Electronic Interpretations of Organic Chemistry

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PREFACE

No doubt the ultimate goal toward which organic chemistry is striving is that state in which fundamental laws and theories will have been developed to such an extent that it will be possible, in advance of experimental trial, to deduce a satisfactory method for the synthesis of any compound and to predict all its properties. Owing to the complex structure of most organic molecules, however, it seems probable that such a Utopian state is impossible of achievement and that organic chemists must content themselves with the more modest aim of augmenting what Gilbert Lewis gallantly calls their "uncanny instinct" by such exact science as they may find applicable. The usefulness of modern physical chemistry for this purpose can be seen clearly at once if we analyze what has been referred to as the ultimate goal of organic chemistry. A satisfactory preparative procedure demands: (1) that the proposed reaction be thermodynamically possible, (2) that the reaction take place with a sufficiently high velocity to be practicable, and (3) that there be as few side reactions as possible and that those which are inevitable take place much more slowly than the main reaction. It should be at once apparent that if we would predict such things we must first understand the effects of structural and environmental changes on both the free energies and activation energies of organic reactions. This seems to be a demand for the fusion of electronic theories of organic chemistry with such modern developments in physical chemistry as the quantum-mechanical concept of resonance and the transition-state theory of reaction rates. The main purpose of this book is to show how this fusion of ideas has been satisfactorily achieved. The pursuit of the sister-problem of predicting the physical properties of substances from a knowledge of their molecular structures would carry us into every remote corner of physical chemistry. Mere contemplation of the field to be covered is staggering. This second subject will be largely although not entirely neglected in the present volume.

It is intended that this book shall serve the dual purpose of a review and an advanced textbook. These two objectives are by no means mutually incompatible, for the advanced student should be given a picture of how his science grows and he should be taught to be critical.

Finally he should feel the thrill of emerging on the frontier of science with a clear understanding of the problems which remain to be solved. Certainly these are also the objectives of a good review. However, a review ideally should be written in such a manner that it presents an unbroken development of the chosen theme, while in the textbook the main theme is apt to be constantly interrupted for the purpose of building up the background of the student. In order to achieve the desired continuity without neglecting the deficiencies of the student's background, several chapters dealing with specialized knowledge not always possessed by students who have completed only one year of physical chemistry have been included as appendixes. References are made to these appendixes at those points in the main body of the book where the knowledge in question becomes prerequisite to the understanding of the main theme. They need not be read by the well-informed chemist.

Another objective, shared by all advanced courses which are "frontier courses," is to give the student such knowledge as is necessary to follow future developments in the field by reading the research literature. It is partly for this reason that the symbolism and the language of the English school have been introduced, despite the fact that they are not popular in this country at the present time.

Finally the author wishes to point out that he has not only attempted to present a critical review of those portions of the field which seem to fit into the general picture outlined above but has also made an effort to show the organic chemist just how this new knowledge may be used in attacking problems. With this idea in mind he has attempted to reduce the most reliable portions of these theoretical developments to a set of working rules which he calls "basic principles." These are introduced as concluding statements all through the book and are numbered so that when they are later used in the solution of problems they may conveniently be referred to by number. They have been reproduced in a group as Appendix V for the purpose of ready reference.

The author wishes to express his indebtedness to his former colleagues, Drs. A. S. Miceli and Lynne L. Merritt, Jr., for their kindness in reading critically several of the later chapters, and to his wife for her loyal aid in the arduous task of proof-reading.

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CHAPTER I

PRE-ELECTRONIC THEORIES OF CHEMICAL AFFINITY

Our modern concepts of the electrical nature of matter owe a considerable debt of gratitude to organic chemistry. The indebtedness arose as a result of the fact that for almost a century organic chemistry presented experimental facts whose interpretations in terms of existent electrochemical theories defied the most ardent and ingenious supporters of those theories. As is always the case in the development of science, the exceptions to the rules lead our wavering steps to the doors of greater generalizations; and organic chemistry, in performing this service, benefited immeasurably in the concomitant clarification of its own concepts. This particular clarification is by no means yet complete, and those who would further the subject can best get the necessary perspective by acquainting themselves with the steps by which the old dualistic electrochemical theories grew into a reconciliation with organic chemistry.

The electrical explanation of chemical affinity was a natural outgrowth of a rapid succession of researches starting with Volta's discovery in the year 1790 of a chemical method of producing an electric current. In 1800 he published a description of the voltaic pile.[1] The next year Nicholson and Carlisle[2] announced their discovery that water could be electrolytically decomposed, and in 1803 Berzelius and Hissinger[3] carried out similar experiments on aqueous salt solutions. These studies led immediately to attempts, notably by Davy in England and Berzelius in Sweden, to relate electrical dualism to chemical affinity.

Davy[4] was the first to announce an electrochemical theory. He explained the theory in a lecture to the Royal Society of London in 1806, and presented the results of 7 years of ingenious experimentation. He pointed out[5] "that hydrogene, the alkaline substances, the metals, and certain metallic oxides are attracted by negatively electrified metallic surfaces; and contrariwise, that oxygene and acid substances are attracted by positively electrified metallic surfaces." He correlated these observa-

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[1] Volta, *Phil. Trans.*, 403 (1800).

[2] Nicholson and Carlisle, *Nicholson's Journal*, **4**, 186 (1801).

[3] Berzelius and Hissinger, *Ann. Chim.*, **51**, 167.

[4] Davy, *Phil. Trans.*, 1 (1807). *See also* Davy's *Elements of Chemical Philosophy*.

[5] *Idem* (*Phil. Trans.*), 28.

tions with his experiments on the production of electrification by friction. Thus when sulfur was rubbed against a metal, the sulfur became negatively and the metal positively charged, which were the same states of electrification they exhibited in the experiments with electrolytic decomposition. Moreover[6] "in the decompositions and changes presented by the effects of electricity, the different bodies naturally possessed of chemical affinities appear incapable of combining or of remaining in combination, when placed in a state of electricity different from their natural order. Thus . . . the acids in the positive part of the circuit, separate themselves from alkalies, oxygene from hydrogene, and so on. . . ."

Chemical combination was accordingly considered to be due to the electrical attraction of oppositely electrified bodies, which, incidentally, he considered to become electrified only on their approach to each other, and chemical affinity was thought to be proportional to difference in electrical condition.

In further support of his contention he pointed out that negatively electrified zinc is incapable of combining with oxygen, while oxygen will combine readily with positively electrified silver.

A clearer insight into his methods of reasoning may be gained by a consideration of the experiment, already mentioned, in which sulfur and copper become electrified by friction. The electrification becomes greater at elevated temperatures, and if the temperature is raised sufficiently heat and light will be given off and the two substances will combine to form a new substance which is "nonelectric." Thus chemical combination was brought about by neutralization of the electric charges, the process being accompanied by the liberation of energy in much the same way as the two coatings of a Leyden jar may be brought to the same potential with the liberation of energy in the form of a spark.

However, Davy seemed to have had in mind also the idea (at least in the cases of those substances which his pupil, Faraday, later called electrolytes) that even after chemical combination the constituent parts of the substance produced retained their own peculiar electrical states and hence could be separated again by electrolysis, for he said:[7] "The coated glass plates of Becarria strongly adhere to each other when oppositely charged, and retain their charges on being separated. The fact affords a distinct analogy to the subject; different particles in combining must still be supposed to preserve their peculiar states of energy."

We also find in this astounding lecture that he suggested explanations for different degrees of chemical reactivity, for the results of competitive reactions, and for the production of complicated molecules; and his sug-

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[6] Davy, *Phil. Trans.*, 38 (1807).

[7] Davy, *Phil. Trans.*, 40 (1807).

gestions for the most part appear as sound approximations to what we consider today as established fact. He also pointed out that the driving force of reactions should depend both on the individual affinities of the reacting particles and on their numbers; and he even suggested that relative degrees of affinity might be determined by measuring "the intensity or quantity" of electricity necessary to just counterbalance the attractive forces holding the two parts of a molecule together. This suggestion was destined eventually to reach maturity in the electromotive series and the thermodynamic interpretation of affinity.

Berzelius brought forward the main outlines of his electrochemical theory in 1812,[8] although he had previously published certain electrochemical speculations, and in 1819 he published a detailed exposition of his theory.[9] In the main his conceptions agreed with those of Davy. But whereas Davy considered that charges were developed only when two suitable substances approached each other, Berzelius considered that the charges were already present in the atoms, each atom possessing both positive and negative electricity, which was more or less concentrated at poles in the atom. However, each atom had a predominant state of electrification, depending upon whether positive or negative electricity predominated in the particle as a whole. Today we would consider instead that different atoms have greater or smaller electron affinities. Following up this idea, he arranged elements in a series in which oxygen was the most negative and the alkali metals the most positive. He considered that oxygen was always negative but recognized that some elements, such as sulfur, were positive to oxygen but negative to the metals and hydrogen. Furthermore, he considered that after atoms had combined to form "compound atoms," these also had electrical properties similar to the simple atoms and hence could combine again to produce still more compound atoms. Here we find the inception of the ideas which culminated in Werner's theory of complex salts and the electronic explanation based on the presence of unshared electrons in the "compound atoms."

Ladenburg [10] says of this period of chemical history: "The further development of the electrochemical theories appeared at that time to be the highest aim of our science; at a later date we see these theories abandoned. The extraordinary enthusiasm was succeeded by an indifference just as extraordinary."

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[8] Berzelius, *Schweigger's Jour.*, 6, 119 (1812).

[9] Berzelius, *Essai sur la théorie des proportions chimique et sur l'influence chimique de l'électricité*, Paris, 1819.

[10] Ladenburg, *History of Chemistry*, translated from the 2nd German ed. by L. Dobbin, 1900, p. 68.

This attitude was due to the rise of organic chemistry and its astounding success in interpreting reactions on the basis of structural theories which took no cognizance of the dualistic electrochemical theory and indeed could not be reconciled with it.

The opening guns of a long and bitter struggle between Berzelius and the French school were fired on the momentous occasion when Dumas' paper on substitution (or metalepsy) was read before the Academy of Sciences at Paris in 1834. On this occasion he directed attention to the fact that in such reactions as the chlorination of acetic acid, hydrogen was replaced by chlorine. We must remember that at this time the structural theory of organic chemistry had not yet been developed and that hence it was by no means obvious to Dumas that the chlorine atom took the exact place in the molecule which had previously been occupied by the hydrogen atom. This assertion was, however, made the following year by Laurent, a student of Dumas. The idea was particularly obnoxious to Berzelius who denied vehemently and repeatedly that a negative chlorine could ever take the place of a positive hydrogen atom in an organic radical.[11] At first Dumas himself agreed with Berzelius, but eventually the pressure of an accumulated array of facts in support of Laurent caused him to transfer his support to his colleague. Old Berzelius, however, never yielded. He was forced to resort to many incongruous makeshifts in order to force newly discovered facts into the mold of his electrochemical theory. These impromptu extensions of his theory, devoid of any experimental foundations, finally drove most of his supporters, including the distinguished Liebig, to the French camp.

This extended controversy marked the parting of the ways for inorganic and organic chemistry. The former continued to use and to develop the electrochemical theory; the latter contented itself, first with the development of structural chemistry culminating in Kekulé's conceptions and then, for a number of years, in determining the structure of organic compounds used and produced in chemical reactions. Electrochemical dualism was ignored by these pioneers of molecular geometry, although they continued to use and even to develop ideas on chemical affinity.

The concept of chemical affinity was, of course, not new. It had been a subject of extensive discussion long before Volta's epoch-making discovery. Thus as early as 1718 Geoffroy [12] drew up tables of "affinity" which are suggestive of our electromotive series. To be sure, the chemical world jubilantly welcomed the electrochemical theories of Davy and

[11] Cf. *Compt. rend.*, **6**, 633 (1838); *Ann. chim. phys.*, **67**, 309 (1838).

[12] J. C. Brown, *History of Chemistry*, 2nd ed., 1920, p. 481.

Berzelius as the long-awaited explanation of chemical affinity, but, as we have seen, their optimism received a severe jolt from the French school of organic chemists. No doubt Maxwell expressed the viewpoint of many chemists when he wrote in 1873 [13] that "the fact that every chemical compound is not an electrolyte shows that chemical combination is a process of a higher order of complexity than any purely electrical phenomenon." Thus organic chemists, while frankly admitting their complete ignorance of the true nature of chemical affinity, recognized its existence and used the concept freely in their development of science.

The next milestone along the road of this development was the concept we now call valence. This conception grew naturally out of work on molecular structure and was developed chiefly by Williamson, Frankland, Odling, and finally Kekulé, who, in 1857, showed that the structure of organic radicals could be successfully explained on the basis of the assumption of the constant tetravalency of carbon and used graphical formulas to picture the structure of organic molecules.[14] Kekulé conceived valence as being a fundamental property of atoms and to be a constant for each element. There certainly is no doubt about the correctness of the first point, but the second was shown to be untenable by the work of Kolbe, Blomstrand, and others.

Soon after this the structures of unsaturated compounds such as the olefins were elucidated by the concept of double and triple bonds. Although this offered a satisfactory explanation for one type of unsaturation, there yet remained to be explained that other type of unsaturation typified by molecular compounds, such as hydrates and complex salts, which Kekulé had distinguished from atomic compounds. It seemed obvious that a molecule which is saturated in the Kekulé sense must still have some "residual affinity" in order to combine with other equally saturated molecules, and it became a matter of much interest to explain the origin of this residual affinity.

Kommrath [15] argued that, e.g., silver has more affinity for chlorine than sodium does, and hence one of two conditions must obtain: either AgCl and NaCl are both saturated, in which event chlorine is assumed to have a different attractive force for "each of the other 62 elements"; or, as Kommrath preferred to believe, NaCl is unsaturated, as would be most if not all other compounds. This unsaturation would be the result of the inability of the sodium atom to use up all of the available affinity of the chlorine atom (silver could use up most of it) and hence there

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[13] Maxwell, *Electricity and Magnetism*, 1873, vol. 1, p. 315.

[14] Kekulé, *Ann. Chem. Pharm.*, **104**, 132 (1857).

[15] Kommrath, *Ber.*, **9**, 1392 (1877).

must remain a small residual affinity which Kommrath considered large enough to produce the weak unions observed in hydrate formation, etc.

Eight years later Pickering [16] and Armstrong [17] suggested similar ideas of residual affinity. Armstrong held that substitution reactions of benzene were preceded by the formation of intermediate addition compounds formed by the exercise of this residual affinity. Pickering developed his conception on the premise that heats of neutralization measure affinity, and he came to much the same conclusion that Kommrath had reached.

The common error of all these investigators is of course obvious today: they failed to recognize that affinity has both quantity and intensity factors. Consequently, when they concluded from thermal measurements that the affinities (intensity factor) of all elements were different, they interpreted it as meaning that valences (quantity factor) could not be equal, being slightly more or less than the small whole numbers commonly used to denote them. In view of the fact that Faraday's laws of electrolysis were certainly known to these investigators, their confusion seems to us somewhat surprising. It was apparently due to the fact that, within the range of their experience, all forces of the type which act from a distance, such as electrostatic or magnetic attraction, seem to distribute themselves uniformly over the surface of any matter imbued with them and do not act as though they are concentrated at a few definite points, as the modern electron theory and the quantum theory take as axiomatic. Granting their premise, it does not seem unreasonable that, when one atom is subjected to the affinity demands of another, varying amounts of this radiating affinity will be harnessed to produce a valence bond and hence varying amounts of residual affinity will be left free. Precisely this point of view was taken by Werner [18] in developing his theory of chemical affinity, first announced in 1891.

In view of the prevalent disregard of chemists for the true significance of Faraday's laws of electrolysis, it is interesting that 10 years before this time the physicist Helmholz, in his famous Faraday lecture, had made clear that he, at least, appreciated the significance of Faraday's work in its relation to the problem of chemical affinity. He said,[19] referring to similar conceptions of affinity held by Berzelius: "According to

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[16] Pickering, *Proc. Chem. Soc.*, 122 (1885); 593 (1887).

[17] Armstrong, *B. A. report*, Aberdeen (1885); *Proc. Roy. Soc.*, 268 (1886); *Proc. Chem. Soc.*, 260 (1887).

[18] Werner, *Vierteljahrsschr. naturforsch. Ges. Zürich*, **36**, 129 (1891); *Neure Anschauungen auf dem Gebiete der anorganischen Chemie*, Braunschweig, Fr. Vieweg & Sohn, 3rd ed., 1913.

[19] Helmholz, *J. Chem. Soc.*, **39**, 285 (1881).

Berzelius's theoretical views, the quantity of electricity collected at the point of union of two atoms ought to increase with the strength of their affinity. Faraday demonstrated by experiment that so far as this electricity came forth in electrolytic decomposition its quantity did not at all depend on the degree of affinity." He then proceeded to give his reasons for believing that chemical unions in nonelectrolytes as well as electrolytes are electrical in nature, thus clearly making his remarks apply to organic chemistry. Following up the same theme he next proceeded to make a remark which already has taken its place in history: "Now the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity." Finally he drew the conclusion that chemical union is somehow associated with these positive and negative "atoms" of electricity and that chemical affinity is merely the force with which they are attracted by the atom.

In the same year that the Helmholz lecture was published there was also published a lecture by another physicist, G. J. Stoney, which had been read before the British association at Belfast in 1874. Like Helmholz, he too had seen the true significance of Faraday's work. He said: "For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases." He estimated the value of this elementary electrical charge to be 0.3×10^{-10} absolute electrostatic unit.[20]

These astounding lectures seem, however, to have been ignored by the proponents of the various theories on residual affinity. Perhaps it is just as well, for they continued in their own peculiar way to follow up the question of molecular compound formation and chemical reactivity and gave to the world a body of well-correlated facts which even today are but partially understood.

Let us, then, return for a moment to a consideration of the Werner theory [21] mentioned above. Although it was first announced in 1891, its development extended into the twentieth century, and many of Werner's ideas and most of his terminology survived the modern electronic reinterpretation of molecular compound formation.[22] Werner did not agree with the Kekulé-van't Hoff conception of valency wherein, as he said,[23]

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[20] Stoney, *Phil. Mag.*, **11**, 384 (1881).

[21] For a more detailed discussion of Werner's theory see Henrich, *Theories of Organic Chemistry*, translated by Johnson and Hahn, John Wiley & Sons, 1922, Chap. 5.

[22] See Chapter II.

[23] Werner, *New Ideas*, 1911, p. 57.

"The fact that an atom is able to combine with a definite number of other atoms is . . . interpreted as meaning that the affinity of an atom only comes into action through a definite number of units of valency which are considered as independent forces." Rather, as pointed out by Waters and Lowry,[24] "Werner appears to have adopted the views of Lossen,[25] who states that 'The valency of an atom is [merely] a number which expresses how many atoms are present in its combining zone,' and of Claus,[26] who said that 'The hypothesis that valency in multivalent atoms is a preexisting force acting in definite units is as unfounded as it is unnatural.' "

It will be observed that the above conception of valency was an attempt at a clarification of the confusion existing between affinity and valence, now relegated more or less to the domain of the geometrical, and was an expression of the number of atoms (or groups) which could cluster over the surface of a given atom.

Werner's conception may be made clearer by the following brief summary of his views. The affinity of a given atom (the "central atom") may be partially saturated by direct union with other atoms ("primary" or "principal valence") producing ordinary molecules, and there remains a residual affinity, as explained above. This residual affinity may frequently operate to produce further chemical union (secondary or auxiliary valence) but does so under different restrictions than those regulating the primary unions. Secondary unions (represented graphically by dotted lines) may bind the central atom to whole molecules, such as water or ammonia, or to ions; but the latter occurs only through the "intervention" of another ion. Thus a nitrogen atom may form primary valence unions with only three hydrogen atoms. In order to attach a fourth hydrogen atom, some anion must also be involved.

The atoms or groups attached directly to the central atom are very firmly bound and are described as being in the "coordination group" or the "first sphere." They are not ionized. The other atoms involved in the molecule are said to be in the "second sphere" and are characterized by being ionized. Graphically the coordination group is enclosed in square brackets. The maximum number of atoms or groups which may be directly bound to the central atom, either by primary or secondary valence, is called the coordination number. The magnitude of this number is governed largely by the amount of space constituting the first zone, and usually is 4 or 6.

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[24] Waters and Lowry, *Physical Aspects of Organic Chemistry,* D. Van Nostrand Co., 1936, p. 7.

[25] Lossen, *Ann. Chem. Pharm.,* **204,** 327 (1880).

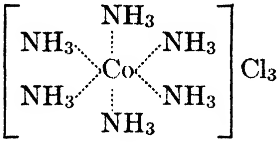
[26] Claus, *Ber.,* **14,** 432 (1881).

Although Werner used both solid and dotted lines to represent valence bonds within the first sphere, Sidgewick[27] says "it was ultimately admitted, if not by Werner at least by his successors, that within the coordination group when once it was constituted, this distinction vanished, and all the valencies attaching the groups to the central atom were identical."

It is an interesting consequence of his theory that in order for a salt to ionize in water, molecules of water must coordinate with the metallic atom thus forcing the negative atoms or groups into the second sphere, where they will be in the ionic condition.

Another noteworthy feature of the theory is that it attempted to answer a question which today is considered of paramount importance, viz., what inner properties of molecules regulate their thermodynamic and kinetic behavior? Werner held that stability is a function of the amount of bound affinity and rectivity a function of the residual affinity.

To illustrate the application of Werner's theory we may turn to the cobalt chloride ammines.[28] The substance $CoCl_3 \cdot 6NH_3$ gives three chloride ions in water solution, which are of course precipitated with silver nitrate. However, if the solution is treated with sulfuric acid the ammonia molecules are not removed. Werner described this behavior by the formula



which shows the six molecules of ammonia attached to the central cobalt atom by auxiliary valences and thus being held in the first sphere, where they do not exhibit the customary properties of ammonia. The three chlorine atoms are in the second sphere and accordingly are ionized.

Other complexes of the same series exist and are shown in Table I. In each case the cobalt becomes "coordinatively saturated," i.e., its

TABLE I

1. $[Co(NH_3)_6]Cl_3$
2. $[Co(NH_3)_5Cl]Cl_2$
3. $[Co(NH_3)_4Cl_2]Cl$
4. $[Co(NH_3)_3(NO_2)_3]$
5. $[Co(NH_3)_2(NO_2)_4]K$
6. $[Co(NO_2)_6]K_3$

coordination number of 6 is in each case used to the utmost. Compound 4 is a nonelectrolyte since the second sphere is empty. Note also that

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[27] Sidgwick, *The Electronic Theory of Valency*, Oxford Press, 1927, p. 110.

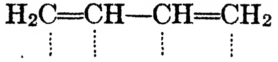
[28] Werner and Miolati, *Z. physik. Chem.*, **14**, 506 (1894).

in the first three compounds the coordination complex is a cation while in the last two it is an anion.

The concept of residual valency formed the basis of another theory developed by Thiele[29] in 1899. Inasmuch as some of the most important concepts in the modern electronic interpretations of organic chemistry are reinterpretations of Thiele's theory, it seems worth while to review it in some detail.

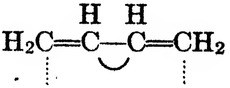
Thiele's particular interest was in compounds containing double or triple bonds, and his particular triumph in explaining the so-called 1,4-additions to conjugated systems. He considered that in multiple linkages the valence bonds beyond the first did not utilize as much of the atomic affinity as a single bond. In such cases, therefore, there was a large though variable amount of affinity left free, to which he gave the name "partial valence." This idea was substantiated by the earlier investigations of Thomson,[30] who showed that the heat of formation of ethylene was less than would be the case if two complete carbon-to-carbon bonds were formed. Since the exercise of affinity results in the liberation of energy (such as in the case of an object falling toward the earth under the influence of its gravitational affinity) this observation was interpreted as meaning that less than that amount of affinity customarily called into play in the formation of two single carbon-to-carbon linkages was utilized in the formation of a double bond between these two carbon atoms.

We may now proceed at once to a consideration of the time-honored example of 1,4-addition, viz., the addition of bromine to butadiene. Each of the four carbon atoms would, according to the above considerations, be possessed of a partial valence, represented as follows:



$$H_2C{=}CH{-}CH{=}CH_2$$

Now if in general singly bound carbon atoms may utilize a further portion of affinity (when available) to form so-called double bonds, then it follows that in the above compound as pictured we would have an improbable distribution of affinity, because the two central carbon atoms are pictured as having free affinity and yet are bound together only by a single bond. Certainly the free affinity on these two atoms would be expected to saturate itself largely or wholly across the single bond, which Thiele pictured as follows:



$$H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2$$

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[29] Thiele, *Ann.*, **306**, 87 (1899); *idem*, **308**, 333 (1899).

[30] Thomson, *Z. physik. Chem.*, **1**, 369 (1887).

It will be immediately evident that this concept pictures conjugated systems as being more saturated than systems containing two pairs of normal double bonds. In support of this prediction we find that the former in general have lower heats of combustion. Obviously the two terminal carbon atoms in 1,3-butadiene have an excess of affinity and the bromine will add to the 1 and 4 positions. The addenda are considered first to attach themselves loosely to the two carbon atoms when there would follow a redistribution of affinity with the production of $H_2CBr—CH{=}CH—CH_2Br$ as the final product.

It should be noted in passing that Thiele's concepts were not involved with the general confusion characteristic of the nineteenth century ideas on residual valence. His "partial valence" had no connection with reactions involving molecules which were saturated in the sense of Kekulé, but involved only the residual affinity associated with multiple linkages.

The initial distribution of chemical affinity (in the diolefin) postulated by Thiele is essentially what the modern proponents of wave mechanics call resonance. Yet without any of the complicated mathematical equipment of these moderns Thiele was able to formulate the concept in a rather satisfactory manner some 30 years before it was "discovered" by the mathematical physicists. Certainly we have here an example of the "uncanny instinct" of organic chemists, referred to in the preface to this volume.

Concerning Thiele's theory we should finally remark that the conjugation need not necessarily involve carbon atoms only but may involve such linkages as $C{=}O$ and $C{\equiv}N$. In these cases the problem is frequently complicated by tautomeric shifts of the keto-enol type subsequent to the formation of the 1,4-addition compound.

The years during which the nonelectrochemical concepts of affinity had been growing saw also the parallel growth of the dualistic electrochemical theory from the pioneer researches of Faraday, who recognized and named electrolytes and ions, to the Arrhenius theory of electrolytic dissociation which was announced in 1887. Naturally this period was not entirely devoid of attempts to bridge the gap between these two self-sufficient theories. As early as 1869 we find Blomstrand[31] trying to reconcile Berzelius's theory with the newer views of affinity. Soon after this we find a few organic chemists talking about the effects of "negative groups" as substituents in organic compounds, seeming to insinuate that electrical forces are factors in determining the affinity relationships even in compounds which do not yield to electrolysis. Thus in 1875 Markownikoff wrote:[32] "When an unsaturated molecule C_nH_mX adds another

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[31] Blomstrand, *Die Chemie der Jetztzeit* (1869).

[32] Markownikoff, *Compt. rend.*, **81**, 670 (1875).

molecular system YZ at a low temperature, the most negative element or group, Y, combines with the least hydrogenated carbon atom, or with that which is already in direct union with some negative element; but at comparatively higher, it is the element Z, which becomes attached to the least hydrogenated carbon, that is to say, for the same substances, the reaction takes a path directly opposite to the first."

Thought provocative research was also being done by Menschutkin. He showed that certain radicals, like methyl or ethyl, could be arranged in a series according to their influence as substituents on the speed or on the equilibrium conversion of certain reactions (e.g., esterification). At first the observations were classified only empirically, but we find in 1885–1889 that Ostwald[33] refers to certain atoms or groups, which by substitution into acetic acid makes it stronger, as "negative groups." He also pointed out that the same substituents which increased the strength of acids increased the velocities of many of their reactions.[34]

Other examples were not wanting. Thus nitromethane had been shown[35] to form salts with alkalies, thus indicating a negative nature for the nitro group. Similarly a methylene group between two carbonyl groups, as in acetoacetic ester, was known to act as a weak acid. Many other examples are cited by Henrich,[36] who points out that the so-called negative groups are all unsaturated groups.

I cannot state definitely by what process of reasoning chemists came to assign a negative electrical nature to these acid-producing groups, but it seems practically certain that they had two ideas in mind. First there was the time-honored idea that negative elements or their oxides produced acids; secondly, certain negative ions like Cl^- and CN^- when substituted into organic acids, made them more strongly acidic. However it may have been, one thing is certain: it was gradually dawning on them that even in the un-ionized linkages of organic molecules manifestations of chemical affinity were found to be related to the electrical properties of the constituents of molecules.

Once the importance of the concept of the "negative nature of atomic groups" was recognized, much research was done on the subject,[37] notably by Victor Meyer and Henrich. A particularly important contribution to the problem was made by Vorländer[38] when he pointed out that the

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[33] Ostwald, *J. prakt. Chem.*, **31**, 433 (1885); *Z. physik. Chem.*, **3**, 170, 418 (1889).

[34] Ostwald, *J. prakt. Chem.*, **30**, 93 (1884).

[35] Victor Meyer, *Ber.*, **5**, 399 (1872).

[36] Henrich, *Ber.*, **32**, 668 (1899).

[37] For a review of the subject and references to the original literature see Henrich, *Theories of Organic Chemistry*, translated by Johnson and Hahn, John Wiley & Sons, 1920, Chap. 8.

[38] Vorländer, *Ber.*, **34**, 1632 (1901).

so-called negative nature of certain unsaturated groups can only become active when the group is in a certain position relative to the hydrogen atom to be activated. He symbolized organic acids by formulas such as

$$\underset{1}{\mathrm{H}}.\underset{2}{\mathrm{E}}.\underset{3}{\mathrm{E}}{=}\underset{4}{\mathrm{E}} \qquad \text{and} \qquad \underset{1}{\mathrm{H}}.\underset{2}{\mathrm{E}}.\underset{3}{\mathrm{E}}{\equiv}\underset{4}{\mathrm{E}}$$

(I) (II)

where E represents a nonmetallic element, and called the unsaturated atoms occupying the positions 3–4 the "reactive group." This term is synonymous with what we have been calling a negative group (e.g., carbonyl). He then points out that if the reactive group is to be effective it must stand in the *beta* position relative to the hydrogen atom which is to be activated. It has no influence on the mobility of the hydrogen atom if it is present in such combinations as H—E=E or H—E—E—E=E.

The importance of these observations to the development of theoretical organic chemistry lies in this: whereas certain negative substituents such as Cl or NO_2 increase the ionization of an organic acid most when substituted on the α-carbon atom and exert a diminishing effect as they are moved farther away, this is by no means the case when we examine the "negative influence" of groups such as C=O, C=C, whose behavior is described by Vorländer's rule, for here the *beta* position is more effective than either the *alpha* or *gamma* positions. The conclusion is inevitable that the so-called negative influence is exerted by at least two different mechanisms. A satisfactory explanation of these facts was not forthcoming until the English school of chemists devised their electronic theories many years later.

In tracing the above developments, which are of particular interest to organic chemistry, we have neglected a parallel development in physics which led ultimately to the discovery of the electron in 1897 by J. J. Thomson[39] and independently by Kaufmann.[40] Since we are not primarily interested in physics, a complete review of these important physical developments would be out of place here, but the high lights of this field of research may profitably be mentioned. In 1870 Sir William Crookes discovered cathode rays by passing an electrical discharge through a partially evacuated tube. The controversy which arose as to the nature of these cathode rays was ultimately solved by the experiments of Lenard, Perrin, and others who showed that the rays were deflected by magnetic or electrostatic fields in such a direction as to suggest that the rays were negatively charged, and cast shadows, penetrated thin sheets of metal, and showed various mechanical effects which

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[39] Thomson, *Phil. Mag.*, **44**, 293 (1897).

[40] Kaufmann, *Ann. Physik.*, n.s., **61**, 544 (1897).

indicated that they must be corpuscular and not wavelike in nature and must be very minute. Today we recognize these cathode ray particles as being electrons, i.e., as being negatively charged particles having a mass vastly less than that of the lightest atom. A satisfactory proof of the existence of such particles would of necessity have to be a quantitative measurement of the charge and the mass of the particles. In this relation it will be recalled that the value of the elementary charge of electricity had been estimated by Stoney from Faraday's electrochemical equivalent and a crude estimation of Avogadro's number based on the kinetic gas theory, but it had not been shown that this elementary charge was of necessity associated with any mass or was the same charge as that carried by cathode ray particles. In later studies carried out in Thomson's laboratory, gases were rendered conducting, not by an electrical discharge such as used in cathode ray tubes, but by X-rays or by the rays from radium. This work ultimately was made to show that gaseous ions were produced by the X-rays or γ-rays, thus rendering the gases conducting, and that the negative ions had the same value of ne (where e is the charge and n is the number of molecules per cc) as univalent ions in electrolysis, and a value of e/m (where m is the mass) about 1800 times less than the value of e/m found for hydrogen ions. The presumption was thus very strong that these negatively charged particles carried the same unit charge as found in electrolysis experiments and had a mass about 1800 times less than the mass of the hydrogen atom. These experiments, then, constituted the "discovery of the electron" already alluded to.[39]

Having made this brief excursion into the realm of physics, let us once more turn our thoughts back to the perplexing galaxy of well-substantiated but uncorrelated theories of chemical affinity which existed on the eve of the discovery of the electron. There was primary valence, which might or might not be accompanied by ionization. Where ionization occurred, electrical dualism offered a satisfactory explanation; in nonionizing linkages such phenomena as the union of two chlorine atoms to form a molecule or the substitution in organic molecules of a "positive" hydrogen atom by a "negative" chlorine atom seemed to preclude the possibility of a dualistic electrochemical explanation. And yet observations on the negative nature of atomic groups, as well as the considerations outlined by Helmholz in his Faraday lecture, made it seem inevitable that even these un-ionized chemical unions must find their explanation in electrical forces. It furthermore appeared that atoms or groups could in some way relay their electrical influence through a molecule. Then there were the mysterious secondary valence phenomena studied by Werner and the forces of cohesion and adhesion operating in solids, liquids, and gases.

The stage was all set for the dramatic entrance of the conquering hero, the electron. No dramatist could have outdone nature in choosing a more perfect moment for ushering in the chief actor.

CHAPTER II

EARLY APPLICATIONS OF THE ELECTRON THEORY TO PROBLEMS OF ORGANIC REACTIVITY

Chemists were quick to pounce upon the newly discovered electron as an aid in untangling their diverse notions of chemical affinity. Clarification started in 1899 with a paper by Abegg and Bodlander [1] who pointed out that the old concept of affinity between atoms should be replaced by the concept of the affinity of atoms for electrons. As a measure of this electron affinity of atoms they used decomposition voltages, as suggested nearly a century before by Davy for the measurement of chemical affinity. A most interesting feature of this paper is the authors' recognition that even secondary valence phenomena line up with electron affinities of the atoms in the complex molecules and that hence even coordination forces must be electrical in nature.

During the last few years of the nineteenth century an explanation of another of the valence anomalies, viz., the union of two like atoms to form an elementary molecule, was forming in the minds of at least three noted chemists. W. A. Noyes and A. C. Lyon [2] in 1901 wrote: "If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of those molecules, it would follow that the elementary molecules as well may ionize into positive and negative parts." They invited discussion of the subject and were rewarded by an immediate reply from Stieglitz,[3] who claimed that he had been using the concept for some time in his lectures at the University of Chicago. He amplified their ideas on the possible existence of positive chlorine ions by pointing out that the action of chlorine on potassium hydroxide solution is readily interpretable by the equation

$$Cl^+ + Cl^- + K^+ + OH^- \rightarrow K^+ + Cl^- + HOCl$$

wherein we observe that the negative hydroxyl ion combines with the positive chlorine ion. He also argued that hypochlorous acid is an

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[1] Abegg and Bodlander, *Z. anorg. Chem.*, **20**, 453 (1899).

[2] Noyes and Lyon, *J. Am. Chem. Soc.*, **23**, 463 (1901).

[3] Stieglitz, *ibid.*, **23**, 797 (1901).

amphoteric compound and that in addition to the usual acid ionization it would be capable of a weak basic ionization: $HOCl \rightarrow HO^- + Cl^+$.

During the same year Lapworth,[4] in England, suggested that in addition reactions bromine might be considered to react according to the equation $Br_2 \rightarrow Br^+ + Br^-$.

These ideas were extended by Abegg[5] in 1904. He argued that *any* element might exhibit either positive or negative valence and pointed out that whereas atoms of one element never exhibit more than one negative valence they frequently exhibit a variable positive valence which tends toward a maximum as the electron affinity of the adjoined atom is increased. He also pointed out the relationship between electron affinity of atoms and their position in the periodic table, a relationship which every chemical tyro knows today. He crowned these theoretical speculations with his famous "rule of eight," which we may state as follows: *Every element (except the inert gases) may have a "normal valence" and also a valence of opposite sign called a "contravalence." The arithmetic sum of the maximum values of these two valences for each element is eight.* This rule formed the basis of the later "octet theory" of valence developed by Lewis and Langmuir and is illustrated in the following table.

Periodic table group number	1	2	3	4	5	6	7
Normal valence	+1	+2	+3	±4	−3	−2	−1
Contravalence	(−7)	(−6)	(−5)		+5	+6	+7

In the same paper Abegg also made another highly important contribution. He discussed the question as to how we may determine the "polar character" of an element in a given compound, i.e., how may we determine whether it is exercising its positive or negative valence? He suggested four different methods, to which we shall append our own examples.

(1) If the compound ionizes in a polar solvent, the "polar character" of its constituents is easily determined by well-known methods.

(2) If the compound hydrolyzes, that molecular fragment which becomes attached to the hydroxyl group must have been positive and the one becoming attached to the hydrogen ion must have been negative. Thus, if a compound XY hydrolyzes as follows: $XY + HOH \rightarrow XH + YOH$, X must have exercised a negative and Y a positive valence in

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[4] Lapworth, *J. Chem. Soc.*, **79**, 1267 (1901).

[5] Abegg, *Z. anorg. Chem.*, **39**, 330 (1904).

the initial compound, even though it is not ionizable in the usual sense. We may take an example from the later writings of Stieglitz.[6] Ethyl iodide always hydrolyzes as follows:

$$C_2H_5I + H^+OH^- \rightarrow C_2H_5OH + HI$$

"We never by any mischance" get C_2H_6 and HIO as hydrolysis products. Thus the iodine atom in ethyl iodide must be negative and the adjoined carbon atom positive.

(3) The "polar character" may be judged from the relative positions in the periodic table of the two atoms adjoined. Thus ICl must have a positive iodine and a negative chlorine atom since both atoms are in the seventh group and I has the higher atomic number, making it more positive.

(4) If a given atom is exercising its maximum valence this in general furnishes a means of establishing its polar character, since negative valence is not variable. Thus in SF_6 the sulfur is exercising its maximum valence and hence must be the positive atom of the combination.

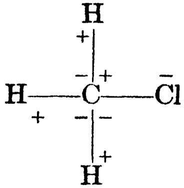
In the same year J. J. Thomson [7] published the first extensive attempt to correlate chemical properties with electronic structure. Since his theory has been shown to be largely erroneous we will not indulge in a detailed discussion, but merely note in passing that he considered valence as arising from a striving of atoms to attain electronic stability. Inert gases are electronically stable and hence exhibit no valence, but all other atoms tend to gain or lose "corpuscles" (i.e., electrons). This they accomplish by transfer of corpuscles from one atom to another and in so doing develop negative or positive charges which operate as valences. This much of his theory continued to live as a part of all later electronic theories of valence. He erred in supposing that the electrons were always completely transferred.

Organic chemists soon attempted to apply this feature of Thomson's theory to the elucidation of their own theoretical problems. Of these many attempts we shall consider only the few which particularly commend themselves to the author; and in discussing these few we shall restrict ourselves to the specific ideas which survived the subsequent discard of the Thomson theory and continued to be genuinely useful in organic chemistry. Accordingly we shall present the theoretical speculations of a group of American chemists: Fry, Falk, Nelson, Noyes, and Stieglitz. All these men seem to have embraced the ideas of Abegg and of Thomson and developed them in a closely similar manner. So closely

[6] Stieglitz, *J. Am. Chem. Soc.*, **44**, 1306 (1922).
[7] Thomson, *Phil. Mag.*, **7**, 237 (1904).

alike are they that it would require much careful study to decide just which of these men deserves credit for being the first to publish each little feature of what one might call their combined theory. It is quite possible that we have erred in some such details.

Fry [8] introduced the convention of indicating the "polar character" of atoms in given molecules by writing + or − over the atom in question. Thus he would have written:



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & {}^{+}| & & \\ & & {}^{-}|^{+} & & {}^{-} \\ \mathrm{H} & \text{——} & \mathrm{C} & \text{——} & \mathrm{Cl} \\ {}^{+} & & {}^{-}|^{-} & & \\ & & |^{+} & & \\ & & \mathrm{H} & & \end{array}$$

He also suggested [9] a new type of isomerism. Thus the compound XY might exist as X^+Y^- or X^-Y^+, differing only in the location of the electrons. This isomerism was referred to as "electronic isomerism" or "electromerism" and the isomerides as "electromers." Fry emphasized that in general only one electromer of a given compound will be stable, the other existing, if at all, only in very minute concentration.

Assuming, as Abegg had done, that hydrolytic decomposition reactions were preceded by ionization, he applied the hydrolytic method of determining polar character to interpret the earlier work of Selivanow [10] and thereby made an important contribution to the problem of the existence of "positive halogen" atoms. Selivanow had observed that in the hydrolysis of the chloroamines, RNHCl and R_2NCl, and in their interaction with hydriodic acid, Cl was replaced by H instead of OH, which was surprising in view of the opposite behavior of alkyl halides.

$$R_2NCl + 2HI \rightarrow R_2NH + HCl + I_2$$

Fry interpreted these reactions as due to the presence of positive chlorine ($R_2N^{-+}Cl$) which, of course, would be replaced by positive H.

Falk and Nelson [11] published the first of their papers very shortly after Fry. They subscribed to Fry's ideas on electromerism and pointed out that olefins would add such reagents as HBr to give, in general, a mixture of isomeric addition products because the olefin existed in two elec-

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[8] H. S. Fry, *The Electronic Conception of Valence and the Constitution of Benzene*, Longmans, Green Co. (1921) and earlier papers.

[9] Fry, *J. Am. Chem. Soc.*, **30**, 34 (1908); *Z. physik. Chem.*, **76**, 387 (1911).

[10] Selivanow, *Ber.*, **25**, 3612 (1892).

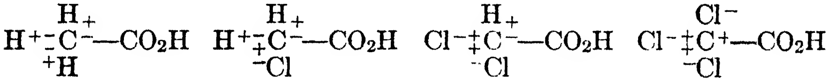
[11] Falk and Nelson, *School of Mines Quarterly*, **30**, 179 (1909); *J. Am. Chem. Soc.*, **32**, 1637 (1910).

tromeric forms each of which would add HBr in a different way. This can be conveniently presented, using Fry's symbolism:

$$\begin{array}{l} R_1R_2C^{+}{=}^{-}CR_3R_4 + \overset{+}{H}\overset{-}{Br} \rightarrow R_1R_2\overset{+}{C}\overset{-}{Br}\cdot\overset{-}{C}\overset{+}{H}R_3R_4 \\ \quad\;\; \downarrow\!\uparrow \\ R_1R_2C^{-}{=}^{+}CR_3R_4 + \overset{+}{H}\overset{-}{Br} \rightarrow R_1R_2\overset{-}{C}\overset{+}{H}\cdot\overset{+}{C}\overset{-}{Br}R_3R_4 \end{array}$$

It will be noticed that two ideas are involved here: (1) Orientation in addition reactions is directed by an attraction of the negative ion of the addendum by the positive carbon atom of the olefin, and the positive ion of the addendum by the negative carbon atom. (2) The formation of two isomeric addition products is due to the presence in significant concentration of the electromers of at least one of the reactants.

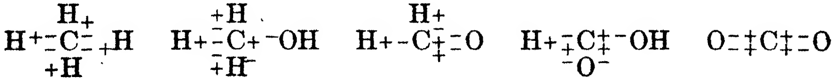
In 1911, Falk[12] made a slight extension of Ostwald's earlier observation that the introduction of negative atoms or groups into acids made them stronger. Thus in the chloroacetic acids



$$H^{+}\substack{-\\-}\overset{H_{+}}{\underset{{}^{+}H}{C}}{}^{-}\text{—}CO_2H \quad H^{+}\substack{-\\+}\overset{H_{+}}{\underset{{}^{-}Cl}{C}}{}^{-}\text{—}CO_2H \quad Cl^{-}\substack{\ddagger\\+}\overset{H_{+}}{\underset{{}^{-}Cl}{C}}{}^{-}\text{—}CO_2H \quad Cl^{-}\substack{\ddagger\\+}\overset{Cl^{-}}{\underset{{}^{-}Cl}{C}}{}^{+}\text{—}CO_2H$$

it will be observed that on successive introduction of chlorine atoms into the molecule more and more electrons are removed from the α-carbon atom. This shift of electrons, they point out, is the direct reason for the increased acidity. Thus the influence of the so-called negative atoms and groups was given an electronic interpretation. It remained for G. N. Lewis and H. J. Lucas some years later to suggest a mechanism by which the removal of electrons from the α-carbon atom might increase the ionization of the relatively distant hydrogen atom.

To Nelson and Falk[13] we also owe a clarification of our ideas on oxidation-reduction reactions. If we accept the definition usually given for oxidation, viz., that it is a loss of electrons, it is not immediately evident how this definition applies to such an oxidation series as $CH_4 \rightarrow CH_3OH \rightarrow HCHO \rightarrow HCO_2H \rightarrow CO_2$. However, if we write the series using directed valences



$$H^{+}\substack{-\\-}\overset{H_{+}}{\underset{+H}{C}}\substack{-\\-}{}_{+}H \quad H{+}\substack{-\\-}\overset{+H}{\underset{\substack{-\\+H^{-}}}{C}}{+}{}^{-}OH \quad H{+}{-}\overset{H+}{\underset{+}{C}}\substack{-\\+}\substack{-\\-}O \quad H{+}\substack{-\\+}\underset{{}^{-}O^{-}}{C}\substack{\ddagger\\+}{}^{-}OH \quad O\substack{-\\-}\substack{\ddagger\\+}C\substack{\ddagger\\+}\substack{-\\-}O$$

it is at once evident that in each successive step electrons are removed from the carbon atom. Lest the reader's foreknowledge of the concept of shared electrons lead him astray at this point he should be

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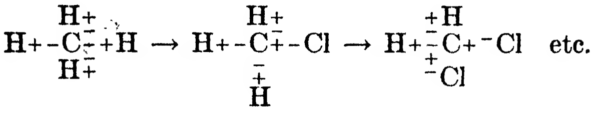
[12] Falk, *J. Am. Chem. Soc.*, **33**, 1140 (1911).

[13] Nelson and Falk, *ibid.*, **35**, 1810 (1913).

reminded that according to the Thomson theory the electrons transferred are *completely* lost by the carbon atom and that hence the above series represents steps of oxidation in strict accord with the definition.

Similarly they showed that chlorination is an oxidation:



$$\begin{array}{ccccc} \mathrm{H+} & & \mathrm{H+} & & \mathrm{+H} \\ \mathrm{H+{-}C\mp{+}H} & \rightarrow & \mathrm{H+{-}C\mp{-}Cl} & \rightarrow & \mathrm{H+\mp C+{}^{-}Cl}\ \text{etc.} \\ \mathrm{H\mp} & & \mp & & \mathrm{\pm{}^{-}Cl} \\ & & \mathrm{H} & & \end{array}$$

They must have had in mind essentially what Stieglitz frequently emphasized later, viz., that the replacement of hydrogen by chlorine takes place as follows:

$$\mathrm{H_3C^{-}{—}^{+}H + Cl^{+}{—}^{-}Cl \rightarrow H_3C^{-}{—}^{+}Cl + H^{+}{—}^{-}Cl}$$
$$\mathrm{H_3C^{-}{—}^{+}Cl \rightarrow H_3C^{+}{—}^{-}Cl}$$

In the first step we note that the positive hydrogen is replaced by the positive chlorine atom. In the second step the chlorine, because of its high affinity for electrons, pulls them away from the carbon atom; thus the carbon becomes oxidized.

This electronic interpretation of the replacement of hydrogen by chlorine solved a very old and very vexing problem, the one which caused all the bitterness between Berzelius and the French school and caused inorganic and organic chemistry to follow different roads for many years. Except for the fact that Thomson's postulate of complete electron transfer has been replaced by Lewis's concept of shared electrons, the interpretation is still in good standing.

The Advent of the Lewis Theory *

In 1916 G. N. Lewis [14] and Kossel [15] independently presented similar electronic theories of valence. Soon thereafter the Lewis theory received further development by Langmuir.[16] Like the Thomson theory before them, both of the new theories contained the idea of complete electron transfer attending the formation of valence bonds (now called electrovalence), but only in the Lewis theory did the idea of shared electrons (covalence) make its debut. The other chief difference between the two theories lay in the fact that Kossel considered that elements of the first two periods of the Mendeleeff table may lose all their valence electrons, while Lewis contended that only the metallic elements are capable of

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* If the reader is not familiar with the elementary details of the Lewis electronic theory he should read Appendix I before proceeding.

[14] Lewis, *ibid.*, **38**, 762 (1916).

[15] Kossel, *Ann. Physik* [4], **49**, 229 (1916).

[16] Langmuir, *J. Am. Chem. Soc.*, **41**, 868 (1919).

doing so. As a result of these differences the Kossel theory is now only a matter of historical interest while the Lewis theory has been universally adopted and much expanded.

The Lewis theory made clear for the first time the electronic nature of the three types of valency recognized by earlier chemists: (1) the ionizable valence, (2) the nonionizing primary valence, and (3) secondary valence, which will be discussed in detail in Chapter III. It also clarified the confused opinions held by opposing schools of thought on whether the affinity of an atom is divided into equal directed portions, like the four tetrahedrally arranged valences of carbon, or whether it could be unequally divided in proportion to the affinity demands of other atoms. It now became clear that a valence bond consists of a pair of shared electrons and that the valence electrons of an atom are divided equally, i.e., in pairs, between the different bonds. However, since the electrons are not equally shared by all atoms, different linkages may be polar in different degrees and thus contribute differently to the effective kernel charges of the atoms and hence to their reactivity. Thus was achieved the reconciliation of the Kekulé and Werner points of view.

Another noteworthy feature of the new theory was its emphasis on the principle that a bond could only be formed if one atom had unshared electrons and another had an incomplete valence shell into which they could be incorporated.

It is interesting that similar features had already appeared in a nonelectronic theory of chemical affinity put forward by Flürscheim long before the advent of the Lewis theory and widely used long afterwards.[17] Flürscheim accepted the Werner point of view on the distribution of affinity and on the facilitation of reaction by the formation of an intermediate complex (Kekulé) at an atom having components of free affinity. He maintained that chemical reactivity in a constant thermodynamic environment is determined by three different factors: (1) The "quantitative factor," which measures the amount of residual affinity available; (2) the "polar factor," which catalogues the affinity as to kind; (3) the "steric factor," which takes into account influences due to steric hindrance. His quantitative factor is strongly suggestive of Lewis's electron affinity though by no means identical with it. His polar factor was introduced to explain why two atoms having sufficient affinity to combine frequently failed to do so. The failure in such cases was attributed to the circumstance that the two atoms had the same polar nature—only atoms having opposite polar natures and sufficient affinity could

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[17] Flürscheim, *J. prakt. Chem.*, **66**, 321 (1902); **71**, 497 (1905); *Ber.*, **39**, 2016 (1906); *J. prakt. Chem.*, **76**, 185 (1907); *J. Chem. Soc.*, **95**, 718 (1909); **97**, 86 (1910); *Chem. and Ind.*, **44**, 246 (1925).

combine. He maintained that his "polar factor" could not be explained by any concept as simple as positive and negative electrostatic charges. The future substantiated this claim. We now clearly see that his "polar factor" is conditioned by one type of atom having unshared electrons and another having room for them in its valence shell.

The Contributions of Julius Stieglitz

Julius Stieglitz was among the foremost pioneers in applying the electron theory to organic chemistry. Apparently he attempted, with a certain amount of success, to apply the dualistic electrochemical theory to organic chemistry before the turn of the century. As contemporary concepts changed and the Thomson and Lewis theories successively enjoyed favor, he found it easy to retranslate his own concepts. He adopted such features of the theories of Abegg, Falk and Nelson, Fry, and W. A. Noyes as appealed to him and, uniting them with his own ideas, developed a course of lectures, delivered at the University of Chicago, which correlated practically the whole field of organic chemistry in terms of electrochemical concepts.

G. N. Lewis at first held that all covalent linkages are nonpolar. This idea clashed with the basic notions upon which Stieglitz had erected his electrochemical philosophy, and he at once appeared in the role of defender of the concept of polarity in un-ionized linkages. So convincingly did he marshal his evidence[18] that we feel safe in saying that he established the validity of the concept upon purely chemical evidence before the advent of Debye's evidence based on measurements of dielectric constants.[19] This statement needs one qualification, however, which Stieglitz did not fail to make clear. The chemical evidence did not prove that such molecules as ethyl iodide have polar linkages in the resting state. But since ethyl iodide hydrolyzes to give ethyl alcohol, never ethane, one could not escape the conclusion that at least in the activated state the binding electron pair is more closely associated with the iodine than the carbon atom; and since the molecule is predisposed to activation in a given direction it seemed highly probable that polarity exists in unactivated molecules and gives direction to the activation process.

This distinction, however, seemed to have no bearing on the practical application of the theory at that time. Certain it was that all organic molecules reacted as though they had polar linkages. Thus in the hydrolysis of Grignard compounds

$$CH_3{}^{-+}MgBr + H^{+-}OH \rightarrow CH_3{}^{-+}H + H\overset{-}{O}\overset{+}{M}gBr$$

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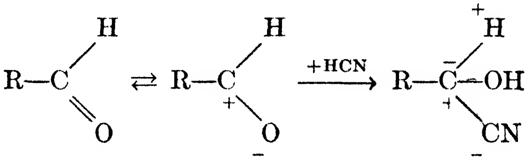
[18] Stieglitz, (a) *Proc. Nat. Acad. Sci.*, **1**, 196 (1915); (b) *J. Am. Chem. Soc.*, **44**, 1293 (1922).

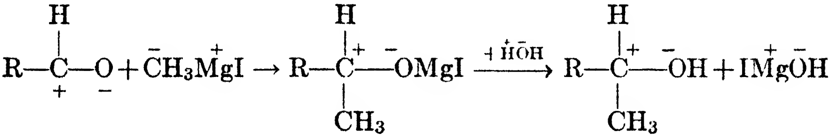
[19] *See* Appendix III.

we would expect the alkyl group to be negative to the magnesium atom and as a result the hydrolysis should and does yield the hydrocarbon in striking contrast to the hydrolysis of alkyl halides where the alkyl group is positive.

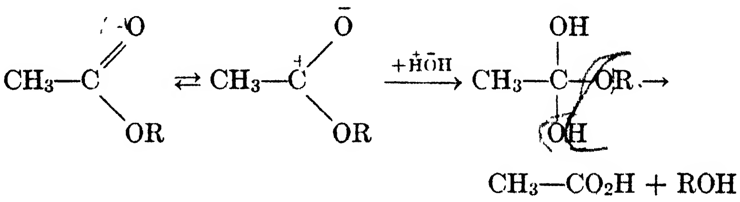
In reactions involving the carbonyl group he considered activation to consist in the opening of the double bond, which always resulted in a positive carbon atom and a negative oxygen atom, thus:



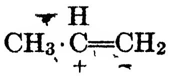
Similarly we have



$$R-\overset{H}{\underset{+}{C}}-\underset{-}{O}+\overset{-}{C}H_3\overset{+}{Mg}I \rightarrow R-\overset{H}{\underset{CH_3}{\overset{+}{C}}}-\overset{-}{O}MgI \xrightarrow{+\overset{+}{H}\overset{-}{O}H} R-\overset{H}{\underset{CH_3}{\overset{+}{C}}}-\overset{-}{O}H+I\overset{+}{Mg}\overset{-}{O}H$$



The addition reactions of olefins also indicate that polar influences are at work. Thus propylene adds halogen hydrides in such a way that the halogen goes preponderantly to the central carbon atom, indicating that polarity in the propylene double bond is as follows:



$$CH_3\cdot\overset{H}{\underset{+}{C}}=\underset{-}{C}H_2$$

Now Stieglitz had previously demonstrated, as was explained in the early part of this chapter, that the chlorine atom in hypochlorous acid is "positive," and hence the fact that it added to propylene to give $CH_3\cdot CHOH\cdot CH_2Cl$ served as a brilliant verification of the polar formula given above.

The fact that two isomers are usually formed in olefin addition reactions he explained on the basis of Fry's theory of electromerism. Thus in addition to the chief electromer pictured above, a small amount of another electromer, $CH_3\cdot\overset{-}{C}H{=}\overset{+}{C}H_2$, also exists. Electromerism may also exist in the addenda. For example, Falk and Nelson[20] had suggested that electromerism was the most likely explanation of the proved existence of two isomeric forms of bromine chloride, $\overset{+}{Br}\overset{-}{Cl}$ and $\overset{-}{Br}\overset{+}{Cl}$. Here the two atoms do not differ widely in their electron affinities and hence there should be very appreciable amounts of each electromer in the equilibrium mixture. We should expect, then, as we actually find, that when bromine chloride is added to propylene we get mixtures of the two isomers $CH_3\cdot CHCl\cdot CH_2Br$ and $CH_3\cdot CHBr\cdot CH_2Cl$ in very fair proportions.

Perhaps the most outstanding feature of the school of thought championed by Stieglitz was this: the details of organic chemistry can be satisfactorily correlated in electrochemical terms if we recognize that the type of reactivity exhibited by any particular atom or group is regulated in a consistent way by its state of electron possession or, as Abegg would have called it, its "polar character." Hence all the reactions of alkyl halides are consistent with the formula $\overset{+}{R}\overset{-}{X}$ and the negative halogen atom is always replaced by other negative groups (unless RX is first acted upon by a reducing agent, which would render the alkyl group negative) as exemplified in reaction with water, alkalies, ammonia, amines, sulfides, and alcoholates.[21] Yet in compounds in which we can demonstrate the presence of "positive halogens" the properties are entirely different. Thus if we grant that Stieglitz had satisfactorily demonstrated the presence of positive chlorine in hypochlorous acid it follows that the chlorine atom in chlorimidoketones must also be positive:[22]

$$R_2C{=}\overset{-}{N}\overset{+}{H} + H\overset{-}{O}\overset{+}{Cl} \rightleftarrows R_2C{=}\overset{-}{N}\overset{+}{Cl} + \overset{+}{H}\overset{-}{O}H$$

A priori it would seem possible that after the positive chlorine had replaced the positive hydrogen atom it would pull the binding electrons over to itself, becoming negative. However, upon hydrolysis the chlorimidoketone regenerates the hypochlorous acid, proving, according to Stieglitz, that the chlorine must have remained in the positive condition. No reactions are known in which the chlorine atom in a chloromidoketone is replaced by a negative group; and it shows the customary

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[20] Falk and Nelson, *J. Am. Chem. Soc.*, **32**, 1637 (1910).

[21] Stieglitz, *ibid.*, **44**, 1306 (1922).

[22] Stieglitz and Peterson, *Ber.*, **43**, 782 (1910).

oxidizing power, diagnostic of positive halogens, in liberating iodine from hydriodic acid.

Similarly the formula $H\overset{+}{O}\overset{-}{N}H_2$ "expresses perfectly the actual behavior of hydroxylamine and its derivatives . . . [and] its positive hydroxyl group is not directly replaceable by Cl^-, Br^-, etc., as is the case for the hydroxyl group of bases, of alcohols, . . . of acids, etc." [23]

Stieglitz is chiefly famous for his extensive work on molecular rearrangements which he attempted, with considerable success, to explain in terms of the electron theory. In this task he was particularly aided by the independent research of his ex-student L. W. Jones. Space cannot be spared in this volume for an adequate discussion of this phase of his work. Suffice it to say that he showed that molecular rearrangements are very apt to occur when a molecule contains oxygen, nitrogen, or halogen atoms in the "positive" condition. The tendency of these atoms to attain their more stable negative states was considered to be the driving force in the rearrangements.

Stieglitz adopted the concept of oxidation held by Falk and Nelson, notwithstanding the fact that whereas those investigators considered electron transfer to be complete in such cases as the chlorination of hydrocarbons, it had since become evident that the electrons are only partially transferred and covalent linkages are formed. This point will be discussed in detail in Chapter IV.

Stieglitz developed an electronic theory to explain orientation in benzene substitution reactions. Since this theory is no longer in favor, I will not attempt the lengthy discussion its explanation would entail.

Electronegativity and Polar Character

No little confusion is inherent in the use of the pair of words "negative" and "positive" for two different meanings. Thus the chlorine atom in hypochlorous acid is said to be positive in the sense that it has a slight deficiency of electrons. Yet we say that this same chlorine atom is strongly oxidizing because chlorine is a negative element, this time meaning that it has a high affinity for electrons. Logical as it would seem to distinguish the second concept by speaking of high or low electron affinity, this term has become well established in recent years as meaning the thermodynamic affinity of a neutral atom for an electron. Thus the equilibrium constant of the reaction $Cl + e \rightarrow Cl^-$ measures the electron affinity of chlorine. It has also become conventional to speak of the electron-attracting powers of an atom *in a molecule* as electronegativity. Thus in methyl chloride the chlorine atom has high and the hydrogen low electronegativity.

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[23] Ref. 21, p. 1307.

In order to avoid the confusion inherent in the double meanings of "negative" and "positive" it would be well to use the terminology indicated in the following table.

TABLE I

Old terms	New terms	
	Electronegativity	Polar character
Negative	High electronegativity	Electron-rich
Positive	Low electronegativity	Electron-poor

Thus in the new terminology we would say that the chlorine atom in HOCl is electron-poor and has high low electronegativity.

Theories of Alternating Polarity

One difficulty in applying the electronic principles developed by this group of American chemists becomes evident when we try to predict how addenda will become oriented upon reaction with various olefins. It is easy enough to see that the carbon atom in a carbonyl group is electron-poor since it has a lower electronegativity than oxygen, but in unsymmetrical olefins no method was available for predicting, in advance of one trial, what the polar character of the doubly bound carbon atoms would be. In an unsuccessful attempt to solve this problem, Cuy devised his theory of alternating polarity.[24]

The theory was based on the observation that certain properties, such as melting points, boiling points, densities, molecular volumes, and viscosities, seemed to be an alternating function of the number of carbon atoms in any homologous series, i.e., if the melting points, for example, were plotted against the number of carbon atoms the curve would have a saw-tooth appearance. He assumed that these properties are directly related to the polarity of the constituent atoms and that the carbon atoms will tend to become polarized alternately positively and negatively. Thus, if we start at one end of a carbon chain with a methyl group, the carbon atom will be electron-rich in regard to the three valences connected with the hydrogen atoms and hence will be predominantly "negative." Having thus established the predominant polar character of one atom, alternating signs can be assigned to the remaining carbon atoms of the chain. Thus in propylene we have

$$\mathrm{H_3\overset{-}{C}{-}\overset{+}{C}H{=}\overset{-}{C}H_2}$$

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[24] Cuy, *J. Am. Chem. Soc.*, **42**, 503 (1920).

which is the polar structure we previously assigned to it on the basis of experiment.

Cuy's idea of an alternating effect was not completely original with him. Many years before, Flürscheim [17] had put forward a theory of "alternating affinity demand." Cuy's theory, however, was based completely on electrostatic considerations, whereas Flürscheim's was not. Fry [25] previously had also postulated an alternate polarity and Lapworth [26] proposed a theory of alternating polarity in the same year that Cuy's paper was published. The idea was soon extended by Kermack and Robinson [27] and by Stieglitz.[18b] It would profit us but little to pursue further the similarities and differences of these theories of alternating polarity. Suffice it to say that they were eventually shown to be wrong,[28] at least in regard to saturated molecules. Cuy's theory is of interest chiefly as an attempt to answer the puzzling question as to how we may determine the polar character of doubly bound carbon atoms without recourse to addition experiments.

The Lewis-Lucas Electron Displacement Theory

A most fruitful suggestion was advanced by Lewis to explain the relative strengths of acids and bases. Falk had already suggested, as we have seen, that the increase in the strength of acetic acid accompanying the substitution of an α-hydrogen atom by chlorine is connected with the corresponding change in polarity of the α-carbon atom. Lewis furthered the idea by suggesting that the substitution is accompanied by a general displacement of electrons throughout the molecule toward the entering chlorine atom because it has a higher electronegativity than hydrogen and thus draws the binding electron pair closer to itself.[29] This pair of electrons, therefore, exercises a smaller repulsion on the other electrons of the carbon atom and they accordingly move closer to the carbon nucleus. The argument may be repeated for the electrons of the C—O and the O—H linkages, with the final result that the O—H bond becomes more polar and hence ionizes more readily. The idea was later amplified somewhat by Lucas.[30] It is now customary to say that the substitution of an electronegative atom or group decreases the

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[25] Fry, *Z. physik. Chem.*, **76**, 385 (1911). Presented before the Cincinnati section of the Am. Chem. Soc. in January 1908.

[26] Lapworth, *Mem. Manchester Phil. Soc.*, **64**, No. 3 (1920).

[27] Kermack and Robinson, *ibid.*, **121**, 427 (1922).

[28] (*a*) Lucas, *J. Am. Chem. Soc.*, **46**, 2475 (1924); (*b*) Ingold, *J. Chem. Soc.*, **127**, 513 (1925).

[29] Lewis, *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Co., N. Y. (1923), pp. 85 and 139.

[30] Lucas, *J. Am. Chem. Soc.*, **48**, 1827 (1926).

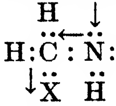
screening effect[31] of the binding electron pair which is initially displaced and that the relaying of the effect down the chain is due to successive alterations of the screening effects of all electrons concerned The screening effect is easily understood when we realize that the effective nuclear charge of an atomic nucleus is less for the outer "shells" of electrons than for the inner ones. This is partly due to the increased distance and partly to the repulsive effect of the inner shells of electrons on those farther out. This repulsive effect makes the inner electrons act as a screen between the nucleus and the outer electrons and accordingly is called the screening effect. Even the valence electrons exert some repulsive effect on each other and thus contribute to the screening effect, although they are less effective than the electrons in the inner shells.

There are three obvious consequences of this postulate. The first is that the effect should die out rather rapidly as it is propagated along a chain of atoms since, in general, the lessened screening effect produced by pulling one electron pair away from the nucleus is compensated by the inward movement of three pairs. Thus a halogen atom would have the greatest effect when substituted in the *alpha* position to the carbonyl group, less in the *beta*, etc. This prediction is readily borne out by the data in Table II.

TABLE II[32]

IONIZATION CONSTANTS OF ACIDS AT 25°

α-Chlorobutyric acid	1.45×10^{-3}
β-Chlorobutyric acid	8.8×10^{-5}
n-Butyric acid	1.50×10^{-5}

The second consequence is that, if a hydrogen atom of an acid is replaced by a group of lower electronegativity than hydrogen, a process of electron release will give rise to a displacement opposite to that given above and the substituted acid will be weaker. The third consequence of the postulate is that a given electron displacement will have opposite effects on the strengths of acids and bases because an electron-attracting group increases the pull on the unshared electrons of bases, like  $\begin{array}{c} \text{H} \quad \downarrow \\ \text{H}:\ddot{\text{C}}\overset{\longleftarrow}{:}\ddot{\text{N}}:\text{H}, \\ \downarrow\ddot{\text{X}} \quad \ddot{\text{H}} \end{array}$ and thus decreases their availability for coordination purposes in salt formation. This means that the base will be weaker, whereas the same substituent would have made an acid stronger.

It should be at once apparent that measurements of the strengths of a series of substituted acids or bases would give us a measure of the rela-

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[31] Sommerfeld, *Atomic Structure and Spectral Lines*, translated by Brose, E. P. Dutton & Co., 1923, p. 7[illegible].

[32] *International Critical Tables*, VI, 266, 267.

tive electronegativities of the substituent atoms or groups. The problem is complicated, however, as Lewis clearly foresaw, by the fact that electrical influences need not be transmitted solely along atomic chains but may also operate directly across space. Thus if the electronegativities of constituent atoms were the only factors involved, fumaric and maleic acids should be equally strong. The fact that they are not is generally interpreted as meaning that their steric differences result in different amounts of electrical influence operating directly through space between the two carboxyl groups. This effect has since become known as the field effect, whereas the electron displacement propagated along atomic chains is now called the normal inductive effect.

Lucas[33] called upon this concept to explain why a hydroxyl group increased the strength of acetic acid, whereas it decreased the strength of benzoic acid when substituted in the *para* position where the field effect should be absent or at least minimized. We shall see later that he erred in his interpretation. However, he considered that to get a true measure of the relative electronegativities of groups, these groups should be substituted into the *para* position of benzoic acid. Thus he offered the following table of relative electronegativities:[34] $NO_2 > CN > SO_2NH_2 > CO_2H > Cl > Br > H > NHCOCH_3 > OEt > Me > OCOMe > OMe > OH > NH_2 > NHMe > NMe_2$.

Despite the anomaly encountered in hydroxyacetic acid, the fact is that the above substituents have a remarkably consistent effect in altering the strengths of acids and bases, even in such different types as phenols and carboxylic acids. Therefore we are reasonably safe in extending Lucas's series somewhat by the inclusion of groups whose electronegativities have been determined by their substitution in acetic acid, and we may add the sequence F > Cl > Br > α-naphthyl > Ph > H.

There are certain inconsistencies in the Lucas theory. Chief among them is the placement of OH, NH_2, etc., below H. It is difficult to see how, on the basis of the electron displacement principle, a union of the two would be less electronegative than either one alone. Also the theory would predict that benzoic acid should be stronger than formic acid, whereas in reality the reverse is true.

The chief feature of the Lucas theory, however, is its application to the problem of orientation in olefin addition reactions.[35] The application can be simply illustrated by considering propylene. The groups attached to the two unsaturated carbon atoms differ in one respect only, viz., that a CH_3 group on one side stands in opposition to a H atom on the other. Since the electronegativity of hydrogen is higher than that of the

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[33] Ref. 30, p. 1831.

[34] Lucas, Ref. 30, p. 1832, and *ibid.*, **51**, 2718 (1929).

[35] Lucas, *idem*, **47**, 1459 (1925); also Ref. 28.

methyl group there will be a net displacement of electrons in a direction away from the methyl group. This gives the following polarity: $\mathrm{Me{-}\overset{+}{CH}{=}\overset{-}{CH_2}}$, which will direct the course of the addition reaction.

The data on orientation in olefin addition reactions which were existent in 1931 were reviewed by Kharasch.[36] He reported that many of the data were contradictory and needed reinvestigation. This task he undertook in collaboration with his students. During the course of these investigations [37] they discovered the now famous "peroxide effect." They showed that certain olefins formed peroxides on contact with air while others did not. In any case, when peroxides were present, whether they were formed spontaneously or were deliberately added, they exerted a powerful catalytic effect in that the orientation of the addenda was the reverse of that observed in the peroxide-free reaction. Thus they found, for example, that allyl bromide and vinyl bromide formed peroxides in contact with air and their addition reactions took place as follows:

Peroxides absent: $\mathrm{BrCH_2CH{=}CH_2 + HBr \rightarrow BrCH_2{\cdot}CHBr{\cdot}CH_3}$ (70–80%)

Peroxides present: $\mathrm{BrCH_2CH{=}CH_2 + HBr \rightarrow BrCH_2{\cdot}CH_2{\cdot}CH_2Br}$ (70–80%)

Peroxides absent: $\mathrm{BrCH{=}CH_2 + HBr \rightarrow Br_2CH{\cdot}CH_3}$ (100%)

Peroxides present: $\mathrm{BrCH{=}CH_2 + HBr \rightarrow BrCH_2{\cdot}CH_2Br}$ (100%)

Propylene does not form peroxides by contact with air. However, if benzoyl peroxide is present during its reaction with hydrogen bromide the reaction product is largely, if not entirely, *n*-propyl bromide.

They found also that if a strong reducing agent was present peroxides were destroyed and "normal addition" ensued. Hydrogen iodide and hydrogen chloride were found always to give normal addition, even in the presence of added peroxides.

Now that many olefin addition reactions have been reinvestigated under peroxide-free conditions, we can say that the Lucas theory gives for the most part correct predictions. Three exceptions have been found, however.[38] Their "normal" reactions are given below.

$$\mathrm{CH_2{=}CHBr + HBr \rightarrow CH_3CHBr_2}$$

$$\mathrm{BrCH_2{\cdot}CH{=}CH_2 + HBr \rightarrow BrCH_2{\cdot}CHBr{\cdot}CH_3}$$

$$\mathrm{Ph{\cdot}CH{=}CH_2 + HBr \rightarrow Ph{\cdot}CHBr{\cdot}CH_3}$$

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[36] Kharasch, *J. Chem. Education*, **8**, 1725 (1931).

[37] For a review of this subject see Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

[38] (*a*) Kharasch, McNab, and Mayo, *J. Am. Chem. Soc.*, **55**, 2521, 2531 (1933); (*b*) Kharasch and Mayo, *ibid.*, **55**, 2468 (1933); (*c*) Walling, Kharasch, and Mayo, *ibid.*, **61**, 2693 (1939).

There is another apparent exception which, however, has not been investigated under peroxide-free conditions, viz., $CH_2{=}C{=}O + HOH \rightarrow CH_3CO_2H$.

Lucas also extended his theory to include substitution reactions of saturated hydrocarbons and orientation in benzene substitution. In this latter phase of his theory he succeeded remarkably well in correlating orientation with activating and deactivating influences of substituents. Substituents which are more negative than hydrogen cause deactivation relative to benzene itself because the electrons are more firmly held and hence less easily attacked by halogens, sulfuric acid, or nitric acid, all of which are oxidizing (electron-seeking) reagents. Substituents which are less electronegative than hydrogen have, conversely, an activating effect since they are electron releasing. This phase of the Lucas theory has been retained in all the later theories of benzene substitution.

In regard to the problem of orientation in aromatic substitution reactions he took as an additional premise to his theory the empirical relationship that the order in which the inductive effect is transmitted from different positions of the benzene ring is $p > o \gg m$. The fact that he chose to picture this effect in terms of an outmoded benzene model suggested by Pauling need not detract from the real value of his contribution. On the basis of his theory, if a group less electronegative than hydrogen is substituted into the benzene ring, it would activate the *para* position most and the *meta* least. Thus it would be an *ortho-para* orienting substituent. If, on the other hand, it was more negative than hydrogen it would deactivate the *meta* position least and hence *meta* substitution would preponderate. The halogens, although they acted as deactivating substituents, caused *ortho-para* orientation and hence formed an obvious exception to the simple theory. He was therefore forced to bolster up his theory by the additional assumption that if the atom directly connected to a benzene carbon atom had unshared electrons *ortho-para* orientation occurred regardless of its electronegativity. He attempted unsuccessfully to explain this phenomenon; however, it proved to be a fruitful suggestion and was developed later by the English school, whose extensions of the electronic theories of the early American school we will consider in Chapter V.

CHAPTER III

APPLICATIONS OF THE LEWIS THEORY TO PROBLEMS OF MOLECULAR STRUCTURE

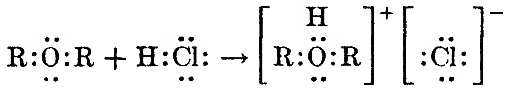
COORDINATION PHENOMENA

"Onium" Compounds

The Lewis theory was the first one to account satisfactorily for the three types of valence recognized in the nineteenth century, viz., ionizable valences and the two types of nonionizable valences: primary and secondary. The first step toward the solution of the problem of secondary valence in general in terms of an electronic theory was made by Huggins[1] when he suggested that atoms having unshared electrons could share them with other atoms or ions having incomplete octets. A few familiar examples of this phenomenon, as it is exhibited in the structures of ammonium chloride and sulfuric acid, are given in Appendix I to this volume. They are no doubt familiar to the average student. A few important applications of the same principle to organic chemistry may, however, consume our attention profitably for a few pages.

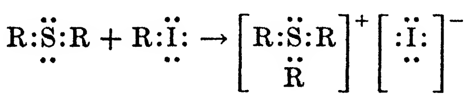
In addition to ammonium compounds there are known several other types of "onium" compounds in which atoms other than nitrogen are responsible for salt formation in virtue of their possession of unshared electrons. Thus iodonium, oxonium, selenonium, telluronium, phosphonium, arsonium, and stibonium compounds are known.

Ethers, when treated with concentrated hydrochloric acid, yield oxonium compounds.



$$\mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{R} + \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow \left[\begin{matrix}\mathrm{H}\\ \mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{R}\end{matrix}\right]^{+}\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\right]^{-}$$

Similarly we have sulfonium compounds.



$$\mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{R} + \mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}: \rightarrow \left[\begin{matrix}\mathrm{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{R}\\ \mathrm{R}\end{matrix}\right]^{+}\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:\right]^{-}$$

The electronic formulation of the other "onium" compounds is deduced in exactly the same way—the atom with the unshared electrons "co-

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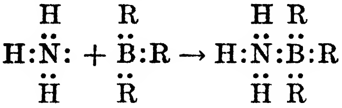
[1] M. L. Huggins: (*a*) undergraduate thesis, University of California, 1919; (*b*) *Science*, **55**, 459 (1922); (*c*) *J. Phys. Chem.*, **26**, 601 (1922).

ordinates" with a positive ion, i.e., shares a pair of its previously unshared electrons with the ion.

Instead of coordinating with ions the atoms bearing the unshared electrons may, of course, coordinate with neutral atoms (as in sulfur dioxide becoming sulfur trioxide) or with neutral molecules containing an atom with an incomplete valence shell, e.g.,



$$\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{N}}}}}: + \underset{\mathrm{R}}{\overset{\mathrm{R}}{\ddot{\underset{\cdot\cdot}{\mathrm{B}}}}}:\mathrm{R} \rightarrow \mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{N}}}}}:\underset{\mathrm{R}}{\overset{\mathrm{R}}{\ddot{\underset{\cdot\cdot}{\mathrm{B}}}}}:\mathrm{R}$$

In such cases the final result is significantly different from the onium compound formation for the coordinate bond is highly polar. The following considerations will make clear the theory involved.

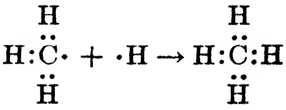
Semi-Ionic Bonds

It has been pointed out by Sidgwick[2] that covalences may be formed in two different ways. If each of the two atoms to be bound together furnishes one electron to the linkage, he calls it "normal covalency"; if, on the other hand, one of them (the "donor") furnishes two electrons and the other (the "acceptor") none, then he calls it "coordinate covalency."

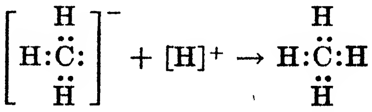
$\mathrm{A}\cdot + \cdot\mathrm{B} \rightarrow \mathrm{A}:\mathrm{B}$ normal covalency

$\mathrm{A}: + \mathrm{B} \rightarrow \mathrm{A}:\mathrm{B}$ coordinate covalency

On first thought one might be inclined to think that the manner in which the linkage is formed is a matter of no consequence since the final states would be indistinguishable. This is true, with certain qualifications. Thus as far as the final state is concerned it makes no difference whether we consider methane to be formed by the first or the second of the following methods:



$$\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\cdot + \cdot\mathrm{H} \rightarrow \mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$$



$$\left[\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}:\right]^- + [\mathrm{H}]^+ \rightarrow \mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$$

But the compound AB in the following illustration would have different properties depending upon whether it could properly be considered to have been formed according to Equation 1 or 2:

$$[\mathrm{A}:]^- + [\mathrm{B}]^+ \rightarrow \mathrm{A}:\mathrm{B} \tag{1}$$

$$\mathrm{A}: \quad + \mathrm{B} \quad \rightarrow \mathrm{A}:\mathrm{B} \tag{2}$$

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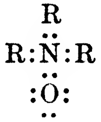
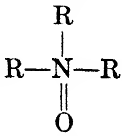
[2] Sidgwick, *The Electronic Theory of Valency*, Oxford Press, 1927, p. 60.

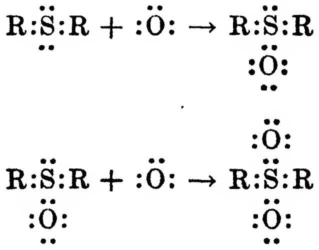
In the first case A^- would lose a half share in two electrons and B^+ would gain equally, thus neutralizing the charges on the two kernels except in so far as a slight polarity of the bond might result in slight residual charges on them. In the second case similar considerations make it appear that in the final state A would bear one (or almost one) unit of positive charge while B would bear an equal negative charge. Each is said to bear a formal charge of one unit regardless of whether or not unequal electron affinities of the two atoms result in a charge slightly less than unity. In this case A would be bound to B not only by a covalent but also by an electrovalent "linkage." This was first recognized by Lowry,[3] and such a "linkage" was called by him a "mixed double bond." Sugden[4] calls it a "semipolar double bond," while Noyes[5] has pointed out certain objections to the above names and prefers to use instead the term "semi-ionic bond."

Such a bond must exist in the addition compounds of ammonia and boron trialkyls mentioned above. Other examples from the field of organic chemistry follow. (1) Amine oxides, formed by the action of hydrogen peroxide on tertiary amines:



$$\begin{array}{c} R \\ R:\ddot{N}:R \\ :\underset{\cdot\cdot}{\ddot{O}}: \end{array}$$

It is worthy of note in passing that according to the classical valence theory the amine oxide would have been written as  $\begin{array}{c} R \\ | \\ R\text{—}N\text{—}R \\ \| \\ O \end{array}$, indicating a double bond where no property of the substance would justify its inclusion. (2) Sulfoxides and sulfones:



$$\begin{array}{l} R:\underset{\cdot\cdot}{\ddot{S}}:R + :\ddot{O}: \rightarrow \begin{array}{c} R:\ddot{S}:R \\ :\underset{\cdot\cdot}{\ddot{O}}: \end{array} \\ \\ \begin{array}{c} R:\ddot{S}:R \\ :\underset{\cdot\cdot}{\ddot{O}}: \end{array} + :\ddot{O}: \rightarrow \begin{array}{c} :\ddot{O}: \\ R:\ddot{S}:R \\ :\underset{\cdot\cdot}{\ddot{O}}: \end{array} \end{array}$$

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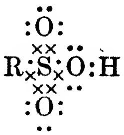
[3] Lowry, *J. Chem. Soc.*, **123**, 822 (1923); *Trans. Faraday Soc.*, **18**, 285 (1933); **19**, 488 (1933).

[4] Sugden, *J. Chem. Soc.*, **127**, 1527 (1925).

[5] W. A. Noyes, *J. Am. Chem. Soc.*, **55**, 4890 (1933).

The sulfur atom in the sulfoxide bears a unit formal positive charge, whereas that in the sulfone bears two units. (3) Sulfonic acids:



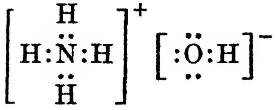
$$\begin{array}{c} :\overset{\cdot\cdot}{\text{O}}: \\ \text{R}{}^{\times}_{\times}\overset{\times\times}{\underset{\times\times}{\text{S}}}{}^{\times}_{\times}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\text{:H} \\ :\underset{\cdot\cdot}{\text{O}}: \end{array}$$

In this formula the six electrons initially belonging to the neutral sulfur atom are indicated by crosses. It will be observed that the linkages with R and OH are normal covalences, whereas the other two are coordinate covalences; hence the sulfur atom bears a positive formal charge of two units.

The concept of the semi-ionic link, born of theoretical necessity, has enjoyed a little supporting evidence, chiefly from determinations of parachors, a subject which will be treated in a later section of this chapter, but to some extent also from dipole moment measurements. It has been shown [6] that the "bond moments" of normal single covalent bonds between nonmetallic elements range from 0 to 1.56 *D*, whereas coordinate covalences have values occurring approximately in the range 2.4 to 3.5 *D*. Normal covalent double and triple bonds have values in the same range as the coordinate linkages, but since the parachor measurements show clearly that coordinate covalences are not double bonds their high dipole moments can best be explained by the Lowry theory discussed above, which insists that the respective donor and acceptor functions of the two atoms linked together would give rise to considerable charge separation and hence to large dipole moments.

Hydrogen Bonds

We could build up the electronic formulas for ammonium hydroxide and its alkyl derivatives exactly as was done for ammonium chloride, giving formulas such as



$$\left[\begin{array}{c} \text{H} \\ \text{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:\text{H} \\ \text{H} \end{array}\right]^{+} \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:\text{H}\right]^{-}$$

but in doing so we at once recognize that the electrovalent union of the two ions would demand that these bases be strong electrolytes, whereas actually they are all weak except the quaternary bases. There is certainly nothing in the electronic formulas to suggest the abrupt transition which we observe between the tertiary and the quaternary bases. This was at first explained by the assumption that the equilibrium point in

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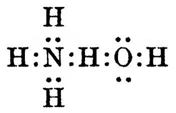
[6] C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).

the hydration of the "anhydro bases," e.g., $R_3N + H_2O \rightleftarrows [R_3NH]^+[OH]^-$, lies far to the left. Then, since an anhydro base corresponding to the tetra-alkylammonium hydroxide is impossible, this would constitute the unique case and would be a strong electrolyte.

Strangely enough, the requisite data for disproving this interpretation had been in existence for years. Moore and Winmill [7] had made measurements on the conductivity of solutions of these ammonium bases and also their partition coefficients between water and an immiscible solvent at several temperatures and were able to calculate therefrom the true dissociation constants. This work showed that all of them are really weak bases except the quaternary base, which is a genuinely strong electrolyte. Sidgewick [8] has pointed out that this work disproves the above interpretation. In seeking a new explanation he says: "If we accept the view that a weak electrolyte exists in solution largely in a covalent form, ammonium bases like $(NR_3H)OH$ must be able to pass over into such a form; but the change must involve a hydrogen attached to the nitrogen, since the base remains weak so long as one such hydrogen is present but becomes strong (i.e., the covalent form vanishes) as soon as the last hydrogen is replaced. This can only mean that the hydroxyl forms a covalent (coordinate) link with this hydrogen."

This suggestion was originally made by Latimer and Rodebush.[9a] The idea necessitates the following formula for the un-ionized base:



$$\begin{array}{ccccccccc} & & H & & & & & & \\ H & : & \underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} & : & H & : & \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} & : & H \\ & & H & & & & & & \end{array}$$

A similar explanation seems necessary for H_2F_2, which may be written as $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$. In such compounds one proton serves to bind together two larger units and accordingly it has come to be called a "hydrogen bond." Hydrogen fluoride apparently forms six-fold polymers in the gaseous state,[9b] showing how strong hydrogen bonds may become.

Hildebrand [9c] has pointed out that although Latimer and Rodebush [9a] deserve credit for being the first to recognize the hydrogen bond as a general phenomenon, certain coordination formulas of Werner suggest that the idea was vaguely forming in his mind many years before and Pfeiffer [9d] had actually suggested in 1913 that hydrogen in *o*-hydroxy-

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[7] Moore and Winmill, *J. Chem. Soc.*, **91**, 1373 (1907); **101**, 1635 (1912).

[8] *The Electronic Theory of Valency*, Oxford Press, 1927, p. 97.

[9] (*a*) Latimer and Rodebush, *J. Am. Chem. Soc.*, **42**, 1419 (1920); (*b*) Simons and Hildebrand, *ibid.*, **46**, 2183 (1924); (c) Hildebrand, *Science*, **83**, 21 (1936); (*d*) Pfeiffer, *Ann.*, **398**, 137 (1913).

anthraquinone is "coordinately" bound to the oxygen of the carbonyl group.

In the years that have followed the paper by Latimer and Rodebush, much evidence has been accumulated in favor of the hydrogen bond or the "hydrogen bridge," as it is sometimes called.[10a] The lattice structure attributed to ice [10b] places hydrogen atoms on lines joining pairs of oxygen atoms. Similar evidence exists for methanol.[10c] Hildebrand [9c] has also lined up a quantity of evidence from solubility relationships. The data in Table I will serve to illustrate the point. Solubility requires strong attractions between the solute and solvent molecules. The two most likely sources of such attraction are the mutual electrostatic attraction of molecular dipoles * and chemical coordinative forces such as involved in the formation of hydrogen bonds. If now the first four liquids in Table I are considered, it is evident that, if solubility depends primarily on dipole attraction, nitrobenzene with its high dipole moment, should be the most soluble. However, it is seen to be only three times as soluble as the nonpolar benzene, whereas phenol, with a low dipole moment, is 137 times as soluble. Since the nonpolar parts of these four molecules must be nearly identical, it seems reasonable to ascribe the higher solubilities of aniline and phenol to hydrogen bond formation involving the oxygen atom of water as donor and the hydrogen atoms attached respectively to the nitrogen and oxygen of aniline and phenol

TABLE I [9c]

SOLUBILITY OF LIQUIDS IN WATER AT 20°

	Solubility (%)	Dipole moment $\mu \times 10^{18}$
Benzene	0.06	0
Nitrobenzene	0.19	4.19
Aniline	3.49	1.51
Phenol	8.2	1.70
Ethyl iodide	0.40	1.66
Ethanol	∞	1.70
Propyl chloride	0.27	2.0
Propyl iodide	0.11	1.6
Propanol	∞	1.7
Water	....	1.85

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[10] (*a*) Huggins, *J. Org. Chem.*, **1**, 407 (1936); (*b*) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); (*c*) Warren, *Phys. Rev.*, **44**, 969 (1933).

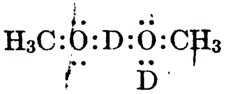
* For an explanation of dipole moments see Appendix III.

as acceptors. A similar argument would apply to the remaining groups of compounds in Table I. Hildebrand also points out that hydrogen bond formation offers a satisfactory explanation for similar trends found when deviations from Raoult's law or deviations from linearity of molar polarization-concentration relationships in solution are considered.

Further evidence of the existence of hydrogen bonds has been given by X-ray studies,[11] electron diffraction investigations,[12] and infrared spectroscopic methods.[13, 14] Much of this evidence can be more effectively discussed under the heading of chelate rings, but we may discuss a portion of the infrared spectroscopic work at this time.

Infrared absorption spectra are due in part to the vibrations of atoms in molecules. It has been found by comparing the spectra of similar molecules that definite linkages have characteristic vibration frequencies which are usually altered comparatively little by substitution. One would expect, however, that if a hydrogen atom attached, for example, to an oxygen in alcohol became a hydrogen bond, its vibration frequency would become significantly altered, thus giving evidence of its altered state of existence. Such has indeed been found to be the case, the formation of hydrogen bonds shifting the O—H band of water or alcohol to lower frequencies.[15] It happens, however, that the O—H band occurs in a region of the spectrum in which many solvents also absorb, and it has been found convenient, therefore, to work with the O—D band of D_2O or CH_3OD instead,[14] since the O—D fundamental is in the region of 4μ, where few solvents absorb appreciably.

In dilute solutions of CH_3OD in benzene the O—D vibrational band is at 3.73μ, which is very close to that observed in the vapor. In liquid CH_3OD, however, the band shifts to 4.01μ and broadens. This makes it amply clear that something startling has happened to the O—D bond in the process of changing from the vapor to the liquid state. If it is a chemical change, as seems certain, it must be a reversible reaction of the CH_3OD with itself, i.e., association. By analogy to the hydration of ammonia and amines we might reasonably expect that the deuterium atom of one molecule had coordinated with the unshared oxygen electrons of the other to yield



$$H_3C:\overset{..}{\underset{..}{O}}:D:\overset{..}{\underset{\overset{..}{D}}{O}}:CH_3$$

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[11] Zachariasen, *J. Chem. Phys.*, **1**, 634 (1933).

[12] Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

[13] Hilbert, Wulf, Hendricks, and Liddell, *J. Am. Chem. Soc.*, **58**, 548 (1936).

[14] (*a*) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939); (*b*) Gordy and Stanford, *ibid.*, **8**, 170 (1940); **9**, 204 (1941).

[15] See Ref. 14*a* for references.

Since the band was not altered appreciably in passing from the vapor to a dilute benzene solution we must conclude that the hydrogen atoms of benzene are incapable of forming hydrogen bonds. In more concentrated benzene solutions the spectra show association of the CH_3OD. Other solvents were investigated in the same manner, using CH_3OD and D_2O as solutes. Amines were found to have a very pronounced effect on the O—D band. Ethers, aldehydes, ketones, esters, and nitro compounds have similar effects decreasing in the order given. Hydrocarbons have no effect, which accords with the Latimer-Rodebush explanation of the strongly basic character of quaternary ammonium bases, viz., that hydrogen attached to carbon has no tendency to coordinate.

The factors which regulate the stability of hydrogen bonds have not yet been worked out in detail, but it is becoming evident that the more electronegative the atom to which the hydrogen is bound the greater the coordinating tendency of the hydrogen atom. Thus for the elements of the first short period of the Mendeleeff table the tendency for hydrogen bond formation increases in the order[16] $H—C < H—N < H—O < H—F$.

The Lewis-Lucas theory of electron displacement offers a ready explanation of this sequence. When a hydrogen atom is attached to a sufficiently electronegative atom the binding electron pair is pulled toward the latter, leaving the effective nuclear charge of the hydrogen atom relatively high. It is thus better able to act as an electron acceptor. We shall see in a later chapter that this is not the complete explanation, but it appears to be correct as far as it goes. If we pursue the concept farther we cannot fail to see the possibility that even though a hydrocarbon hydrogen atom does not have sufficient electronegativity to form a coordinate covalence, the hydrogen in compounds like $CHCl_3$ might well be able to do so in virtue of the electron affinity induced in both the carbon and hydrogen atoms by the electronegative chlorines. Such, indeed, has been shown to be the case by the solubility studies of Zellhoeffer, Copely, and Marvel,[17] who interpret departures from ideality as being due to association, in many cases most readily interpretable as due to hydrogen bond formation.

Chelate Rings

Another manifestation of coordination is found in compounds in which ring closure has been effected through some coordinating atom, very fre-

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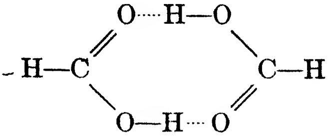
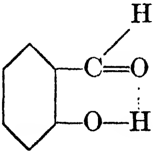
[16] Sidgwick, *The Covalent Link in Chemistry*, Cornell University Press, 1933, pp. 164–165.

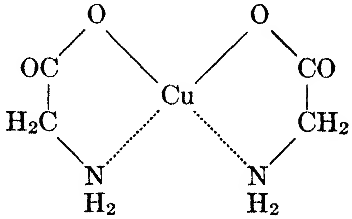
[17] Zellhoeffer, Copely, and Marvel, *J. Am. Chem. Soc.*, **60**, 1337 (1938) and later papers.

quently hydrogen. Such compounds are said to contain "chelate rings," a term introduced in 1920 by Morgan and Drew.[18] For example, Pauling and Brockway [12] showed by electron diffraction studies that the dimer in formic acid vapor has the structure



Other examples of chelate rings are the following:





Evidence for the existence of chelate rings comes from several diverse sources. Lassettre [19] discusses in detail evidence from molecular weight determinations. It was found that in general the molecular weights of organic compounds containing the groups $-NH_2$, $-OH$, $-CO_2H$, $=NOH$, and $=NH$ are abnormally high in nonpolar solvents, such as benzene and carbon tetrachloride, while their molecular weights in such solvents as glacial acetic acid are often found to be normal. This behavior is, of course, due to association, presumably brought about by hydrogen bond formation. It is a matter of great importance to our present thesis that in many cases where *meta* and *para* isomers are polymerized the *ortho* isomers are not. Sidgwick attributes this behavior to the formation in the *ortho* compounds of chelate rings involving as the coordinating atom the hydrogen which would otherwise have produced association by inter-molecular hydrogen bond formation. Thus association is precluded. That chelate ring formation would be possible only in the *ortho* isomer is of course a direct consequence of the proximity of the donor and acceptor groups in *ortho* compounds. Among the compounds whose *ortho*, *meta*, and *para* isomers have been shown to exhibit this relationship are nitrophenol, hydroxybenzaldehyde, methyl hydroxy benzoate, and nitroacetanilide.

This evidence based on polymerization is not, of course, conclusive proof of chelate ring formation, but the fact that a very large number of

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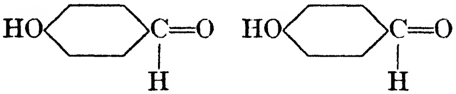
[18] **Morgan and Drew, *J. Chem. Soc.*, 117, 1457 (1920).**

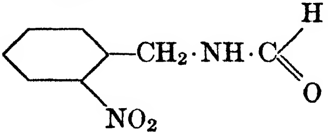
[19] **Lassettre, *Chem. Rev.*, 20, 267 (1937).**

such data are satisfactorily correlated by the hypothesis is a strong indication in favor of its validity. Better evidence is furnished by infrared spectroscopy. Wulf and his collaborators [13] have shown that absorption in the region of the spectrum characteristic of the OH group is absent for dilute CCl_4 solutions of phenols containing as *ortho* substituents groups such as $-COH$, $-COMe$, $-NO_2$, and $CONH_2$ (any one of which could act as electron donor) but is present in the *meta* and *para* isomers. This shows clearly that the hydrogen atom of the hydroxyl group is not present in its customary condition in the *ortho* substituted phenols where the *ortho* substituent is capable of acting as donor. This is interpreted as being due to chelate ring formation involving a hydrogen bond as pictured above for orthohydroxybenzaldehyde. It should be noticed that association of the *meta* and *para* isomers in these dilute solutions would not obliterate the hydroxyl absorption band since one unassociated hydroxyl group would be left intact:

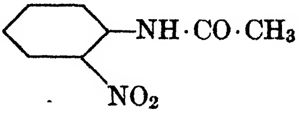


Direct evidence of ring formation in similar compounds is furnished by electron diffraction studies of formic acid, already referred to, and by the demonstration of Mills and Gotts [20] that the beryllium, copper, and zinc derivatives of benzoyl pyruvic acid may be resolved into optically active forms, and this resolution is a consequence of these metallic atoms acting as coordination centers in producing chelate rings.

Studies of the stereochemical properties of chelated compounds [21] show that six-membered chelate rings are somewhat more stable than five-membered rings, which are in turn much more stable than seven-membered rings. Thus the compound



which could only form a seven-membered ring, is not chelated to any large extent while the compound



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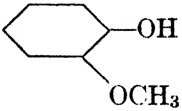
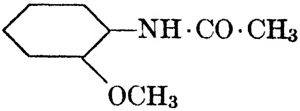
[20] Mills and Gotts, *J. Chem. Soc.*, 3121 (1926).

[21] See Ref. 19; also Wulf and Liddell, *J. Am. Chem. Soc.*, **57**, 1469 (1935).

which forms a six-membered ring, is strongly chelated. The following compounds are weakly chelated (five-membered rings):





The Werner Complexes and Coordination in General

It cannot be said that the Lewis theory has as yet made many significant additions to our knowledge of molecular compounds of the Werner type, but at least it has fitted them pretty well into the general picture,[22] albeit the accommodation was consummated only with bothersome growing pains. The subject has been admirably reviewed by Sidgwick [23] and need not be discussed in detail here since it is chiefly of interest to inorganic chemists. Our discussion of coordination would, however, be incomplete without at least a brief reference to the subject.

All coordination phenomena are the result of the union of a donor atom, possessing unshared electrons, with an acceptor atom whose valence shell is incomplete. It makes no fundamental difference whether the unshared pair is on a neutral molecule or a charged ion. But in case both reactants are ions we fall back into the category of ordinary covalence, which lacks the semi-ionic character of a true coordinate link. Now there are reasons to think that cases exist in which the valence shell may accommodate more than the octet of electrons found in the valence shells of the inert gases terminating each period of Mendeleeff's table. Thus OsF_8 presumably has sixteen electrons in the valence shell of the osmium and SF_6 twelve in that of the sulfur. Of course, we could resort to an explanation based on single electron linkages, but the fact that the larger atoms, which on the basis of geometrical considerations would be expected to be able to accommodate more electrons in their valence shells, actually do have higher coordination numbers furnishes us with a consistent and reasonable theory, making it unnecessary to resort to any concept so violent as "singlet linkages."

Sidgwick [24] has formulated a set of rules, based on careful and extensive consideration of chemical evidence, which limit the covalence that any atom may exercise. The maximum covalence is (1) for hydrogen, 2; (2) for elements of the first short period, 4; (3) for elements of the second short period and the first long period, 6; and (4) for heavier elements, 8.

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[22] Sidgwick, *J. Chem. Soc.*, **123,** 725 (1923).

[23] Ref. 2, Chapters VII and IX.

[24] Sidgwick, *Trans. Faraday Soc.*, **19,** 469 (1923); Sidgwick and Callow, *J. Chem. Soc.*, **125,** 532 (1924).

It is possible that certain of the heavier elements may exercise a maximum covalence of 10. These figures represent the maximum covalences attainable under the most favorable conditions. Under less favorable conditions the covalence may be any number between the maximum and the normal covalence.

As an example of the electronic interpretation of Werner's complexes, we may return to the cobalt ammines referred to in Chapter I. In $[Co(NH_3)_6]Cl_3$ the cobaltic ion is the acceptor and is utilizing its maximum covalence, viz., 6 (Werner would have called this the coordination number) in coordinating with the lone pairs of the six ammonia molecules (the donors). Now turning to $[Co(NH_3)_5Cl]Cl_2$, we may say that the chloride ions, having complete octets, may act as donors just as well as ammonia molecules and hence may replace one or more molecules of ammonia from the coordination sphere. Thus, as Werner had already pointed out, ions or neutral molecules may play the same role in the coordination sphere. However, the electron theory would place a definite limitation on this process of replacement, viz., that the atom or molecule which is to become coordinated with the cobalt ion must have an unshared electron pair so that it may act as donor.

THE PARACHOR

Many attempts have been made to find properties of atoms or of linkages which are additive in the sense that the total measured value of some such property for a molecule may be calculated by adding together the constant contributions of each atom or linkage. *A priori* one might think that the molecular volume would be an additive function of the atomic volumes, but experiment shows that this is only too frequently far from the case. Sugden [25] argued that this lack of additivity was due to the unequal "internal pressures" under which different molecules exist even when external conditions are equal. This "internal pressure" is a term lacking precise definition, but it is generally considered to manifest itself in the phenomenon of surface tension. Sugden considered, therefore, that if he could measure the molecular volumes at a standard internal pressure, it should be an additive function of the atomic volumes similarly measured. The molecular or atomic volumes measured at an arbitrary and constant value of the surface tension, i.e., at standard internal pressure, he designated as the molecular or atomic parachors, respectively.

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[25] Sugden, *J. Chem. Soc.*, **125**, 1185 (1924); *The Parachor and Valency*, Alfred A. Knopf, London, 1930.

The parachor is defined by the equation

$$[P] = \frac{M\gamma^{1/4}}{D - d}$$

where $[P]$ = the parachor,
M = the molecular weight,
γ = the surface tension,
D = density of the liquid,
d = density of vapor.

Since Sugden's first paper was published, much experimental work on the subject has firmly established the parachor as an additive property. It is not dependent on the atoms alone, however, but also on the types of linkages. The ordinary single covalent linkage was chosen in the mathematical analysis as an arbitrary level to which all measurements were referred, i.e., its parachor was considered to be zero.

Experimental work has established not only the values of the parachors of all elements commonly of interest in organic chemistry but also that 23.2 parachor units should be assigned to double bonds regardless of the elements involved (e.g., C═C, C═O, C═N, N═O) and 46.6 units to triple bonds. Allowances also have to be made for ring structures, e.g., 6.1 units for a six-membered ring.

The application of parachor measurements to structural problems in organic chemistry should be obvious. If alternative structures for a molecule seem possible we may decide between them, if their calculated parachors are different, by comparing the calculated values with experimentally observed values.

When a parachor was determined for a molecule whose structure indicated the presence of a semi-ionic link, it was found that a value of −1.6 units must be ascribed to such a link. The negative sign, corresponding in a sense to a negative volume, merely means that the semi-ionic link uses less space than a single covalent linkage, to which we previously assigned a parachor of zero. That it is entirely different from a covalent double bond is evidenced by its vastly smaller parachor. Thus, although we may feel a little uneasiness about distinguishing between single covalent bonds and semi-ionic bonds on the basis of 1.6 parachor units (only slightly greater than experimental error), we must admit that the difference of 24.8 units between the semi-ionic and true double bonds forms a completely convincing substantiation of G. N. Lewis's conviction that the double bonds demanded by the classical valence theory in such cases are nonexistent.

FREE RADICALS

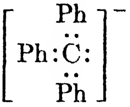
The first experimental evidence of the existence of free radicals was furnished by Gomberg's well-known discovery [26] that hexaphenyl ethane dissociates in polar solvents to give ions:

$$\mathrm{Ph_3C\cdot CPh_3} \rightleftarrows \mathrm{Ph_3C^+ + Ph_3C^-}$$

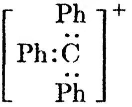
and in nonpolar solvents to give free radicals which are electrically neutral:

$$\mathrm{Ph_3C\cdot CPh_3} \rightleftarrows \mathrm{2Ph_3C}$$

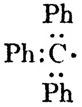
The electronic structures must be as follows:



$$\left[\mathrm{Ph}:\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}:\right]^{-}$$



$$\left[\mathrm{Ph}:\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\right]^{+}$$



$$\mathrm{Ph}:\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\cdot$$

All free radicals are characterized by the presence of an "odd electron," as in triphenylmethyl above.

G. N. Lewis pointed out in his monograph that atoms containing an odd number of electrons should possess a magnetic moment. Each electron, owing to its spin energy, confers on the atom a definite magnetic moment. Two electrons will pair together in such a way that the magnetic field of one just counterbalances that of the other: hence the stability of the electron pair. When the atom contains an odd number of electrons, one must remain unpaired (the odd electron) and its magnetic moment is uncompensated. This gives a magnetic moment to the atom or molecule in question. Thus all free radicals are paramagnetic.

Another property common to all free radicals which have been isolated is color, which Lewis also attributed to the odd electron. This subject will be treated in more detail in Chapter VI.

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[26] Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); **36**, 1144 (1914); *Chem. Rev.*, **1**, 91 (1924); **2**, 301 (1925).

CHAPTER IV

THE GENERALIZED CONCEPT OF OXIDATION-REDUCTION

The universally accepted definition of oxidation is that which classifies it as a chemical transformation involving the loss of electrons. It is also universally conceded that oxidation must always be accompanied by the reverse process, reduction, since electrons cannot exist in the free condition in appreciable amounts for any length of time. The term had been used previously in a more restricted sense, but redefinition seemed justified by the greater generality thus obtained for what was deemed to be a mode of chemical reaction fundamentally different from double decomposition and from many "single" decompositions.

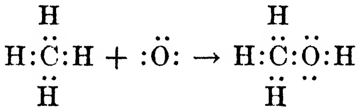
The fact that the oxidation-reduction reactions of ions always involved valence changes at first obscured the application of the new concept to organic chemistry. However, as we already have seen, Nelson and Falk were able to demonstrate, on the basis of Thomson's theory of complete electron transfer, that such a series of reactions as the stepwise oxidation of a hydrocarbon to carbon dioxide was clearly in accord with the electronic definition of oxidation. But no sooner was this apparent accord achieved than Lewis demonstrated that in nonionizing linkages electrons are not completely transferred. It should thereupon have become clear that chemists should reexamine their definition of oxidation to ascertain whether only in complete electron transfer did they encounter reactions fundamentally different from double decompositions or whether partial electron transfer also constituted a unique case.

Stieglitz proceeded to apply the Nelson-Falk concept to what he knew to be covalent linkages without offering any justification, so far as I am aware, beyond the statement that whereas previously $H_3C^+Cl^-$ was understood to mean complete electron transfer it now was understood to mean a polar covalent bond in which the chlorine atom had the lion's share of the electrons, and that the usefulness of the polar formula was in no way altered by its new physical interpretation. Whatever ideas he may have had in his mind concerning electronic fundamentals, it is certain that he demonstrated this last point admirably.

In order fully to understand the very useful ideas of Stieglitz on this subject and further to gain a much-needed clarification of its more fundamental aspects, the whole subject must necessarily be examined in some detail.

Let us start this task by first ignoring the bothersome question of the relative degrees of electron sharing in covalent linkages, and then proceeding to determine whether or not we may demonstrate that oxidation involves an actual loss of electrons.

In the oxidation of methyl alcohol to formaldehyde it is easy to show, by writing Lewis's electronic formulas, that there is an actual loss of electrons, since there are fourteen valence electrons in the alcohol and twelve in the aldehyde. If, however, we apply the same procedure to the oxidation of methane to methyl alcohol we see that the organic molecule gains electrons, even if we neglect the four unshared electrons brought in by the oxygen atom.



$$\mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}}}:\mathrm{H} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}: \rightarrow \mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

Our assurance that nevertheless the organic molecule must have become oxidized is strengthened by the observation that the oxygen atom has gained electrons and hence become reduced. If we restrict our attention merely to counting electrons we are driven to the untenable conclusion that although oxygen was reduced, nothing was oxidized.

We have a similar reaction in the oxidation of trinitrobenzene to picric acid by aqueous potassium ferricyanide, and considerable light may be thrown on the difficulty by formulating the reaction in hypothetical steps which would lead from the initial state to the established final state.

$$\begin{array}{rcll}
\mathrm{RH} & \rightarrow & \mathrm{R}^- + \mathrm{H}^+ & \text{ionic dissociation} \quad (1a) \\
\mathrm{H_2O} & \rightarrow & \mathrm{H}^+ + \mathrm{OH}^- & \text{ionic dissociation} \quad (1b) \\
\mathrm{R}^- & \rightarrow & \mathrm{R}^+ + 2e & \text{oxidation} \quad (1c) \\
2\mathrm{Fe(CN)}_6^{\equiv} + 2e & \rightarrow & 2\mathrm{Fe(CN)}_6^{\overline{\equiv}} & \text{reduction} \quad (1d) \\
\mathrm{R}^+ + \mathrm{OH}^- & \rightarrow & \mathrm{ROH} & \text{ionic association} \quad (1e)
\end{array}$$

$$\begin{aligned}
\mathrm{RH} + \mathrm{H_2O} + 2\mathrm{Fe(CN)}_6^{\equiv} \rightarrow & \\
& \mathrm{ROH} + 2\mathrm{Fe(CN)}_6^{\overline{\equiv}} + 2\mathrm{H}^+ \qquad (1f)
\end{aligned}$$

Now it is seen clearly in the third step (1*c*) that the carbon atom loses electrons, but in the last step it partially regains them. Is this oxidation? Whether it is or not, the ferricyanide ion was clearly reduced.

In the present state of our knowledge it is desirable that the definition of oxidation-reduction be independent of any mechanism, real or assumed, and that only a knowledge of the initial and final states be necessary to its application. In the above case, if we attempt to judge by consideration of the initial and final states whether or not the hydrocarbon is oxidized, we can only say that during the process electrons were moved farther away from a carbon atom. Now we might justly ask if this is oxidation according to the usual definition. If we define oxidation as a loss of electrons, do we mean complete or partial loss? If we mean complete loss, then the ferricyanide ion was reduced but the carbon was not oxidized. If we mean partial loss, then the organic molecule may be said to be reduced in such a reaction as

$$\mathrm{RCl + KI \rightarrow RI + KCl} \tag{2}$$

since the electron pair in RI is closer to R than it was in RCl. But this is a typical double decomposition reaction!

Where then does oxidation-reduction stop and double decomposition begin? In all chemical reactions there are shifts of electrons from one energy level to another, and it is obvious that at one extreme we have complete loss (or gain) while at the other extreme we have only a slight shift of electrons away from (or toward) a given atom. Thus oxidation-reduction merges gradually into double decomposition, and there is certainly no fundamental difference between them, unless it is involved in the mechanism of the reaction,* which possibility we have agreed is to be ignored in formulating our definition. This point of view is referred to as the generalized concept of oxidation and reduction. We will consider it in detail later in this chapter.

Even though there is no fundamental difference between double decomposition and redox reactions, it may be that there is a practical advantage to using as a working tool the formulations used by Stieglitz, Nelson, and Falk. Let us consider this question carefully by reexamining the two reactions we have been using as examples, writing them as Stieglitz would have done.

$$\overset{-}{\mathrm{R}}\overset{+}{\mathrm{H}} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}} + 2\mathrm{Fe(CN)}_6^{\equiv} \rightarrow \overset{+}{\mathrm{R}}\overset{-}{\mathrm{OH}} + 2\mathrm{H}^+ + 2\mathrm{Fe(CN)}_6^{\substack{-\\-\\-\\-}} \tag{3}$$

$$\mathrm{R^+Cl^-} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{I}} \rightarrow \mathrm{R^+I^- + K^+Cl^-} \tag{4}$$

Since in the first reaction the hydrocarbon radical changes from an electron-rich to an electron-poor condition, Stieglitz would have said

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* It is conceivable that in some reactions electrons could momentarily be freed, giving rise to what might be considered statistically as an electron atmosphere while in other redox reactions this might not occur. Such an electron atmosphere would give rise to a definite electron fugacity, which is envisioned in certain modern explanations of the action of reversible electrodes.

that it became oxidized; since in the second reaction none of the atoms change their polar character, he would have catalogued it as a double decomposition. Thus his formulation at least disposed of the verbal tangle we previously encountered provided we redefine oxidation as the change of an atom from the electron-rich to the electron-poor condition (in regard to one or more of its electron pairs). It must be remembered that in reaction 4 above, although electrons are being moved closer to R, the polar character of R has not changed: it was electron-poor at the start and is still electron-poor at the end of the reaction.

It is obvious that a position of particular importance has been assigned to what, in terms of our simple picture of the atom, we call the mid-point between the two atoms. If during the course of a reaction the electrons move across this point we catalogue the reaction as an oxidation-reduction. In terms of Abegg's ideas, there is a practical justification for this arbitrary choice and it is this: If such compounds become oxidized or reduced then they will undergo reactions of the hydrolytic type in the reversed electronic sense to what they would have done before the oxidation or reduction. For example, methyl iodide hydrolyzes as follows:

$$H_3C^{+}I^{-} + H^{+}OH^{-} \rightarrow H_3C^{+-}OH + H^{+}I^{-}$$

Here the methyl group acts as an electron-poor group. But if methyl iodide is converted into the Grignard reagent, its hydrolysis will then be in the reversed electronic sense: the methyl group will act as though it were electron-rich and hence on hydrolysis will yield methane instead of methyl alcohol.

$$H_3C^{+}I^{-} + Mg \rightarrow H_3C^{-+}Mg^{+}I^{-}$$

$$H_3C^{-+}Mg^{+-}I + H^{+}OH^{-} \rightarrow H_3C^{-}H^{+} + IMgOH$$

Thus we conclude that in the reaction with magnesium the organic halide was reduced. Conversely, if the electron theory would enable us to predict that magnesium would "reduce" methyl iodide, we would then know that the hydrolysis of the organic reductant would proceed in the reversed electronic sense to that of the oxidant (if it would hydrolyze at all). Our definition does, then, seem to have a practical advantage: an "oxidation-reduction" reaction is one which changes a very important property of an atom, viz., its polar character, which in turn directs its subsequent reactions with hydrolytic reagents if the linkage in question is a covalence.

Where the oxidation involves electrovalences, the situation is much simplified, for here there is complete transfer of electrons.

There are also cases, like the oxidation of sulfite to sulfate, where unshared pairs of electrons become shared or vice versa. In such cases if, after the covalence has become established, the newly shared electrons lie on the acceptor atom's side of the "midpoint" between the two atoms, oxidation obviously has occurred. Such is the case in the transformation of sulfite to sulfate, whereas it is not the case in the transformation of ammonia to the ammonium ion. Thus we term any atom holding unshared electron pairs as electron-rich in regard to transformations involving those particular electrons.

A few clarifying examples are given below. To facilitate the presentation the symbol Ⓡ will be used to denote "electron-rich" while Ⓟ will denote "electron-poor."

1. $H^{+-}\underset{\text{Ⓡ}}{C_6H_5} + HO^{-+}\underset{\text{Ⓟ}}{NO_2} \rightarrow O_2\underset{\text{Ⓡ}}{N}{}^{-+}\underset{\text{Ⓟ}}{C_6H_5} + HOH.$

Carbon is oxidized; nitrogen is reduced.

2. $2H_3\underset{\text{Ⓟ}}{C}{}^{+}Cl^{-} + 2\underset{\text{Ⓡ}}{Na} \rightarrow H_3C^{+-}\underset{\text{Ⓡ}}{CH_3} + 2\underset{\text{Ⓟ}}{Na}Cl.$

Carbon is reduced; sodium oxidized. Note that the formula for activated ethane is used.

3. $2\ :\underset{\text{Ⓡ}}{C}::\ddot{O}: + :\ddot{O}\underset{\cdot\text{Ⓟ}\cdot}{:}\ddot{O}: \rightarrow 2\ :\overset{\cdot\cdot\,-}{\underset{\text{Ⓡ}}{O}}:\overset{+}{:}\underset{\text{Ⓟ}}{C}::\ddot{O}:.$

Carbon is oxidized by giving up preponderant share of lone pair.

4. $C_6H_5\underset{\text{Ⓟ}}{N}{}^{+}O_2{}^{-} + 3\underset{\text{Ⓡ}}{Zn} + 6HCl \rightarrow$

$C_6H_5\underset{\text{Ⓡ}}{N}{}^{-}H_2{}^{+} + 3\underset{\text{Ⓟ}}{Zn}{}^{++} + 6Cl^{-} + 2H_2O.$

Nitrogen is reduced, zinc oxidized. Possible changes in the polar character of the C—N link are neglected.

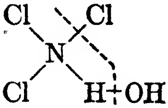
5. $2C_6H_5\underset{\text{Ⓡ}}{S}{}^{-}H^{+} + \text{oxidizing agent} \rightarrow C_6H_5\underset{\text{Ⓡ}}{\overset{-}{S}}\text{—}\underset{\text{Ⓟ}}{\overset{+}{S}}C_6H_5$

The arguments advanced so far in this chapter were advanced to show that the extended Nelson-Falk-Stieglitz concept of oxidation-reduction is justified only by its practical utility in describing chemical reactions and this in turn rests on the assumption that the course of hydrolytic reactions is determined by the polarity of the hydrolyzable bond. Before we rest too complacently with this concept, however, we must extend our critical inquiries somewhat farther. Since we have defined oxidation in terms of polar character we must have a reliable means of measuring the latter. Of the four methods suggested by

Abegg, the first, dealing with ions, is completely reliable. The third, dealing with relative positions of elements in the periodic table, cannot be reliable if Noyes and Stieglitz were correct on the existence of positive halogens. Even aside from this it seems possible that the electron affinity of an atom might become so much augmented by substitution of "negative" groups that we would be bound to have occasional exceptions to the third rule. The fourth rule, dealing with the variable positive valence and invariable negative valence, can only be infrequently applied in organic chemistry. This leaves the second rule, dealing with hydrolysis, to bear almost the entire burden in cases of covalent unions. The basic assumption made in applying the rule was the assumption that during hydrolysis covalent linkages first ionize, thus $X^+Y^- \rightarrow X^+ + Y^-$, and then the ions so produced unite respectively with the ions from water, or at least that the molecules react "as though" this were the mechanism.

Now the ionic theory of organic reactions has not lacked supporters but it is equally true that much evidence has been amassed in support of Kekulé's theory of intermediate compound formation. If hydrolysis proceeds by the preliminary formation of unstable intermediate complexes, it may well be that the polar characters of the atoms in the original molecule may be changed by this complex formation.

Closely related to this phase of the subject is a suggestion by Sidgwick[1] concerning the hydrolysis of nitrogen trichloride. He suggested that the water molecule might become coordinated with the nitrogen atom through the latter's lone pair and that this would be followed by the elimination of HOCl as indicated below. This explanation would not necessitate Noyes's assumption of positive chlorine atoms.



It is obvious that if such a mechanism applies to many hydrolytic reactions (and it will be shown later that it probably does) they cannot be relied upon to give us information concerning the polarity of hydrolyzable linkages, and conversely, the course of hydrolysis cannot always be predicted on the basis of a knowledge of the polar character of linkages even if we are fortunate enough to know them with certainty. These considerations lead to the final blow: the concept of oxidation-reduction, except in complete electron transfer, can hardly be said to be of any general practical importance. There seems to be no further necessity for distinguishing it from double decomposition.

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[1] Sidgwick, *The Electronic Theory of Valency*, Oxford Press, 1927, p. 158.

THE GENERALIZED CONCEPT OF OXIDATION-REDUCTION

The only clear-cut cases of oxidation-reduction reactions are those in which electron interchange occurs between ions. We have seen that this complete transfer of electrons shades off gradually through reactions in which unshared electrons become shared, to those in which shared electrons remain shared but move to different energy levels. All these reactions are alike in one respect, viz., electrons move away from certain atoms and toward certain others. Ingold[2] points out "that reduction and oxidation are to be regarded as the prototypes of a more general classification based on the reception and donation of electrons." This is the "generalized concept of oxidation-reduction" and it includes all chemical reactions.

It seems reasonable to suppose that if an electron-rich and an electron-poor reagent are brought together there will be a reaction only if the former has a sufficiently low and the latter a sufficiently high electronegativity. That this must be so for the occurrence of oxidation-reduction reactions (in the old sense) has long been recognized, but that it is equally true for all types of reactions was apparently first recognized by Lapworth.[3] If electron-rich substances show a readiness to give up their electrons in whole or in part he speaks of them as having a high "anionoid reactivity," i.e., they are behaving analogously to very reactive anions. Conversely, electron-poor reagents of high electronegativity are said to exhibit high "cationoid reactivity." Ingold[4] uses the term "nucleophilic" in place of "anionoid" and "electrophilic" in place of "cationoid."

We may now come at once to the main point of Lapworth's theory. Anionoid substances may only react with cationoid substances and will do so only when their relative electron affinities are favorable to reaction. Molecules always have both anionoid and cationoid centers, but usually if the reactivity of one is high, that of the other is low and the molecule as a whole may be catalogued as predominantly cationoid or anionoid. Lapworth also maintains that the point of initial attack in a cationoid molecule is the cationoid center, whereas in an anionoid molecule it is the anionoid center. After the initial attack, secondary reactions may occur involving the other centers.

The theory is supported by the experimental work of Lapworth[5] himself. He showed that cyanohydrin formation is accelerated by the addition of bases or salts of weak acids, is not appreciably affected by neutral

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[2] Ingold, *Chem. Rev.*, **15**, 266 (1934).

[3] Lapworth, *Nature*, **115**, 625 (1925); *Mem. Manchester Phil. Soc.* (1925).

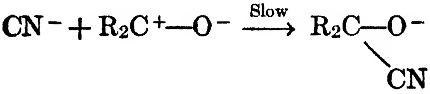
[4] Ingold, *J. Chem. Soc.*, 1120 (1933).

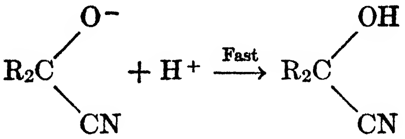
[5] Lapworth, *J. Chem. Soc.*, 995 (1903); 1206 (1904).

salts, and is retarded by acids. These observations prove that HCN is not added directly. If its ions add simultaneously the reaction would be trimolecular and the speed would depend on the product of the concentrations of the two ions, which should not change on the addition of small amounts of acid or base. However, if the cyanide ion is first added slowly and the hydrogen ion is then added rapidly, the predicted effects of acids or bases would be those actually observed.

The steps in the reaction, according to the Lapworth theory, are, therefore, as follows:[6]

$$R_2C{=}O \xrightarrow{\text{Fast}} R_2C^{+}{-}O^{-} \qquad (1)$$


(2)


(3)

The first step is the same as that commonly assumed by the early American school. The second step involves logic peculiar to the Lapworth theory. It is argued that the positive carbon atom has a much greater tendency to form a covalence than has the negative oxygen atom. This is deduced from common experience, since many stable ions are known involving negatively charged oxygen, whereas an ion involving a positively charged carbon atom would not be stable except under extraordinary conditions. It follows, therefore, that a covalence would first be formed at the carbon atom and hence the aldehydes are electrophilic and should react most readily with nucleophilic compounds. As a matter of fact they do not add hydrogen chloride, which is seen to be electrophilic, since the chloride ion is known to have such a slight tendency to lose or share electrons. But aldehydes do add hydrogen cyanide, for here the cyanide ion has a great tendency to share its electrons, as is shown by the low ionization constant of HCN (ca. 10^{-10}), and is accordingly to be classified as nucleophilic.

It is well known that the reagents which add to aldehydes and ketones do not add to olefins, and vice versa. If the carbonyl compounds are electrophilic substances, the olefins would be presumed to be nucleophilic. Substantiation of this idea will be given in Chapter V, under the heading

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[6] R. Robinson, *Outline of an Electrochemical Theory of the Course of Organic Reactions*, Inst. Chem. Great Britain and Ireland, 1932, p. 16.

"Applications of the Theory." Suffice it to say that the particular triumph of Lapworth's theory lies in the fact that it makes clear, at long last, why this selectivity is manifested in addition reactions. Fundamentally it rests on the same foundation as the selectivity of oxidizing and reducing agents: we would ordinarily not expect one reducing agent to react with another.

Further evidence for Lapworth's theory is to be found in certain addition reactions of olefins and related substances. Terry and Eichelberger[7] observed that a mixture of bromine and potassium chloride reacted with sodium maleate in water solution to produce the chloro-bromo but not the dichloro-addition compound. They were unable to explain their results. Similarly Francis[8] observed the formation of α-chloro-β-bromo ethane from ethylene and bromine in neutral sodium chloride solution. No trace of ethylene dichloride was found. Similarly when sodium nitrate solution was used one product was $BrCH_2 \cdot CH_2 \cdot ONO_2$. In both cases the dibromoethane was also produced. The explanation suggested by Francis is in complete accord with the Lapworth theory and may be rephrased as follows: Olefins are nucleophilic and will accordingly first be attacked by the electron-poor halogen ion (possibly the attack and the formation of the ion are simultaneous).

$$CH_2{=}CH_2 + Br^+ \rightarrow CH_2Br \cdot \overset{+}{C}H_2$$

This intermediate ion is then free to react with any negative ions in solution, e.g., Br^-, Cl^- or NO_3^-.

$$CH_2Br \cdot \overset{+}{C}H_2 + Cl^- \rightarrow CH_2Br \cdot CH_2Cl$$

The dichloro compound could not be formed, however, because no electron-poor chlorine is present to make the initial attack.

Similarly it has been shown that the halogenation of an olefin in organic media in the presence of a silver salt resulted in the addition of an atom of halogen and the anion from the salt.[9] Other similar examples are known.[10]

Watson[11] considers that the experiments just discussed prove the correctness of the Lapworth theory. In the opinion of the present author, they demonstrate clearly that the addition reactions take place in steps but they certainly do not offer unequivocal proof that the initial attack

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[7] Terry and Eichelberger, *J. Am. Chem. Soc.*, **47,** 1067 (1925).

[8] Francis, *ibid.*, **47,** 2340 (1925).

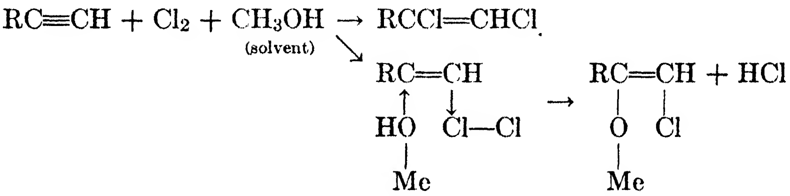
[9] Ushakov, Christov, and Zelinski, *Ber.*, **68B,** 824 (1935).

[10] For literature references see Ref. 12 below.

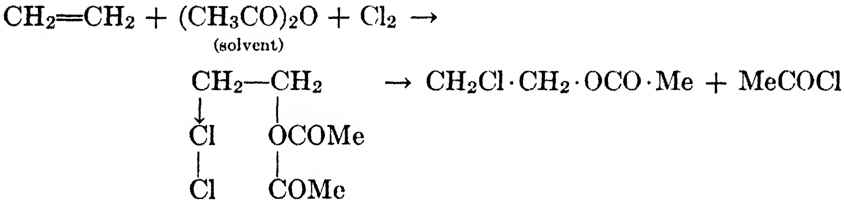
[11] Watson, *Modern Theories of Organic Chemistry,* Oxford Press, 1937, p. 100.

takes place at the electron-rich carbon atom. If, in a solution containing ethylene, bromine, and sodium chloride, a bromide or chloride ion led the attack, then the only electrophilic atoms present to complete the reaction would be the electron-poor bromine or the hydrogen ion of water. The former, being much more electrophilic, would then be the one to react. The net result of the reaction would thus be the same as though the electron-poor bromine had led the attack.

Further work along similar lines has been done by Hennion and his collaborators,[12] who have demonstrated that the nucleophilic addendum need not be an ion; the presence of unshared electron pairs seems to be sufficient. Among the reactions they studied are the following, in which we may follow the authors in representing the intermediate steps as involving the simultaneous processes of bond formation and bond rupture.



$$\mathrm{RC{\equiv}CH + Cl_2 + \underset{(solvent)}{CH_3OH}} \rightarrow \mathrm{RCCl{=}CHCl}$$
$$\searrow \begin{array}{ll} \mathrm{RC{=}} & \mathrm{CH} \\ \uparrow & \downarrow \\ \mathrm{HO} & \mathrm{Cl{-}Cl} \\ | & \\ \mathrm{Me} & \end{array} \rightarrow \begin{array}{ll} \mathrm{RC{=}} & \mathrm{CH + HCl} \\ | & | \\ \mathrm{O} & \mathrm{Cl} \\ | & \\ \mathrm{Me} & \end{array}$$



$$\mathrm{CH_2{=}CH_2 + \underset{(solvent)}{(CH_3CO)_2O} + Cl_2} \rightarrow$$
$$\begin{array}{ll} \mathrm{CH_2{-}} & \mathrm{CH_2} \\ \downarrow & | \\ \mathrm{Cl} & \mathrm{OCOMe} \\ | & | \\ \mathrm{Cl} & \mathrm{COMe} \end{array} \rightarrow \mathrm{CH_2Cl{\cdot}CH_2{\cdot}OCO{\cdot}Me + MeCOCl}$$

Similar reactions have been carried out by others.[10] The existence of acetate ions seems improbable in dry acetic anhydride, and hence the above interpretation appears to be justified. Like the work of Francis, this work seems to demand the theory of stepwise addition, although it does not establish that the initial attack is made by an electrophilic reagent. However, their study of the rate of addition of hydrogen chloride or hydrogen bromide to cyclohexene or 3-hexene[12b] supplies the desired evidence on this point. They found that the rates of addition in electron-donor solvents like ether or dioxane are much slower than in inert solvents like heptane or benzene. It is well known that ethers tend

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[12] (*a*) Verbanc and Hennion, *J. Am. Chem. Soc.*, **60**, 1711 (1938); (*b*) O'Connor, Baldinger, Vogt, and Hennion, *ibid.*, **61**, 1454 (1939); (*c*) Weber, Hennion, Vogt, *ibid.*, 1457; (*d*) Baum, Vogt, and Hennion, *ibid.*, 1460; (*e*) Norris, Vogt, and Hennion, *ibid.*, 1460; (*f*) Hennion and Wolf, *ibid.*, **62**, 1368 (1940); (*g*) Irwin and Hennion, *ibid.*, **63**, 858 (1941); (*h*) Emling, Vogt, and Hennion, *ibid.*, 1624.

to coordinate with protons to yield oxonium compounds, whereas hydrocarbons do not. Hence the protons are bound rather firmly to the solvent molecules when the reactions are carried out in donor solvents and are loosely attached to halogen atoms when hydrocarbon solvents are used. It follows that if the rate determining step is an attack by the electrophilic hydrogen ion on the nucleophilic olefin, then the rate of addition should be less in the donor solvents, as was actually found to be the case.

Further pertinent evidence relating to the Lapworth theory will be given in the last chapter. It is of a stereochemical nature and cannot be discussed without a knowledge of the transition state theory, which will be presented in Chapter VII.

CHAPTER V

OUTLINE OF THE ELECTRONIC THEORY OF THE ENGLISH SCHOOL

[NOTE: Students who are not acquainted with modern theories of refractivity and dipole moments should read Appendixes II and III before attempting this chapter.]

The electronic theory of the early American school underwent considerable development as a result of the combined efforts of a group of English chemists under the leadership of Lapworth, Robinson, and Ingold in particular. I shall not attempt to follow through the historical development of the theory within this group; rather, I propose to present their combined views, divorced from all polemical growing pains, as they appear to exist today.[1] This task is facilitated by the fortunate fact that these chemists seem to be in essential agreement among themselves at the present time.

Inasmuch as their theory forms the best working tool with which our knowledge of the electron has provided organic chemists, it seems well to discuss their theory in detail. Lest the basic principles be buried too deeply in this mass of details I will present first as concise an exposition of these principles as is consistent with clarity. This done, I will then turn to an examination of the evidence on which the theory is based, and finally conclude the chapter by reviewing the essential details connected with the application of the theory.

BASIC PRINCIPLES

Electrophilic and Nucleophilic Reagents

The generalized theory of oxidation-reduction, discussed in Chapter IV, is one of the cornerstones of the theory of the English school.

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[1] (*a*) Ingold, *Chem. Rev.*, **15**, 225 (1934); (*b*) R. Robinson, *Outline of an Electrochemical Theory of the Course of Organic Reactions*, The Institute of Chemistry of Great Britain and Ireland; (*c*) Waters and Lowry, *Physical Aspects of Organic Chemistry*, D. Van Nostrand Co., 1937; (*d*) Watson, *Modern Theories of Organic Chemistry*, Oxford Press, 1937; (*e*) R. Robinson, *Quatrième Conseil de la Inst. Chim. Solvay*, 423 (1931); (*f*) Hunter, *The Electron Theory of Valency*, E. Arnold & Co., London, 1934.

Intramolecular Transmission of Electrical Charge

Inductive Effect. The mode of electronic displacement envisioned by G. N. Lewis and developed by Lucas has been adopted by the English school and called the inductive effect.[1a, 2b] It is symbolized by I_s, the subscript *s* standing for the word "static," which is meant to convey the impression that this is a "polarization effect" characteristic of a molecule in equilibrium with its environment. It is characterized by four traits: (1) This mode of electron displacement is relayed from atom to atom along a chain without the transference of any electron from the octet of one atom to that of another. (2) Changes in polarity produced by such a displacement are all in the same direction; hence this effect could not produce alternating polarity. (3) The effect becomes progressively less as it proceeds away from the atom or group producing it. (4) It is a polarization effect, not a polarizability effect, and the dipoles it produces are present in molecules which are in their normal states, i.e., disturbing electric or magnetic fields are absent.

The inductive effect is considered to be due to changes in the screening effect, as already explained when discussing the Lucas theory, and its magnitude is determined by the electron-attracting powers (electronegativity) of the atom or group in question. However, most of the English chemists prefer not to rely on the ionization constants of acids and bases as a measure of relative electronegativities. They consider the relationships immediately deducible from the periodic table as being more free from complicating influences and hence more reliable.

The way in which they proceed to establish relative electronegativities will be evident from the following considerations. The term "pole" is used to indicate the seat of an electric charge in a polyatomic ion.[2] These poles have the highest electron-attracting or repelling powers. Thus the positive pole in the anilinium ion would have very great electron-attracting powers, whereas the negative pole in the phenolate ion would powerfully repel electrons.

Somewhat less powerful in their I_s effects are dipoles resulting from coordinate covalence, such as $\mathrm{O{=}\underset{|}{\overset{+}{N}}{-}\overset{-}{O}}$, which, in virtue of the positive charge on the nitrogen atom, strongly attracts electrons from any group R in a compound $\mathrm{R{-}NO_2}$. The I_s effects of ordinary dipoles associated with normal covalences between atoms of unequal electronegativity, such as C—Cl, are smaller still.

If an atom or group attracts electrons more than hydrogen does, it is said to exhibit a $-I_s$ effect; if it attracts electrons less than hydrogen

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[2] (*a*) Ingold, *Ann. Repts. Chem. Soc.*, **23**, 129 (1926); (*b*) *Idem*, p. 140.

(or if it repels them) it exhibits a $+I_s$ effect and is said to be an electron-releasing group.

The relative magnitudes of the I_s effects may be judged from the periodic arrangement of the elements. Thus, if the group number and charge are constant, the $-I_s$ effect will decrease or the $+I_s$ effect will increase as the atomic number becomes greater. On the other hand, if the periodic number and charge are constant, an increase in atomic number will cause the reverse changes. Thus we have[3]

TABLE I

$+I_s$ Effect

$-\overset{-}{N}R > -O^-$

$-O^- > -S^- > -Se^-$

$-I_s$ Effect

$-\overset{+}{O}R_2 > -\overset{+}{N}R_3$

$-\overset{+}{N}R_3 > -\overset{+}{P}R_3 > -\overset{+}{A}sR_3$

$-\overset{+}{N}R_3 > -NO_2$

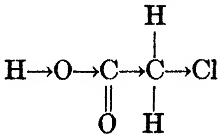
$-\overset{+}{N}R_3 > -NR_2$

$-F > -OR > NR_2 > -CR_3$

$-F > -Cl > -Br > -I$

$=O > =NR > =CR_2$

Inductive displacements are indicated in structural formulas by substituting arrows for the customary bond signs. The arrows point in the direction of the electron displacement, but there seems to be no agreement on whether an arrow indicates the direction of the partial moment of a given bond or merely the direction in which electrons are displaced by a given substituent. Thus chloroacetic acid might be written



$$H\rightarrow O\rightarrow \underset{\underset{O}{\|}}{C}\rightarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\rightarrow Cl$$

to show that the substitution of chlorine causes an electron displacement in the direction indicated, although the polarity of the C—O bond is almost certainly in the reverse direction.

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[3] Ref. 1*a*, p. 238.

The signs $\delta+$ and $\delta-$ are used for a similar purpose. They indicate minute electrical charges on atoms due to polar bonds, not free poles. Thus we may write

$$\underset{\delta+}{H_3C}\rightarrow\underset{\delta-}{Cl}$$

Field Effect (*Direct Effect*). This effect has already been discussed in Chapter II. It is characterized by the fact that here the electrical fields of two atoms (not directly bound to each other) interact owing to the transmission of electrical influence directly through empty space instead of through a chain of electronic linkages. In practice it has so far been found impossible to disentangle the field effect from the inductive effect,[4] and many authors use the latter term to designate the combined effect of the two.

Ingold and Vass [5] symbolize this direct effect as $\pm D$, the signs having their usual significance.

Inductomeric Effect. The inductive effect represents a permanent state of polarization, owing its existence to an electronic displacement which may be considered to have taken place along the lines of the valence linkages. This mode of electron displacement is referred to as the "inductive mechanism" and is symbolized by I. In addition to this permanent I_s effect, a further electronic displacement may be called into play by any change in the electrostatic environment such as would be produced by placing the system between the plates of an electrical condenser or adding some new substance to the system. Forces such as these would start the system off toward a new equilibrium, and since their effects on the initial molecules would vary during the period of adjustment they are called "time-variable" or "polarizability" effects. A time-variable effect operating by the inductive mechanism is called the "inductomeric effect" [6] and is symbolized as I_d, the subscript meaning "dynamic."

The extent to which the inductomeric effect is called into play, as is known from studies of refraction and dielectric phenomena, will depend on the strength of the polarizing field and on the polarizability of the bond in question. This is expressed by the familiar equation $P = F\alpha$, where P is the total induced polarization, F the strength of the polarizing field, and α the polarizability. The magnitude of the polarizability might be expected (1) to decrease with an increase of positive charge on either of the adjoining atoms, since a positive charge attracts electrons, thus putting them under greater constraint; (2) to decrease with increas-

[4] Lapworth and Manske, *J. Chem. Soc.*, 2536 (1928).

[5] Ingold and Vass, *ibid.*, 418 (1928).

[6] Ingold, *ibid.*, 1120 (1933).

ing group number of the adjoined atoms when the periodic number is constant, since this means greater electronegativity and hence more constraint; and (3) to increase with increasing periodic number when the group number is constant.

We thus get the following table of inductomeric polarizabilities:[7]

$$-\overset{-}{\mathrm{O}} > -\mathrm{OR} > -\overset{+}{\mathrm{O}}\mathrm{R}_2$$

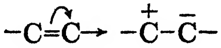
$$-\mathrm{CR}_3 > -\mathrm{NR}_2 > -\mathrm{OR} > -\mathrm{F}$$

$$-\mathrm{I} > -\mathrm{Br} > -\mathrm{Cl} > -\mathrm{F}$$

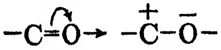
Ingold[7] states: "It is provisionally assumed that an inductomeric polarizability along any linking is the same for both directions; this would surely hold for small electron displacements, but it is unlikely to be more than roughly true for displacements of the magnitude of those which occur during reactions."

Polarizability effects are of importance in chemistry chiefly because chemical reactions are thought to take place as the result of deformation brought about in molecules by the electrical fields of attacking reagents. Of course these deformations may also result from such a source of electrostatic disturbance as an electrical condenser, but such cases are rare. In so far as ordinary chemical reactions are concerned, it is clear that the inductomeric effect is brought into play only at the moment of reaction and only on demand of the attacking reagent.

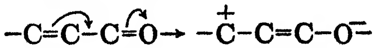
Electromeric Effect. In addition to the polarizability effect brought about through the inductive mechanism, there is possible an additional polarizability effect having its origin in a different mechanism of electron displacement known as the "tautomeric mechanism" (symbol, *T*) which was first postulated by Lowry.[8] This mechanism may operate only in conjunction with multiple bonds and, in contrast to the inductive mechanism, involves a change in the octet affiliations of one or more electron pairs. This occurs without decomposition of the molecule. This process may be illustrated as follows, using curved arrows to symbolize tautomeric (*T*) displacements of electron pairs.



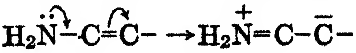
$$-\mathrm{C}{=}\mathrm{C}- \rightarrow -\overset{+}{\mathrm{C}}-\overset{-}{\mathrm{C}}- \tag{1}$$



$$-\mathrm{C}{=}\mathrm{O} \rightarrow -\overset{+}{\mathrm{C}}-\overset{-}{\mathrm{O}}- \tag{2}$$



$$-\mathrm{C}{=}\mathrm{C}-\mathrm{C}{=}\mathrm{O} \rightarrow -\overset{+}{\mathrm{C}}-\mathrm{C}{=}\mathrm{C}-\mathrm{O}^{-} \tag{3}$$



$$\mathrm{H_2\ddot{N}}-\mathrm{C}{=}\mathrm{C}- \rightarrow \mathrm{H_2}\overset{+}{\mathrm{N}}{=}\mathrm{C}-\overset{-}{\mathrm{C}}- \tag{4}$$

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[7] Ref. 1*a*, p. 263.

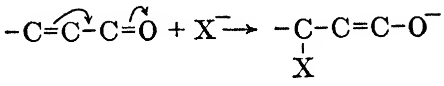
[8] Lowry, *J. Chem. Soc.*, **123**, 822 (1923).

This effect, in so far as it is purely a polarizability phenomenon, is called the electromeric effect (symbol, E).

Different atoms and groups are considered to have $+E$ or $-E$ effects according to whether they release electrons to or attract them from the rest of the molecule, respectively. Thus in Equation 3 the carbonyl group is said to exhibit a $-E$ effect, whereas the amino group in Equation 4 shows a $+E$ effect.

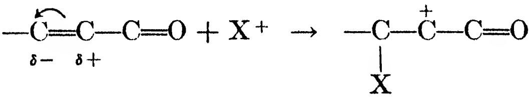
Like the inductomeric effect, the electromeric effect is brought into play only at the moment of molecular collision, i.e., when the attacking molecule is so close that the electrostatic field is a distorting influence of importance.* Unlike the inductive effect, it produces activation of a molecule in the old sense that free poles or "exposed charges" are created which are free to combine with other free poles of the opposite sign.

A statistical point of view must be taken in regard to the direction of an electromeric displacement just as it was in regard to Fry's electromerism. Thus Equation 2 shows the most probable direction of electromeric displacement in a carbonyl double bond. The reverse displacement, in which the carbon atom would pull an electron pair entirely away from the more electronegative oxygen atom, is much less probable, even when aided by an attacking reagent. Thus we say, in the parlance of the English school, that the carbonyl group has a $-E$ effect because, in comparison, its $+E$ effect is negligibly small. Now, in order to comprehend a related point of much importance, consider an unsaturated carbonyl compound to be attacked in the *beta* position by a nucleophilic ion X^- as follows:



$$-C{=}C{-}C{=}O + X^- \rightarrow -\underset{X}{C}{-}C{=}C{-}O^-$$

It is clear that the $-E$ effect of the carbonyl group aids this particular reaction. On the other hand, if X had been an electrophilic reagent it would have attempted to induce an electromeric displacement in the opposite direction when it collided with the *beta* carbon atom.



$$-\underset{\delta-}{C}{=}\underset{\delta+}{C}{-}C{=}O + X^+ \rightarrow -\underset{X}{C}{-}\overset{+}{C}{-}C{=}O$$

Such a displacement obviously could not be aided by the $-E$ effect of the carbonyl group while the $+E$ effect is too small to make any practi-

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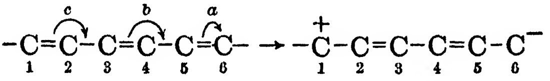
* It may, of course, also be brought into play by placing the system between the plates of a charged condenser, but inasmuch as this is not common to chemical practice it will hereinafter be ignored.

cal difference. But in addition to these points it is important to realize that the $-E$ effect of the carbonyl group could not possibly *hinder* the reaction because an electrophilic reagent attacking as postulated would attract electrons, not repel them, and hence the $-E$ effect of the carbonyl group would not be called into play. This leads to one of the basic principles of the English theory, that the electromeric effect is called into being only in a manner to aid a reaction.

Robinson [9] considers that the recognition of an electromeric polarizability, fundamentally different from inductomeric polarizability, is necessitated by the behavior of an isolated double bond, as in Equations 1 and 2, as well as by that of conjugated double bonds, as in Equations 3 and 4. This is no doubt true in the sense that in the E effect an electron pair may, as a limiting condition, be completely removed from the octet of one atom without disruption of the molecule. The present author, however, is unable to see that there is any fundamental difference between the breaking of a C—H bond in a saturated hydrocarbon attacked, let us say, by chlorine, and the breaking of one bond of C=C by the same attacking reagent. Of course, the polarizability of the latter bond is much greater, but that constitutes a difference in degree rather than in kind. However, he considers that one must envision a polarizability mechanism truly different from inductomeric polarizability when consideration is given to conjugated systems, for here a new phenomenon is present in the relay of electric charge from atom to atom down a chain:



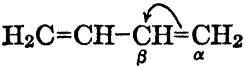
$$-\underset{1}{\mathrm{C}}=\underset{2}{\overset{c}{\mathrm{C}}}-\underset{3}{\mathrm{C}}=\underset{4}{\overset{b}{\mathrm{C}}}-\underset{5}{\mathrm{C}}=\underset{6}{\overset{a}{\mathrm{C}}}- \rightarrow -\underset{1}{\overset{+}{\mathrm{C}}}-\underset{2}{\mathrm{C}}=\underset{3}{\mathrm{C}}-\underset{4}{\mathrm{C}}=\underset{5}{\mathrm{C}}-\underset{6}{\mathrm{C}}^{-} \tag{5}$$

Let us suppose that this electron displacement was initiated by an electrophilic attacking reagent which happened to approach the organic molecule from the right-hand side. It would demand a high electron density on carbon atom number 6 and the shift *a* would take place. The positive charge left on carbon atom number 5 would impede the approach of the attacking reagent if it remained there, but it is transferred by electromeric relay ($b + c$) to carbon atom number 1, where it is too far away to impede the reaction. If this over-all displacement does not take place 100 per cent owing to the incomplete operation of displacements *b* and *c* it is evident that there will at any rate be a localization of negative charge and a distribution of positive charge with the same net effect—the facilitation of the reaction by the removal of the charge uncalled for by the attacking reagent.[10]

[9] Ref. 1*b*, p. 16.

[10] Ref. 1*b*, p. 20.

According to this principle, if butadiene were attacked by an electrophilic reagent, the second of the two following electromeric shifts would be more probable and hence C_α would be the atom initially attacked.

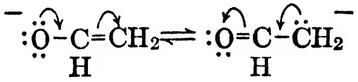


$$H_2C{=}CH{-}\underset{\beta}{C}H{=}\underset{\alpha}{C}H_2$$

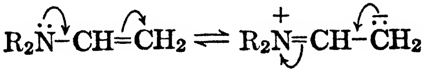
$$H_2C{=}CH{-}\underset{\beta}{C}H{=}\underset{\alpha}{C}H_2$$

It is a matter of passing interest to note that the operation of a alone (Eq. 5) would put a positive charge on the fifth carbon atom, that $a + b$ would put it on the third, whereas $a + b + c$ would put it on the first, thus producing alternating polarity. It is obvious that this could not occur in a saturated carbon chain without disrupting the chain, and thus the concept is not a modernization of Cuy's utterly erroneous theory of alternating polarity.[11]

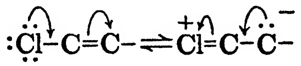
The next question to be considered is the prediction of the direction in which the electromeric effect may operate. In unsaturated compounds any atom having unshared electrons or any multiple linkage may act as an "electron source," while any coordinatively unsaturated atom or any multiply linked atom may serve as an "electron sink." For example, we may take Equation 5 and also the following:



$$^{-}:\ddot{O}{-}\underset{H}{C}{=}CH_2 \rightleftharpoons :\ddot{O}{=}\underset{H}{C}{-}\ddot{C}H_2^{-} \qquad (6)$$



$$R_2\ddot{N}{-}CH{=}CH_2 \rightleftharpoons R_2\overset{+}{N}{=}CH{-}\overset{-}{\ddot{C}}H_2 \qquad (7)$$



$$:\ddot{Cl}{-}C{=}C{-} \rightleftharpoons \overset{+}{Cl}{=}C{-}\ddot{C}^{-}{-} \qquad (8)$$

The relative ease with which two electromeric displacements may take place, either in different molecules or in the same one, can be predicted by the use of Fajan's rules[12] in much the same way as was done before, except that one complicating factor occurs here which had no counterpart in the inductomeric effect and which was not initially recognized by Ingold[13] when he deduced the relative electromeric effects of groups. This change of viewpoint resulted from a mass of evidence, which will be discussed later, indicating that the order within each Mendeleeff group is the reverse of that which would have been predicted by the applica-

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[11] See p. 27.

[12] See p. 439.

[13] Ref. 1a, pp. 244 and 265.

tion of Fajan's rules. Thus the $+E$ effect of the halogens would occur in the order: $F > Cl > Br > I$ despite the fact that fluorine has the firmest grip on its unshared electrons and hence would be expected to release them for double bond formation (Eq. 8) with the least ease. This phenomenon is not understandable on the basis of relative polarizabilities. However, an early suggestion of G. N. Lewis [14] seems to have a bearing on the question. It was his opinion that only elements of the first short period are capable of forming double bonds. Although modern investigations do not give complete verification to his viewpoint, it seems probable that at least such a tendency exists and that the larger atoms find it more difficult to increase their covalences, as they must if their $+T$ effects are to operate.

A consideration of all the factors under discussion leads to the relationships given in Table II.

TABLE II [1a]

RELATIVE ELECTROMERIC EFFECTS

$+E$ EFFECT

$-O^- > -OR > -\overset{+}{O}R_2$

$-\bar{C}R_2 > -\bar{N}R > -\bar{O}$

$-F > -Cl > -Br > -I$

$-OR > -SR > -SeR$ etc.

$-E$ EFFECT

$=\overset{+}{N}R_2 > =NR$

$=O > =NR > =CR_2$ etc.

When a multiple linkage occurs between unlike atoms the E effect will, of course, occur much more easily in the direction which produces a negative pole on the more electronegative atom. Thus the displacement $\overset{\curvearrowleft}{C{=}O}$ would not be expected. However, when the multiple bond is between two like atoms, we must make our decision on the basis of other considerations. It seems reasonable that if in a molecule X—CH=CH—Y the X—C bond is more polarizable than the C—Y bond the electromeric shift would operate preferably in a direction away from X. An example is the time-honored propylene, in which the high $+I_d$ effect of the methyl group gives direction to the shift:[14a]

$$CH_3-CH\overset{\curvearrowright}{=}CH_2 \rightarrow CH_3-\overset{+}{C}H-\overset{-}{C}H_2$$

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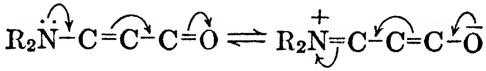
[14] See p. 429.

[14a] See, however, hyperconjugation, pp. 150 and 164.

The same result would be expected if X had a strong $+I_s$ effect, for it would produce a high electron density on the left-hand carbon atom, and this would repel the electrons of the double bond.

Mesomeric Effect. C. K. Ingold and E. H. Ingold[15] were the first to point out that there was reason to suspect the existence of a permanent polarization which is produced by the tautomeric mechanism of electron displacement. In such a system as



$$R_2\ddot{N}-C=C-C=O \rightleftharpoons R_2\overset{+}{N}=C-C=C-\bar{O}$$

they considered the most stable form to lie somewhere between the two extremes pictured, and the electrons involved are considered to be in the permanent possession of one more atom than is apparent from the formulas for either the neutral or the dipolar forms. Thus one pair of electrons contributes to the octets of three carbon atoms, etc. This concept is a modernization as well as an extension of Thiele's theory of partial valence. It is called the "mesomeric effect" (symbol, M).

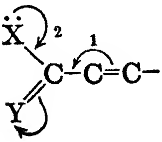
It should be emphasized that the two extreme structures ("unperturbed structures") given in the above equation represent exceedingly improbable states and that the actual state of the molecule lies in between them. This actual state is called the mesomeric state. Mesomerism is not to be thought of as a kind of tautomerism, for in the latter the molecules spend almost all of their time in one extreme configuration or the other, while the reverse is true of mesomerism.[16]

The relative mesomeric susceptibilities ($\pm M$ effects) of atoms and groups are the same as those already given for the electromeric effect ($\pm E$ effects) since they are produced by the same mechanism of electron transfer ($\pm T$).

The same remarks concerning the necessary conditions for operation of electron sources and sinks apply here as to the electromeric effect.

The direction of one M or E displacement may be influenced by that of another. Thus Ingold[1a] gives the following examples.

If a group X—C=Y is attached to an unsaturated system, we may expect the following electron displacements:



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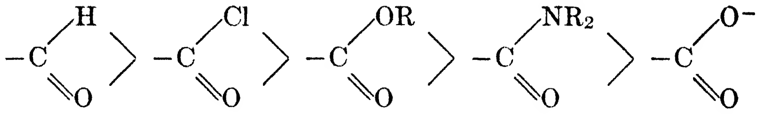
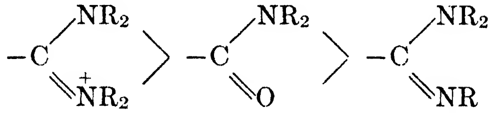
[15] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 1310 (1926).

[16] Ingold, *Nature*, **133**, 946 (1934); see also Ref. 1*a*, p. 251.

It is at once evident that displacements 1 and 2 may not both occur since they are in opposition. The greater the $+M$ effect of X, the less will displacement 1 take place, which is equivalent to saying that the less will be the $-M$ effect of the group $X{-}\dot{C}{=}Y$ as a whole. Thus we may deduce the following series, in which the groups are arranged in the decreasing order of their $-M$ effects.



Note that in H—C=O the hydrogen exerts no mesomeric opposition at all. The following sequence is also obvious:



A final point of importance should be noted. Whereas the electromeric effect is only called into play on the demand of the attacking reagent, and hence may not impede a reaction, the mesomeric effect is in operation at all times and therefore may impede a reaction.[17]

Summary of Electron Displacement Effects

Ingold's summary [18] of the four main electron displacement effects are given in Table III.

TABLE III [1a]

Electronic mechanism	Electrical classification	
	Polarization	Polarizability
General inductive (→) (I)	Inductive (I_s)	Inductomeric (I_d)
Tautomeric ($\curvearrowright$) (T)	Mesomeric (M)	Electromeric (E)

Summary of Basic Principles

In the application of any theory it is convenient to condense it into a set of working rules. If these rules are unambiguous and reliable the theory is an ideally successful one; if they must be bolstered by impromptu

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[17] Shoppee, *J. Chem. Soc.*, 698 (1932); Baddely and Bennett, *ibid.*, 265 (1933).

[18] Ref. 1*a*, p. 233. The modern symbols I_s and I_d have been added to his table.

vagaries so that one can only feel confidence when applying them *a posteriori,* then either the theory is in its infancy or it is a snare and a delusion.

Let us, then, try first to catalogue these working rules so that we may, without fear of omission, examine the evidence on which they are based and then proceed to the interesting task of studying the manner in which they have been applied by their sponsors.

In addition to Lewis's main ideas on atomic structure and the English classification of electrical influences as polarization and polarizability effects, and of the mechanisms of electron transfer as inductive and tautomeric, the theory of the English school involves the basic principles (symbolized by **P**) set forth below. This list does not include all the postulates which have been used by the English theorists, and some of those included have never been definitely set forth as postulates by anyone. The list merely represents the author's attempt to reduce the ideas of the English school to a set of reliable and useful working rules.

P 1. Substances react as a result of their affinities for electrons (electrophilic or cationoid) or atomic nuclei (nucleophilic or anionoid). Bimolecular reactions are initiated by and at those parts of molecules which are most strongly electrophilic and nucleophilic in such a way that nucleophilic and electrophilic centers are brought together.

P 2. If, by substitution or change in the thermodynamic environment, the electron density is increased at a given atom in a molecule, there will result an increase in the nucleophilic and a decrease in the electrophilic properties of that atom. Electrons are more easily removed from an atom the higher the electron density around it.

P 3. The relative magnitudes of the inductive, inductomeric, electromeric, and mesomeric effects of different atoms and groups may be deduced by well-established methods from considerations of atomic diameters, nuclear charges, and screening effects, except that the $+T$ effects decrease with increasing atomic number in any periodic group.

P 4. The magnitude of an inductive displacement becomes progressively and rapidly less as it proceeds away from the atom producing it. The extent to which the effect is transmitted is greater, the greater the polarizability of the intervening bonds.

P 5. Polarizability effects are brought into operation only under the influence of an external field; in chemical reactions this means only at the moment of reaction and only if they meet the electronic demands of the attacking reagent.

P 6. The extent (P) to which a polarizability effect is brought into play is given by the equation $P=\alpha F$, in which P is the induced polarization, α is the polarizability of the bond in question, and F is the strength of the distorting electrical field.

P 7. The change in electron density produced at a given atom by the operation of polarizability effects is proportional to the sum of the polarizations induced in the valence electrons of that atom.

P 8. Other things being equal, the electromeric effect will operate more readily the more extended the conjugation becomes.

P 9. The electromeric effect, except when unusually weak, is a much more powerful electron displacement agency than the inductive or inductomeric effect.

P 10. If it is possible to write two or more electronic structures for a given molecule without changing the arrangement of the atoms, then none of these structures represents the true state of the molecule, which is correctly represented by an intermediate mesomeric state. Thus the contributing structures will always undergo a mesomeric displacement in the direction of this intermediate state.

The above statement of the principle of mesomerism anticipates certain information to be presented in the next chapter. This procedure is employed because it is undesirable to reword any of the basic principles later.

EVIDENCE FOR THE BASIC PRINCIPLES

Inductive and Field Effects

It is well known that the measurements of the permanent dipole moments of molecules have given us excellent physical evidence that many covalent linkages are polar. That the polarity is transmitted through the molecule by an inductive mechanism demands independent verification.

The ideas that prompted Lewis to postulate an inductive displacement of electrons have already been reviewed. One supporting argument is found in the rapid diminution in the strengths of substituted fatty acids as the electronegative substituent is placed successively farther away from the carboxyl group. This behavior would, of course, be equally characteristic of the field effect and hence does not serve to distinguish between the two.

If we turn to dipole moment measurements for evidence we are naturally concerned with the manner in which the partial moment of a given bond is altered by substitution in other parts of the same molecule. It will be at once recognized that we are here dealing with the widely discussed and as yet unconquered problem of the mutual interaction of dipoles. In examining experimental data from this field we must be on our guard against work done on unsaturated molecules since it is not convincingly free from the taint of mesomerism.

One case free from this taint is the following.[19] Octachloropropane has no dipole moment. If one chlorine atom is replaced by hydrogen the resultant heptachloropropane has a moment of 0.8 *D*, which accordingly represents the difference of the partial moments of C—Cl and C—H. However, the moment of propyl chloride is 2.0 *D* which again may be taken as the difference of the same partial moments since propane itself has no moment. Obviously the chlorine atoms in the first example are exerting a strong influence on the bond in question. As to whether this influence is to be ascribed to the *I* or *D* effects, it is again difficult to surmise. We may say, however, that the presence of many chlorine atoms in the molecule has decreased the value of $\bar{\mu}_{\text{CCl}} - \bar{\mu}_{\text{CH}}$ and that this would be predicted if the *I* effect alone were responsible.* This follows quite simply from the basic theory of the *I* effect by the following argument. The value of $\bar{\mu}_{\text{CH}}$ in propane is zero or nearly so; hence the introduction of electronegative substituents, which would increase the effective kernel charge of the carbon atom, would increase $\bar{\mu}_{\text{CH}}$. The same influence would, however, decrease $\bar{\mu}_{\text{CCl}}$, since the chlorine atom is the electron-rich one of the C—Cl combination. Thus the value of $\bar{\mu}_{\text{CCl}} - \bar{\mu}_{\text{CH}}$ would be smaller in the highly chlorinated derivatives.

Results obtained in the study of electronic spectra of molecules also seem to demand the existence of the I_s effect.[20] Thus it is found that the ionization potentials of the electrons (presumably the unshared electrons) of the halogen atoms in alkyl halides are at least one volt lower than in the halogen hydrides. This is interpreted to mean that a larger negative charge exists on halogen atoms in the former, which in turn indicates that alkyl groups are more electron releasing than hydrogen.† Similarly, the most prominent bands in the spectra of alkyl substitution compounds of water, hydrogen sulfide, and ammonia are displaced to longer wave lengths with successive alkyl substitution.[21]

Further evidence in favor of the *I* effect is found in the recent paper of Remick [22] in which he attempts to calculate semi-quantitatively the effects of dipole interaction on the assumption that only the inductive mechanism is operative. He points out that, in considering the interac-

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[19] Boeseken, Henriquez, and Van der Spek, *Rec. trav. chim.*, **55**, 145 (1936).

* The symbol $\bar{\mu}_{\text{XY}}$ means the partial moment of the bond X—Y. The molecular moment is the vector sum of the partial moments of the constituent bonds.

[20] W. C. Price, *Ann. Repts. Progress Chem.* (London), 47 (1939).

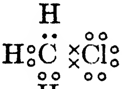
† See, however, the subject of "hyperconjugation" in the next chapter.

[21] Ley and Arends, *Z. physik. Chem.*, **B15**, 311 (1932); Herzberg and Schiebe, *Z. Physik*, **B7**, 390 (1930); Price, *J. Chem. Phys.*, **3**, 256 (1935).

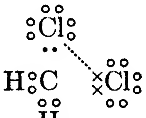
[22] Remick, *J. Chem. Phys.*, **9**, 653 (1941).

tions of partial dipole moments of bonds which involve a common atom, it would be a mistake to consider the "effect" operating by the inductive mechanism and the one operating across space to be two independent agencies, since the alteration of the effective kernel charge of the central atom (which is considered responsible for the operation of the inductive mechanism) is thought to be due to the altered screening effect of attached electron pairs, i.e., to their altered repulsions of other electron pairs attached to the same central atom. These repulsions would be expected to operate directly across space. In other words, the inductive mechanism itself is due to forces acting directly across space. The important point to be grasped with respect to the inductive mechanism is that it does not ignore the *direct* interaction of the electron pairs attached to the same central atom but replaces this interaction by an equivalent alteration in the effective kernel charge of the central atom which attracts electrons along the lines of the valence bonds.

As an example, let us consider the alteration in $\bar{\mu}_{CCl}$ which occurs when CH_3Cl is converted into CH_2Cl_2. The following pair of formulas will be helpful in concentrating attention on the electron pair symbolized by the black dots (:) and that symbolized by ××.



(I)



(II)

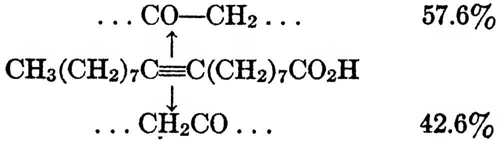
The substitution of chlorine for hydrogen causes this electron pair (:) to move away from the carbon atom, because chlorine is more electronegative than hydrogen. Since the molecules have tetrahedral configurations this means that the average distance (indicated by the dotted line between the pairs : and ××) becomes greater and the repulsive force between them therefore becomes less. Since the actual kernel charge (as contrasted with the effective kernel charge) of the carbon atom is a constant, the result is that the electron pair (××) moves in toward the carbon atom. Now the argument is that this sequence of interactions can be represented by an exactly equivalent though different mental picture as follows: When the electron pair (:) moves out the effective charge on the carbon kernel increases. This effective kernel charge is considered to operate from the center of the carbon atom and as a result of its increase the C—Cl electron pair (××) is drawn toward the carbon atom as before. Note that the second picture involves the consideration of no forces except those which operate along the lines of the valence bonds. This is the inductive mechanism.

It should now be clear that there is no justification for considering the inductive effect and the effect "operating directly across space" to have separate existences when we are considering the dipole interactions of two bonds attached to the same central atom. But in chloroacetic acid, for example, the electrical field of the chlorine atom might conceivably affect the O—H bond by two fundamentally different mechanisms: (1) the inductive mechanism, operating along the path of the intervening bonds and (2) the field effect, operating directly across the empty space between the C—Cl and the O—H bonds. At first thought it might seem that the transmission of electrostatic influence would depend on the polarizabilities of the intervening bonds in the *I* effect but not in the *D* effect; but this can hardly be true because in the latter case the extent to which the substitution alters the polarity of the O—H bond will depend on its polarizability which, in turn, will depend on the polarizability of the adjacent C—O bond, etc. Quantitatively, of course, there may be differences which could serve diagnostic purposes and in extreme cases, such as stereochemical approaches to ring formation, it is conceivable that the *D* effect could operate when the *I* effect would have been damped out on its passage through a long chain of atoms; but in general it seems that for qualitative purposes consideration of the *I* effect alone will serve to take care of both influences.

With this clarification of basic concepts we may quickly dispose of the question of just how much support this paper [22] gives to the concept of the inductive mechanism. The original paper should be consulted for mathematical details but the essential picture may be given here. Every molecule is considered to have been formed by substitution of a reference molecule, CH_3Y, the four "standard bond moments" of which may be calculated from the measured molecular dipole moment and equations based on the mathematical model described below. The substitution alters the effective kernel charge of the central carbon atom because $\bar{\mu}$ for the new bond is different from the standard moment of the bond replaced. This change in the effective kernel charge of the carbon alters the partial moments of the other bonds in proportion to their polarizabilities. These secondary alterations exert a back inductive effect on the first bond, changing its value. This back and forth interaction finally results in equilibrium values for all bond moments concerned, which values emerge from the mathematics. Their vector addition gives the "calculated value" of the molecular dipole moment. The mathematical treatment is rendered comparatively simple by the assumption that no interactions take place except along the lines of the valence linkages, i.e., by the inductive mechanism. The calculations were made for a number of polyhalogenomethanes and ethanes and for isopropyl and *tert.*-butyl chlorides and gave values of molecular dipole moments in rough accord with measured values. In the few cases where comparison was possible the accord between theory and experiment was just as good as that achieved by Smyth and McAlpine,[23] who set up a model involving only direct electrostatic interactions between the parts of the molecule. Although both methods involve questionable assumptions, it seems safe to conclude that they demonstrate that the two modes of electron displacement are really equivalent and that the concept of the inductive mechanism as used by the English school is not only justified for qualitative deductions but for semi-quantitative ones as well. It was also shown [22] that if the "bond refractions" of the carbon-halogen bonds were empirically reduced to correct for the contributions of the unshared electrons whose polarizabilities are unavoidably included in the "bond refractions" and if a similar empirical increase is allowed in the C—C bond refraction to correct for another error inherent in the mathematical method, the result is a good agreement between calculated and experimental values. The success of these empirical adjustments, made as they were in directions dictated by the theory itself, give added weight to the argument. Furthermore, the agreement achieved in cases where one or more methyl groups were substituted into halogenomethanes probably indicates that it is semi-quantitatively legitimate to consider the perturbations produced by the C—Cl dipole as being transmitted along a chain of atoms, thus: $H \rightarrow C \rightarrow C \rightarrow Cl$.

These arguments conclude the evidence in favor of the inductive effect and they make clear certain limitations in regard to the usefulness of the concept of a field effect without throwing the least doubt on its actual existence. It is one thing, however, to recognize the certain existence of such an effect and quite another to demonstrate that its magnitude is such as to exert an appreciable influence in relation to other effects or that it operates in a manner which would distinguish it from the inductive effect. Let us, therefore, turn to the evidence which has been presented in attempts to answer these questions.

Robinson [24] cites, as proof of the existence of an appreciable field effect, the hydration of stearolic acid by means of sulfuric acid and water in which unequal amounts of the two isomers are formed:



$$\begin{array}{cc} \ldots CO{-}CH_2\ldots & 57.6\% \\ \uparrow & \\ CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2H & \\ \downarrow & \\ \ldots CH_2CO\ldots & 42.6\% \end{array}$$

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[23] Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

[24] Robinson and Robinson, *J. Chem. Soc.*, 2204 (1926); also Ref. 1*b*, p. 32.

Since the inductive effect of the carboxyl group would not be transmitted through a chain of seven carbon atoms he deemed it necessary to assume that the chain is bent around in space until the carboxyl group is in close proximity to the triple bond, when electrostatic influences could operate directly across space from one to the other. It would be further necessary to suppose that the carboxyl group is closer to one of the unsaturated carbon atoms than to the other. If this were so, the effect might well be of a purely mechanical nature.

He also cites the work of Walker and Lumsden [25] who found that the addition of hydrogen bromide to undecylenic acid yields one isomer in toluene and the other in ether solution.

$$\mathrm{HBr} + \mathrm{CH_2{=}CH\cdot(CH_2)_8CO_2H} \left\langle \begin{array}{l} \xrightarrow{\text{toluene}} \mathrm{BrCH_2CH_2(CH_2)_8CO_2H} \\ \xrightarrow{\text{ether}} \mathrm{CH_3CHBr(CH_2)_8CO_2H} \end{array} \right.$$

Here again he assumes a bending of the chain bringing the carboxyl group close to the double bond and devises an explanation to render reasonable the greater intervention of the field effect in the case of the toluene solution. It has since been shown,[26] however, that this is merely another case of the "peroxide effect" discussed in Chapter II.

The work of Bennett and Mosses [27] is also quoted by Robinson as bearing on the question. They showed that when phenyl-γ-hydroxypropyl sulfide, phenyl-δ-hydroxybutyl sulfide and phenyl-ϵ-hydroxyamyl sulfide are subjected to the action of fuming hydrobromic acid under identical conditions, the extent to which they react in equal lengths of time is: 1.0% for the γ-compound, 90% for the δ-compound, and 1.3% for the ϵ-compound. The γ- and ϵ-compounds form the phenylbromoalkyl sulfides while the δ-compound forms the cyclic sulfonium bromide. They argued that the fact that the δ-compound underwent ring closure showed that the δ-substituent must be close to the sulfur atom in space. Furthermore, since the normal induction would not exert any appreciable influence through four carbon atoms, the increased reactivity of the δ-hydroxyl group must be ascribed to the direct influence of the sulfur atom acting across space. One might think their argument invalid since they seem to be comparing the speeds of two different kinds of reactions. However, they presented evidence to show that in the δ-compound the open chain bromide was first formed, cyclization occurring subsequently; and it is obvious that if these two reactions together occur

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[25] Walker and Lumsden, *J. Chem. Soc.*, **79**, 1191 (1901).

[26] (*a*) Ashton and Smith, *ibid.*, 435 (1934); (*b*) Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **13**, 331 (1938); (*c*) J. C. Smith, *Chem. and Ind.*, 461 (1938).

[27] Bennett and Mosses, *J. Chem. Soc.*, 2364 (1930).

more rapidly than the reactions of the γ- or ε-bromides, then the first step must also occur more rapidly. The first step is of the same type as the reactions of the other two compounds and hence, they argued, strictly comparable.

There is, however, one adverse criticism that might justly be made of their contentions. The conversion of the various hydroxy compounds into open chain bromides is probably a reversible reaction. Hence it is possible that the reversible conversion of the δ-hydroxy-compound into the open chain bromide is accelerated by the removal of one of its reaction products. Since the other two reactions are not subject to such an influence, there would be no basis for comparison.

Lapworth and Manske[28] suggested that the fact that all *ortho*-substituted benzoic acids are stronger than benzoic acid itself is to be ascribed to the field effect of the *ortho*-substituent on the carboxyl group. This argument was extended by Bennett and Mosses.[27] Watson[29] discusses this and other related phenomena under the heading of "the *ortho* effect" and comes to the conclusion that at least in a large number of cases the phenomenon is due to chelation.

Another entirely different avenue of approach is suggested when one considers that strong repulsive or attractive field effects between two neighboring substituents should change the angles of the bonds concerned. If the two substituent atoms or groups are so large that ordinary space requirements demand a spreading of the valence bonds, the compound cannot serve as a test case. But if small substituent atoms of high electronegativity are used, the situation is ideal. This suggests fluorine or chlorine. Following up this avenue of approach we may examine Table IV. The bond angles there listed were determined by electron diffraction measurements.[30] Although there is a slight indication of bond spreading, it is to be noted that within the limit of experimental error no departure from the tetrahedral angle, 109°28′, has been definitely demonstrated. If this angle really obtains in these cases it means either that

TABLE IV[30]

ANGLES BETWEEN C—Cl BONDS

Compound	Angle
CH_2Cl_2	111° ± 2°
$CHCl_3$	111° ± 2°
CCl_4	109° 28′

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[28] Lapworth and Manske, *J. Chem. Soc.*, 2539 (1928).

[29] Ref. 1*d*, p. 205.

[30] Sutton and Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).

the electrical field at small distances from chlorine atoms is slight or that it is of about the same magnitude as that of hydrogen atoms. The latter alternative seems unlikely.

It is significant that if two chlorine atoms do not repel each other appreciably when they are in such close proximity they can hardly be expected to exert an appreciable field effect between more or less remote parts of a molecule. This is borne out by dipole moment measurements on *cis*-2,3-dichloro-2-butene from which it is concluded that there is no deformation of the carbon tetrahedra.[31] Similarly Johnston and Dennison [32] have concluded from moments of inertia that the methyl group has the same dimensions in methane and in the methyl halides. While these few examples do not exhaust the literature on the subject they make it sufficiently clear that the field effect of chlorine atoms is not strong enough to produce appreciable change in bond angles. Since the transverse polarizability of the electrons in a C—Cl bond is about 57% as great as the longitudinal polarizability,[33] it would seem that the field effect must be small indeed. Since the C—Cl bond is highly polar, this conclusion can probably be extended to other atoms bound to carbon by ordinary covalences. The case is presumably different, however, for atoms which are free poles, as the following evidence indicates.

Years ago it was shown that, if each hydrogen atom in a symmetrical dicarboxylic acid ionizes independently, statistical considerations require that $K_1/K_2 = 4$, where K_1 and K_2 are respectively the first and second ionization constants.[34] This result has been found to hold true in many cases (both phenols and carboxylic acids). Where there are deviations from this rule interaction between the two groups is assumed. If these two groups are separated by more than two saturated carbon atoms, the internally propagated effect (I_s) becomes negligible and the interaction is ascribed to the field effect. This assumption has been rendered plausible by the mathematical treatment of the problem given by Bjerrum [35] who has shown that the deviation is a function of the distance between the two carboxyl groups. His mathematical treatment took into consideration the accumulation of hydrogen ions around the free negative pole of the acid, thus producing locally an excess over the average distribution in the solution. The work of Bjerrum has been extended by others and the resultant calculations are well in accord with those from X-ray

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[31] Mikhailov and Tischenko, *J. Gen. Chem. (U.S.S.R.)*, **9**, 782 (1939).

[32] M. Johnston and D. M. Dennison, *Phys. Rev.*, **48**, 868 (1935).

[33] Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

[34] (*a*) Wegscheider, *Monatsh.*, **16**, 153 (1895); (*b*) Adams, *J. Am. Chem. Soc.*, **38**, 1503 (1916).

[35] Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

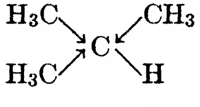
data.[36] It is of particular interest that Ingold [37] has successfully extended the treatment to include a theoretical calculation of the ratio of the velocity constants of the first and second steps in the hydrolysis of esters of dicarboxylic acids.

In conclusion we may say that a combined I_s and D effect operating essentially in accord with the theoretical requirements of the I_s effect has been convincingly demonstrated. Tentatively it seems that the D effect is negligible in cases involving only normal covalences and is operative in cases in which a free pole can cause ions of the opposite charge to cluster around it in solution.

Inductomeric Effect

If we accept the modern theory of refraction we must admit the existence of inductomeric polarizability, which is the only type admissible in saturated compounds in general.*

If we seek evidence that inductomeric polarizability is called into play during chemical reactions and that it may direct the course of the reactions, we may turn to an argument by Ingold.[38] The most acceptable definition of group dipole moments is given, for a group X, by the equation $\bar{\mu}_X = \mu_{RX} - \mu_{RH}$. This gives the moment of X relative to hydrogen. Since the moments of all saturated hydrocarbons are zero, it follows that the moment of the methyl group (relative to hydrogen) is zero. Yet, when paraffins are nitrated, the tertiary hydrogen atoms are most readily attacked notwithstanding that in the case of isobutane, for example, there are nine primary hydrogen atoms to one tertiary atom. The most reasonable explanation would be the assumption that polarity was induced in the methyl groups by the field of the attacking reagent, thus:



"The possibility of an inductomeric ($-I_d$) effect of alkyl groups in the presence of nucleophilic reagents may be foreseen."

Evidence in favor of the English school's method of deducing relative inductomeric polarizabilities of bonds is to be sought in refraction data. We are, however, immediately faced with the difficulty that it is at present impossible to calculate the contribution made to the group

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[36] For a review of the subject see Greenspan, *Chem. Rev.*, **12**, 339 (1933).

[37] Ingold, *J. Chem. Soc.*, 1375 (1930).

* As far as can be judged at the present time second order hyperconjugation (see next chapter) does not operate in compounds such as CCl_4.

[38] Ingold, *J. Chem. Soc.*, 1125 (1933).

refraction by the shared electrons in a bond such as $\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ since the contribution of the unshared electrons is not known. However, if we proceed cautiously we may find strong supporting evidence in the data of Table V. The comparison of C—H with Si—H, and C—C with Si—C involves no unshared electrons. In each case the polarizability becomes greater when silicon is substituted for carbon. This is in accord with the theory. Since the halogens all have the same number of unshared electrons we may also make a valid comparison of their polarizabilities.

TABLE V

MOLAR REFRACTIONS OF ELECTRON GROUPS

		Lit.			Lit.
C—H	1.61 cc	39	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$	1.82 cc	39
C—C	1.41	39	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$	6.57	40
Si—H	2.99	39	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:$	9.47	40
C—Si	2.30	40	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:$	14.51	40

Again the facts accord with the theory.

One point which deserves special comment relates to the polarizabilities of the C—H and C—C bonds. Lewis, Lucas, and the whole English school agree that the methyl group is less electronegative than the hydrogen atom. Since, as was pointed out at the beginning of this section, C—C and C—H seem to have equal bond moments in hydrocarbons, this viewpoint can only be interpreted as meaning that the I_d effect of C—C is greater than that of C—H. But this is contrary to the refraction data of Table V. Recently an explanation has been found in terms of a peculiar type of mesomerism (or resonance) involving the methyl group. This phenomenon will be discussed in the next chapter under the heading of "hyperconjugation." For the moment, however, I wish to consider another possible explanation of the apparent fact that alkyl groups in saturated hydrocarbons show a larger I_d effect than hydrogen despite the lack of parallelism in their polarizabilities. This may possibly be due to the fact that bond polarizabilities are made up of both transverse and longitudinal components. Denbigh[33] gives the values in Table VI for the bond refractions (P_E), the longitudinal polarizabilities (b_l), and the transverse polarizabilities (b_t). It is evident from these

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[39] Calculated from the data of Watson and Ramaswamy, *Proc. Roy. Soc.* (*London*), **A156**, 144 (1936).

[40] C. P. Smyth, *Dielectric Constant and Molecular Structure*, The Chemical Catalog Co., 1931, p. 152.

data that although the C—H bond is the more polarizable its longitudinal component is less than that of the C—C bond. It seems reasonable to suppose that in chemical reactions it is the ease with which the electrons can approach the carbon atom which is most important. Thus the longitudinal component of polarizability is indicated as the best measure of the I_d effect.

TABLE VI

Bond	P_E	$b_l \times 10^{25}$ (cc)	$b_t \times 10^{25}$ (cc)
C—C	1.25	18.8	0.2
C—H	1.69	7.9	5.8

That an atom affects the polarizability of electrons in the same molecule even though not directly united with them is proved by an argument given in Appendix II. There it is shown that if we ascribe to the unshared electrons in HCl the same polarizability that they evidence in the chloride ion, the contribution made by the covalent pair is practically zero; in certain other cases it is a negative number. This shows clearly that the unshared electrons are put under more constraint when the chloride ion becomes attached to a positive ion. If this is true for unshared electrons it is surely true also for shared electrons, and we may say with confidence that the constraints under which electrons exist in molecules are altered by substituents. This conclusion fits in well with our ideas on the inductive mechanism.

The effect of substituents on the inductomeric polarizability of a given bond is not very great, however, as judged by refraction data. Thus Denbigh [33] has compared the observed values of the molar refractions of about 130 compounds with those calculated by the addition of the component "bond refractions" and has found that the average error is 0.7% and is seldom greater than 1.5% except in compounds containing C—F and C≡C where it may be as much as 4%. This means that substitution does not much alter the constant values of the bond refractions (polarizabilities) used.

Let us next consider the evidence relating to the magnitude and direction of the small effect produced on bond polarizability (I_d) by substitution. In Table VII are listed the molar refractions of molecules produced by the successive substitution of chlorine. In the third column are given the differences in $[R_M]_D$ between each pair of successive compounds. The two figures in parentheses were obtained by dividing by two the difference between the $[R_M]_D$ values of methane and methylene chloride. This procedure was necessitated by the lack of data for methyl chloride. No doubt the first of these figures should be slightly smaller and the second slightly larger than 4.89.

TABLE VII[41]

Compound	$[R_M]_D$	$\Delta[R_M]_D$
CH_4	6.60	
		(4.89)
CH_3Cl	.....	
		(4.89)
CH_2Cl_2	16.38	
		4.99
$CHCl_3$	21.37	
		5.07
CCl_4	26.44	

If the bond refractions were not altered by substitution the figures in the third column would, of course, be constant and equal to the difference between the refraction of the C—Cl bond which was introduced and the C—H bond which was removed. Since these figures are not constant it shows that the refractions of both the C—H and the C—Cl bonds are altered by substitution since it is quite inconceivable that only one of them would be altered. Now, since the values of $\Delta[R_M]_D$ depend on a *difference* of bond refractions, $(P_E)_{C\text{-}Cl} - (P_E)_{CH}$, there are two possible explanations of the trend observed on successive substitution of chlorine: (1) the polarizability of the C—Cl bond becomes smaller and that of the C—H bond becomes still smaller, or (2) the polarizability of the C—H bond becomes larger and that of the C—Cl bond becomes still larger.

The first possibility is in accord with the English theory since the substitution of a chlorine atom would be expected to put all electrons under greater constraint. Furthermore, in view of the magnitudes and directions of the two bond moments concerned, the electrons of the C—H bond must be closer to the carbon atom and hence their polarizability would be more altered by the change in effective kernel charge of the carbon atom produced by the substitution. Thus the polarizability of the C—H bond "becomes still smaller."

The second of the above-mentioned possibilities is favored by Stevels.[41] He devised a method for calculating the refractions of the bonds in halogenated methanes, assuming that these bond refractions varied from compound to compound. The results of his calculations are given in Table VIII. It is unfortunate that he felt compelled to use in his calculations for *covalent bonds* a formula developed by Fajans for use with *ions* of the alkali metal halides. In the author's opinion this throws grave doubts on the validity of his method. Stevels also attaches considerable importance to the fact that the trends of the calculated bond

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[41] Stevels, *Trans. Faraday Soc.*, **33**, 1381 (1937).

TABLE VIII [41]

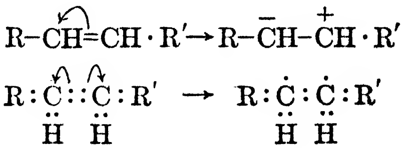
Compound	Calculated bond refractions	
	C—H	C—Cl
CH_4	1.65	....
CH_3Cl	1.77	6.19
CH_2Cl_2	1.89	6.33
$CHCl_3$	2.01	6.47
CCl_4	....	6.61

refractions for C—Cl parallel the bond stretching polarizabilities as deduced from Raman spectra. However, if the same comparison is made for his calculated values of C—H refractions, the reverse is found to be true.[42]

It is apparent that this controversial question must be settled before we can definitely state whether or not refraction data bear out this phase of the English theory.

Electromeric Effect

The electromeric effect has been defined as a displacement of electron pairs by the tautomeric mechanism under the influence of an electric field external to the molecule under consideration. It can be demonstrated that such a movement must frequently take place in compounds containing double bonds under the influence of an attacking reagent, for if at the outset the structure of an olefin is correctly represented by the formula R—CH═CH·R′, then it is obvious that at some stage of the process one of the following electronic shifts must have taken place:



$$R-CH{=}CH\cdot R' \rightarrow R-\overset{-}{CH}-\overset{+}{CH}\cdot R'$$

or

$$R:\underset{\underset{H}{\cdot\cdot}}{C}::\underset{\underset{H}{\cdot\cdot}}{C}:R' \rightarrow R:\underset{\underset{H}{\cdot\cdot}}{\dot{C}}:\underset{\underset{H}{\cdot\cdot}}{\dot{C}}:R'$$

The first case represents an electromeric displacement. These two possibilities are considered in detail by Waters and Lowry [43] who present evidence to show that each type is possible under the proper conditions. They classify the first type as "ionic reactions" and the second as "nonionic reactions." Nonionic reactions are characteristic of gases, particularly in cases where photochemical activation is concerned, although

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[42] See Chap. VI, p. 171.

[43] Ref. 1*e*, Chapters V, VI, VII, VIII.

they may also take place in nonionizing solvents of low dielectric constant where the formation of ions would be difficult. A discussion of this type of reaction is reserved for a later chapter. Ionic reactions, on the other hand, take place in solution at low temperature in the dark, particularly if there is present any polar substance such as the solvent itself, the glass walls of the containing vessel, or an ionized reactant or catalyst.

Certain reactions of unsaturated substances have been demonstrated to occur by the ionic mechanism. Stewart and Edlund[44] showed that the interaction of ethylene and bromine vapor takes place mainly, if not entirely, on the glass walls of the reaction vessel. Norrish[45] studied the same reaction, coating the walls of the reaction vessel with substances of different degrees of polarity, and found that the catalytic effectiveness of the various surfaces is in the order: stearic acid > glass > cetyl alcohol > paraffin wax. These experiments indicate that a polar catalyst is needed to promote the reaction and hence strongly indicate that an ionic mechanism is involved since it is difficult to imagine the electrical field of the polar catalyst forcing the two electrons in opposite directions.

Lapworth's work[46] on the addition of hydrogen cyanide to aldehydes and ketones makes it clear that this also involves an ionic mechanism.

In relation to reactions involving acids, Waters and Lowry conclude ". . . nearly every action of any acid, occurring at moderate temperatures and in the absence of photochemical activation, depends upon a process of ionization."

Certain heterogeneous reactions with sodium and certain other metals seem to involve the nonpolar mechanism.[47] We may satisfy our immediate objective by coming to the point at once and concluding that most homogeneous addition reactions involving multiple bonds are of the "ionic type," and that all of the "ionic type" must involve an electromeric displacement at some stage of the reaction.

Thus the existence of the effect cannot be doubted. However, certain of its characteristics already outlined have yet to be justified. For evidence on these points we may turn to the study of refraction, which is a phenomenon depending on polarizability.

The significance of the exaltation of the refraction is apparent from the well-known equation[48]

$$n^2 = 1 + \frac{e^2}{\pi m} \sum \frac{N}{(\nu_0{}^2 - \nu^2)}$$

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[44] Stewart and Edlund, *J. Am. Chem. Soc.*, **45**, 1014 (1923).

[45] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923); **129**, 55 (1926).

[46] See Chap. IV, p. 53.

[47] See Chap. IX.

[48] Appendix II, Eq. 5.

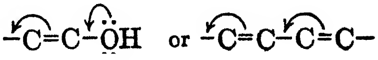
from which it is evident that an unexpectedly large value (exaltation) of n for a given substance and given light source would require that ν_0 be abnormally small; this would mean that the electrons concerned must be under unexpectedly small constraints.

Thus in speaking about the effects of structure on the properties of the molecules we may say that "elements perturbateurs" produce a loosening of the electrons and this of course means greater polarizability.

There are certain difficulties involved in the interpretation of refraction data, however. In the first place, as pointed out by Ingold,[49] it is impossible to analyze refractometric data adequately without more knowledge concerning molecular anisotropy, since this factor is assumed absent in the derivation of the Lorentz-Lorenz equation. Furthermore, it is impossible accurately to ascribe the exaltation to a given bond since it is measured for all the electrons in the molecule, shared and unshared. However, if we concern ourselves exclusively with cases involving large exaltations, it is reasonably certain that the polarizabilities of the bonds of the "elements perturbateurs" are at least roughly given, in comparison to normal bonds, by the exaltations observed.

It has been observed that in all cases where the theory would predict the operation of the electromeric effect we find the polarizability, as measured for example, by refraction data, considerably greater than in the corresponding cases where only inductomeric polarizability is possible. This clearly shows the relative magnitudes of these two effects. The following facts bear out this contention.

Unconjugated multiple bonds are not ordinarily considered to involve exaltation of the refraction. However, the fact remains that a positive correction has to be made for their presence, and this is equivalent to saying that their polarizability is higher than that of a single bond between the same two atoms. If the multiple bond is conjugated the exaltation indicates a further increase in polarizability, successive conjugation producing successive increases (cf., **P 8**). It is thus apparent that refraction studies show that there must be strong interaction between the unsaturated units of a conjugated system. Since these units are peculiar only in that they contain unshared electrons or multiple bonds, it appears likely that the interaction depends on the possibility of their mutual donation and reception of electrons. This possibility becomes almost a certainty when we further observe that the unsaturated units must be in just the right relative positions for this relay of electrons or exaltation of the refraction will not occur, for example:



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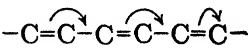
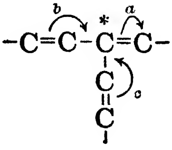
[49] Ref. 1*a*, p. 265.

In regard to crossed conjugations, the theory would predict that they would be less effective. Thus in the following examples I would be ex-



I



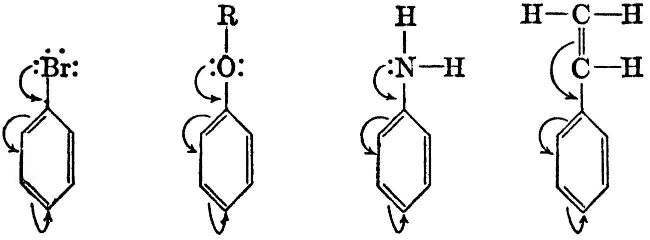
II

pected to show more exaltation than II because in the former the transmission of electromeric shifts may operate unimpeded through six carbon atoms, whereas in the latter displacement "a" may be followed by "b" or "c" but not by both at once unless the octet limitation of the starred carbon atom is to be ignored. The data given in Table II of Appendix II are in accord with our theoretical predictions and thus support those portions of the theory used.

Additional support for the theory may be obtained from a consideration of data such as those given in Table IX. In each case the theory would predict the operation of the electromeric effect, thus (showing just one of the possible series of shifts):

TABLE IX [50]

Compound	T., °C	EM_D	$E\Sigma_D$
Benzene	20	−0.17	−0.218
Bromobenzene	20	−0.240	−0.154
Anisole	16.5	+0.305	+0.273
Aniline	20	+0.868	+0.932
Styrene	20	+1.27	+1.221



As one proceeds down the table the substituents become less electron attractive and the loosening up of the electrons should become progressively greater, as shown actually to be the case by the distinct trend of the exaltations. This trend would have been predicted by **P 3** which,

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[50] Calculated from data in *International Critical Tables*, 7, except for benzene and styrene, which were taken from Hückel's *Theoretische Grundlagen der Organischen Chemie*, Akademische Verlagsgesellschaft, Leipzig, 1935, pp. 130, 134.

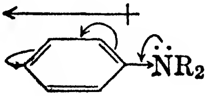
incidentally, has already been justified by the discussion of Fajan's rules in Appendix II.

Thus we see that where the theory would predict electromeric displacements we actually observe greater polarizabilities, the increases brought about by certain combinations of atoms and bonds being in the same relative order of magnitudes as the theory would predict. This is a strong indication that such induced polarizations operate largely by the tautomeric mechanism.

Mesomeric Effect

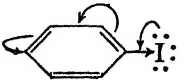
Ingold [51] has given a detailed discussion of the evidence for the mesomeric effect. Since mesomerism has come to be recognized as an example of resonance, which concept had its inception in quantum mechanics, much of the evidence naturally comes from the field of chemical physics and accordingly will be discussed in the next chapter. We may, however, examine certain other evidence at once.

In 1926 Ingold [52] suggested that dipole moment measurements on aromatic and aliphatic amines should yield evidence of the existence of mesomerism. In the case of the aliphatic amines only the inductive effect can be operative while in the aromatic amines there will be a mesomeric displacement opposing the inductive displacement. Since nitrogen has a low electronegativity it seems possible that the mesomeric would outweigh the inductive effect in an aromatic amine with the result that the direction of the electric moment associated with the linkage in question would become reversed.



$$\overset{+\!\!\longrightarrow}{H_3C \rightarrow NR_2}$$

The first tests of this kind were made subsequently by Højendahl [53] with definitely positive results. Later Sutton [54] made more extensive investigations on the difference between the dipole moments of a number of similar pairs of compounds, i.e., Ar—X and Al—X. The significance of this difference becomes apparent when we consider, for example, the pair of iodides:



$$H_3C \rightarrow \underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}:$$

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[51] Ingold, Ref. 1*a*, p. 253.

[52] Ingold, *Ann. Repts. Chem. Soc.*, **23**, 144 (1926).

[53] Højendahl, *Studies of Dipole Moments*, Bianco Lunos Bogtrykkeri, Copenhagen, 1928.

[54] Sutton, *Proc. Roy. Soc.* (London), **133A**, 668 (1931).

If a negative sign is given to the value of a dipole when it is directed away from the carbon atoms, it is apparent that the $+M$ effect of iodine in iodobenzene will make that moment less negative than it would be in the absence of mesomerism. Thus if a $+M$ effect is operating, $\mu_{Ar-X} - \mu_{Al-X}$ will be a positive number and it will be more positive the greater the value of the $+M$ effect. On the other hand, if the effect is $-M$, as would be expected with the nitro group, the difference should be negative. His results are given in Table X.

TABLE X[54]

Group	$\mu_{Ar-X} - \mu_{Al-X}$	Group	$\mu_{Ar-X} - \mu_{Al-X}$
I	0.86	O	(0.23)
Br	0.69	S	(0.10)
Cl	0.59	CN	−0.43
CH_3	0.45	CCl_3	−0.50
NH_2	(0.32)	NO_2	−0.88

The parentheses indicate uncertainty due to ignorance of the angles involved. The other groups have the relative values to be expected from the theory except that CH_3 and CCl_3 would not have been expected, on the basis of any theory known at that time, to show any mesomeric effect. This apparent anomaly suggested strongly that at least part of the effect at first ascribed to mesomerism is in reality due to another type of mutual interaction between the hydrocarbon radicals and the substituent groups, viz., an interaction of the inductomeric type, if we may stretch the definition of that term to include intramolecular alteration of permanent polarization.

Groves and Sugden[55] improved on Sutton's work by devising an approximate method for calculating the magnitude of the induced moments.[56] They were thus enabled to apply a correction for them and on doing so they obtained fairly consistent bond moments for polar groups from the data for aliphatic compounds. For example, from the data for acetonitrile, they calculated μ_{CN} to be 2.97, while from propionitrile the value turned out to be 3.03 *D*. However, when these bond moments were used to compute the moments of aromatic compounds it was found that additional moments ("mesomeric moments") were present, much as was found in Sutton's work. Their results are given in Table XI. While the signs of the mesomeric moments are those predicted by the theory, it will be noticed that the order of the halogens is the reverse of that to be expected on the basis of Fajan's rules. As already mentioned,

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[55] Groves and Sugden, *J. Chem. Soc.*, 1992 (1937).

[56] The method was a development of that suggested by Frank, *Proc. Roy. Soc.*, **152A,** 171 (1935).

TABLE XI [57]

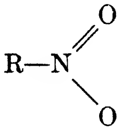
Mesomeric Moments

Phenol	1.12	Diphenyl ether	0.47 (in each Ph group)
Fluorobenzene	1.00	Anisole	0.40
Chlorobenzene	0.97	Benzonitrile	−0.05
Bromobenzene	0.89	Acetophenone	−0.17
Iodobenzene	0.87	Nitrobenzene	−0.29

this situation is found in a large number of other cases and will be further discussed later in this chapter. It has already been discussed earlier in this chapter in relation to the concepts of Lewis.[14]

Thus we find that on turning to the field of dipole moments in search for evidence substantiating the concept of mesomerism, the evidence clearly indicates the operation of some such factor in conjugated systems; but owing to the complexity of the problem of quantitatively correcting for inductive interactions, we feel uncertain that the magnitude of the effect can be adequately predicted on the basis of simple considerations of kernel charges and the screening effect.

If we next turn our attention to justifying the concept of the mesomeric state as one of resonance between the two extreme contributing forms we find that the evidence from dipole moment measurements is more convincing.[58] Thus the two contributing forms of a nitro compound would be represented as



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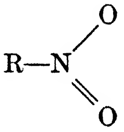
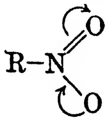


while we would symbolize the mesomeric state as



The fact that *p*-dinitrobenzene and 4-4′-dinitrodiphenyl have zero dipole moments indicates that the nitro group has a symmetrical structure as the mesomeric form would and the contributing forms would not have.

Ingold [58] also cites certain chemical evidence. For example, in cases involving the keto-enol type of tautomerism ("prototropy") many pairs of hydrogen isomerides have been isolated, but no single pair of corre-

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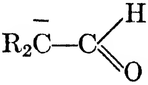
[57] The signs have been changed to make them consistent with the convention used by Sutton.

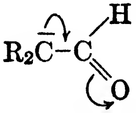
[58] Ingold, *J. Chem. Soc.*, 1120 (1933).

sponding alkali salts. This would mean either that the anion has the enol structure $R_2C{=}CH\cdot O^-$ which is incapable of tautomerizing to the keto form,



$R_2\overset{-}{C}\text{—}C\begin{smallmatrix}\diagup H\\ \diagdown\!\!\diagdown O\end{smallmatrix}$

, or that the ion has a mesomeric structure



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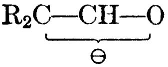


$\underbrace{R_2C\text{—}CH\text{—}O}_{\ominus}$

more or less midway between the two contributing structures. The first interpretation seems unlikely in view of the extreme mobility of electrons.

APPLICATIONS OF THE THEORY

In the foregoing discussions an attempt has been made to summarize under the heading of "basic principles" only those ideas which seem to be best substantiated and most widely accepted by the proponents of the English theory. Many other principles have been used from time to time by individual investigators who were hard pressed to explain their experimental results. We thus find ourselves beset by many different effects, including such concepts as "reversed effects," and we are dismayed to find in many cases that we may obtain a complete reversal of our predictions by assuming somewhat different yet completely reasonable magnitudes for opposing effects. In fact we cannot avoid the suspicion that one could explain any reaction, *a posteriori*, by the simple expedient of ignoring certain effects, reversing others, augmenting and diminishing magnitudes until a proper balance is obtained and then, if all this failed to give satisfaction, employing the field effect to administer the *coup de grâce* to the writhing victim.

In view of such difficulties it seems best to avoid consideration of those published papers which employ ill-founded concepts not included in our table of basic principles. The field effect will not be given separate recognition from the inductive effect. The quantitative shortcomings of the theory, however, will be emphasized since improvement in these represent the direction in which the theory must grow. Emphasis will also be given to the best substitute that has yet been found for a quantitative theory, viz., the establishing of trends which are in accord with the theory. The great success achieved in this department of research is the strongest argument in favor of the essential validity of the theory.

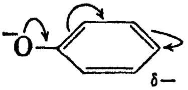
Aromatic Substitution

The theoretical interpretation of aromatic substitution has long been a favorite topic among organic theorists. We have already seen how Lucas attacked the problem. Not long after his publications on the subject we find Robinson[59] and Ingold[60] combining Lewis's electron displacement concept with Lowry's[61] electromeric displacement and demonstrating that the combination gives a satisfactory interpretation of aromatic substitution.

There are two important phases of aromatic substitution which have been extensively discussed, viz., orientation, and nuclear activation and deactivation. There have been several empirical rules proposed in regard to orientation phenomena, the most famous of which was the Crum-Brown-Gibson rule. In regard to the activation and deactivation phenomena, it has long been recognized that all the *meta* directing groups are deactivating, whereas the *ortho-para* directing groups cause activation of the benzene ring, except for the halogens.

Let us proceed at once to a study of the way in which the English school has explained these phenomena.

Activation and Deactivation. The common aromatic substitution reactions are all brought about by electrophilic reagents and hence should be accelerated by the presence of electron-releasing groups and impeded by electron-attracting groups. Thus toluene is more active than benzene, which in turn is more active than nitrobenzene. Similarly, if an electron-releasing group is substituted in naphthalene or anthraquinone further substitution will normally take place in the substituted ring; if the substituent is electron attracting the other ring will be attacked.

Orientation in Benzene Derivatives. Since in these substitution reactions equilibrium between the various isomers is never attained, it is obvious that the relative proportions of the different isomerides formed depend on the relative speeds of their formation. We may say as a first approximation that they depend on the relative extents to which the various ring positions become activated. Thus, since an electron-releasing group causes *o-p* orientation it must mean that the electron release is transmitted more effectively to the *ortho* and *para* positions than to the *meta* position. This is readily explained as follows: If the electron-releasing group contains a free negative pole, as in the phenolate ion,  , the mesomeric effect would operate to change the extreme contributing form into the more stable mesomeric state, as indicated by the arrows (**P 10**). Furthermore, since the attacking reagent is electrophilic and the nucleophilic reactivity of carbon is greater than that of oxygen, the electromeric effect will operate in the same

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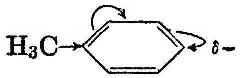
[59] R. Robinson, *J. Chem. Soc.*, 401 (1926).

[60] Ingold, *ibid.*, 1310 (1926); *Ann. Repts.*, 129 (1926).

[61] Lowry, *ibid.*, **123**, 822, 1866 (1923); *Nature*, **114**, 376 (1925).

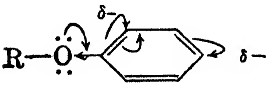
direction (**P 5**). The net result is an activation at the *ortho* and *para* positions due to increased electron density at those points (**P 2**).

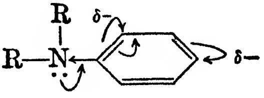
The above is an example of the ($+I,+T$) category. The case of toluene is slightly different. Here the substituent group is classified as "$+I$ only." The $+I$ effect of the methyl group in toluene is justified[62] by dipole moment measurements. However, since it has the same electronegativity as hydrogen in hydrocarbons, as judged by dipole moment measurements on saturated hydrocarbons, it used to be commonly assumed that its electron-releasing properties in toluene arise as a result of the act of substituting the electron-attracting mesomeric phenyl group for a hydrogen atom of methane, this act calling on the $+I_d$ effect of the methyl group. Since the electron-attractive power which called the $+I_d$ effect into being during the substitution still persists after the act is complete, the electron release suffered by the methyl group becomes a permanent effect ($+I_s$) in the toluene molecule. This idea can be pictured as follows:



etc. Such a mesomeric shift would lower the electron density on the substituted ring carbon atom, thus increasing its electronegativity and attracting electrons from the methyl group. Such an effect no doubt is operative, but modern research (to be discussed in the next chapter) makes it evident that the $+I_d$ effect of methyl is not large enough to account for the observed electron-releasing effect of that group. For the purposes of this chapter it will be sufficient to accept the experimental fact that the methyl group shows strong electron-releasing properties when substituted into aromatic rings. It should be noticed in the above electronic formula for toluene that the *ortho* and *para* positions have attained high electron density and hence have become activated. Furthermore toluene should be less easily substituted than the phenolate ion since the negative pole in the latter is more strongly electron releasing (**P 3**). The prediction is in perfect accord with the facts.

The following compounds (both *o-p* orienting) again present a different problem.





Here we observe two opposing effects ($-I,+T$) in relation to the substituents. Everything we know about these groups seems to indi-

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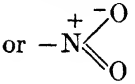
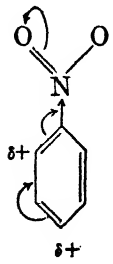
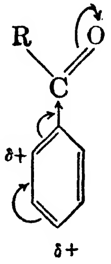
[62] Ingold, *Rec. trav. chim.*, **48**, 800 (1929).

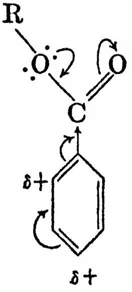
cate that $+T > -I$. For example, the corresponding *para*-substituted benzoic acids are weaker than benzoic acid itself, indicating $+M > -I$. Hence $+T > -I$ since the E effect operates in the same direction as the M, (**P 5**) and as a result the compounds are more easily substituted than benzene and are *ortho-para* orienting. It is worthy of note that OEt has a greater *ortho-para* orienting influence than OMe.[63] Since dipole moment measurements show no inherently different electron-attractive powers for methyl and ethyl, we must ascribe the difference to the greater polarizability of the ethyl group, which would increase the electromeric conjugation of the oxygen atom with the ring (**P 7** and **2**).

Groups of high electron-attractive power, like $-\overset{+}{N}R_3$ (a positive pole) or  $-\overset{+}{N}\begin{smallmatrix}\nearrow O^{-}\\ \searrow O\end{smallmatrix}$ (where the N is at the positive end of a dipole) are *meta* orienting and deactivating. The deactivation is an obvious consequence of the attraction of electrons away from the points of attack on the ring toward the groups in question, thus lessening the electron density at all ring carbon atoms.

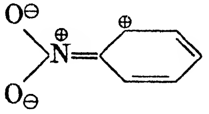
In regard to the *meta* orientation, let us first discuss the case of groups falling in the $(-I, -T)$ category.

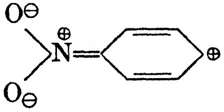






It will be observed from the above pictures that the M effect operates (**P 10**) so as to deactivate selectively the *ortho* and *para* positions. This is, perhaps, more easily understood by reference to the two following contributing forms of nitrobenzene:





Hence the *meta* positions will be most reactive, although even they have been deactivated somewhat by the $-I$ effect. The E effect will not operate (**P 5**).

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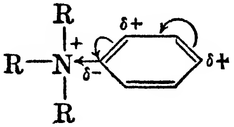
[63] Allan, Oxford, Robinson, and Smith, *J. Chem. Soc.*, 401 (1926).

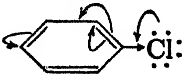
We may now turn to the ammonium salt, where the substituent contains a free positive pole and no unshared electrons on the atom next to the ring ($-I$ only). Here it will be impossible for the atom attached to the benzene ring to increase its covalence, as it did in nitrobenzene. But the strong $-I_s$ effect of the positive pole lowers the electron density on the substituted ring carbon atom and according to **P 2,** this carbon atom therefore tends to take electrons from the *ortho* carbon atom, thus initiating a mesomeric displacement toward the NR_3 group. This will deactivate the *ortho* position. A second tautomeric shift will also occur as pictured to deactivate the *para* position. The other *ortho* position may become deactivated by a third tautomeric shift or by Kekulé resonance. Thus, with the *ortho* and *para* positions most deactivated and substitution in general impossible at the ring carbon which already is substituted, further substitution would be most apt to occur at the *meta* positions.



If the nitrogen atom in these ammonium salts is replaced by P, As, or Sb there result changes shown in Table XIV (nos. 4, 6 and 7). Ingold[64] explains these as being due to the decreasing $-I$ effect produced by greater electron screening in the larger atoms. Since, however, the charge on the -onium group is due to a methyl ion located on the periphery of the central atom, it seems more likely that the observed decrease in *meta* directive influence is due to the greater inductomeric polarizability of the larger atoms, an effect which would cause some measure of electron release to the benzene nucleus and thus like toluene result in a proportionate *o-p* directive influence.

The last case to be discussed is that of the halogens. They fall in the ($-I, +T$) category and differ from $-OR$, $-NR_2$, etc., in that $-I > +T$. Here we have *o-p* orientation accompanied by deactivation.

Ingold has offered an explanation of this perplexing case.[65] The strong $-I$ effect of the halogen atom deactivates the entire ring by induction. The $+M$ effect is too small to be of importance. Then the electrophilic attacking reagent calls into play the $+E$ effect of the halogen atom



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[64] Ingold, *Rec. trav. chim.*, **48,** 805 (1929); *Ann. Repts. Chem. Soc.*, **23,** 134 (1926).
[65] Ref. 58, pp. 1122–23.

(P 5). This raises the nucleophilic reactivity of the *ortho* and *para* positions above that of the *meta* positions, thus producing *o-p* orientation, but the increase is insufficient to bring the reactivity up to the level of benzene itself; hence we say deactivation has occurred.

The foregoing discussion is summarized in Table XII.

TABLE XII

POLAR CATEGORY OF SUBSTITUENT	ORIENTATION	ACTIVATION
$+I$ only	*o,p*	+
$-I$ only	*m*	−
$+I, +T$	*o,p*	+
$-I < +T$	*o,p*	+
$-I > +T$	*o,p*	−
$-I, -T$	*m*	−

Alpha substituted toluene derivatives present an interesting problem in relation to orientation. On nitration the following percentages of *meta*-nitro compounds are obtained.[66]

PhMe	4.4%		$PhCHCl_2$	33.8%
$PhCH_2Cl$	(4.2%)	12%[64]	$PhCCl_3$[67]	64.5%

The sequence is not adequately explained by saying that three chlorine atoms must be substituted before the inductive effect of the side chain operates to draw electrons away from the ring, because even a chloromethyl group appears to be more electron attractive than either hydrogen or the phenyl group, if we may judge from measurements of the ionization constants of substituted acetic acids [68] (β-chloropropionic acid is stronger than either phenylacetic or acetic acid). It has been suggested [69] that the *o-p* directive action is to be ascribed to the inductomeric polarizability of the group in question. Thus we know that carbon has a high polarizability and it might very well be that although the $-I_s$ effect of a $-CH_2Cl$ group would by itself deactivate the ring,* the inductomeric electron release of this same group (at the moment of reaction and on demand of an electrophilic attacking reagent) would be an overbalancing factor and *o,p* orientation would result. The inductomeric electron release would grow smaller in the order $\cdot CH_2Cl > \cdot CHCl_2 > \cdot CCl_3$ while the inductive electron attraction would grow larger and

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[66] Holleman, *Chem. Rev.*, I, 197 (1924).

[67] Latimer and Porter, *J. Am. Chem. Soc.*, **52**, 206 (1930). Orients *o,p* in chlorinations.

[68] *International Critical Tables*, VI, 264.

[69] Baddeley, Bennett, Glasstone, and B. Jones, *J. Chem. Soc.*, 1830 (1935).

* The *o/p* ratio obtained on nitration of these compounds bears out the contention that the side chains exert a $-I$ influence. See p. 103.

hence a point is finally reached in $PhCCl_3$ where the inductomeric effect cannot overpower the inductive attraction. At this point the net effect is an electron pull away from the ring and *meta* substitution preponderates for the same reason, presumably, that anilinium salts undergo *meta* substitution. Here again the obvious weakness of the theory lies in the fact that at least roughly quantitative values for the magnitudes of the two opposing effects must be known before we can test the theory, and such quantitative information is lacking.

Another influence must be recognized in the hyperconjugative[69a] ability of side chains with α-hydrogen atoms. It is perhaps significant that the preponderance of electron release from the side chain stops when all three hydrogen atoms have been substituted.

Competitive Reactions. So far we have been considering only the question of the electronic explanation of *ortho-para* as opposed to *meta* orientation. Further examples are to be found in Table XIV. We recognize such orientations as a direct consequence of the relative effects of activating or deactivating substituents on the different ring carbon atoms. Such a classification is rough, however, because it places the substituent groups in only two categories: *o-p* or *m* orienting. A more critical test of the theory may be made by examining data on the relative speeds of substitution of different benzene derivatives. From such an examination we can arrange the groups in the order of their activating powers and explain, if we can, the complete sequence.

In choosing this test we must realize that the velocities of substitution at different ring positions may be individually and differently affected by substitution. Hence we will have three rate constants, k_o, k_m and k_p, involved in each reaction. If we measure the relative amounts of isomers produced, these are related to the ratios of the above constants; and if we measure the rate of total substitution, this involves their sum.[70] If we wish to know the individual values of the constants, both measurements must be used simultaneously.

Experimental data of the desired kind are, unfortunately, rare. Ingold and his collaborators have carried out careful measurements on the nitration of certain benzene derivatives by acetyl nitrate in acetic anhydride solution, choosing this combination because it gives a homogeneous system when benzene or its homologs are added. Two groups of experiments were made. In the first group they measured, by a competition method, the ratio of the rates of mononitration of benzene and one of its homologs mixed in equivalent proportions. In the second they measured the proportions of the three isomeric disubstituted derivatives formed.

[69a] See pp. 150 and 164.

[70] Ingold, Lapworth, Rothstein, and Ward, *J. Chem. Soc.*, 1959 (1931).

They defined the partial rate factor (*F*) of the orienting group at the nuclear position considered as the ratio of the number of molecules substituted during a small element of time at the given nuclear carbon atom to the number which would have been substituted during the same element of time at the same carbon atom had the orienting group been absent.[71] Or in other words,[72] the partial rate factor is "the factor by which the replacement of a hydrogen atom in benzene by an orienting substituent alters the probability of substitution at an individual carbon atom." Cognizance was taken of the fact that there is only one *para* position, whereas the *ortho* and *meta* positions occur in pairs. Their results are summarized in Table XIII.

TABLE XIII

NITRATIONS BY ACETYL NITRATE IN ACETIC ANHYDRIDE

Substance nitrated	Temp. (°C)	Isomers formed, %			*F*			Lit.
		Ortho	*Meta*	*Para*	*Ortho*	*Meta*	*Para*	
Toluene	30°	59	4	37	40	3.0	51	72
Toluene	18°				43	3	55	73
Ethyl benzoate	18°	24.1	72.0	4	.0026	.0079	.0009	73
Chlorobenzene	18°				.030	.000	0.139	74
Chlorobenzene	25°	31.0	0	69.0				74
Bromobenzene	18°				.037	.000	.106	74
Bromobenzene	25°	41.4	0	58.6				74

The partial rate factor is defined in such a way that if it is larger than unity it means that the substituent group has an activating influence, while if it is less than unity it means a deactivating influence. It will be observed that the recorded values of *F* show the methyl group to activate the *ortho* and *para* positions strongly and the *meta* slightly, the carbethoxy group to deactivate all positions, but the *meta* least; while each of the halogens deactivates all positions but affects the *meta* the most. All these measurements bear out the theoretical conclusions previously reached on the basis of less exact work.

For the remainder of our test we must content ourselves with total rate constants. The above investigators[73] also made determinations of

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[71] (*a*) Ingold and Shaw, *J. Chem. Soc.*, 2918 (1927); (*b*) Ref. 70.

[72] Ingold and M. S. Smith, *ibid.*, 917 (1938).

[73] Bird and Ingold, *J. Chem. Soc.*, 918 (1938).

a rougher sort on fluorobenzene and iodobenzene which indicated the following order for the total rates of nitration of the halogenobenzenes: PhH $\gg$ PhF $\sim$ PhI $\gg$ PhCl $>$ PhBr. This order was confirmed by other experiments of a different nature.[74] Ingold has suggested an explanation of the observed order.[75] A more convincing explanation has been offered by Dippy and Lewis,[76] who represent the possible complex interrelations of the $-I$ and $+E$ effects by the diagrams reproduced in Figure 1. Each of these effects varies in the order F $>$ Cl $>$ Br $>$ I (**P 3**) but since they are opposing effects their relative magnitudes become very important. In this figure the total line represents the $-I$ effect, the dotted part the opposing $+T$ effect and the solid line the resultant of the two (the resultant being an electron-attractive effect). Three different resultant sequences for the net electron-attracting effects of the halogens is thus obtained, despite the fact that in each case the required sequence F $>$ Cl $>$ Br $>$ I was maintained for the opposing effects. Thus it once more becomes apparent that until the theory can be made more quantitative, it may frequently be difficult to apply it in advance of knowledge of the experimental facts.

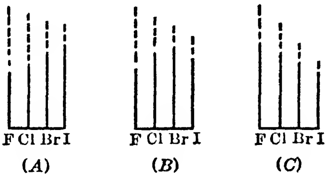

FIG. 1.[76]

We find further support for the theory in examples 21 to 26 of Table XIV. Here the confusion due to simultaneous substitution at two positions in the benzene ring has been eliminated by using the phenolic ethers substituted in the *para* position by chlorine. In such cases the entering chlorine will only attack the position *ortho* to the highly activating OR group. As R becomes more highly electron attracting, the theory would predict slower rates of chlorination. The sequence observed, viz., nPr $>$ Et $>$ Me $>$ $PhCH_2$ $>$ p-$Cl\cdot C_6H_4CH_2$ $>$ p-$NO_2\cdot C_6H_4CH_2$ is that which would have been predicted by the theory. A similar series of experiments was performed on compounds of the type p-$CO_2H\cdot C_6H_4OR$. The agreement with the theory was equally satisfactory.

It was at one time suspected that the relative influences of two groups could be determined by substituting both into the same benzene nucleus and then determining the ratios of isomers found when this compound underwent further substitution. It was demonstrated, however, that there is interaction between the two substituents which alters their relative directive powers.[77] As a result of this fact many anomalies might

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[74] Benford and Ingold, *ibid.*, 929 (1938).

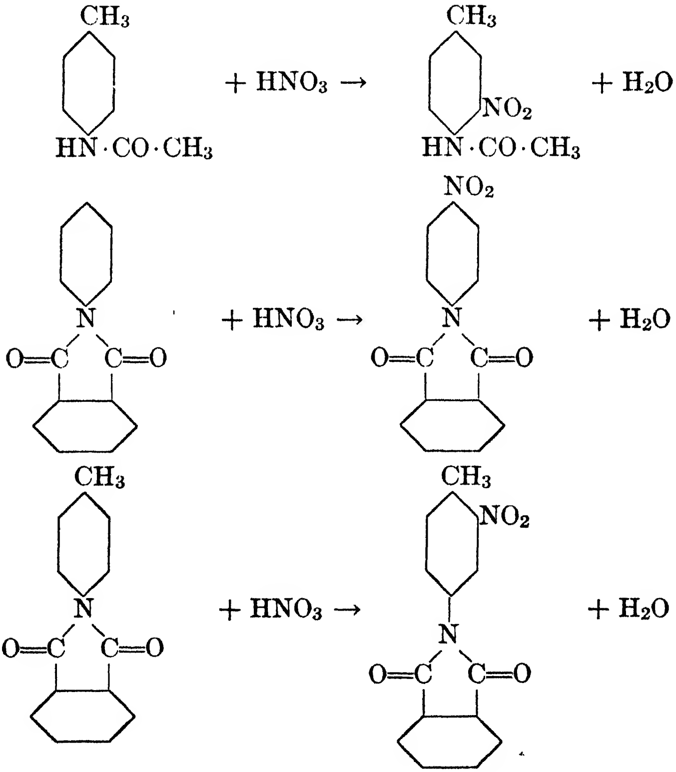
[75] Ref. 73, p. 928.

[76] Dippy and Lewis, *ibid.*, 649 (1936).

[77] Ref. 66, p. 204.

be expected. Many, in fact, do occur, but not so many that they mask the essential correctness of the simple theory. For example, an *o-p* directing group will usually, if not always, overpower a *meta* directing group in the same molecule. There is also observed a tolerable consistency in the order of directive influence of different groups in general which accords fairly well with the theory.

In relation to this general topic of the competitive action of groups, Robinson[78] points out one rule that seems to be of general application, viz., that when a substituent possesses unshared electrons on the atom next to the benzene ring, it will compete successfully with an alkyl group for control of direction in poly-substituted benzenes. This rule only fails in cases where the $+T$ influence is exceedingly weak. This is illustrated by the following series of reactions.[79]



The first reaction shows that even with the highly electron-attractive acetyl group its $+T$ influence overpowers not only its own $-I$ effect but

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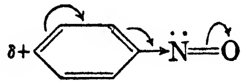
[78] Ref. 1*b*, p. 41.

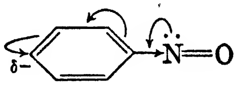
[79] Brady, Quick, and Welling, *J. Chem. Soc.*, **127**, 2264 (1925).

also the $+I$ effect of the methyl group. The second equation above shows that even with the more electronegative phthalimido group, the $+T$ influence still is preponderant, but it has been so weakened that (third equation) it no longer can compete with the methyl group. In these examples we find again that although the trend is predictable, the actual turning point could not definitely have been foretold without a more quantitative set of relations to guide us.

A complication which awaits adequate explanation is the fact (illustrated by examples 36 to 42 of Table XIV) that the ratios of isomers formed is frequently changed significantly by using different substituting reagents. Holleman has called attention to the difficulty of choosing truly comparable conditions for comparison of such different reactions as sulfonation and nitration.[80]

The outstanding anomaly encountered in orientation studies is the *o-p* directive influence of the NO group.[81, 82] Unlike most other *o-p* directive groups, the nitroso group, when substituted in benzene, shows a large dipole moment in the negative sense: $\underset{+\!\!\longrightarrow}{\mathrm{C{-}N{=}O}}$; moreover, when the dipole moments of aromatic and aliphatic nitroso compounds are compared, it is found that the NO group has a $-M$ effect.[83] As a matter of fact, it quite outdoes the nitro group in its ability to activate *para*-substituted halogen atoms in the reaction with silver nitrate.[82, 84] Probably, as suggested by LeFevre,[84] the explanation is to be found in Robinson's prediction that in nitrosobenzene and its derivatives, either a $+T$ or $-T$ effect may operate,[85, 86] thus:





The direction of the electromeric portion of either of these displacements is determined by the electronic demands of the attacking reagent (**P 5**). Thus an electrophilic substituting reagent would demand a $+E$ shift resulting in *o-p* orientation while the reaction of *p*-bromonitrosobenzene with silver nitrate would demand a $-E$ shift because the nucleophilic nitrate ion seeks a carbon nucleus. Incidentally, in so doing, it ejects a bromide ion. This type of reaction will be more thoroughly discussed later.

[80] Ref. 66, p. 204.

[81] Ingold, *J. Chem. Soc.*, 513 (1925).

[82] Hammick and Illingworth, *ibid.*, 2358 (1930).

[83] Hammick, New, and Sutton, *ibid.*, 742 (1932).

[84] LeFevre, *ibid.*, 810 (1931).

[85] R. Robinson, *Chem. and Ind.*, **44,** 456 (1925).

[86] Francis, *J. Am. Chem. Soc.*, **48,** 1631 (1926).

TABLE XIV

MISCELLANEOUS EXAMPLES OF AROMATIC SUBSTITUTION

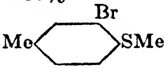
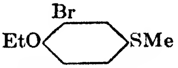
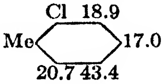
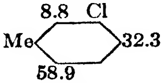
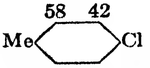
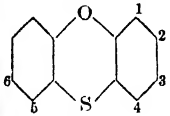
No.	Aromatic substance	Entering group	Position of entering group	Vel. const.	p/o	Lit.
1	$\mathrm{Ph\overset{+}{N}Me_3}$	NO_2	$m = 100\%$			64
2	$\mathrm{PhCH_2\overset{+}{N}Me_3}$	NO_2	$m = 88\%$			64
3	$\mathrm{PhCH_2CH_2\overset{+}{N}Me_3}$	NO_2	$o + p = 81\%$			64
4	$\mathrm{Ph\overset{+}{P}Me_3}$	NO_2	$m = 100\%$			64
5	$\mathrm{PhCH_2\overset{+}{P}Me_3}$	NO_2	$o + p = 90\%$			64
6	$\mathrm{Ph\overset{+}{As}Me_3}$	NO_2	$m = 98\%$			64
7	$\mathrm{Ph\overset{+}{Sb}Me_3}$	NO_2	$m = 86\%$			64
8	$\mathrm{PhB(OH)_2}$	NO_2	$m = 72\%$			107
9	$\mathrm{PhCH_2Br}$	NO_2	$o + p = 93\%$			64
10	$\mathrm{PhCH_2Cl}$	NO_2	$o + p = 88\%$			64
11	$\mathrm{PhCH_2F}$	NO_2	$o + p = 88\%$			64
12	$\mathrm{PhCH_2NO_2}$	NO_2	$o + p = 52\%$			64
13	$\mathrm{PhCH_2CH_2NO_2}$	NO_2	$p = 52.3\%$, $m = 13\%$, $o = 34.4\%$		1.52	87
14	ω-Nitrostyrene	NO_2	$o = 30\%$, $m = 2\%$, $p = 67.5\%$		2.24	87
15	PhSMe	Br	$o = 5$–6%, $p = 94$–95%		15.8	88
16	PhSMe	SO_3H	$o = 10\%$, $p = 90\%$		9.0	88
17	*p*-$\mathrm{MeC_6H_4SMe}$	Br				89
18	*p*-$\mathrm{OEtC_6H_4SMe}$	Br				89
19	$\mathrm{PhC{\equiv}C{\cdot}CO_2H}$	NO_2	$o = 27\%$, $m = 7.7\%$			90
20	PhCN	NO_2	$m = 81\%$			90
21	*p*-$\mathrm{ClC_6H_4OMe}$	Cl		1.226		91
22	*p*-$\mathrm{ClC_6H_4OEt}$	Cl		2.443		91
23	*p*-$\mathrm{ClC_6H_4OPr}$	Cl		2.756		91
24	*p*-$\mathrm{ClC_6H_4OCH_2Ph}$	Cl		0.8371		91
25	*p*-$\mathrm{ClC_6H_4OCH_2{\cdot}C_6H_4NO_2}$(*p*)	Cl		0.1742		91
26	*p*-$\mathrm{ClC_6H_4OCH_2{\cdot}C_6H_4Cl}$	Cl		0.4834		91
27	PhBr (0°)	NO_2	$o:p = 37.6:62.1$		1.65	92
28	PhCl (0°)	NO_2	$o:p = 30.1:69.9$		2.32	92
29	PhI (0°)	NO_2	$o:p = 41.1:58.7$		1.43	93
30	$\mathrm{PhNO_2}$ (0°)	NO_2	$o:m = 8.3:91.0$			92
31	PhMe (0°)	NO_2	$o:m:p = 56:3:41$		0.73	92
32	$\mathrm{PhCO_2H}$ (−30°)	NO_2	$o:m:p = 14:85:0.6$		0.04	92
33	*o*-Chlorotoluene	NO_2				94
34	*m*-Chlorotoluene	NO_2				94
35	*p*-Chlorotoluene	NO_2				94
36	PhCl	Cl	$o:m:p = 39:6:55$		1.41	95
37	PhCl	Br	$o:m:p = 11:1.6:87$		7.77	95

TABLE XIV—*Continued*

MISCELLANEOUS EXAMPLES OF AROMATIC SUBSTITUTION

No.	Aromatic substance	Entering group	Position of entering group	Vel. const.	p/o	Lit.
38	PhCl	NO_2	$o:p = 30:70$		2.32	95
39	PhCl	SO_3H	$p = 100\%$		∞	95
40	PhMe	Br	$o:p = 39:60$		1.52	95
41	PhMe	NO_2	$o:m:p = 56:3:41$		0.73	95
42	PhMe	SO_3H	$o:m:p = 32:6:62$		1.94	95
43	*o*-Fluoroanisole	NO_2	68% 2-F,4-NO_2			96
44	4-Acetyldiphenyl	NO_2	2,4'-dinitro-4-acetyl diphenyl			97
45	*p*-Phenylbenzaldehyde	NO_2	2,4'-dinitro-4-carboxylic acid			97
46	*p*-Phenylbenzoic acid	NO_2	2,4'-dinitro comp.			97
47	$PhSO_2NH_2$	NO_2	*o,p*			98
48	Pyrazole	Cl,Br	4-halopyrazole			99
49	Thionaphthene	NO_2	3-nitro compound			100
50	Thionaphthene	Br	3-bromo			101
51	Thiazole	Br	2-bromo			102
52	Dibenzofuran	NO_2	3-nitro			103
53	Dibenzofuran	Cl,Br	2-halogeno			104
54	Quinoline	Br	3-bromo			115
55	Quinoline	SO_3H	8-sulfo (220°) 6-sulfo (300°)			116
56	Benzo [*f*] quinoline	NO_2	7,9-dinitro			105
57		Br	3- and 3,6			106
		MeCO	3			
		SO_3H	3- and 3,6			

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[87] J. W. Baker and Wilson, *J. Chem. Soc.*, 842 (1927).

[88] Van Hove, *Bull. sci. acad. roy. Belg.* [5], **12,** 929 (1926).

[89] *Idem,* **13,** 206 (1927).

[90] J. W. Baker, Cooper, and Ingold, *J. Chem. Soc.*, 426 (1928).

[91] Bradfield and Brynmor Jones, *J. Chem. Soc.*, 1006 (1928). Measurements made in 99% acetic acid.

[92] Holleman, *Die direkte Einfuhrung von Substituenten in den Benzolkern,* Leipzig, 1910.

[93] Holleman, *Rec. trav. chim.*, **32,** 134 (1913).

[94] Wibaut, *ibid.*, **32,** 244 (1913).

[95] Holleman, *Chem. Rev.*, **1,** 218 (1925).

[96] Schiemann and Miau, *Ber.*, **66B,** 1179 (1933).

[97] Grieve and Hey, *J. Chem. Soc.*, 968 (1933).

[98] Shriner, Goebel, and Marvel, *J. Am. Chem. Soc.*, **54,** 2470 (1932).

[99] (*a*) Balbiano, *Ber.*, **23,** 1453 (1890); (*b*) Severini, *Gazz. chim. Ital.*, **23,** I, 284 (1893); (*c*) Knorr, *Ber.*, **28,** 715 (1895).

[100] Fries and Hemmecke, *Ann.*, **470,** 1 (1929).

[101] Komppa, *J. prakt. Chem.*, **122,** 319 (1929).

[102] Wibaut and Jansen, *Rec. trav. chim.*, **53,** 77 (1934).

[103] Gilman, Bywater, and Parker, *J. Am. Chem. Soc.*, **57,** 885 (1935).

[104] Bywater, Smith, Brown, and Gilman, *Proc. Iowa Acad. Sci.*, **41,** 166 (1934).

[105] Clem and Hamilton, *J. Am. Chem. Soc.*, **62,** 2349 (1940).

[106] Suter, McKenzie, and Maxwell, *J. Am. Chem. Soc.*, **58,** 717 (1936).

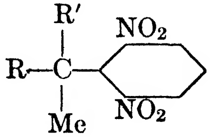
[107] Ainley and Challenger, *J. Chem. Soc.*, 2171 (1930).

The suspicion that the directive influence of the nitroso group is dependent on the association of nitrosobenzene [82] seems to be without foundation.[84]

As a concluding remark on "competitive reactions" it should be mentioned that Francis [86] made an exhaustive study of the relative bromination rates and came to certain conclusions that are highly thought provocative and difficult to explain.

The Ortho-Para Ratio. The basic principles already developed serve rather adequately to explain the relative amounts of substitution observed in the *ortho* and *para* positions of benzene derivatives. Since we have agreed not to recognize the field effect as distinct from the inductive effect, we will ignore the theory of the *ortho-para* ratio put forward by Ingold.[108]

Lapworth and Robinson [109] pointed out that most of the data on the *ortho-para* ratio could be explained if it was recognized that substituents showing $+I$ effects activate the neighboring *ortho* positions more than the remote *para* positions (**P 4**) while those showing $-I$ effects deactivate the *ortho* more than the *para* positions. They also found it necessary to employ the concept of steric hindrance by large substituent groups to explain such observations as the almost complete absence of *ortho* substitution when diphenyl is nitrated. Apparently Kehrmann [110] was the first to suggest that steric effects are of importance in aromatic substitution and more recently LeFevre [111] also has joined the ranks of those defending the hypothesis. He argued that the probability of *ortho* substitution will be lessened by the size of the substituent group in the order Me < Et < Pr^{β} < Bu^{γ}. He supported his contentions by constructing scale diagrams of compounds of the type



from which it became evident that steric interference is a reality; and he also demonstrated that nitration, sulfonation, and halogenation of 1-methyl-4-isopropylbenzene yields 2-derivatives preponderantly.

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[108] Ingold, *Rec. trav. chim.*, **48**, 797 (1929).

[109] Lapworth and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1927).

[110] Kehrmann, *Ber.*, **23**, 130 (1890).

[111] (*a*) LeFevre, *J. Chem. Soc.*, 977, 980 (1933); 1501 (1934); (*b*) Ganguli and LeFevre, *ibid.*, 848, 852 (1934).

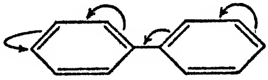
Let us now turn back to the interesting task of seeing how well predictions made on the basis of the up-to-date English theory accord with existing data on the *ortho-para* ratio. We must first recognize that if a given substituent had exactly the same influence on *ortho* and *para* substitutions, the ratio *p/o* would be 0.5 since there are two *ortho* positions and only one *para* position. Accordingly the ratio *p/o* will be greater or less than 0.5, depending on whether the *para* or *ortho* substitution is favored. Lapworth and Robinson [109] give the data reproduced in Table XV. Since $-I > +T$ for all halogens they are deactivating and the *ortho* positions are most affected, thus $p/o > 0.5$. Furthermore the ratio should be and is greatest for F and least for I since the $-I_s$ effect decreases in going from F to I. The ratio also changes in the expected direction as the α-hydrogen atoms of toluene are successively substituted by chlorine. The only surprising fact is that $p/o > 0.5$ in the case of toluene. This is not understandable on the basis of random orientation accompanying collision between reactants if we assume that the methyl group exerts only $+I_s$ or $+I_d$ effects when it is a ring substituent. If, however, we ascribe to the methyl group a $+T$ effect (this is "hyperconjugation," already alluded to several times) and involve **P 8**, it becomes apparent that the *para* position should become more activated than the *ortho* position and hence that the ratio *p/o* should be greater than 0.5. If it also is conceded that only α-CH links can exhibit hyperconjugation, then LeFevre's observation that methyl is more strongly activating than isopropyl can be explained without recourse to steric hindrance.

TABLE XV [109]

RATIO OF *Para* TO *Ortho* SUBSTITUTION ACCOMPANYING NITRATION

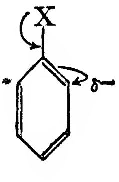
Substance	*Ortho* (%)	*Para* (%)	*p/o*	Substance	*Ortho* (%)	*Para* (%)	*p/o*
PhF	12.4	87.6	7.06	$PhCH_2Cl$	41	55	1.34
PhCl	30.1	69.9	2.32	$PhCHCl_2$			1.84
PhBr	37.6	62.4	1.66	$PhCCl_3$			4.22
PhI	41.1	58.7	1.43	PhMe	58	38	0.65

The very low yield of the *ortho* compound observed in the nitration of diphenyl need not be explained by steric hindrance if we rely on **P 8**, since the extended conjugation possible between the two benzene rings would favor *para* substitution:

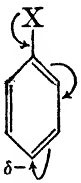


The same principle applied to the $-M$ effect of the carboxyl group in benzoic acid (Table XIV, no. 32) serves to explain the strong deactivation of the *para* position observed there. The same explanation applies to nitrobenzene (no. 30) where no *para* nitration is observed.

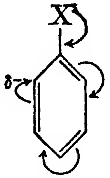
There is one point regarding the application of **P 8** which is not entirely clear. An electron-releasing ($+T$) substituent X might lead to any of the following situations:



I



II

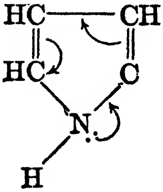


III

Although the conjugation is more extended in II than I, thus favoring *para* substitution, it is equally true that it is more extended in III than in II. However, in accord with the discussion of this principle given in part II of this chapter, it may be that the point of greatest importance in relation to extended conjugation is that the charge uncalled for by the attacking reagent can thus be removed as far as possible from the point of attack. From this viewpoint situation II would be most likely to lead to reaction. Unfortunately the same point of view does not seem to be applicable to such cases as furan, as will be shown in the next section.

Heterocyclic and Fused Ring Systems. The English theorists seem to have published but little on the subject of directive influence in ring systems other than benzene. It is a temptation, therefore, to apply their basic principles ourselves and appraise the results in the light of our findings.

One of the few cases discussed by them is that of pyrrole.[112] Examination of the electronic formula



leads us to expect facile substitution due to the conjugation of the nitrogen atom with the ring, thus allowing the activating $+T$ effect to oper-

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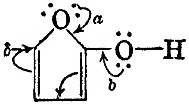
[112] Ref. 1*b*, p. 43.

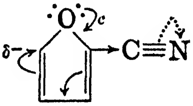
ate. The same would, of course, be true with furan and thiophene. In accordance with the theory, all are more readily substituted than benzene. This was illustrated in the case of furan by Gilman [113] in a very convincing manner. Thiophene is the least easily substituted of the three. This is in accord with the weaker +*E* effect of sulfur.

The position of the entering group would be predicted, on the basis of the conjugative relay of the +*T* electron displacement, to be principally *alpha* (**P 8**), although some *beta* substitution would be expected. All three compounds exhibit a strong *alpha* orientation. In relation to the *beta* substitution, Gilman remarks that it would be unwise to assert that none occurred, since the yields are low, but at any rate none has been observed.[114]

Gilman also asserts that any *alpha*-substituted furan will undergo further substitution in the other *alpha* position. This would have been predicted by consideration of the two following cases:



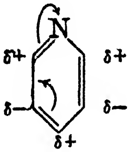
I



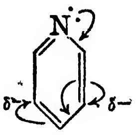
II

In case I, where the substituent is electron releasing, either displacement *a* or *b* would lead (**P 8**) to *alpha* activation: In case II, where the substituent is electron attractive (−*I*,−*T*) the −*E* effect of the CN group will not be brought into play (**P 5**) while the +*E* effect of the heteroatom will operate in addition to its +*M* effect. We would therefore surely predict the preponderance of displacement *c* with its resultant *alpha* activation.

Pyridine could conceivably undergo either of two electromeric displacements:



III



IV

III would be somewhat analogous to nitrobenzene, with deactivation of the entire ring. In so far as it is an *E* effect it would not be called into play by an electrophilic reagent (**P 5**). The electromeric displacement

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[113] Gilman, *Chem. Rev.*, **11,** 323 (1932).

[114] Ref. 113, p. 330.

shown in IV would be called on and would be activating, leading to *beta* substitution by an electrophilic reagent. It is well known that substitutions of pyridine occur in the *beta* position, which would accord with either III or IV, but one finds frequent statements in organic textbooks that pyridine is less easily substituted than benzene. Apparently such statements are made on the basis of its slow sulfonation, which surely involves not pyridine but its salt. In such cases the positive charge on the nitrogen atom would be expected to be deactivating as a result of its high electronegativity. In that case mechanism III would operate.

The bromination of quinoline seems to indicate that pyridine is more easily substituted than benzene, since the first bromine atom enters the nitrogen-containing ring.[115] This stands in contrast to the nitration and sulfonation, both of which cause substitution in the homocyclic ring of quinoline,[116] a result of the deactivation discussed above. Likewise iodination in concentrated sulfuric acid solution yields the 5-iodoquinoline.[117]

Apparently, then, mechanism IV operates when pyridine itself is substituted by electrophilic reagents, the substitution taking place with more ease than in benzene.

The whole problem is complicated by the discovery that the bromination of pyridine [118] and quinoline [119] (as well as that of bromobenzene [120]) produces different isomers at different temperatures.

Aromatic compounds containing more than one heteroatom and all fused ring structures present alternative activation mechanisms between which we cannot make unequivocal choices on the basis of the theory in its present form.[121] Examples will be found in Table XIV.

One unambiguous and noteworthy case, however, is phenoxthin (Table XIV, no. 57). Here either the oxygen or sulfur atom might be expected to increase its covalence, resulting in *ortho-para* orientation relative to either one. The fact that the substituents enter *para* to the oxygen atom would definitely have been predicted by consideration of **P 3** and **P 8.**

Electrophilic Reactions of Aromatic Compounds. The foregoing common substitution reactions of aromatic compounds all involve attack of the aromatic nucleus by a strongly electrophilic reagent. Substitution

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[115] LaCoste, *Ber.*, **14**, 915 (1881).

[116] Georgievics, *Monatsh.*, **8**, 577, 641 (1888); Koenigs, *Ber.*, **12**, 449 (1879) and many others.

[117] Istrati, *Compt. rend.*, **127**, 520 (1898).

[118] denHertog and Wibaut, *Rec. trav. chim.*, **51**, 381, 940 (1932).

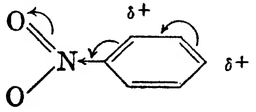
[119] Jansen and Wibaut, *ibid.*, **56**, 699 (1937).

[120] Wibaut, deLande, and Wallagh, *ibid.*, **52**, 794 (1933).

[121] See, however, Ref. 1c, p. 462.

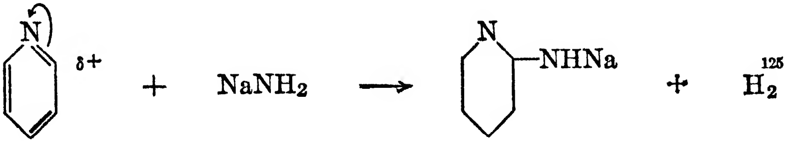
reactions are also possible in which the attacking reagent is nucleophilic. In such cases, of course, the aromatic compound exhibits electrophilic reactivity. Such cases have been discussed by Robinson[122] and by Waters and Lowry.[123]

The general theory of the English school would predict that the electrophilic reactions of aromatic compounds would be facilitated by substituents exerting strong $-I$ or, more particularly, strong $-T$ effects since the attacking reagent is acting as an electron donor. If we consider the nitro group as an example it is apparent that the *ortho* and *para* positions would become activated.

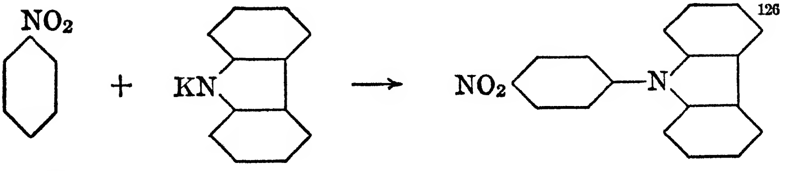


In accord with the theoretical predictions, we find that nitrobenzene reacts with strong sodium hydroxide solution to give *o*-nitrophenol.[124] These electrophilic substitution reactions offer a sharp contrast to nucleophilic substitutions also in a second way, viz., that if a negative ion (e.g., OH^- above) is to replace a hydrogen atom, the bonding electrons of the latter must also be displaced. This requires the presence of an oxidizing agent. Frequently the air performs the necessary oxidation. Sometimes other oxidizing agents must be added. Sometimes the aromatic substance itself performs the function and becomes partially reduced.

A few other examples follow.



[125]



[126]

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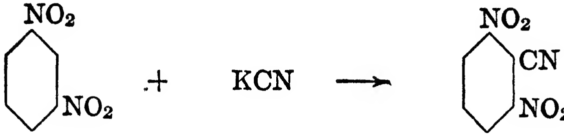
[122] Ref. 1*b*, p. 46.

[123] Ref. 1*c*, p. 453.

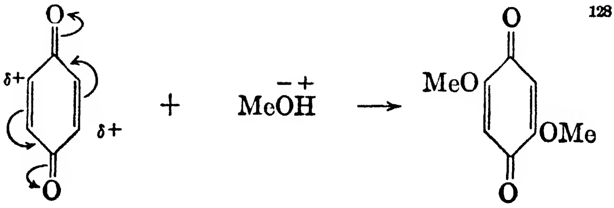
[124] Wohl, *Ber.*, **32**, 3486 (1899); **34**, 2444 (1901).

[125] Tschitschiabin and Zeide, *J. Russ. Phys.-Chem. Soc.*, **46**, 1216 (1924).

[126] G. and M. de Moutmollin, *Helv. Chim. Acta*, **6**, 94 (1923).



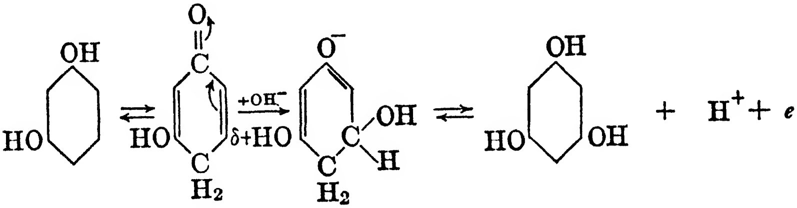
[127]



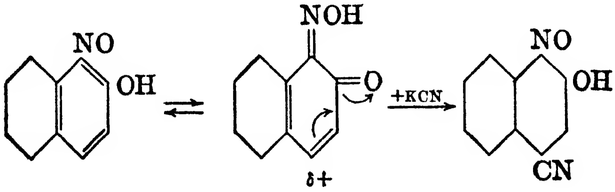
[128]

Likewise quinones react with amines to give aminoquinones, with sulfinic acids to give sulfones, with cyanides to give nitriles, etc.[129]

Sometimes the quinonoid system is not evident until after tautomeric change, but even here the activating effect of the doubly bound oxygen (or nitrogen) is evident. An example is found in the reaction of fused sodium hydroxide on resorcinol:[129]



and in the similar reaction:[130]



Waters and Lowry formulate the well known reaction for the production of alizarin as follows. Here the oxidizing agent is a chlorate or

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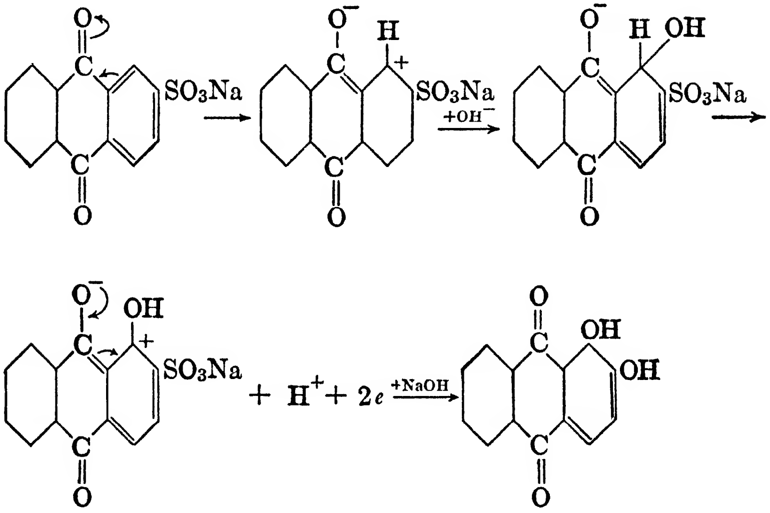
[127] Lobry de Bruyn, *Rec. trav. chim.*, **2**, 210 (1899).

[128] Knoevenagel and Buckel, *Ber.*, **34**, 3993 (1901).

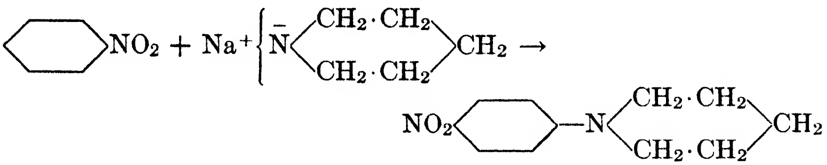
[129] W. Bradley and R. Robinson, *J. Chem. Soc.*, 1254 (1932).

[130] *Idem*, 1484 (1934); see also: Bradley, *ibid.*, 1091 (1937), and Bradley and Jadhav, *ibid.*, 1791 (1937).

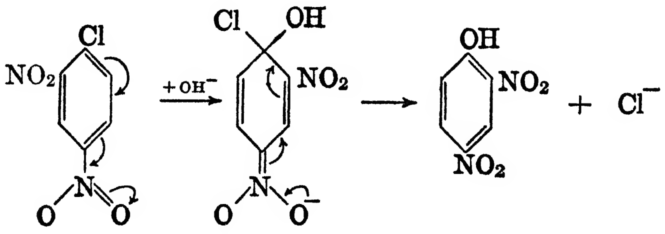
nitrate and the $-E$ effect of the carbonyl group makes the compound sufficiently electrophilic.



The following reaction seems to indicate that the piperidine anion is strongly nucleophilic.[129]



When a compound contains a group with a strong $-T$ effect capable of producing an electrophilic center in the compound and when that center is also attached to an atom or group which can exist as a stable anion (e.g., Cl) then the latter may be replaced by anions of less electron affinity. For example, the reaction of 2,4-dinitrochlorobenzene with alkalies may be represented as follows:



The similar activating effect of the nitroso group has already been mentioned.[131] Thus *p*-bromonitrosobenzene produces silver bromide in a solution of silver nitrate in glacial acetic acid. Likewise there is the well-known example of the hydrolysis of *p*-nitrosodimethylaniline to yield *p*-nitrosophenol.

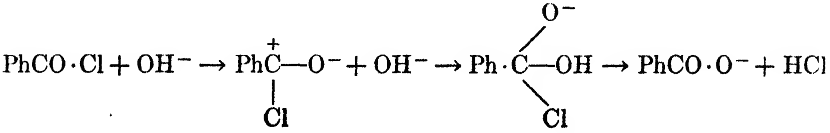
If the attacking reagent is very strongly nucleophilic, the presence of an activating group in the aromatic ring is no longer necessary to eliminate the halide ion. Examples are to be found in the reactions of metals such as magnesium and sodium with organic halides.

Hydrolysis

Although the subject of hydrolysis is to be considered in some detail in a later chapter, an introductory discussion will be included at this point since the subject is well suited to the illustration of certain important points of the English theory.

Olivier[132] studied the hydrolysis of substituted benzyl chlorides in aqueous alcohol, $XC_6H_4\cdot CH_2Cl + H_2O \rightarrow XC_6H_4\cdot CH_2OH + HCl$, and found the relative effectiveness of the substituents, X, in increasing the velocity to be $Me > H > Hal > NO_2$. It will be observed that electron-releasing groups accelerate the reaction (as was found to be the case in benzene substitutions[133]). Since this is also observed to occur in a large number of other reactions it has become conventional to classify all such reactions as type A.[134] The molecules bearing the substituents must exhibit nucleophilic reactivity in such reactions, since nucleophilic reagents give up their electrons, in whole or in part, and this procedure would be facilitated by electron-releasing substituents.

There is another large class of reactions in which substituents have just the reverse effect. This is called type B. Alkaline hydrolyses, such as the hydrolysis of substituted benzoyl chlorides, fall in this class. The substituted molecules are obviously electrophilic. This may be made clear by formulating the reaction as follows:



$$\mathrm{PhCO\cdot Cl + OH^- \rightarrow Ph\underset{\displaystyle |\atop Cl}{\overset{+}{C}}{-}O^- + OH^- \rightarrow Ph\cdot \underset{\diagdown\atop Cl}{\overset{O^-\atop \diagup}{C}}{-}OH \rightarrow PhCO\cdot O^- + HCl}$$

It must not be imagined, however, that all reactions fall unequivocally in one or the other of these two classes. Baker[135] points out that usually

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[131] See p. 99.

[132] Olivier, *Rec. trav. chim.*, **42,** 775 (1923).

[133] This parallelism was apparently first pointed out by Olivier.

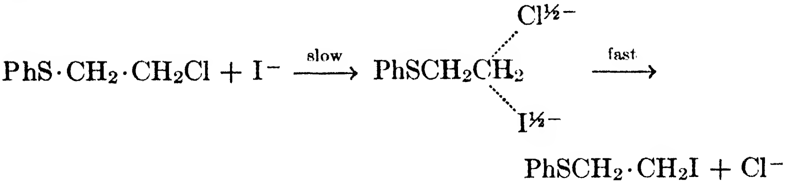
[134] Ingold and Rothstein, *J. Chem. Soc.*, 1217 (1928).

[135] J. W. Baker, *ibid.*, 1128 (1933); Shoppee, *ibid.*, 1117.

a reaction depends on the joint operation of at least two rate-determining stages of opposite polar character. Hence reactions may frequently be classified as belonging to each category in stated proportion.

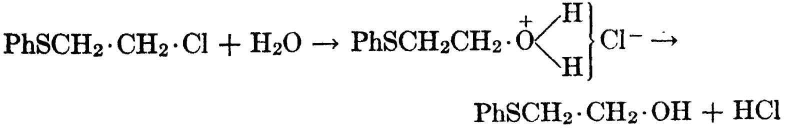
An example of the influence of mesomerism on hydrolysis is discussed by Baddeley and Bennett.[136] The rate of hydrolysis of certain substituted benzyl bromides was found to be:[137] *p*-MeO > *o*-MeO > H > *m*-MeO. Since the reaction falls in class A, acceleration by substituents must be ascribed to their electron-releasing powers. The methoxyl group falls in the $-I, +T$ category and since the T mechanism can only operate from the *ortho* and *para* positions, it is apparent that in these two positions the $+T$ effect overpowers the $-I$ effect, as was also found in benzene substitution. The *para* would be favored over the *ortho* according to **P 8.** In the *meta* position, where only the $-I$ effect is operative, we observe deactivation. Whether the tautomeric electron displacement is to be ascribed to the E and M effects, or both, it is difficult to say; the M effect may always operate in such structures and inasmuch as the attacking reagent is electron-seeking, the $+E$ effect may be called into play (**P 5**). It is interesting, therefore, to note that the velocity of reduction of the same compounds decreases in the order: *m*-MeO > *o*-MeO > *p*-MeO and unsubstituted. Here the attacking reductant is electron-donating and hence the $+E$ effect will not be called into operation. However, electron release is apparently occurring more from the *ortho* and *para* positions than from the *meta*. Since it cannot be a $+E$ effect it must be a $+M$ effect.

Baddeley and Bennett [136] studied the following reactions; their results and their interpretation are indicated.



$$PhS\cdot CH_2\cdot CH_2Cl + I^- \xrightarrow{slow} PhSCH_2\overset{Cl^{\frac{1}{2}-}}{\underset{I^{\frac{1}{2}-}}{CH_2}} \xrightarrow{fast} PhSCH_2\cdot CH_2I + Cl^- \quad (1)$$

Type B. Rate-determining step: capture of I$^-$. Relative speeds (*para* substituents in the phenyl group): MeO < Me < H < I < Br < Cl < NO_2.



$$PhSCH_2\cdot CH_2\cdot Cl + H_2O \rightarrow \left. PhSCH_2CH_2\cdot\overset{+}{O}\begin{matrix}H\\H\end{matrix}\right\}Cl^- \rightarrow PhSCH_2\cdot CH_2\cdot OH + HCl \quad (2)$$

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[136] Baddeley and Bennett, *J. Chem. Soc.*, 265 (1933).

[137] Lapworth and Shoesmith, *ibid.*, 1391 (1922); 214 (1926).

Type A. Rate-determining step: incipient ionization of Cl^-. Relative speeds (*para* substituents in phenyl group): $NO_2 < I < Br < Cl < MeO$. Whatever one may think about their pictures of the mechanism, if we grant the two groups of reactions to be respectively of types B and A, it is evident that the influence of substituents on reaction (1) is what would have been predicted if again we ascribe high powers of electron release to the methoxyl group ($+T > -I$). In reaction 2 the influence of substituents is what we would predict for type A reactions except that the order of the halogens is the reverse of that originally postulated.* This would demand $+T$ effects for the halogens in the order $Cl > Br > I$. The authors point out that this "anomalous" order for halogens is found in many other cases. They offer as supporting evidence the data in Table XVI. "In reactions of type A the inductive effects of the halogens must retard and their electromeric effects should accelerate the reaction for the *para* isomeride. In the *meta* isomeride, on the other hand, the inductive effect is weaker and the electromeric almost or quite inoperative. Consequently the relative forces of the electromeric effects of the halogens are indicated by the variation of the ratio of velocities *p/m*, or by the order of velocities of the *p*-isomerides." However, in type B reactions, indications of the relative values of the $+M$ effect is given by the *m/p* ratios, since a *p*-halogen atom must conversely cause acceleration by its *I* and retardation by its *M* effect.

TABLE XVI [138]

Reaction	Order of velocities of *p*-halogenated compounds	*p/m velocity ratio*
Type A		
Hydrolysis: $ArSC_2H_4Cl$	$Cl > Br > I$	
Do. $ArCH_2Cl$	$F > Cl > Br > I$	$F > Cl > Br > I$
Do. Ar_2CHCl	$Cl > Br$	
Do. $ArCH_2Br$	$F > Cl > Br$	
$ArNH_2 + ClC_6H_4 \cdot NO_2$	$Cl > Br > I$	$Cl > Br > I$
Redn. of $ArNH \cdot NH_2$	$Cl = Br$	$Cl > Br$
Type B		*m/p ratio*
Hydrolysis: $ArCO_2R$	$Cl < Br < I$	$Cl > Br > I$
Do. Phthalides	$Cl < Br < I$	
Action of RCN with H_2S	$Cl < I$	
Benzoylation of ArOH	$Cl < Br$	
Tautomerism of $ArCH_2N{=}CHAr'$	$Cl > Br > I$	$Cl > Br > I$
Hydrol. of aryl succinimides	$Cl < Br$	$Br > Cl$
Redn. of $ArCH_2Br$	$F < Cl$	

These data complete the argument, started earlier in this chapter, that the $+T$ effects of the halogens vary in the order $F > Cl > Br > I$

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* See p. 66.

[138] See Ref. 137 for references to the original papers on which this table is based.

despite the facts that their inductomeric polarizabilities vary in the reverse order and their relative I_s effects would make fluorine the least electron-releasing. It will be recalled that the mesomeric moments determined by Groves and Sugden have already been presented as evidence for this sequence and that it was suggested, in line with an early idea of G. N. Lewis, that the explanation lies in the probable fact that double bond formation is more difficult with larger atoms.

Let us return again to the subject of the mechanism of hydrolysis. From what has already been said it is evident that once we determine whether a given type of reaction is to be classified as type A or B, the effect of variation in substituents can be rather well predicted from theory. But the theory does not enable us to make a prediction of the mechanism to be encountered. Indeed, it has been found in the alkyl halide series that the mechanism of hydrolysis changes as heavier alkyl groups are introduced. In this particular case the theory has been developed by Hughes and Ingold and their collaborators.[139] It has to do with various substitutions (in the broad sense) taking place at saturated carbon atoms. These reactions are classified as follows:

Nucleophilic substitutions (S_N):

$$\begin{gathered} \mathrm{Y} + \mathrm{Alk}\vdots\!-\mathrm{X} \rightarrow \mathrm{Alk}-\mathrm{Y}+\mathrm{X} \\ \mathrm{R}\vdots\!-\mathrm{Y} + \mathrm{Alk}\vdots\!-\mathrm{X} \rightarrow \mathrm{Alk}-\mathrm{Y}+\mathrm{RX} \end{gathered}$$

Electrophilic substitutions (S_E):

$$\begin{gathered} \mathrm{Z} + \mathrm{Alk}-\!\vdots\mathrm{X} \rightarrow \mathrm{Alk}-\mathrm{Z}+\mathrm{X} \\ \mathrm{R}-\!\vdots\mathrm{Z} + \mathrm{Alk}-\!\vdots\mathrm{X} \rightarrow \mathrm{Alk}-\mathrm{Z}+\mathrm{R}-\mathrm{X} \end{gathered}$$

The fate of the binding electrons, as symbolized in this classification, is particularly to be noted, as are also the type symbols, S_N and S_E, meaning respectively nucleophilic substitution and electrophilic substitution.

Two different types of mechanism are possible for either of the above categories; one is monomolecular (3), the other dimolecular (4). This may be illustrated as follows.

$$(S_N1)\quad \begin{array}{l} \mathrm{Alk}\vdots\!-\mathrm{X} \xrightarrow{\text{Slow}} \mathrm{Alk}^+ + \mathrm{X}^- \\ \mathrm{Alk}^+ + \mathrm{Y} \xrightarrow{\text{Fast}} \mathrm{Alk}-\mathrm{Y} \end{array} \tag{3}$$

$$(S_N2)\quad \mathrm{Y} + \mathrm{Alk}\vdots\!-\mathrm{X} \longrightarrow \mathrm{Alk}-\mathrm{Y}+\mathrm{X} \tag{4}$$

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[139] (*a*) Hughes, Ingold, and Patel, *J. Chem. Soc.*, 526 (1933); (*b*) Hughes and Ingold, *ibid.*, 1571 (1933); (*c*) Gleave, Hughes, and Ingold, *ibid.*, 236 (1935); (*d*) Hughes and Ingold, *ibid.*, 244 (1935); 225 (1936); (*e*) Hughes, *ibid.*, 255 (1935); (*f*) Hughes and Shapiro, *ibid.*, 1177 (1937); (*g*) Cooper and Hughes, *ibid.*, 1183 (1937); (*h*) Bateman and Hughes, *ibid.*, 1187 (1937); (*i*) Hughes and Shapiro, *ibid.*, 1192 (1937); (*j*) Bateman, Hughes, and Ingold, *ibid.*, 881 (1938).

It is apparent that reaction S_N1 would be monomolecular if, as postulated, the second step is fast compared to the first; while reaction S_N2, which assumes the intermediate formation of a complex between Y and Alk − X, would be bimolecular. The ionization involved in the S_N1 mechanism is considered to be a solvolytic ionization. This means that the "unimolecular" ionization is in reality "polymolecular," since water molecules enter into the reaction.[140] Hughes and Ingold [141] point out, however, that from this point of view all reactions taking place in solution would be polymolecular, and it is desirable to distinguish between the reactions in solution in which only one molecule is necessarily undergoing covalence change (unimolecular) and those in which two molecules undergo covalence change (bimolecular).

In reaction S_N1 an increase in the electron-releasing powers of the alkyl group ($Me < RCH_2 < R_2CH < R_3C$) should favor the ionization and increase the speed, as should also an increase in the electronegativity of X. The electronegativity of Y should be without effect on the speed. In reaction S_N2, on the other hand, the higher the electronegativity of the alkyl group, the greater should be its tendency to accept electrons from Y (ordinarily this will result in sharing of electrons). The same tendency will be favored by a low electronegativity of Y. Apparently, then, changes in the electronegativity relationships should favor one mechanism at the expense of the other and we should not be surprised to find different members of a given series of compounds, Alk − X, reacting by different mechanisms to form the same type of products. The manner in which a change in alkyl groups may effect a change in mechanism is represented in Figure 2 for the hydrolysis of alkyl iodides.

As already explained, increasing electron-releasing tendencies in the alkyl groups should favor mechanism S_N1 at the expense of S_N2. Therefore as we increase the size of the alkyl groups by successive substitution of the methyl group (Fig. 2) the reaction, proceeding at first according to mechanism S_N2, becomes slower. Finally a minimum is reached (the "mechanistic critical point"), after which there is a change in mechanism to S_N1, which is further favored by the change from the isopropyl to the tertiary butyl radical. The upper curve on either side of the critical point is the experimentally realizable curve.

A similar but different relationship is observed when Y is changed. This is illustrated in Figure 3 where, from left to right, Y becomes progressively more electron-attractive. The changes observed have already been explained.

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[140] Cf. Farinacci and Hammett, *J. Am. Chem. Soc.*, **59**, 2544 (1937).

[141] Bateman, Church, Hughes, Ingold, and Taher, *J. Chem. Soc.*, 1008 (1940).

It must be realized that the precise location of the critical point will depend on the thermodynamic environment, although in general it may well be that changes within practical limits will not suffice to shift the critical point a whole place in the chemical series.

A number of different cases are discussed by the authors, and the reader must refer to their papers for the details, as well as for the literature references. They checked the experimental observations against the theory from a number of different points of view and found a highly satisfactory concordance. A few clarifying examples are given below in a more or less condensed form.

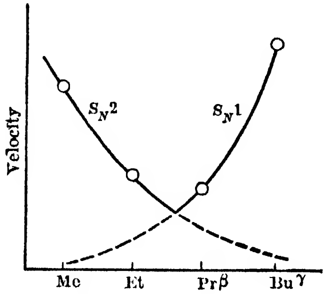


FIG. 2.[139c] The velocity of hydrolysis of alkyl iodides as a function of the substituent groups.

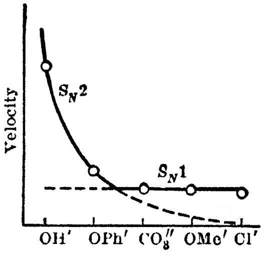


FIG. 3.[139c] Velocity of substitution of halogen ions from an alkyl halide by different negative ions.

Hydrolysis of Alkyl Iodides

$RI + OH^- \rightarrow ROH + I^-$

Solvent: water.

Reagent: alkali hydroxides.

Mechanism: Me and Et,S_N2; *iso*-Pr and *t*-Bu,S_N1. Curve as in Figure 2 with mechanistic critical point between Et and *iso*-Pr. In the case of EtI there was a side reaction producing ethylene.

Hydrolysis of Aryl-Alkyl Halides.

Series: Me, $PhCH_2$—, Ph_2CH—, Ph_3C—.

Theory: The phenyl group may exhibit either $+E$ or $-E$ effect, depending on the electronic demands of the reaction. In mechanism S_N2 it is hard to say what those demands are since the separation of X as a negative ion demands electron release and the simultaneous formation of a covalence with the OH^- (Y) demands electron attraction. Probably the influence on S_N2 would be slight in traversing the series to the right. But S_N1 would be favored by the same changes since electron release by the organic radical is definitely demanded for the ionization. Hence in going from left to right in the series the mechanism might be expected to change from S_N2 to S_N1. Before the change the velocity curve might be irregular, but after the change it should increase.

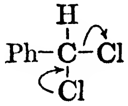
The following experimental data substantiate the theory.

MeX·S_N2.

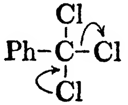
$PhCH_2 \cdot Cl$. Falls on S_N2–S_N1 borderline, kinetics complex.

Ph_2CHCl. S_N1. Speed independent of reagent hydroxide.

Hydrolysis of Polyhalides.



S_N1



S_N1

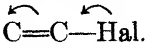
However, if the second and third halogens are attached to other carbon atoms their $+E$ effects cannot operate and their $-I$ effects will. This inhibits S_N1 and facilitates S_N2. Thus the following relative rates of reaction with MeO^- ion have been observed:[142] PhBr (5), Me_2CHBr (1), $CH_2BrCH_2CH_2Br$ (12), $CH_3 \cdot CHBr \cdot CH_2Br$ (33), $CH_2Br \cdot CHBr \cdot CH_2Br$ (2450).

Hydrolysis and Alcoholysis of α-Halogenated Acids and Esters:[143]

$BrCHMe \cdot CO_2R$ and $BrCHMe \cdot CO_2H$

The mechanism is S_N2 under conditions which result in mechanism S_N1 for secondary alkyl halides; this is due to the $-I$ effect of the carboxy and carboalkoxy groups. In sufficiently basic solution the ionization of the carboxyl group results in the production of a free negative pole which is electron repelling $(+I)$ and therefore aids the ionization of bromine and favors mechanism S_N1. It is claimed that actually the mechanism of hydrolysis of $BrCH_2 \cdot CO_2$ is $S_N1 + S_N2$ and that the proportion of S_N1 increases successively in $BrCH(Me)CO_2^-$ and $BrCH(Et)CO_2^-$ as it should since the alkyl groups $(+I)$ aid in the ionization. Finally in $BrCHPhCO_2^-$ the mechanism becomes exclusively S_N1 owing to the strong electromeric effect of the phenyl group.

Hydrolysis of Unsaturated Aliphatic Halides.



$C{=}C{-}Hal$. Mechanism S_N2, slow hydrolysis. Halogen inhibits both mechanisms but affects S_N1 the more.

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[142] Tronov and Gersevic, *J. Russ. Phys.-Chem. Soc.*, **59**, 727 (1927).

[143] (*a*) Cowdrey, Hughes, and Ingold, *J. Chem. Soc.*, 1208 (1937); (*b*) Cowdrey, Hughes, Ingold, Masterman, and Scott, *ibid.*, 1252.

$\mathrm{C{=}\overset{\curvearrowright}{C}{-}C{-}\overset{\curvearrowright}{Hal}}$ or $\mathrm{\overset{\curvearrowleft}{C}{=}C{\leftarrow}C{-}Hal}$. The first assists S_N1, the second S_N2. Hence under all conditions these halides are highly reactive in nucleophilic substitutions.

Formation of Quaternary Ammonium Salts.

$$\mathrm{NR_3 + Alk{\cdot}Hal \rightarrow Alk{\cdot}\overset{+}{N}R_3 + Hal^-}$$

Velocity changes due to variation of alkyl: Me $\gg$ Et $\gg$ *iso*-Pr and Et $>$ *n*-Pr $\sim$ higher primary groups.

Mechanism: S_N2. Note that greater powers of electron release in the alkyl group slow up the reaction in accord with the theory.

The discussion of "substitution" reactions given in this section exemplifies the way in which the simpler details of the English theory may be applied to such reactions. Further discussion of the subject will be postponed until the last chapter because a thorough consideration of hydrolytic reactions demands the application of certain knowledge from the fields of quantum mechanics and kinetics which will be considered in the intervening chapters.

Addition Reactions of Unsaturated Systems

An unsaturated substance may owe its additive properties to the presence of multiple bonds, to the possession of unshared electrons, or to the circumstance that it can accommodate additional electrons in its valence shell. It is only the first of these topics with which we shall attempt to deal here. For convenience the subject will be subdivided according to the kinds of atoms joined by the multiple linkages, viz., C═C, C═O, C≡N and N═N.

Olefins. Many of the older data on addition of acids to olefins have been rendered of questionable value by Kharasch's discovery of the "peroxide effect." This effect has already been discussed in Chapter II.[144] A summary of the facts which have been established in relation to this phenomenon has been given by Kharasch.[145] For our immediate purpose it will be sufficient to emphasize that this catalytic effect has not been observed in addition reactions involving as addenda HCl, HI, or H_2SO_4. Most of the recorded cases of the peroxide effect in addition reactions involve HBr. The theory proposed by Kharasch to explain the phenomenon and its criticism by Michael[146] need not concern us here. Our chief concern will be to restrict our test cases to those reactions in which peroxides have been shown to be without effect, or those in which the "normal" product has been established.

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[144] See p. 31.

[145] Kharasch, Englemann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

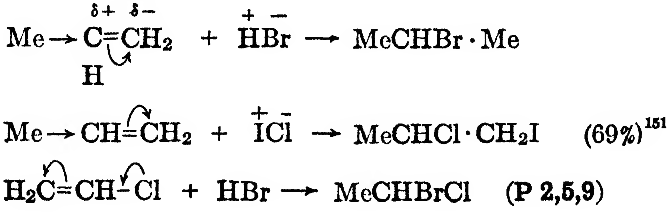
[146] A. Michael, *J. Org. Chem.*, **4**, 519 (1939); Michael and Weiner, *ibid.*, 531.

The manner in which the English school has applied its theory to addition reactions may be most readily understood if we simply state that they added to the old Lucas theory[147] (which recognized only the inductive effect as an orienting influence) their other electrical effects and their concept of nucleophilic and electrophilic reactivity.

Olefins are nucleophilic substances. *A priori* this could hardly have been predicted, since the polarized form $-\overset{\curvearrowleft}{\underset{\delta-}{\mathrm{C}}}{=}\underset{\delta+}{\mathrm{C}}-$ presents both electron-rich and electron-poor carbon atoms, either of which would have been predicted to have a strong tendency to form covalences. However, the fact that olefins add electrophilic substances such as ozone, halogens, and strong acids and the fact that among the halogens the ease of addition parallels the electron affinity, force us to conclude that olefins are nucleophilic. Further support comes from its lack of reactivity with nucleophilic substances, such as weak acids, and ammonia and its derivatives. Robinson[148] also finds support for the idea in experiments of J. J. Thomson on the discharge of electricity through rarefied gases. Thomson observed that no hydrocarbon radicals so produced carried negative charges except HC_2^-, which is the anion of the exceptional substance acetylene. This seems to indicate that carbon is normally in a more stable condition when electron-poor than when electron-rich and hence would exhibit nucleophilic reactivity.

Further supporting evidence is to be found in the work of Hennion, which was discussed in Chapter IV.[149] The possibility that activation of olefins involves the symmetrical rupture of the double bond has already been discussed.[150]

With the foregoing facts in mind we may now quickly dispose of the problem of predicting orienting influences in olefin addition reactions. The following examples of "normal" addition reactions (taken from the papers of Kharasch unless otherwise specified) make the application of the theory plain.



$$\mathrm{Me}\rightarrow\underset{\mathrm{H}}{\overset{\delta+}{\mathrm{C}}}{=}\overset{\delta-}{\mathrm{C}}\mathrm{H_2} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{Br}} \longrightarrow \mathrm{MeCHBr\cdot Me}$$

$$\mathrm{Me}\rightarrow\mathrm{CH}\overset{\curvearrowright}{=}\mathrm{CH_2} + \overset{+}{\mathrm{I}}\overset{-}{\mathrm{Cl}} \longrightarrow \mathrm{MeCHCl\cdot CH_2I} \quad (69\%)^{151}$$

$$\mathrm{H_2}\overset{\curvearrowleft}{\mathrm{C}}{=}\mathrm{CH}\overset{\curvearrowleft}{-}\mathrm{Cl} + \mathrm{HBr} \longrightarrow \mathrm{MeCHBrCl} \quad \mathbf{(P\ 2,5,9)}$$

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[147] See p. 28.

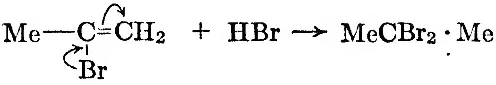
[148] R. Robinson, *J. Chem. Soc.*, 401 (1926).

[149] See p. 55.

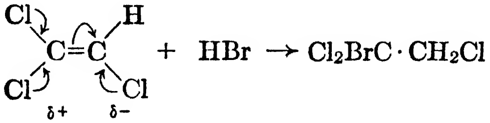
[150] This chapter, p. 82.

[151] Ingold and H. G. Smith, *J. Chem. Soc.*, 2742 (1931). Probably ICl addition is not subject to the peroxide effect.

Presumably the high dipole moment of HBr is here responsible for calling the $+E$ effect of Cl into operation to such an extent that $+E > -I$ (**P 6**).



$$\mathrm{Me{-}C(Br){=}CH_2 + HBr \rightarrow MeCBr_2\cdot Me}$$



$$\mathrm{Cl_2C{=}CHCl + HBr \rightarrow Cl_2BrC\cdot CH_2Cl}$$

The last reaction above does not occur without a catalyst. The catalyst used was $FeCl_3$, which had been shown to catalyze the "normal" additions.

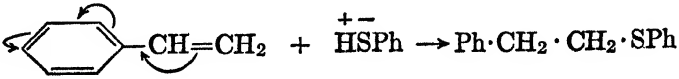
$$\mathrm{Me{\rightarrow}C{\equiv}CH + HBr \rightarrow MeCBr_2Me}$$

$$\mathrm{MeCH_2{\rightarrow}CH{=}CH{\rightarrow}CO_2H + HCl{\rightarrow}MeCH_2{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H}^{152}$$

β-Ethylidene propionic acid also adds HCl in such a way that the chlorine atom goes to the carbon farthest from the carbonyl group, while in allyl acetic acid the reverse is true.[152] In the latter the carbonyl group is apparently so far removed from the double bond that its inductive influence is not of consequence and addition proceeds as it would in propylene.

The case of styrene is interesting. According to the English theory the phenyl group may act either as an electron source or sink, depending on the demands of the attacking reagent. If the attacking reagent were electrophilic (e.g., HBr) the phenyl group would act as a source (**P 5**):

Thiophenol, however, adds to styrene in the reverse direction, and Ingold [153] explained the fact by assuming that thiophenol reacts as a nucleophilic reagent, which might be expected in view of its weakly acidic nature. If this is true the electron demand would be the reverse of that in the reaction with HBr and the phenyl group will act as an electron sink:



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[152] Schjanberg, *Ber.*, **70B**, 2385 (1937).

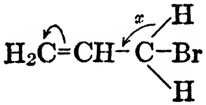
[153] Ingold, *Ann. Repts. Chem. Soc.*, 146 (1928).

Shortly after the peroxide effect had been discovered Burkhardt[154] suggested that thiophenol might act as an antioxidant and hence give results opposite to those observed with HBr, but this criticism was ultimately disposed of by Walling, Kharasch, and Mayo[155] when they showed that the normal reaction of HBr with styrene yields the *alpha*-bromo compound. In fact, further work from Kharasch's laboratory made it appear probable that the thiophenol reaction was peroxide catalyzed since styrene reacted with thioglycollic acid in the presence of ascaridole to give $PhCH_2 \cdot CH_2 \cdot SCH_2 \cdot CO_2H$, while no reaction occurred in the presence of a strong antioxidant.[156] Obviously further work is desirable before final judgment can be passed on Ingold's explanation, but on the basis of existing evidence it seems that the dual electronic functions of the phenyl group have not been demonstrated in the above case.

Allyl bromide seems to be a case where the older qualitative theory of the English school would not have made the proper prediction. It would have been applied as follows:

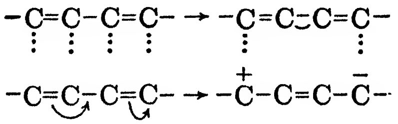
$$H_2C{=}CH\rightarrow CH_2\rightarrow Br \ + \ HBr \longrightarrow CH_2Br\cdot CH_2\cdot CH_2Br$$

Actually the 1,2-dibromo compound is formed. This can be explained on the basis of the newly discovered effect, hyperconjugation, as indicated below.



The $+T$ effect indicated by x is hyperconjugative.

The English theory has been particularly successful in dealing with many types of reactions involving conjugation. The earlier partial valence theory of Thiele finds a natural explanation in terms of the electron theory, as is indicated by the similarity of the following representations:



In addition to this, however, the English have extended the theory to include prediction of whether 1,2- or 1,4-addition is to be expected in any given case.

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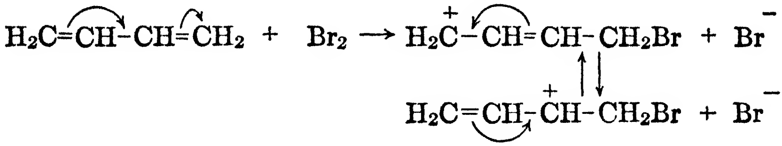
[154] Burkhardt, *Trans. Faraday Soc.*, **30,** 18 (1934).

[155] Walling, Kharasch, and Mayo, *J. Am. Chem. Soc.*, **61,** 2693 (1939).

[156] Kharasch, Read, and Mayo, *Chem. and Ind.*, 752 (1938).

The general application of the theory may be illustrated as follows:[157]



$$H_2C{=}CH{-}CH{=}CH_2 + Br_2 \longrightarrow H_2\overset{+}{C}{-}CH{=}CH{-}CH_2Br + \overset{-}{Br}$$
$$\updownarrow$$
$$H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br + \overset{-}{Br}$$

The initial attack is by the electron-poor bromine atom (as was previously demonstrated for the alkenes) and, according to **P 8**, it must occur preponderantly at the end of the chain. This yields an ion which may tautomerize as indicated, yielding two possible points for attack by the negative bromide ion. The relative amounts of the 1,2- and the 1,4-isomers finally produced will depend on the equilibrium concentrations of the two intermediate ions, if a sufficient time is available for equilibrium to be established, and the relative values of the velocity constants associated with the formation of covalences between the bromide ion and either of the two isomeric anions.

Of further importance to the subject of conjugative addition is the work of Kharasch and his collaborators who have studied the peroxide effect in the addition of hydrogen bromide to butadiene.[158] They found that in the absence of oxygen and peroxides and in the presence of an antioxidant a 1,2-addition occurs. At higher temperatures under the influence of hydrogen bromide, and particularly under the combined influence of hydrogen bromide and peroxides, the above addition product rearranges to give the product which would have been formed by 1,4-addition. Such results as these naturally dictate caution in theorizing on the basis of the older data.

In addition to the orientation problem there is also the problem of predicting the effects of substituents on the speed of olefin addition reactions. The basic theory for this problem has been expounded by the Ingolds.[159] They emphasize that a given substituent group may facilitate different reactions much or little, depending on the strength of the polarizing field of the attacking reagent (**P 6**). Thus chlorine, which falls in the $-I,+T$ category, exerts a constant $-I$ influence and a variable $+T$ influence. It follows that either influence may be preponderant, depending on the strength of the polarizing field of the attacking reagent, and hence the substituent chlorine may facilitate one reaction and inhibit another even though both are nucleophilic in character. Hence "be-

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[157] Burton and Ingold, *J. Chem. Soc.*, 910 (1928); Ingold, *Ann. Repts. Chem. Soc.*, **25**, 131 (1928).

[158] Kharasch, Margolis, and Mayo, *J. Org. Chem.*, **1**, 393 (1936).

[159] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931).

cause it is not possible accurately to gauge the electrical requirements of additions in comparison with those of other reactions, it is also not possible theoretically to deduce a complete sequence representing group effects on additions by interpolation from known group-series relating to other reactions." [159]

The experimental data necessary for the test and the elucidation of the theory have been supplied by the carefully planned work of Ingold and Anantakrishnan.[160] They carried out competitive brominations of various olefins, expressing their results as "reduced rates," i.e., as the ratio of the rate of reaction of each substance to that of ethylene. They demonstrated that the "reduced rates" are independent of the catalytic effects investigated. Their results are summarized in Table XVII.

TABLE XVII [160]

REDUCED RATES OF BROMINE ADDITION IN CH_2Cl_2 SOLUTION AT −78°

$Me_2C=CMe_2$	14.0	$CH_2=CH \cdot CHO$	1.5
$Me_2C=CHMe$	10.4	$CH_2=CH_2$	1.0
$Me_2C=CH_2$	5.53	$MeCH=CH \cdot CO_2H$	0.26
$PhCH=CH_2$	3.35	$CH_2=CH \cdot CO_2H$	small
$MeCH=CH \cdot CHO$	3.0	$CH_2=CHBr$	small
$MeCH=CH_2$	2.03		

It will be observed that the successive introduction of electron-releasing methyl groups into ethylene causes increases in reaction velocity. The strong $-T$ effect of the carboxyl group is seen to be deactivating to such an extent that even the substitution of a methyl group in the same molecule fails to overbalance it. The bromine atom $(-I,+T)$ is found to be deactivating, a fact which may seem surprising in view of the explanation given previously for the orientation observed in the addition of HBr to vinyl bromide, viz., that $+T > -I$. The explanation is presumably to be found in **P 6**: the electrical field around the dipolar HBr is stronger than around the nonpolar Br_2 and hence the $+T$ effect is called into play to a greater extent by the HBr.

The aldehyde group is found to be activating, a result which would not have been predicted from its $-I,-T$ influence. There is, however, an interesting possible explanation.[160b] The theory would certainly predict that if a sufficiently electronegative group were substituted into ethylene the reactivity might change from nucleophilic to electrophilic because the electron-rich carbon atom of the activated molecule would hold its electrons so firmly that it would have but little tendency to share

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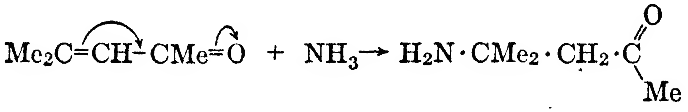
[160] (*a*) Anantakrishnan and Ingold, *ibid.*, 984 (1935); (*b*) *idem*, 1396; (*c*) Anantakrishnan and Venkataraman, *ibid.*, 224 (1939).

them, while the electron-poor carbon atom would find its acceptor qualities much enhanced. If the aldehyde group is sufficiently electron-attractive to bring about this condition the attack would be made by the electron-rich bromine atom and would be facilitated by electron-attractive substituents. The powerful $-E$ effect of the aldehyde group makes this seem plausible.

If the unsaturated aldehydes do exhibit electrophilic properties in their reactions with the halogens we should expect that the relative reactivities of the halogens in these cases would be $I_2 > Br_2 > Cl_2$, the reverse of the order which obtains with other olefinic compounds. In accord with this prediction White and Robertson[161] have shown that crotonaldehyde in glacial acetic acid solution reacts more rapidly with bromine than with chlorine, although they prefer another interpretation than that of Ingold.

The idea that acrolein exhibits electrophilic character when bromine is the attacking reagent is rendered still more plausible by the fact that it frequently exhibits electrophilic character in reactions with other reagents. For example, acrolein adds two molecules of $NaHSO_3$. Since only one of these is removed by heating with acids, the other must have been added to the C=C, which normally would not react with the bisulfite. Another similar example is the following:[162]



$$Me_2C{=}\overset{\curvearrowright}{CH{-}}CMe{=}\overset{\curvearrowright}{O} + NH_3 \rightarrow H_2N{\cdot}CMe_2{\cdot}CH_2{\cdot}C(=O)Me$$

These reactions are explained by Robinson[162] as due to the ability of the carbonyl group to impose electrophilic character on the olefin carbon atom by electromeric relay. Thus while normally the carbonyl carbon atom is electrophilic, $R_2\overset{\curvearrowright}{C{=}O}$, this reactive center is relayed down the carbon chain if a conjugated system is present: $\overset{\curvearrowright}{C{=}C}{-}\overset{\curvearrowright}{C{=}O}$. Thus **P 8** would lead us to the prediction that if a nucleophilic reagent attacked the acrolein molecule, the β-carbon would be most susceptible to attack.

Further indirect support for Ingold's suggested explanation of the addition of bromine to acrolein is found in an early paper by Kohler.[163] He showed that the following reaction occurs when vinyl sulfonic acid is heated with water or alkalies:

$$H_2\overset{\curvearrowright}{C{=}CH}{\rightarrow}SO_3H + H_2O \rightarrow HOCH_2{\cdot}CH_2{\cdot}SO_3H$$

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[161] E. P. White and P. W. Robertson, *J. Chem. Soc.*, 1509 (1939).

[162] Ref. 1*b*, p. 25.

[163] Kohler, *Am. Chem. J.*, **20**, 689 (1898).

Now the electrophilic properties of water are so weak that ordinarily it will not react with olefins, and the introduction of a strongly electron-attractive group like SO_3H into the olefin would render attack by the hydrogen ion still less probable. The converse is true in regard to attack by the hydroxyl ion and the fact that vinyl sulfonic acid reacts better with water in basic solutions seems to indicate that the hydroxyl ion really is the attacking reagent.* Note that the SO_3H is more electron-attractive than the CO_2H group and hence the possibility of a mechanistic critical point lying between them on an electronegativity scale is in complete accord with the theory.

Carbonyl Compounds. These compounds show additive properties in virtue of the following electromeric shift: $\overset{\curvearrowright}{C{=}O}$. Since the shift is toward the oxygen atom (**P 3**) the orientation of the fragments of the addenda is unambiguous. The carbonyl compound is electrophilic, since the electron-poor carbon atom has much more tendency to take up electrons than the electron-rich oxygen atom has to share them. Thus only nucleophilic substances may normally be expected to add to the carbonyl group, and we thus find a natural explanation for the fact that the typical carbonyl reagents do not add to olefins.

The nucleophilic reagents under discussion include ammonia and its derivatives, HCN, $NaHSO_3$, and Grignard reagents. Lapworth's proof of the electrophilic nature of carbonyl compounds has already been discussed.[164] The reactions in question are all reversible and all similar in mechanism to the cyanhydrin formation.[164]

Water is not sufficiently nucleophilic to react with carbonyl compounds in general. However, if strongly electron-attractive atoms or groups are substituted in the aldehyde or ketone molecule its electrophilic reactivity may be increased to the point where even water may add. This is illustrated in the formation of hydrates of mesoxalic acid and chloral.

Watson[165] shows that these same general considerations may be applied to the elucidation of the formation of oximes and phenylhydrazones and of various other condensation reactions. The reader is referred to his book for the details.

The reactions of nucleophilic reagents with carbonyl compounds show the following order of decreasing tendency to occur: aldehydes > ketones > esters > acids. In acids the electrophilic power of the carbonyl car-

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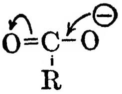
* Ingold considers ethylene sulfonic acid to behave as a nucleophilic reagent when attacked by ICl. Ref. 151.

[164] Chap. IV, p. 54.

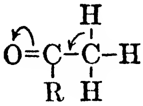
[165] Ref. 1*d*, pp. 107–112.

bon atom is much weakened by the $+M$ effect of the carboxylate ion, thus:[1b]



$$O{=}\underset{\displaystyle R}{C}{-}O^{\ominus}$$

In esters the effect is less. In ketones there is only the weak hyperconjugative influence of the alkyl group:



$$O{=}\underset{\displaystyle R}{C}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H$$

while in aldehydes there is no influence to oppose the electrophilic tendency of the carbonyl carbon atom.

Amides exhibit the same type of mesomerism that esters do, but it is stronger: $O{=}\underset{\displaystyle R}{C}{-}\ddot{N}H_2$. In this case it has the effect of rendering the amide less basic than amines.

Cyanides. Here the expected electromeric shift would be represented as follows: $R{-}\overset{\curvearrowright}{C{\equiv}N}$. Since electron-poor carbon has a greater tendency toward covalence formation than electron-rich nitrogen (assumed, e.g., from the fact that liquid ammonia ionizes while liquid hydrocarbons do not) the theory would predict that cyanides should be preponderantly electrophilic in their reactivity. This is borne out by the following reactions with nucleophilic substances.

$$Me{-}C\overset{\curvearrowright}{\equiv}N + H_2S \rightarrow MeCS{\cdot}NH_2$$

$$RC\overset{\curvearrowright}{\equiv}N + R'MgI \rightarrow RR'C{=}NMgI$$

In the presence of anhydrous HCl they add ethanol: $MeC{\equiv}N + EtOH \rightarrow MeC(OEt){=}NH$. However, if only anhydrous HCl is present it adds to the triple bond: $RC{\equiv}N + HCl \rightarrow RC({=}NH)Cl$, which seems to indicate that cyanides may exhibit nucleophilic properties also. In view of their dual reactivity it is difficult to say *a priori* in which class we should place their hydrolysis.

Azo Compounds.

$$R{-}N{=}N{-}R'$$

Here again we would expect electrophilic reactivity to be preponderant, in so far as reactions involving addition to the double bond are concerned. Owing to the fact that azo compounds usually show a preference for other kinds of reaction, addition reactions are rare. We have, however, the following addition reaction:[166]

$$PhSO_2H + PhN{=}NPh \rightarrow PhNH{\cdot}N(Ph)SO_2Ph$$

The nucleophilic character of the sulfinic acid is inferred from the fact that it adds to the double bond of aldehyde.[167]

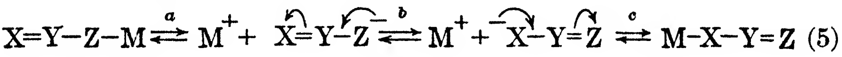
Tautomerism

The subject of tautomerism boasts of an exceedingly extensive literature. This is true also of its interpretation in terms of the English theory. In view of the space limitations of this monograph and in view of the fact that the subject has been reviewed from the electronic standpoint in a highly satisfactory manner by Baker,[168] an extensive review of the subject here is uncalled for. Consequently nothing will be attempted except to indicate the general outline of the theory.

The basic idea back of the modern interpretation is due to Knorr.[169] Phrased in modern terms it pictures tautomeric change as taking place in three steps: (1) ionization, (2) internal transfer of electrons within the unsaturated ion resulting in two possible points of recombination with the other ion, and (3) reunion of the two ions.

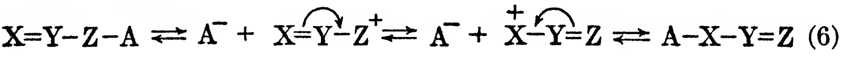
When the "other ion" is positive the tautomeric change is said to be cationotropic and when negative, anionotropic. The all-important case of cationotropy involving the release of a proton is called prototropy. The two cases may be pictured as follows:[168]

cationotropy:



$$X{=}Y{-}Z{-}M \overset{a}{\rightleftharpoons} M^+ + X{=}Y{-}Z^- \overset{b}{\rightleftharpoons} M^+ + {}^-X{-}Y{=}Z \overset{c}{\rightleftharpoons} M{-}X{-}Y{=}Z \quad (5)$$

anionotropy:



$$X{=}Y{-}Z{-}A \rightleftharpoons A^- + X{=}Y{-}Z^+ \rightleftharpoons A^- + \overset{+}{X}{-}Y{=}Z \rightleftharpoons A{-}X{-}Y{=}Z \quad (6)$$

In each example it will be noticed that the initial and final forms represent the two tautomerides and that these establish equilibrium with each other through an intermediate "common ion" whose structure is properly represented not by either extreme contributing form but by the intermediate mesomeric state.

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[166] Hantzsch and Glogauer, *Ber.*, **30**, 2555 (1897).

[167] Kohler, *J. Am. Chem. Soc.*, **31**, 166 (1909).

[168] J. W. Baker, *Tautomerism*, D. Van Nostrand Co., 1934.

[169] Knorr, *Ann.*, **293**, 38 (1896).

The success of the initial ionization and the final association naturally depends on the thermodynamic environment as well as upon internal factors. In regard to the former, it is easy to see how the solvent may facilitate the reaction by its ability to act as a proton donor or acceptor. The relationship may be pictured as follows:[170]

$$-\underset{|}{C}H-\underset{|}{C}=O \xrightleftharpoons{+H^+} -\underset{|}{C}H-\underset{|}{C}=OH^+ \xrightleftharpoons{-H^+} -\underset{|}{C}=\underset{|}{C}-OH$$

$$-\underset{|}{C}H-\underset{|}{C}=O \xrightleftharpoons{-H^+} -\overset{-}{\underset{|}{C}}-\underset{|}{C}=O \rightleftarrows -\underset{|}{C}=\underset{|}{C}-O^- \xrightleftharpoons{+H^+} -\underset{|}{C}=\underset{|}{C}-OH$$

A more detailed consideration of environmental factors, especially the solvent, will be given in Chapter X.

The "internal factors" are two in number: (1) the "mobility," which is defined as the sum of the velocity coefficients of the forward and backward reactions, and (2) thermodynamic affinity, which controls the equilibrium point. For this, the ratio of the rate constants forms a satisfactory measure under suitable conditions.[171]

The mobility obviously depends on the ease of removal of the migrating ion. If this is a cation the reaction will be facilitated by any electron-attracting substituent ($-I$ or $-T$) and vice versa if it is an anion. Experience has shown that the mobility also depends on a second factor, viz., the presence of an atom in the "common ion" which can provide a suitable seat for the electric charge, i.e., an atom which is capable of acting as an electron source or sink and is in a reasonably stable condition when accommodating the charge. The significance of the stability is understandable when we consider that, if the electromerization of the ion is a slow process (Eqs. 5, 6), the speed will depend on the concentration of these ions, which in turn is dependent on their ionic stability. The other factor (capability of acting as an electron source or sink) is exemplified by the $-\overset{+}{N}R_3$ group which, although it facilitates the release of a proton, does not form a suitable seat for the remaining negative charge, while the carbonyl group does both.

The influence of substituent groups may be deduced by the usual methods. In regard to the hindrance of tautomeric change by substitution, it should be pointed out that, for example, in prototropic change the tautomerization depends on the separation of a proton and hence is facilitated by reaction with a nucleophilic reagent. Or, looking at the matter from the opposite angle, prototropic changes are electrophilic,

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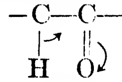
[170] Ref. 1*d*, p. 128.

[171] Ref. 168, p. 42.

the electronic demands of the reactions being low electron density at the seat of reaction. Hence they may be facilitated by substituents with $-T$ effects but cannot be hindered by $+E$ effects since the latter are not called for.[172] Of course there is always a possibility that a $+M$ effect may be operative. Here again we are confronted with the desirability of a more quantitative method of deducing the relative magnitudes of the various effects.

There is one case, however, in which $+T$ effects may hinder, viz., where the group in question is part of the activating group.[172] Thus in a system  $-\underset{H}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-R$, if R exhibits a $+T$ effect it will be called into play by the $-T$ effect of the carbonyl group and hence will compete with the electromeric process causing ionization of the proton, cutting down the ionization. But a $+E$ effect of the activating group as a whole, or of any other substituent group as a whole, would be without influence. If R exhibits a $-I$ effect, it will aid in the ionization. We thus deduce the following sequence of groups, arranged in decreasing order of their effectiveness in producing tautomeric mobility when substituted for R in the above formula: $CO_2Et > H > Me > Hal > OR > NH_2 > O^-$.

The effects of groups substituted in other parts of the molecule may also be deduced by a similar straightforward application of the basic principles of the theory.

In regard to the influence of internal factors on the equilibrium point, Equations 5 and 6 make it clear that three equilibria are involved and naturally the final position of the over-all equilibrium depends on the factors governing each of these three. For the initial and final steps this means the factors governing the stability of the covalent linkages of M^+ (or A^-) to Z and X, while for the intermediate step it means the factors regulating the distribution of the charge in the electromeric ions. In general, therefore, the problem is apt to be complex. If, however, we are dealing with prototropic systems in basic solutions, the equilibria *a* and *c* (Eq. 5) are ruled out to a large extent because in basic solutions the tautomeric substance is apt to exist largely in the ionic form. Under such circumstances the tautomeric equilibrium may be discussed as though only the equilibrium *b* (Eq. 5) exists.

Miscellaneous Applications of the Theory

Methylation of Alcoholic Hydroxyl.[173] Methylation with dimethyl sulfate and alkali is rendered easier by the proximity of a phenyl group, as

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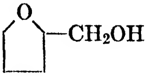
[172] Shoppee, *J. Chem. Soc.*, 969 (1930).

[173] Von Braun, Anton, and Weissbach, *Ber.*, **63B**, 2847 (1930).

in $PhCH_2 \cdot OH$. In the field of tautomerism, ease of methylation has for long been regarded as a criterion of mobility of the proton. Hence here it seems that we must ascribe to the phenyl group a $-I$ influence (which is indicated in many other cases, e.g., in the fact that phenyl acetic acid is stronger than acetic acid) which increases the ionic character of the O—H bond by induction. The results given in Table XVIII are in accord with this idea and with our general principles. They represent the per cent yield of methyl ether obtained under identical conditions.

TABLE XVIII

	%		%
$PhCH_2 \cdot OH$	64		70
$PhCH_2 \cdot CH_2 \cdot OH$	19		
$Ph(CH_2)_3OH$	5		
$Ph(CH_2)_5OH$	0	PrOH	0
$PhCMe_2 \cdot OH$	0	$Me_2N(CH_2)_3OH$	100
$PhCH{=}CH \cdot CH_2 \cdot OH$	53	$EtSO_2 \cdot CH_2 \cdot CH_2 \cdot OH$	100

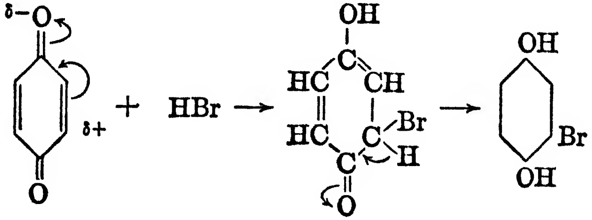
Von Braun believes that quaternary salt formation of amines occurs with dimethyl sulfate. This would put a positive pole on the nitrogen atom of the amino compound in Table XVIII and thus explain the high yield of ether obtained.

Halogenation with Interhalogen Compounds. BrCl is a powerful brominating agent, since brominating agents are electrophilic and here Br^+ is more electrophilic than it is in Br_2. It does not chlorinate. Likewise ICl is a much stronger iodinating agent than iodine.[174] Electrolysis studies show that [175] $IBr \rightarrow I^+ + Br^-$.

The following case seems to be exceptional: [176]

$$PhOH + IBr \rightarrow p\text{-}BrC_6H_4 \cdot OH + HI$$
$$HI + IBr \rightarrow HBr + I_2$$

Electrophilic Reactivity of Quinones. In this case the carbonyl group imposes electrophilic reactivity on the ring carbon atoms.



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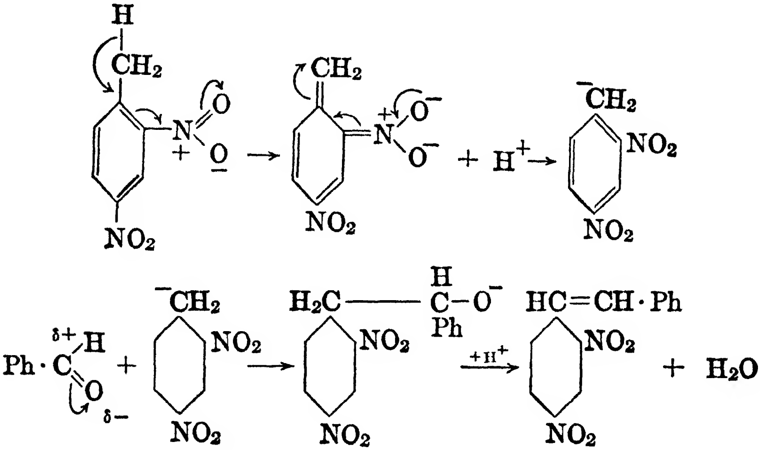
[174] Ingold, *Rec. trav. chim.*, **48**, 809 (1929).

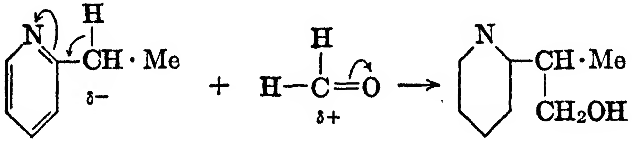
[175] Finkelstein, *Z. physik. Chem.*, **124**, 285 (1926).

[176] Militzer, *J. Am. Chem. Soc.*, **60**, 256 (1938).

Nucleophilic Condensations. Here nucleophilic reactivity is induced in the side chain by the nitro groups.

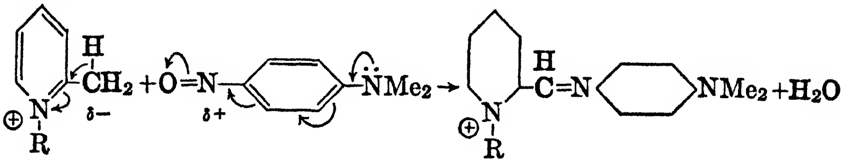


It is well known that α- or γ-alkyl derivatives of pyridine and quinoline undergo similar condensations, whereas the β-derivatives do not.



The activation is due to the $-T$ effect of the nitrogen atom and obviously can be relayed to the *gamma*-position but not to the *beta*. Similarly only one of the methyl groups in dimethylbenzimidazole is capable of forming condensation products with aldehydes.[177]

α-Picoline will not undergo the following condensation but its quaternary salt will.



The nitroso compound is apparently weakly electrophilic because the positive pole produced at the nitroso nitrogen atom is partially annulled by the conjugative relay of electrons from the Me_2N— group. Thus reaction is only rendered possible by increasing the $-I$ effect of the hetero atom in picoline through salt formation.

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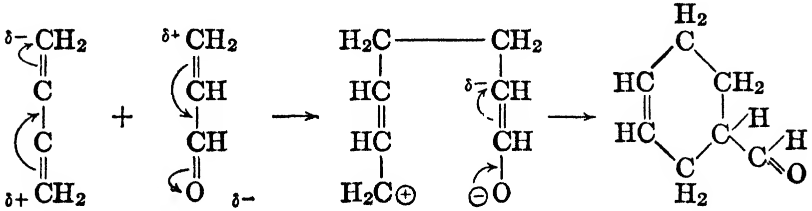
[177] Bamberger and Berle, *Ann.*, **273**, 277 (1893).

Diels-Alder Diene Synthesis.[178] The reaction consists of the addition of dienes to conjugated systems such as quinones, maleic anhydride, acrolein, crotonaldehyde, crotonitrile, acetylene, and dicarboxylic esters. These are characterized by groupings such as $-\overset{\curvearrowright}{C{=}\underset{\delta+}{C}}-\overset{\curvearrowright}{C{=}\underset{\delta-}{O}}$ or $-\overset{\curvearrowright}{\underset{\delta+}{C}{=}C}-\overset{\curvearrowright}{\underset{\delta-}{C{\equiv}}N}$. In all these compounds the electrophilic center is passed along to the β-carbon atom. The dienes are more strongly nucleophilic than mono-olefins, as shown by the exaltation of the molar refraction characteristic of conjugated systems. Addition thus becomes extraordinarily facile. Example:



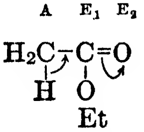
Pyrrole, furan, pyridine, and quinoline have been successfully substituted for the alkadiene.

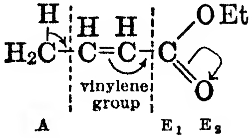
The effect of substitution in causing failure of the reaction has not been explained.[179]

The Principle of Vinylogy. This principle has been stated by Fuson [180] as follows: "When, in a compound of the type $A{-}E_1{=}E_2$ or $A{-}E_1{\equiv}E_2$ a structural unit of the type $-(C{=}C-)$ is interposed between A and E_1 the function of E_2 remains qualitatively unchanged but that of E_1 may be usurped by the carbon atom attached to A."

The resulting compound will have the form $A-(C{=}C)_n-E_1{=}E_2$ and in any given series of this type the members will differ from each other by one or more vinylene residues. It is proposed to call such a group of compounds a vinylogous series. The members of such a series will then be vinylogs of one another.

Thus ethyl crotonate is a vinylog of ethyl acetate, in which A is CH_3, E_1 is C, and E_2 is O.





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[178] Diels, *Z. anorg. Chem.*, **42**, 480, 913 (1929); C. F. H. Allen, *J. Chem. Education*, **10**, 494 (1933); above explanation suggested by Robinson, Ref. 1*b*, p. 29.

[179] Coffman and Carothers, *J. Am. Chem. Soc.*, **55**, 2043 (1933).

[180] Fuson, *Chem. Rev.*, **16**, 1 (1935).

The power of ethyl acetate to condense with diethyl oxalate is due to the activation mechanism symbolized above. It would obviously follow from the English theory that the conjugated vinylene group in ethyl crotonate would relay the active electrophilic center to the β-carbon atom with resultant activation of a neighboring C—H linkage, as required by the principle.

Further examples need not be given as the principle is obviously nothing but a nonelectronic way of dealing with the conjugative relay of electrons, which is so adequately encompassed in the principles of the English theory.

Concluding Remarks

The application of the electron theory reviewed in this chapter demonstrates sufficiently well the methods used by the English school. Further detailed discussions of the way in which those investigators have applied the qualitative principles thus far discussed to other types of reactions would serve no further purpose except to render an account of the mechanisms assumed or established for many reactions. Such knowledge, although admittedly important, is far too extensive to be reviewed in a book the size of this one. Accordingly we will turn instead to a study of the physico-chemical extensions of this qualitative electronic theory which I have chosen to call the electronic theory of the English school. Whether or not the extended theory should bear the same name is a question of no real importance, but it is certainly a fact that the English chemists have been notably aided in the work of extension by the chemists of other nations, particularly by the Americans. A study of these extensions will, among other things, render mesomerism a more valuable tool, show that reaction velocity is a function of other factors than activation, present a clearer picture of the mechanism of activation, thereby paving the path toward the solution of the problem of the *a priori* determination of reaction mechanism, and acquaint us with certain physico-chemical methods which aid in the all-important problem of rendering the theory more quantitative so that less is left to the intuition and wishful thinking of the theorist.

CHAPTER VI

SOME CONTRIBUTIONS FROM THE FIELD OF CHEMICAL PHYSICS

The concept of mesomerism was originally developed on chemical grounds by the Ingolds [1] in the year 1926. In that same year recognition of the same phenomenon emerged from Heisenberg's study [2] in the field of quantum mechanics and was called resonance.

Application of the quantum-mechanical principles involved in the concept of resonance was soon made to the field of chemistry by several scientists, chief among whom was Linus Pauling. Unfortunately but few chemists have the necessary training in physics and mathematics to handle the subject of quantum mechanics with confidence. Consequently chemists in general should feel deeply grateful to Pauling for his book *The Nature of the Chemical Bond*,[3] in which he explains without detailed mathematical treatment the knowledge which has been contributed to that subject by quantum mechanics.

An adequate appraisal of the English theory cannot be made without a review of these quantum mechanical contributions to chemistry. Moreover, our concept of mesomerism will thereby be rendered more exact and we will also gain other knowledge which will be helpful in solving the theoretical problems of organic chemistry. Thus, although the subject has been given a masterful review by Pauling, the continuity of our present thesis requires that we discuss the subject here. Unfortunately mathematical complexities can only be avoided by making the treatment dogmatic.

The Concept of Resonance [3, 4]

The quantum theory has demonstrated that it is impossible to specify accurately the position and motion of an electron at each instant of time. The best that we can do is to get a time-blurred picture of it, which enables us to describe it as a wave motion. The frequency of the wave is related to its energy by the equation $E = h\nu$ (in which h is Planck's constant), while the amplitude measures the probability that the electron is

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[1] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, **130**, 1310 (1926).

[2] Heisenberg, *Z. Physik*, **39**, 499 (1926).

[3] Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, 1939.

[4] Ingold, *Nature*, **141**, 314 (1938).

in a given elementary volume. Confined waves, like the electron wave we are considering, have a property known as "self-interference" which results in the annihilation of all frequencies except those that can form standing waves. The properties of these "stationary quantum states" of a molecule are described by means of the wave functions of the standing waves. The total energy of these states is definitely restricted by the laws of quantum mechanics. Each of these states is designated by a quantum number, n, or by a set of quantum numbers; and each quantum number can assume any one of certain integral values.

The "normal state" or "ground state" of a system is the stationary quantum state which has the lowest value of the total energy. It is thus the most stable state. Quantum numbers are usually assigned values of 1 or 0 for this state.

From the standpoint of this monograph the most important principle derived from quantum mechanics emerges from a consideration of the change in the quantum state of an electron brought about by the process of covalence formation. When an electron becomes shared it falls under the influence of two atomic nuclei and hence there results an "interaction." The nature of this interaction can most easily be understood by consideration of a mechanical analogy.[4] Imagine two like pendulums hung from the same horizontal string. If one pendulum is set in motion its interaction with the string causes the vibratory motion gradually to become transferred to the other pendulum, after which it travels back to the first, etc.

There are only two sets of conditions under which the pendulums, when coupled, can undergo singly periodic motion: (1) The pendulums are started with equal amplitudes in phase, with the result that they keep in phase. The resultant frequency, $\nu - \epsilon$, is less than the frequency, ν, of either uncoupled pendulum because each is interacting with the string in such a way that it lessens the restoring force acting on the other. (2) The pendulums are started with equal amplitudes out of phase with the result that they remain out of phase. In this case the resultant frequency is $\nu + \epsilon$.

If ψ_1 and ψ_2 are the coordinates measuring the displacements of the two pendulums, it is found that the linear combination, $\psi_1 + \psi_2$, has the frequency $\nu - \epsilon$. Thus $\psi_1 + \psi_2$ represents the displacement coordinate of the coupled system 1 above. Likewise $\psi_1 - \psi_2$ represents system 2.

If now we return to the system first mentioned where neither condition 1 nor 2 obtains but where the mutual perturbations result in a surging of energy back and forth between the two pendulums, resulting in motions lacking simple periodicity, it is found that this complex motion can be described as a superimposition of the periodic motions separately described in 1 and 2. Thus the general effect of coupling is to replace two identical periodic motions by two other periodic motions, one of increased and one of decreased frequency.

We may now leave our mechanical analogy and continue the discussion in terms of subatomics. In this case ψ is called the "wave function," and it represents the quantum state or "structure" of a system. If the normal state of a system could conceivably be represented by either of two structures I or II, then ψ_{I} or ψ_{II} would be the respective wave functions for the two unperturbed states, each corresponding to a standing wave. Now if there may be an interaction (coupling) between these two waves their mutual perturbation replaces them by new standing waves. The wave function of one of these may be represented as $\psi_{\mathrm{I}} + \psi_{\mathrm{II}}$, which, as we saw above, corresponds with a decreased frequency relative to the unperturbed states and hence a decreased energy (since $E = h\nu$). This means greater stability. Since all mobile systems spontaneously move into states of lower energy content, this state must be the state which actually obtains, corresponding to an equilibrium condition. If the interaction in question involves an electron pair between two nuclei, this state corresponds to covalence formation, i.e., there *is* interaction and there *is* stability. On the other hand the standing wave corresponding to $\psi_{\mathrm{I}} - \psi_{\mathrm{II}}$ has an increased frequency and greater energy; hence it corresponds to no stable state and represents a condition under which the two atoms would separate. It does not figure in the characterization of the covalent state.

The most important consequence of the above argument is that when coupling can occur the energy of the resultant state is reduced by perturbation or resonance, with the result that the resonating structure is more stable than either of the unperturbed structures whose interaction was considered to give rise to the resonating state. The mesomeric state is such a state.*

The term "resonance energy" is used to indicate the difference in energy which exists between the system in its most probable state and in its most stable unperturbed structure. It thus indicates the amount of extra stability that can be conferred on its most stable unperturbed structure by resonance.

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* The word "mesomeric" means "between the parts." Since the energy of the mesomeric structure is not between that of the two unperturbed structures, but lower than either, Pauling thinks the term an unfortunate one. It should be pointed out, however, that the word was coined to describe the actual state of the system in terms of a geometrical picture, not in terms of the energy picture used in quantum mechanics. Nevertheless, it is important to keep the distinction in mind.

In general we may represent the wave function of a system by the equation[5]

$$\psi = a\psi_{\mathrm{I}} + b\psi_{\mathrm{II}} \tag{1}$$

in which a and b are arbitrary numerical coefficients, the squares of which determine the extent to which each constituent structure contributes to the average structure represented by ψ. A value of b/a may now be found which gives a minimum value to the total energy of the system. The corresponding wave function is then the best approximation to that for the normal state which can be found by the assumption of the particular states I and II, which were arbitrarily chosen at the outset. If the value of b/a thus found is small it shows that structure II contributes but little to the average state, i.e., structure II is an improbable structure. If the value of b/a is close to unity it shows that each structure makes about the same contribution to the normal state of the system. We say then that the system resonates between structures I and II.* When $b/a = 1$ the resonance energy reaches a maximum. Hence the *greatest resonance stabilization occurs when the two unperturbed forms are identical.*

A study of the quantum-mechanical viewpoint makes it clear that resonance is a much more general phenomenon than one would expect from a study of the English concept of mesomerism. Thus we find resonance in saturated molecules such as hydrogen; in fact we find it in all covalent bonds and even in one-electron bonds such as the one which must exist in the hydrogen molecule-ion, H_2^+.

For purposes of quantum-mechanical calculation the hydrogen molecule-ion may be considered to be formed from a proton and a hydrogen atom. If these two particles approach each other without alteration of structure the calculated interaction energy, when plotted against the distance between them (r_{ab}), gives the dotted line curve shown in Figure 1, from which it is apparent that the two particles would repel one another. But if it is considered that resonance occurs between the two forms:

$$\underset{\text{(I)}}{H_A{}^+\cdot H_B} \qquad \text{and} \qquad \underset{\text{(II)}}{H_A\cdot H_B{}^+}$$

(in which the subscripts are used to tag two individual but identical protons) the lower curve of Figure 1 is obtained. Since the two forms are completely equivalent, each would contribute equally to the normal structure, and resonance would be at a maximum. In this lower curve we observe a minimum, which means that the two particles would

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[5] Ref. 3, Eq. 3-1.

* Of course we need not limit ourselves to two contributing structures—any number may be chosen.

attract each other until the distance between them became equal to the value of r_{ab} at the minimum of the curve. Thus we see that the stability of this system is due to the existence of resonance energy.*

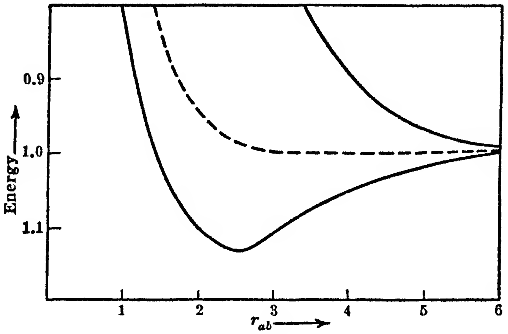

FIG. 1. Energy of interaction of a hydrogen atom and a proton. (Reproduced from *The Nature of the Chemical Bond* by Linus Pauling, Cornell University Press (1939), p. 15.)

The one-electron bond is very rare, and quantum-mechanical considerations make it seem highly unlikely that such a bond could be formed between atoms which are not practically identical in electronegativity.

Partial Ionic Character

The quantum-mechanical treatment of the hydrogen molecule is similar to that just given for the hydrogen molecule-ion. Here, however, four unperturbed forms may contribute to the total energy of the system:

$$\underset{\text{(I)}}{H_A\cdot^1 \quad ^2\cdot H_B} \qquad\qquad \underset{\text{(II)}}{H_A\cdot^2 \quad ^1\cdot H_B}$$

$$\underset{\text{(III)}}{H_A\overset{-}{:} \quad \overset{+}{H}_B} \qquad\qquad \underset{\text{(IV)}}{\overset{+}{H}_A \quad \overset{-}{:}H_B}$$

The total energy of the bond is found to be made up as follows:[6]

I and II	80%
III and IV	5%
Deformation	15%

The two electrons are considered to have opposite spins (this is indicated in structures I and II by the small arabic numerals). These spins have associated with them magnetic fields and hence when two electrons of opposite spin come together there is a mutual neutralization of mag-

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* Refinements in the calculation may be made by including a consideration of deformation (polarization).

[6] Ref. 3, pp. 23, 24.

netic properties and the pair forms a stable unit. The electrons are then said to be "paired" regardless of whether they are shared. Thus covalent bonds in general are formed by the pairing of electrons and owe their stability largely to resonance of the type illustrated in hydrogen by I → II. However, there is always present an additional amount of resonance energy due to resonance involving the ions. The extent to which this contributes to the total bond energy depends upon the difference in electronegativity between the two atoms joined and is at a minimum when this difference is zero, as it is in the hydrogen molecule. In cases where the two atoms have widely different electronegativities, as in HCl, the contribution made by the more probable ionic structure H^+Cl^- (H^-Cl^+ contributes negligibly) becomes very considerable and the bond is said to have a large amount of "ionic character." This is equivalent to the older expressions "polar character" or "polarity" but carries with it the additional implication of quantum-mechanical resonance between the covalent and ionic extremes.

Pauling[7] warns us that we must not confuse the amount of ionic character of a bond with its tendency to ionize in a polar solvent, although there is a certain parallelism between them. "The ionic character of the bond is determined by the importance of the ionic structure (A^+B^-) when the nuclei are at their equilibrium distance . . . whereas the tendency to ionize in solution is determined by the relative stability of the actual molecules in the solution and the separated ions in the solution." Thus H and I have about equal electronegativities and hence HI has very little ionic character. But HI ionizes completely in water, whereas the largely ionic HF is only partially ionized.[8]

Accurate quantitative calculations of the amount of ionic character of a bond can only be made by the methods of quantum mechanics. However, Pauling[9] indicates a simple method of approximating the figure when internuclear distances (R_0) and dipole moments (μ) are known. For HCl the calculation is as follows.

R_0 = 1.28 A°.

e = charge on the electron.

$eR_0 = 6.07 \times 10^{-18}$ e.s.u. = dipole moment if the structure corresponded to the extreme ionic type.

$\mu = 1.03 \times 10^{-18}$ e.s.u. = actual dipole moment.

$\frac{\mu}{eR_0} = 0.170$ = amount of ionic character (i.e., 17%).

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[7] Ref. 3, p. 36.

[8] Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

[9] Ref. 3, p. 46.

Bond Energies

The term "bond energy" is defined as the energy which must be absorbed to break a bond of a gaseous molecule with the production of neutral gaseous atoms or radicals.[10] The less the total energy of a diatomic molecule, for example, the greater the amount of energy it must absorb to rupture the bond. Thus a low value of the total energy corresponds to a high value of bond energy (D).

A method of estimating bond energies from thermal data was first devised by Fajans [11] and soon thereafter developed by others.[12] More recently Pauling [13] has calculated the strengths of a number of bonds in organic molecules. The following example will serve to illustrate the method.

$$\begin{array}{rcl@{\qquad}rcl}
H_2 + \tfrac{1}{2}O_2 & \rightarrow & H_2O\ (g) & \Delta H & = & -57.8\ \text{kcal} \\
2H & \rightarrow & H_2 & \Delta H & = & -103.4 \\
O & \rightarrow & \tfrac{1}{2}O_2 & \Delta H & = & -59.1 \\
\hline
2H + O & \rightarrow & H_2O\ (g) & \Delta H & = & -220.3\ \text{kcal}
\end{array}$$

Thus 220.3 kcal of heat is evolved when two O—H bonds are formed. It is, of course, highly unlikely that in this or in other similar cases the energy of forming the first bond is the same as that involved in forming the second, etc. In fact it has been pointed out by Mecke [14] and later by Norrish [15] that the successive formation of the four C—H bonds in methane may involve widely different amounts of energy. However, precise information on this point is lacking in general, and by almost universal accord the difficulty has been avoided by ignoring it. Thus the O—H bond energy is taken as one-half of 220.3 kcal and the C—H bond energy as one-quarter of the energy liberated in the reaction: $C(g) + 4H\ (g) \rightarrow CH_4\ (g)$.

A summary of bond energies, obtained in this way by Pauling, is given in Table I.

A bond between two identical atoms may be considered to be a normal covalent bond.[8] The wave function for the bond is

$$\psi = a\psi_{A:A} + b\psi_{A^+A^-} + b\psi_{A^-A^+} \tag{2}$$

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[10] H. J. Lucas, *Organic Chemistry*, American Book Co., p. 25.

[11] Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922).

[12] (*a*) Weinberg, *ibid.*, **53**, 1347, 1353, 1519 (1920); (*b*) W. Huckel, *ibid.*, **55**, 2839 (1922); (*c*) Thiel, *ibid.*, **55**, 2844 (1922).

[13] Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

[14] Mecke, *Z. physik. Chem.*, **B7**, 108 (1930).

[15] Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).

When two different atoms of equal electronegativity are joined, the same kind of an equation can be applied. If one atom is more electronegative than the other, the wave function can be formed by adding to the normal covalent bond wave function an additional ionic term. This corresponds to the addition of ionic resonance energy to the normal covalent bond, making it more stable. The term "ionic resonance energy" refers to this additional ionic resonance energy and not to the total ionic resonance energy; i.e., it is the amount of ionic resonance energy in excess of that which would be calculated from Equation 2. Likewise the term "ionic character of the bond" refers to the additional ionic character.

There is considerable evidence from the field of quantum mechanics which shows that the energy of a bond between two given atoms is not much affected by other atoms in the molecule.[16] If this is so, it should follow that the energy of a normal covalent bond A—B is the arithmetic mean of the two bond energy values for A—A and B—B. This relationship is known as the "postulate of the additivity of normal covalent bonds."

Now, as was pointed out above, the actual bond A—B is either a normal covalent bond or it has additional ionic resonance energy. Hence, if the postulate is true, the actual bond energy D(A—B) would always be equal to or greater than the energy of the normal covalent bond A—B calculated according to the additivity rule; i.e., the difference

$$\Delta = D(\mathrm{A{-}B}) - \tfrac{1}{2}\{D(\mathrm{A{-}A}) + D(\mathrm{B{-}B})\} \geqq 0 \qquad (3)$$

It is obvious that Δ of Equation 3 is equal to $-\Delta H$ for the reaction

$$\tfrac{1}{2}\mathrm{A_2}\ (\mathrm{g}) + \tfrac{1}{2}\mathrm{B_2}\ (\mathrm{g}) \rightarrow \mathrm{AB}\ (\mathrm{g}) \qquad (4)$$

and hence the truth of Equation 3 can be easily checked by reference to thermal data. Such a comparison [17] shows Δ to be usually positive and to have larger values as the difference in electronegativities of A and B become greater. This twofold check makes it seem that the postulate is a good approximation. Somewhat better agreement can be gained if the geometric mean is used instead of the arithmetic mean, but in general the gain is hardly worth the increased difficulty of the calculation.[18]

By thermochemical or spectroscopic methods it is possible to determine the heat of dissociation of diatomic molecules into neutral atoms. By definition these heats of dissociation are the respective bond energies.

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[16] (*a*) Pauling, *J. Am. Chem. Soc.*, **53,** 1367, 3225 (1931); **54,** 988 (1932); (*b*) Slater, *Phys. Rev.*, **37,** 481 (1931); **38,** 1109 (1931); (*c*) Hund, *Z. Physik*, **73,** 1, 565 (1932); cf. Ref. 8.

[17] Pauling and Yost, *Proc. Nat. Acad. Sci.*, **18,** 414 (1932).

[18] Ref. 3, p. 50.

In more complicated molecules (e.g., H_2O or NH_3) Pauling takes the bond energy to mean the average of the sum of the energies of all the individual bonds.

In Table I are recorded a few bond energy values.[19]

TABLE I

BOND ENERGY VALUES (kcal/mole)

H—H	103.4	P—H	63.0	C—Br	54.0	
C—C	58.6	O—H	110.2	C—I	45.5	
N—N	23.6	S—H	87.5	C=C	100	
P—P	18.9	H—F	147.5	C≡C	123	
O—O	34.9	H—Cl	102.7	C=O	142	(formaldehyde)
S—S	63.8	H—Br	87.3	C=O	149	(other aldehydes)
F—F	63.5	H—I	71.4	C=O	152	(ketones)
Cl—Cl	57.8	C—N	48.6	C=N	94	
Br—Br	46.1	C—O	70.0	C≡N	144	(HCN)
I—I	36.2	C—S	54.5	C≡N	150	(other cyanides)
C—H	87.3	C—F	107.0	C=S	103	
N—H	83.7	C—Cl	66.5			

These bond energies should only be used where the atoms concerned exhibit their normal covalences. With this understanding, heats of formation may be calculated from the bond energies and the data in Table II. Pauling claims that usually the values thus calculated agree with experimental values to within a few kcal per mole. An impressive example is found in $CH_2F \cdot CH_2OH$, where the calculated and experimental values agree to better than 0.1 kcal/mole, despite the fact that we might expect here, if ever, to find bond energies altered by the inductive effect.

TABLE II *

HEATS OF FORMATION OF ELEMENTS IN THEIR STANDARD STATES FROM MONATOMIC GASES (kcal/mole)

H	51.7	P	31.6	F	31.8
C	124.1 (graphite)	O	59.1	Cl	28.9
	124.3 (diamond)	S	66.3	Br	26.9
N	85.1			I	25.6

In order to illustrate the method of calculating the heat of formation of a compound, I have chosen at random trimethyl amine.

$$3C(g) + 9H(g) + N(g) \rightarrow Me_3N(g) \qquad (5)$$

$$3C(\beta \text{ graph.}) + 4\tfrac{1}{2}H_2(g) + \tfrac{1}{2}N_2(g) \rightarrow 3C(g) + 9H(g) + N(g) \qquad (6)$$

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[19] Ref. 3, pp. 53, 123.

* From *The Nature of the Chemical Bond,* by Linus Pauling, Cornell Univ. Press.

Addition of Equations 5 and 6 gives:

$$3C(\beta \text{ graph.}) + 4\tfrac{1}{2}H_2(g) + \tfrac{1}{2}N_2(g) \rightarrow Me_3N(g) \tag{7}$$

$$\Delta H_7 = \Delta H_5 + \Delta H_6 \tag{8}$$

To calculate ΔH_5, use bond energy values from Table I as follows:

$$\begin{aligned} 9\ \text{C—H bonds};\ \Delta H &= 9(-87.3) = -785.7 \text{ kcal} \\ 3\ \text{C—N bonds};\ \Delta H &= 3(-48.6) = \underline{-145.8} \\ \Delta H_5 &= -931.5 \text{ kcal} \end{aligned}$$

To calculate ΔH_6, use the values in Table II as follows:

$$\begin{aligned} 3C(\beta \text{ graph.}) \rightarrow 3C(g);\quad \Delta H &= 3(124.1) = 372.3 \text{ kcal} \\ 4\tfrac{1}{2}H_2(g) \rightarrow 9H(g);\quad \Delta H &= 9(51.7) = 465.3 \\ \tfrac{1}{2}N_2(g) \rightarrow N(g);\quad \Delta H &= \underline{85.1} \\ \Delta H_6 &= 922.7 \text{ kcal} \end{aligned}$$

The values of ΔH_5 and ΔH_6 may now be substituted into Equation 8:

$$\Delta H_7 = -931.5 + 922.7 = -8.8 \text{ kcal}$$

The experimentally determined value[20] of ΔH_7 is -26 kj or -6.2 kcal. Owing to the small value of ΔH_7 the percentage error is high but the absolute error of 2.6 kcal/mole is not excessive.

While it may be true that bond energies are independent of substituents within the limit of error of ordinary calorimetric data, it has been clearly demonstrated by Kistiakowsky and his collaborators that highly accurate thermal data show definite and orderly trends as the result of substitution.[21] Figure 2 shows graphically their results for the heats of hydrogenation and bromination of ethylene and its homologs. Since, for example, the

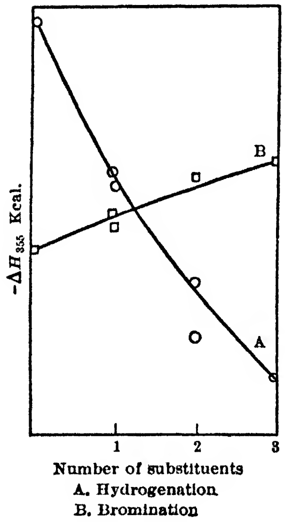

FIG. 2.[21e] Heats of hydrogenation and bromination of ethylene and its homologs.

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[20] *International Critical Tables*, **5**, 182.

[21] (*a*) Kistiakowsky, Romeyn, Ruhoff, H. A. Smith, and Vaughan, *J. Am. Chem. Soc.*, **57**, 65 (1935); (*b*) Kistiakowsky, Ruhoff, Smith, and Vaughan, *ibid.*, **57**, 876 (1935); **58**, 137, 146 (1936); (*c*) Dolliver, Gresham, Kistiakowsky, and Vaughan, *ibid.*, **59**, 831 (1937); (*d*) Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan, *ibid.*, **60**, 440 (1938); (*e*) Conn, Kistiakowsky, and Smith, *ibid.*, 2764 (1938); **61**, 216, 1868 (1939).

heat of bromination is twice the C—Br bond energy minus that for Br—Br and that for one bond of C═C, it is evident that the heat of bromination would be constant for members of this homologous series if the bond energies were constant. It will be observed, however, that the effect of substituting methyl groups is appreciable although not large, three of them changing the heat of bromination by only about 1.3 kcal. Other substituents with electronegativities more different from that of hydrogen would, of course, be expected to exert a greater effect. The effect is greater in hydrogenation, where three methyl groups change the ΔH by about 6 kcal/mole. In any case, the influence is not transmitted far. Kistiakowsky et al. conclude from their experience that a methyl group has a significant effect only on bonds attached to the same carbon atom which holds the methyl group.

The Electronegativity Scale

The terms electronegativity, electron affinity, and electron attraction have been used in the past by some writers as synonymous. Various methods have been proposed for their common measurement. Among them ionization potentials seemed one of the most hopeful. Measurements by the various methods proposed lacked concordance, however, owing to the fact that the thing they were trying to measure had never been accurately defined. This difficulty has been partially remedied. It is now customary to use the following definitions:

The ionization potential [22, 23] (I_A) is the potential concerned in the reaction: $A \longrightarrow A^+ + e$.

The electron affinity (E_A) is measured by the energy of the reaction: $A + e \longrightarrow A^-$.

The electronegativity is taken to mean the attraction of a neutral atom in a stable molecule for electrons. The concept is probably incapable of exact definition. We have already seen that differences in what we believe to be electronegativity of atoms make it necessary to add another term to Equation 2. This confers an additional amount of resonance energy, Δ, on the system, and the value of Δ increases as the electronegativity difference increases. This suggests at once that we should seek in the values of Δ a measure of relative electronegativities.

Now if we are to assign to each atom a number (x) representing its electronegativity, it would then seem desirable that these numbers satisfy the following relationship:

$$x_A - x_B = \Delta(\text{A—B})$$

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[22] Ref. 3, p. 66; also Ref. 8.

[23] Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).

It is found, however, that the values of Δ do not satisfy such an additivity relationship, but the values of $\sqrt{\Delta}$ do satisfy it approximately. Accordingly Pauling has devised a table of electronegativities on the basis of values of $\sqrt{\Delta}$, expressed in electron volts and containing a convenient additive constant. These values are given in Table III, from which it is apparent that they are in keeping with the trend of electronegativities which we would expect from the positions of the atoms in the periodic table.

TABLE III

PAULING'S ELECTRONEGATIVITY VALUES *

H	2.1						
C	2.5	Si	1.8				
N	3.0	P	2.1	As	2.0		
O	3.5	S	2.5	Se	2.4		
F	4.0	Cl	3.0	Br	2.8	I	2.5

The electronegativity scale is meant to be used only in cases of neutral molecules with electron-pair bonds which are not too strongly polar.[23] Mulliken [23] has shown from quantum-mechanical considerations that the average of the ionization potential and electron affinity gives us a measure of electronegativity and on this basis he defines the "absolute electronegativity."

Resonance between Several Valence Bond Structures

In addition to the type of resonance existing in single bonds quantum mechanics has adduced evidence that a second type of resonance is possible in conjugated structures. This is the type to which Ingold gave the name "mesomerism." In choosing the various unperturbed forms which might contribute to a state of resonance in such a molecule, quantum mechanics has not improved much on the method used by the English chemists for deducing possible electromeric shifts in the days before mesomerism had been thought of. The best that can be done at present is to consider that all the "reasonable" structures which we can write for a given molecule contribute in proportion to their stabilities. However, the following conditions for resonance are important:

(1) Each contributing form must be represented by the same geometrical arrangement of the atomic nuclei.

(2) Each form must have the same number of unpaired electrons.

(3) An appreciable contribution to the resonance will be made only by those forms having about the same amount of energy.

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* From *The Nature of the Chemical Bond*, by Linus Pauling, Cornell Univ. Press.

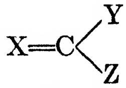
(4) With atoms arranged in a ring, only those valence bond structures for which the bonds do not cross need be considered as contributing to the resonance; all others can be represented as resonance combinations of these.

(5) Unperturbed structures in which adjacent atoms have electrical charges of the same sign are much less important than other structures. (This is the "adjacent charge rule.") [24]

Judging the relative stabilities of the different possible contributing forms is an important and complex problem. The stabilities may be calculated from data on resonance energies, interatomic distances, force constants of bonds, bond angles, dipole moments, etc. When such data or the knowledge of handling them are lacking, more simple considerations sometimes help. For example, we have the following two contributing factors. Other things being equal, the most stable form will (1) have the greatest number of covalent bonds and (2) will have a formal negative charge on the atom of highest electronegativity. These two factors frequently work against each other. Thus in ketones the form $R_2C{=}O$ satisfies the first requirement, whereas $R_2C^+{-}O^-$ satisfies the second. Thus it is not surprising to find that each form of acetone is about equally probable. This can be shown to be roughly true by a simple calculation.[25] For the first structure we would expect a very small dipole moment; for the second, the dipole moment can be calculated by multiplying the electronic charge by the C—O internuclear distance, 1.24 A°. It is thus calculated to be 5.95×10^{-18} e.s.u. The observed moment, 2.8×10^{-18}, shows that the bond has about 47 per cent ionic character.

In general the application of the principle of resonance to organic molecules containing multiple bonds is identical with the application of mesomerism as discussed in the last chapter, and hence such applications need not be discussed again. However, there are certain ways in which the quantum-mechanical treatment has extended the subject, and it is mainly to these that the rest of this chapter will be devoted.

Resonance and Coplanarity [26]

In molecules of the type  $X{=}C\langle^{Y}_{Z}$ all four atoms should lie in a plane unless extraordinary distorting forces are in operation. Determinations of molecular geometry by X-ray and electron diffraction methods

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[24] Pauling and Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

[25] Ref. 3, p. 75.

[26] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

in particular have established the validity of this point of view. For example, $COCl_2$ and $CSCl_2$ have been shown to have planar structures.[27]

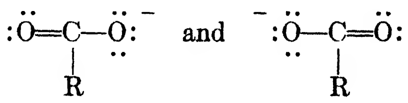
If, then, coplanarity is demanded for a doubly bound carbon atom and the three atoms attached to it, it seems reasonable to suppose that, if resonance imposes partial double bond character on a given linkage, coplanarity should similarly be demanded for the atoms bound by this link and the other atoms attached directly to them. This situation would be expected in the extreme position of resonance where 100 per cent double-bond character has been achieved and should be maintained during resonance since the electronic resonance frequency is so great that the heavy atoms would not have time to get out of planar alignment during an electronic cycle. Experimental results bear out this contention also. Thus, although cyclohexane has a puckered ring in order to maintain the tetrahedral single-bond angles, the resonating benzene molecule has a planar structure.

The Strength of Acids and Bases

Effect of Resonance. The influence of substituents on the strengths of acids and bases is a topic whose history we have already traced at some length. It will be recalled that Lewis attributed the influence to the I_s effect alone and that Lucas based his electronegativity series on the ionization constants of *para*-substituted benzoic acids. This was a most unfortunate choice, since resonance effects may enter which far outweigh the possible field effect which he was trying to avoid.

The inadequacy of the Lewis theory of acid strength must have been evident to organic chemists as soon as it was published, for it had been pointed out years before by Vorländer[28] that the carboxyl group owes its acid character not to either the carbonyl or hydroxyl groups separately but to their combined influence. There was nothing in the Lewis theory to make clear the nature of this interaction.

The extension of the electronic theory to furnish an adequate explanation of this interaction was made possible by quantum mechanics. Pauling[29] treats the problem as follows: The carboxylate ion can resonate between the two equivalent structures



$$:\ddot{\text{O}}{=}\underset{\substack{|\\ \text{R}}}{\text{C}}{-}\underset{..}{\ddot{\text{O}}}:^{-} \quad \text{and} \quad {}^{-}:\underset{..}{\ddot{\text{O}}}{-}\underset{\substack{|\\ \text{R}}}{\text{C}}{=}\ddot{\text{O}}:$$

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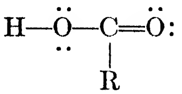
[27] Brockway, Beach, and Pauling, *J. Am. Chem. Soc.*, **57**, 2693 (1935).

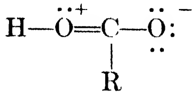
[28] Vorländer, *Abhandl. der naturforschen Gesellschaft zu Halle*, **21**, 235 (1899); *Ber.*, **34**, 1632, 1637 (1901); *Ann.*, **320**, 66, 99 (1901).

[29] Pauling in Gilman's *Organic Chemistry*, John Wiley & Sons, 1938, p. 1871.

Hence the stability of the ion is great. The corresponding ionogen, however, cannot produce two equivalent structures, although it resonates somewhat between the following:



and

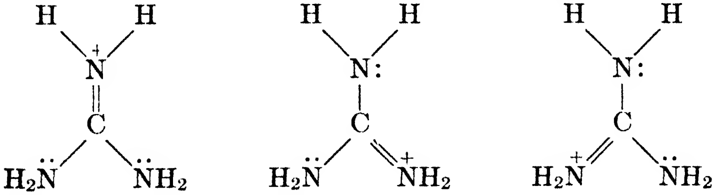


Owing to the lack of symmetry, however, the stabilization by resonance is less here than that observed in the ion. Thus the ion is stabilized more than the ionogen and this explains why a carboxylic acid is so much more acidic than an alcohol.

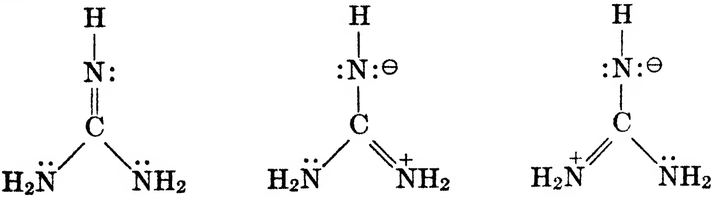
An alternative point of view is provided by a consideration of the last structure pictured above, where it would be predicted that the positive charge placed on the hydroxyl group by resonance would repel the proton.

An example of the application of this point of view is found in a paper by Branch, Yabroff, and Bettman.[30] They point out that the resonance of a system like $PhNO_2$, which contains a group having a $-M$ effect, is much enhanced by the introduction of a group having a $+M$ effect, like OH. Thus in *p*-nitrophenol the quinoidal form  contributes considerably to the structure of the molecule and enhances the ionization by placing a positive charge on the oxygen atom. *p*-Nitrophenol is about ten times as strong an acid as its *meta*-isomer.

Guanidine is ideally suited to illustrate the application of the resonance principle to the explanation of base strength. The guanidinium ion can resonate between three equivalent structures:[29]



The triple equivalence gives the ion very high stability. On the other hand, guanidine itself resonates between three structures that are not equivalent:



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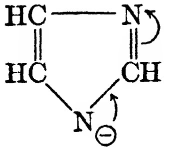
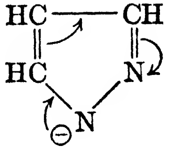
[30] Branch, Yabroff, and Bettman, *J. Am. Chem. Soc.*, **56**, 939 (1934).

Thus here again the ion is the more stabilized by resonance and this contributes to greater base strength.

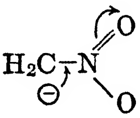
The way in which quantum mechanics has introduced considerations of molecular symmetry into our theorizing is particularly to be noted. The very wide application of this symmetry principle will become evident as we proceed.

A number of acidic substances seem to owe their acid properties to stabilization of the anion by resonance. Thus pyrazole and imidazole, which readily form metallic salts, should allow more complete resonance in their anions, owing to increased symmetry.

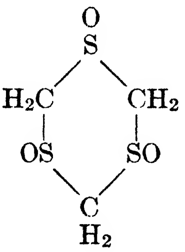




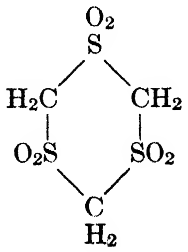
The anion of nitromethane is also stabilized by resonance, which accounts for its acidic nature.



However, it is difficult to see how resonance can similarly be a factor in the ionization of halogen hydrides, of sulfonic acids, or of substances like trimethylene sulfoxide (I) and trimethylene sulfone (II).



(I)



(II)

The sulfoxide dissolves in aqueous alkali, whereas the sulfone will even dissolve in sodium carbonate solution. The relative acidic strengths of these two seem to depend entirely on the inductive effect. We must conclude, therefore, that although resonance of the mesomeric type may be an important factor in acidic ionization, it is not a necessary one.

With the views of Pauling and the English school in mind, let us turn to a consideration of the general problem of the effects of substituents on the strengths of acids and bases in aqueous solutions.* A review of this subject has been given recently by Dippy.[31] In Table IV will be found his values for a number of thermodynamic dissociation constants.[32]

TABLE IV

THERMODYNAMIC DISSOCIATION CONSTANTS FOR SUBSTITUTED BENZOIC ACIDS AT 25°

Position of substitution	$10^5 K_{th}$					
	CH_3	C_2H_5	*iso*-Pr	*tert.*-Bu	OH	OMe
o	12.3				105 (107)	8.06 (8.2)
m	5.35				8.3 (8.71)	8.17 (9.0)
p	4.24	4.43	4.43	3.98	2.9 (3.31)	3.38 (3.6)

	F	Cl	Br	I	NO_2	H
o	54.1	114 (119.7)	140	137	671	6.27–6.52
m	13.6	14.8 (15.06)	15.4	14.1	32.1	
p	7.22	10.5 (10.4)	10.7		37.6	

Influence of Alkyl Groups. In general the substitution of alkyl groups decreases acid strength. Since the negligible dipole moments of paraffins seem to indicate that CH_3 and H are equally electronegative, it has become common to consider that negative groups in the molecule stimulate electron release in the alkyl groups, giving them a $+I$ influence. It is interesting to note, therefore, that substitution of the methyl group in various aromatic acids shows its power of electron release to be greater in the *ortho* and *para* positions than in the *meta*. This suggests that the methyl group is in some way associated with a $+T$ effect.

The following order is usually assigned to the $+I$ effects of alkyl groups: $Bu^{\gamma} > Pr^{\beta} > Et > Me$. This is essentially the order indicated by their substitution into the *para* position of phenyl acetic acid (Table V, K_u = ionization constant of unsubstituted acid). But it is to be noted that the order is very different in the *p*-alkyl benzoic acids.

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* The extension of the problem to nonaqueous solutions will be discussed in Chapter X.

[31] Dippy, *Chem. Rev.*, **25**, 151 (1939).

[32] (*a*) Dippy and Williams, *J. Chem. Soc.*, 1888 (1934); (*b*) Dippy, Williams, and R. H. Lewis, *ibid.*, 343 (1935); (*c*) Dippy and Lewis, *ibid.*, 645 (1936).

TABLE V[32]

Acid	K/K_u			
	Me	Et	*iso*-Pr	*tert.*-Bu
p-Alkylbenzoic acid	0.68	0.71	0.71	0.63
p-alkylphenylacetic acid	0.87	0.87	0.83	0.78

An explanation of this anomaly is possible on the basis of a resonance effect suggested by Baker and Nathan.[33] They made the suggestion as a means of explaining the interaction of pyridine with alkyl substituted benzyl bromides in dry acetone.[34] They observed (1) that all alkyl groups increased the reaction velocity, thus demonstrating that electron release facilitated the reaction; and (2) that with a single *p*-alkyl substituent, the velocity decreased in the order Me > Et > Pr^β > Bu^γ, which suggests that the powers of electron release of these groups are in the reverse order to that generally accepted. Their explanation is as follows. When a methyl group is attached to a conjugated system, the following type of resonance may occur: $H{-}\overset{\curvearrowright}{C}{-}C{=}\overset{\curvearrowright}{C}{-}C{=}\overset{\curvearrowright}{C}{-}$. Thus the following unperturbed forms would be involved: $H{-}C{-}C{=}C{-}C{=}C{-}$ and $H^+\ C{=}C{-}C{=}C{-}C^-{-}$. Such resonance is sufficiently like the resonance observed in hydrogen molecules to appear reasonable. Now if it is conceded that such resonance could not involve a C—C bond it follows that each substitution of a methyl hydrogen atom decreases the possible number of unperturbed forms by one, thus decreasing the amount of resonance. Accordingly the *tert.*-butyl group would have no $+T$ effect.

It is apparent that if alkyl groups exert $+I$ effects in the order Bu^γ > Pr^β > Et > Me and $+T$ effects in the opposite order, then, depending on the quantitative relationships of the two effects, almost any order of influence might be observed. Thus different orders were found for the alkyls in the reaction of benzyl bromides with pyridine, the ionization of substituted benzoic acids, and the ionization of *para*-substituted acetic acids. In the last-named case the order is that of the $+I$ effects, since the absence of a suitably conjugated system would preclude the operation of a $+T$ effect.

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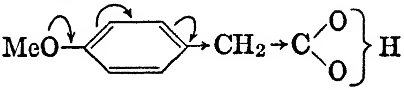
[33] (*a*) J. W. Baker and Nathan, *J. Chem. Soc.*, 1844 (1935); (*b*) J. W. Baker, *ibid.*, 1150 (1939).

[34] Baker and Nathan, *ibid.*, 1840 (1935).

Baker points out that the observations of LeFevre on the nitration, sulfonation, and halogenation of *p*-cymene,[35] showing the methyl group to be more strongly *ortho*-directive than the isopropyl group, find a ready explanation in terms of the Baker-Nathan effect without resorting to the steric hindrance theory of LeFevre, although steric hindrance may well be a factor.

Influence of Hydroxyl and Alkoxyl Groups. These groups strengthen acetic acid; they weaken benzoic acid in the *para* position and strengthen it in the *meta* (Table IV). These effects are obviously due to the fact that only the $-I$ effects may operate in acetic or *meta*-substituted benzoic acids, while in *para*-substituted benzoic acids the stronger $+M$ effects predominate.

It is interesting that *p*-methoxy-β-phenylpropionic acid is weaker than β-phenylpropionic acid itself, whereas the *m*-methoxy acid is stronger. The explanation given[36] is that "the electromeric displacements initiated by methoxyl proceed to the *p*- (or *o*-) carbon atom, whence the influence of the resulting negative charge is propagated inductively to the carboxyl."



Influence of Nitro Group. This group falls in the $-I, -T$ category and hence always increases the strengths of acids. Since the $-M$ effect does not operate to the *meta* position, *p*-nitrobenzoic acids are stronger than the *m*-isomers.

It is an interesting fact that the difference between *meta*- and *para*-nitro substituted acids is greater in the phenyl acetic and β-phenylpropionic acid series than in the benzoic acid series. Dippy and Lewis[37] explain this unexpected result by stating that in the *para* series the hydrogen ion arises to some extent from the methylene group, making a mesomeric displacement possible. In support of this idea they point out that the methylene group in phenylacetic acid is highly reactive and that salts of the postulated formula $Et \cdot O \cdot CO \cdot CH{=}C_6H_4{=}NOOM$ have been isolated.[38] The fact that in the above cases *ortho* substitution does not result in so large an increase in acid strength is explained by Dippy and Lewis[39] as being due to chelation of the methylene and nitro groups, which they claim would oppose the ionization of the former.

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[35] See p. 102.

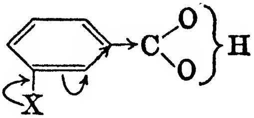
[36] (*a*) Dippy and Page, *J. Chem. Soc.*, 357 (1938); (*b*) Dippy, Watson, Williams, *ibid.*, 346 (1935); cf. Ref. 31.

[37] Dippy and Lewis, *ibid.*, 644 (1936).

[38] Opolski and Zwislocki, *Ber.*, **49**, 1606 (1916).

[39] Dippy and Lewis, *J. Chem. Soc.*, 1426 (1937); 357 (1938).

Influence of Halogens. Most of the data on the strengths of halogen acids are readily explained by assuming a $-I$ effect decreasing from F to I and a $+T$ effect decreasing in the same order. In certain cases, however, it has been necessary to assume that a halogen atom in the *meta* position can stimulate a mesomeric displacement, the effect of which is relayed by an inductive mechanism, thus:[37]



Aromatic Character

There is no agreement on the definition of aromatic character (or aromaticity). It is associated vaguely in the minds of chemists with the peculiarly unreactive double bonds supposed to be in benzene and certain other cyclic compounds and with their susceptibility to certain types of substitution reactions such as nitration, sulfonation, the Friedel-Crafts reaction, and mercuration. Thus Gilman[40] maintains that furan is a superaromatic compound because it undergoes nuclear substitution much more readily than benzene. On the same basis he classifies aniline as more aromatic and nitrobenzene as less aromatic than benzene.[41] He also observed what at first he took to be a parallelism between the degree of aromaticity and ease of cleavage of organic radicals attached to lead or mercury when treated in benzene solution with dry hydrogen chloride. For example,

$$Ph_2Pb(C_4H_3O)_2 + 2HCl \rightarrow Ph_2PbCl_2 + 2C_4H_4O$$

This shows the furyl radical to be more electronegative in the Kharasch sense[42] (since on cleavage it retains the binding electron pair) and together with other similar experiments suggests that the order of relative "electronegativities" thus determined is also the relative order of aromaticities. However, when he later discovered that such radicals as allyl and styryl are more "electronegative" than phenyl, he admitted the inadequacy of the supposed parallelism.[43] Nevertheless, he apparently still prefers to define aromaticity in terms of the relative speeds of nuclear substitution reactions.

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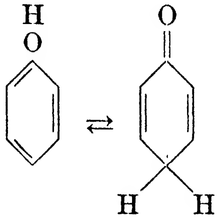
[40] Gilman and Wright, *Chem. Rev.*, **11**, 323 (1932).

[41] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

[42] Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

[43] Gilman, Towne, and H. L. Jones, *J. Am. Chem. Soc.*, **55**, 4689 (1933); cf. also Austin, *ibid.*, **53**, 3514 (1931).

Fieser,[44] on the other hand, maintains that aromaticity should be defined in terms of the thermodynamic reluctance of the double bonds to undergo addition reactions. This means that the stability of the unsaturated molecule relative to that of its addition compound is taken as the measure of aromaticity. In line with this definition it is found[45] that whereas the ΔH of hydrogenation of one double bond in various alkenes and alkadienes runs from −22 to −41 kcal, it has a positive value (5.57 kcal) in benzene. On this basis nitrobenzene would be more aromatic than benzene, since its hydride is still more unstable. Closely related to this viewpoint is the well-known stability of aromatic enols, which Fieser related to the thermodynamic instability of the dihydride structure of the keto form.



It seems probable, therefore, that a complete parallelism will be observed between the stability of the hydrides of unsaturated compounds and the stability of the enolic forms of their hydroxy derivatives. Hence either of these methods may be used to determine relative aromaticities according to Fieser's definition.

In seeking an explanation of aromatic character, chemists at one time suspected that it was in some way due to the symmetrical arrangement of conjugated linkages in a ring. An equally symmetrical arrangement would, of course, occur in cyclooctatetrene and cyclobutadiene. The latter has never been prepared but the former was presumably prepared by Willstatter,[46] who found that it has aliphatic properties. The validity of Willstatter's proof of its structure has recently been questioned,[47] however, and it is possible that future research may show that the substance he used did not have its double bonds symmetrically arranged. Be that as it may, Willstatter's contentions convinced chemists at the time that the existence of a symmetrical ring of conjugated linkages is not a sufficient condition for aromatic stability and that hence a six-membered conjugated ring must possess a stability not found in other conjugated rings.

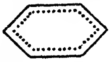
[44] Fieser, *Organic Chemistry*, edited by Gilman, John Wiley & Sons, 1938, p. 52.

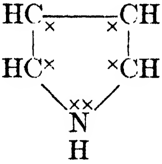
[45] Kistiakowsky, Ruhoff, and H. A. Smith, *J. Am. Chem. Soc.*, **58**, 146 (1936).

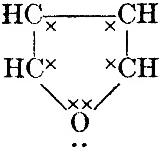
[46] Willstatter and Waser, *Ber.*, **44**, 3430 (1911).

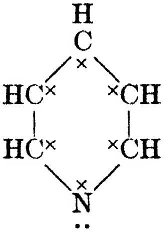
[47] Hurd and Drake, *J. Am. Chem. Soc.*, **61**, 1943 (1939).

This was not, of course, a new thought. Bamberger,[48] in the nineteenth century, had suggested that the six valences unnecessary for the formation of the benzene ring saturated each other in some mysterious fashion and that rings having more or less than six such valences could not attain the same stability. He explained the occurrence of aromatic stability in five-membered heterocyclic rings, like pyrrole, by assuming that the two latent valences which the hetero atom was capable of using in salt formation interacted with the four unused bonds of the carbon atoms to produce the valence sextet required for stability. Accordingly pyrrole would be expected to be a weak base, whereas pyridine, in which the latent valences of the nitrogen are not required for sextet formation, would be much stronger.

In this approach to the problem of aromatic character we find two important concepts, viz., the intramolecular stabilization of the extra valences and the numerical requirement of the sextet. The former has been expressed in the Armstrong-Baeyer centric formula for benzene, which suggests that the interaction takes place at the center of the ring, and in the Thiele formula, , which pictures the interaction as peripheral. The numerical requirement of the sextet, as used essentially by Bamberger in relation to pyrrole and pyridine, has found a ready interpretation in terms of the unshared electrons of the hetero atoms.[49] The application will be obvious from the following formulas, in which the crosses represent the electrons required for the "aromatic sextet."







Cyclopentadiene is not aromatic in character, nor would it be expected to be on the basis of the above theory. But it was pointed out by Goss and Ingold[50] that cyclopentadiene and the closely related indene and fluorene form a unique group of hydrocarbons inasmuch as they are capable of forming stable metallic compounds with the alkali metals.

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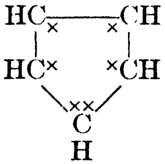
[48] Bamberger, *Ber.*, **24**, 1758 (1891); **26**, 1946 (1893); *Ann.*, **273**, 373 (1893).

[49] Kermack and Robinson, *J. Chem. Soc.*, 437 (1922); Armit and Robinson, *ibid.*, 1604 (1925).

[50] Goss and Ingold, *ibid.*, 1268 (1928).

This stability they ascribe to the presence of the aromatic sextet in the ion in which the free electron pair on the erstwhile methylene carbon atom is considered to contribute to the sextet as illustrated in the following formula.



Hückel[51] discusses the theory of the aromatic sextet in considerable detail. In relation to pyrrole, furan, etc., he points out that salt formation can only take place with the disruption of the sextet and hence the loss of aromatic character, which would in turn render the double bonds susceptible to attack by acids. The fact that diphenylene oxide and carbazole are not sensitive to acids results from the fact that the double bonds of the five-membered rings are also part of the six-membered rings and hence, even after salt formation, their electrons are members of aromatic sextets and hence stabilized. As would be expected, indole and cumaron (benzofuran) are attacked by acids.

Hückel also points out that if there are two or more hetero atoms in the ring the unshared electrons of only one of them are required for the formation of the sextet; this leaves the basic properties of the other relatively unimpaired. Thus imidazole is a stronger base than pyrrole and is more stable in the presence of acids.

One point on which these arguments are open to question is the following: since the oxygen and sulfur atoms have two unshared pairs of electrons, why cannot one pair contribute to the sextet while the other becomes involved in salt formation? The easiest guess would be that the free positive pole produced in salt formation attracts the remaining unshared electrons so strongly that they cannot contribute to the sextet formation. Some support for this idea is to be found in the fact that quaternary pyridinium salts easily yield to ring cleavage by hydrolysis.[52] Pyridine itself, however, is not subject to cleavage by acids, like furan is, despite the fact that in each a proton has become attached to the hetero atom. It seems possible that the inferior stability of furan is due to the fact that in forming the aromatic sextet its oxygen acts as a donor atom, thus leaving itself with a formal positive charge. Now when salt formation gives an additional positive charge to the oxygen atom, the total

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[51] W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, Akademische Verlagsgesellschaft, M.B.H., Leipzig, 1934, p. 386; *Z. Physik*, **70**, 204 (1931).

[52] Zincke and Krollpfeiffer, *Ann.*, **408**, 285 (1915).

charge is greater than that on the pyridinium nitrogen atom, which is not required to act as a donor atom in forming an aromatic sextet. Hence in furan, sextet formation is restrained by a larger formal charge on the hetero atom, as well as its greater electronegativity, and this substance is accordingly less stable and less aromatic than pyridine.

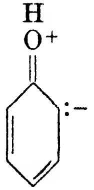
Let us now turn again to the field of quantum mechanics and survey the contributions it has made to the question of aromatic behavior.

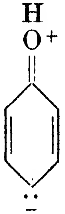
The stability of benzene is readily explained from the resonance point of view.[53] The two Kekulé structures are entirely equivalent and hence would enter into complete resonance with each other, producing a great increase in stability. This viewpoint, incidentally, favors the Thiele concept of a peripheral mechanism of double bond stabilization. Slight contributions are made by other structures. Furthermore, as Pauling points out, this resonance confers on every bond in the ring a large amount of double-bond character from the statistical viewpoint.

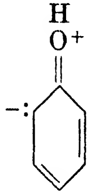
Substituted benzene derivatives, like phenol, are considered to resonate chiefly between the two Kekulé structures

and

However, the following forms also make a small but significant contribution to the normal state of the molecule:[54]







These last three structures contain the same number of double bonds as the two Kekulé forms, but since they involve an unstable separation of charge (the more electronegative oxygen is positively charged) they are less stable.

The amount of stabilization produced by resonance can be obtained by comparing the energy of formation determined by adding up bond energies (Table I) with that obtained experimentally. When the comparison is made for a molecule which does not permit of resonance the two values agree to within a few kcal/mole. When, however, the com-

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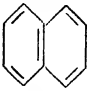
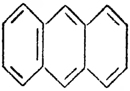
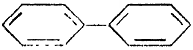
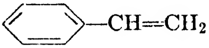
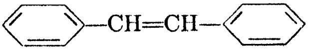
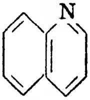
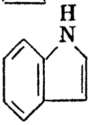
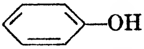
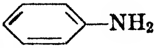
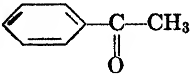
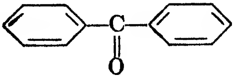
[53] J. C. Slater, *Phys. Rev.*, **37**, 489 (1931); E. Hückel, *Z. Physik*, **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932); Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[54] Wheland and Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

TABLE VI

EMPIRICAL RESONANCE ENERGY VALUES[55]

Substance	*Resonance energy* (kcal/mole)	*Reference structure*
Benzene	39	
Naphthalene	75	
Anthracene	105	
Diphenyl	*8	
Styrene	*7	
Stilbene	*15	
Pyridine	43	
Quinoline	69	
Pyrrole	31	
Indole	54	
Furan	23	
Thiophene	31	
Phenol	*7	
Aniline	*6	
Acetophenone	*7	
Benzophenone	*10	

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[55] Pauling and Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

* Resonance energy in addition to that in the benzene ring.

parison is made for a resonating molecule, it is found that the experimental value is always significantly greater. The difference is the resonance energy. In benzene the resonance energy, calculated by this method, is 1039–1000 = 39 kcal/mole. The calculated value (1000 kcal) was obtained by assuming a molecule with the Kekulé structure. Thus the resonance energy is measured relative to this particular unperturbed form.

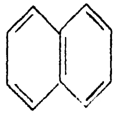
Speaking generally, it is desirable that the unperturbed form chosen as the basis of resonance energy calculations be the most stable of those forms which would be expected to contribute to the resonance.

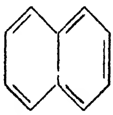
If we accept the thermodynamic definition of aromaticity, it is obvious that we have found in the resonance energy a key to the quantitative measurement of this property. A comparison of the energies of various aromatic compounds is given in Table VI.

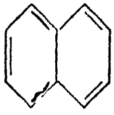
The resonance energies of monocyclic aromatic compounds are largely dissipated when the first double bond is broken and hence they measure the resistance to the first step of saturation, i.e., they measure aromaticity. However, in case there are two or more fused rings, breaking a double bond in one ring would not destroy the aromatic resonance in the others. Hence the total resonance energy is greater than the decrease in resonance energy accompanying the saturation of the first double bond, and it is therefore not a proper measure of aromaticity. However, it seems likely that a rough comparison of aromaticities of polycyclic compounds containing an equal number of aromatic rings can be made by comparing their resonance energies. In all cases an accurate measure of aromaticity should be found in the decrease in resonance energy attending the saturation of one double bond.

If one compares the resonance energy of benzene (39 kcal) with that of furan (23 kcal) it is again evident that furan is not "superaromatic" from this point of view.

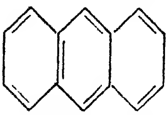
In regard to polycyclic ring systems we may again return to Pauling's concepts.[56] Naphthalene may resonate between three forms:

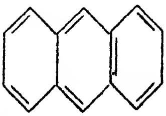


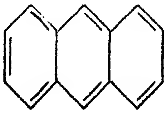


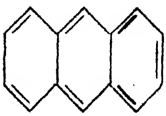


For anthracene there are four forms:









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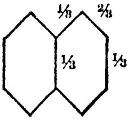
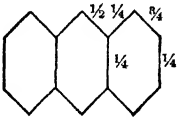
[56] Ref. 3, pp. 132–134.

Similarly five forms may be written for phenanthrene. Since for each compound all the structures written would be expected to have about the same energy and the same arrangement of atomic kernels, they should contribute about equally to the normal states of the molecules. The greater the number of forms between which resonance can occur, the greater the resonance energy should be, other things being equal. In accord with this statement we find the following resonance energies: benzene, 39; naphthalene, 75; anthracene, 105; and phenanthrene, 110 kcal/mole.

Pauling makes the further observation that each C—C union in benzene may be considered to have ½ double bond character, since in one Kekulé form it is a double bond and in the other a single bond. This obviously does not mean that the given union is a full-fledged double bond half of the time, since it remains in neither extreme position for an appreciable time. Rather it should be considered as "a bond of a new type, very much different from a double bond and with properties intermediate between those of a double bond and a single bond."

Arguing in the same fashion, Pauling deduces the following amounts of double bond character for the various bonds of naphthalene and anthracene. He warns that these numbers are not to be given any quantitative significance but are qualitatively useful inasmuch as they give a rough measure of the relative reactivity of the bonds in question.

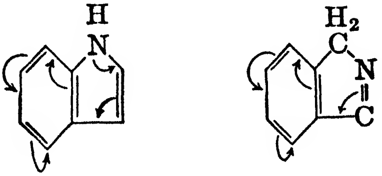




In concluding this brief review of the theory of aromaticity it may be emphasized that quantum mechanics has given us a picture of the mechanism by which the "aromatic sextet" operates. Thus the lone pair of electrons on the nitrogen atom of pyrrole really is responsible for the stabilization, since it is required for the conjugation which increases the resonance; and clearly it cannot enter into this resonance if it is being used in salt formation. However, the significance of the number six does not at once emerge from these considerations. On this point Hückel[51] has remarked, "Ein Verstandnis fur die Sonderstellung der zahl 6 auf Grund irgendwelcher chemischer Tatsachen ist nicht zu gewinnen; sie schient ein an sich unverstandenes Axiom zu bleiben."

The explanation of this "unverstandenes Axiom" is suggested, however, by a combination of the Baeyer strain theory with the principles of resonance. Ring strain is a disruptive influence and thus works against the stabilizing influence of resonance. In benzene the resonance energy is more than sufficient to overcome the ring strain, and three electron pairs (the sextet) enter into resonance. In cyclooctatetrene the coplanarity of the eight carbon atoms, which is a condition for resonance, presumably introduces sufficient ring strain to overcome the resonance effect; hence an aromatic octet is not permitted. In cyclopentadiene, where only a quartet of electrons is available, only a limited resonance is possible; but formation of the negative ion produces an "aromatic sextet" and increases the possibility of resonance. Furthermore, ring strain is at a minimum in a five-membered ring. The argument is readily extended to furan, thiophene, pyridine, etc., and in this extension it is apparent in each case that a sextet of resonating electrons is required for the maximum effect.

In the light of the above discussion it is apparent that the resonance theory has not overthrown the theory of the aromatic sextet but has definitely extended it. As an example of the greater usefulness of the resonance viewpoint Ingold [57] has pointed out that ψ-isoindole lacks the aromatic stability of the isomeric indole despite the fact that it has the necessary six electrons required for stability by the theory of the aromatic sextet. This is readily explained from the resonance viewpoint: ψ-isoindole does not have as many unperturbed forms as indole.



Free Radicals

The most satisfactory theory for explaining the stability of free organic radicals like triphenylmethyl and diphenyl nitrogen was originally put forward in a qualitative way by Burton and Ingold.[58] Later Pauling and Wheland [59] put the theory on a more quantitative basis by the application of quantum mechanics. Hückel,[60] who had worked along similar lines, gave his approval to the idea in question.

The stability of triphenylmethyl, either as a free radical or as an ion,

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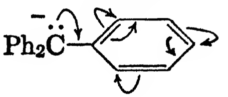
[57] Ingold, *J. Chem. Soc.*, 1127 (1933).

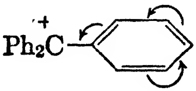
[58] Burton and Ingold, *Proc. Leeds Phil. Soc.*, **1**, 421 (1929); Ingold, *Trans. Faraday Soc.*, **30**, 52 (1934).

[59] Pauling and Wheland, *J. Chem. Phys.*, **1**, 363 (1933).

[60] E. Hückel, *Trans. Faraday Soc.*, **30**, 59 (1934).

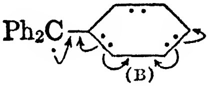
is attributed to resonance stabilization. The resonance in the ions may be understood from the following abbreviated pictures.





In the free radical Ingold points out that the usual concept of tautomeric displacement of electron pairs is no longer sufficient and that we must think of the individual electrons in each pair as being displaced in opposite directions. He reasons that this second type of electron displacement is also required by the principle of maximal octet preservation. The reason for this assumption can most easily be understood from careful study of the following diagrams, in which an arrow is drawn for each electron.

(A)



(B)

In A the resultant unperturbed form would have an unpaired electron in the *ortho* position, whereas in B it would be in the *para* position. When we consider all three phenyl groups we find that the odd electron can resonate among ten positions: the methyl carbon and the *ortho* and *para* positions on each of the three rings. The amount of resonance stabilization would, of course, depend on the number of unperturbed forms. The resonance energy must attain the same general order of magnitude as the bond energy of the C—C link or appreciable dissociation cannot take place. Furthermore, if the electrons are to move in both directions simultaneously, as Ingold maintains, the conjugated system through which they are conducted must allow conduction in both directions (which the phenyl group is well known to do) and must not be a one-way conductor, as certain unsaturated groups practically are.

When naphthyl groups are involved instead of phenyl groups we find that the number of unperturbed forms in which the odd electron is in the ring is increased from three to seven in the *alpha* or six in the *beta* form. In *p*-diphenyl it is six. The theory would predict the relative stabilities to be in the same order as the number of unperturbed forms. The prediction is very nearly fulfilled: the observed order is α-naphthyl > β-naphthyl > *p*-diphenylyl > phenyl.

In the above discussion the only factor recognized as contributing to resonance stabilization was the number of unperturbed forms. However, the relative stabilities of the unperturbed forms must also be an important influence, and no doubt this is partly responsible for the failure of β-naphthyl and *p*-diphenylyl to be exactly equal in their influence. It is possible that steric hindrance is a factor of appreciable magnitude.[61] This could very easily become highly important if it prevented a planar configuration and thus interfered with the development of resonance. With this in mind it is evident that although the replacement of phenyl groups in triphenylmethyl by larger aromatic groups should increase the stability of the free radical up to a certain point, after this point has been passed the steric effect destroying the planar configuration should decrease the stability.[62] Evidence for this viewpoint emerges from recent work by several investigators. Müller and Kruck [62] have shown that the introduction of large groups such as chrysyl and phenanthryl increases the stability of the triarylmethyl radicals. But Bachmann and Kloetzel[63] have found that although the stability of the radicals 1-, 2-, and 3-phenanthryldiphenylmethyl is relatively high in the dark, both the 9-phenanthryldiphenylmethyl and 9-phenanthryldiphenylenemethyl decompose spontaneously. This may be interpreted to mean that prevention of planar configurations by the greater steric hindrance of the 9-phenanthryl group has cut down or destroyed the resonance which stabilizes the free radical against any change, be it association or decomposition, with the result that decomposition occurs. This parallelism between the stability of a radical toward dissociation or disproportionation, on the one hand, and the extent of dissociation of the hexa-arylethane into free radicals on the other hand, has been established in other cases.[64]

It should be noted that Marvel, Mueller, and Ginsberg [65] have questioned the importance of resonance as a factor in the dissociation of hexa-arylethanes. Table VII shows the lack of correlation between the number of resonance forms and the per cent dissociation of the hexa-arylethane.

TABLE VII

Radical	No. of Resonance Forms	Per Cent Dissociation
Triphenylmethyl	10	2– 3
Diphenyl-3-diphenylylmethyl	10	11–12
Tri-3-diphenylylmethyl	10	60
Diphenyl-4-diphenylylmethyl	13	13–14
Phenyl-di-4-diphenylylmethyl	16	75
Tri-4-diphenylylmethyl	19	100

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[61] Bent, Cuthbertson, Dorfman, and Leary, *J. Am. Chem. Soc.*, **58**, 165 (1936).

[62] Müller and Kruck, *Ber.*, **71**, 1778 (1938).

[63] W. E. Bachmann and Kloetzel, *J. Org. Chem.*, **2**, 356 (1937).

[64] (*a*) Hey, *Ann. Repts. Chem. Soc.*, **37**, 255 (1940); (*b*) Marvel, Mueller, Himel, and Kaplan, *J. Am. Chem. Soc.*, **61**, 2771 (1939).

[65] Marvel, Mueller, and Ginsberg, *ibid.*, **61**, 2008 (1939).

Resonance Involving Hydrogen Bonds

Molecular structures involving hydrogen bonds present the possibility of two more or less equivalent electronic modifications involving the same geometrical configuration of nuclei: A H—A′ and A—H A′. This presents the possibility of a resonance between these contributing structures which would account for the stability of the hydrogen bond. The same type of resonance is equally to be expected in chelate rings.

Interatomic Distances and Resonance

Modern research in the realm of chemical physics has given us means of measuring interatomic distances. The diffraction of X-rays by crystals and of electrons by gases has been convincingly demonstrated to yield reliable results, as has also spectroscopy.

A great mass of experimental work has indicated that in general the distance between any two given atoms linked by a covalence of definite type (single, double, or triple) is remarkably constant and depends only slightly on the environment. Thus the length of the C—C bond in saturated and unsaturated hydrocarbons, saturated cyclic compounds, aldehydes, and in diamond varies between the limits of 1.52 and 1.55A°.[66] Moreover, these interatomic distances are related by a simple additive rule.[66] The bond distance A—B is equal to the arithmetic mean of the distances A—A and B—B. Obviously it should be possible to assign covalent radii to atoms; the sum of the radii for any two atoms would then be equal to the interatomic distance when the atoms are covalently linked. Values for such covalent radii have been worked out.[66] Their use is restricted to atoms exercising their normal covalence, although it is found that they apply even to atoms having considerable ionic character, but they may not be used in extreme cases; for these ionic radii should be used instead.

As the multiplicity of the bond increases, the covalent radius decreases. This is illustrated in carbon by the following:

C—C	0.77A°
C═C	0.67
C≡C	0.60

It is also found that the covalent radii of atoms in the same period of Mendeleeff's table decrease as the atomic number increases. This is ascribed to the accompanying increase in the effective nuclear charge. This would lead one to expect that the radius would be decreased if the

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[66] Ref. 3, Chapter V.

atom became the seat of a positive charge and increased if the charge was negative. If, however, one atom gained a negative charge while the atom bound to it gained a positive charge, the effects would be expected to cancel, since one radius would be increasing and the other decreasing (e.g., the S—O bond in dimethyl sulfoxide). These predictions cannot yet be tested rigorously because the necessary data are lacking, but such data as we have seem to support them.[66]

In view of the fact that the formation of a double bond brings two atoms close together, it would be expected that the C—C bonds in benzene, each of which has one-half double bond character due to resonance, would have an interatomic distance whose value would lie between those for C—C (1.54 A°) and C=C (1.34 A°). Such is found to be the case, the value being 1.39 ± 0.01 A°.

The effect of resonance in benzene is a completely general effect: resonance always brings the bound atoms closer together. The fact that interatomic distances are always found to be shortened in just those cases where the English theory would predict mesomerism is a strong indication of the correctness of the theory. The concept is further supported, as we have already seen, by the fact that unusually high bond energy is found whenever the theory predicts mesomerism.

If a C—C distance of 1.39 A° corresponds to what we have called "one-half double bond character" and the values 1.34 A° and 1.54 A° correspond respectively to 100 per cent and 0 double bond character, it is apparent that we could construct a curve relating per cent double bond character with interatomic distances in C—C bonds.[67] A fourth point can be added by using the value for graphite, in which it can be shown that each bond has one-third double bond character. This curve can be expressed by the following equation:

$$R = R_1 - (R_1 - R_2)\frac{3x}{2x + 1} \tag{9}$$

in which R is the value of the interatomic distance for a bond of intermediate type, R_1 that for a single bond, R_2 that for a double bond, and x the amount of double bond character.

Hyperconjugation

The peculiar type of resonance postulated in the "Baker-Nathan effect" has persistently forced itself into various theoretical investigations with the result that it has come to be regarded very seriously. Even before the paper of Baker and Nathan, Wheland[68] had suggested

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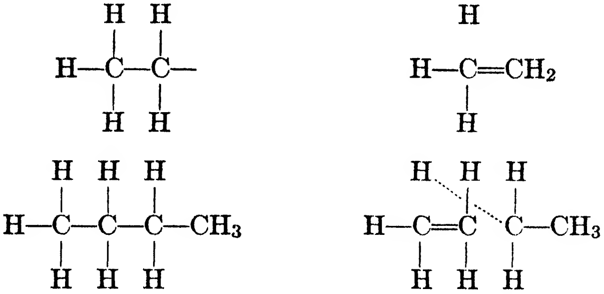
[67] Pauling, Brockway, and Beach, *J. Am. Chem. Soc.*, **57**, 2705 (1935).

[68] Wheland, *J. Chem. Phys.*, **2**, 478 (1934).

that a similar type of resonance was responsible for the stabilizing effect of methyl substituents on free radicals of the triphenylmethyl type. He even went farther in suggesting a more extreme type of resonance, such as



and supported his contentions by rough quantum-mechanical calculations. It appears also that E. Hückel[69] was working along similar lines at the same time.

G. N. Lewis[70] had also, previously to Baker and Nathan's paper, pointed out the necessity of a similar assumption to explain the existence of diborane. He suggested that the six electron-pair bonds resonate between seven positions,

etc.

this resonance stabilizing the substance. Pauling[71] later subscribed to Lewis's explanation but held that resonance structures with one-electron bonds are also involved in this particular case.

Hughes, Ingold, and Taher[72] later suggested that "Baker and Nathan's hypothesis may be accepted provisionally as expressing a general property of all H—X bonds—even those that do not ionise." Hughes, Ingold, Masterman, and McNulty[73] speak of the Baker-Nathan type of resonance as "quasi-conjugation" and point out that the long-sought explanation of the electron-repelling properties of alkyl groups attached to unsaturated centers (as illustrated, for example, in the dipole moment of toluene) is to be found in this hypothesis. Ingold et al.[72] also succeeded in showing that kinetic studies of carefully chosen reactions can also be

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[69] Private communication from L. Pauling to Wheland; see Ref. 68.

[70] G. N. Lewis, *J. Chem. Phys.*, 1, 17 (1933).

[71] Ref. 3, p. 260.

[72] Hughes, Ingold, and Taher, *J. Chem. Soc.*, 949 (1940).

[73] Hughes, Ingold, Masterman, and McNulty, *ibid.*, 909 (1940).

made to yield evidence of quasi-conjugation. They pointed out that whereas considerations of the *I* effect alone lead to the following sequence of electron releasing ability:

$$H < Me < Et < Pr^{\beta} < Bu^{\gamma} \tag{I}$$

considerations of the quasi-conjugative *T* effect lead to the alternative sequence:

$$H < \{Me > Et > Pr^{\beta} > Bu^{\gamma}\} \tag{II}$$

It is rather difficult to predict, in any given case, whether the *I* or *T* influence will predominate, but if we seek a case most likely to exhibit sequence II it should, according to Ingold, be a strongly electron-demanding reaction, such as a "unimolecular nucleophilic substitution." The hydrolysis of the *p*-alkylbenzhydryl chlorides proceeds by the S_N1 mechanism, the rate-controlling step of which is the electrophilic attack by the solvent on the halide, causing its ionization. The effect of substituents on the speed of this reaction is given by sequence II.

Recent quantum-mechanical studies [74] have also indicated the necessity of introducing the concept of quasi-conjugation, although it is customary in this field to refer to it as "hyperconjugation." Basically Mulliken's treatment amounts to a comparison of the theoretically calculated values of conjugation and hyperconjugation with the empirically observed defects from bond-energy additivity, the latter being detected by comparisons with thermal data. The comparison is highly gratifying.[74c]

There are two methods of quantum-mechanical calculation referred to as the molecular orbital (MO) and the atomic orbital method (AO). From the viewpoint of the former the three bonds in a methyl group are likened to a triple bond, the similarity being emphasized by writing $-C{\equiv}H_3$. The difference in conjugating power between $-C{\equiv}H_3$ and a true triple bond such as $-C{\equiv}CH$ is considered to be quantitative rather than qualitative. The former, although much more saturated, has considerable conjugating power, as shown by calculations taken in connection with thermal and bond-distance data.

"In general, three ordinary single bonds from carbon to any three other atoms may be regarded as constituting a quasi-triple bond whenever there is an opportunity for conjugation, across the intervening C—C single bond, with a second (quasi or ordinary) multiple linkage. Some

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[74] (*a*) Pauling, Springall, and Palmer, *J. Am. Chem. Soc.*, **61**, 927 (1939); (*b*) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (*c*) Mulliken, Ricke, and Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

simple examples of conjugated systems, in the generalized sense, are the following: "[74c]

$HC{\equiv}C{-}C{\equiv}CH$ \
$N{\equiv}C{-}C{\equiv}N$ } Ordinary (first order) conjugation.

$H_3{\equiv}C{-}C{\equiv}CH$ Second order conjugation (first order hyperconjugation).

$H_3{\equiv}C{-}C{\equiv}H_3$ • Third order conjugation (second order hyperconjugation).

In all types of conjugation we have donor bonds and acceptor bonds. In first order conjugation it has been shown repeatedly that there is a shortening of the acceptor bond and a slight lengthening of the donor bond and there is a net stabilization which we have previously referred to as resonance energy. Quantum-mechanical calculations show that this net stabilization is the sum of a positive stabilization energy occurring in the acceptor bonds and a smaller negative energy in the donor bonds. Mulliken's computations[74c] indicate that in hyperconjugation the acceptor bonds are very appreciably strengthened and shortened but that the donor bonds are almost inappreciably affected.

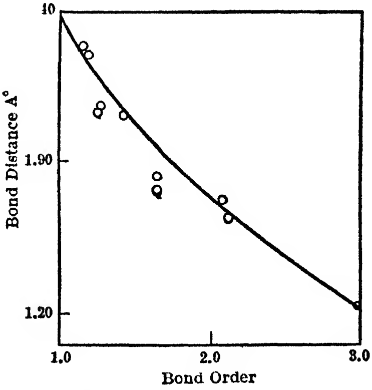
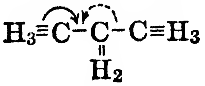


FIG. 3.[74c] Variation of bond distance with bond order.

In third order conjugation in saturated hydrocarbons the C—H bonds act only as donors and the C—C bonds predominantly as acceptors. The C—C bonds serve only as acceptors in ethane, $H_3{\equiv}C{-}C{\equiv}H_3$, but in propane and the higher hydrocarbons they are simultaneously acceptor and donor  $H_3{\equiv}C{-}\underset{\underset{H_2}{\|}}{C}{-}C{\equiv}H_3$ but always more acceptor than donor.

Hyperconjugation, like ordinary conjugation, results in changing the percentage of double bond character in a bond. This may alternatively be expressed in terms of "bond order"[75] which is defined in such a way that bond orders of 1, 2, or 3 would respectively express pure single, double, or triple bonds. Pauling[3] has drawn curves showing that there is a relationship between bond distance and percentage of double bond character. Figure 3 shows that hyperconjugation also fits rather

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[75] Coulson, *Proc. Roy. Soc.* (London), **169A**, 419 (1939).

well into this same picture. In this figure the bond order refers to C—C acceptor bonds. The third order conjugation in ethane gives its C—C bond an order slightly greater than unity; second order conjugation in ethylene results in a bond order greater than 2, while in acetylene the bond order is found to be 3, showing no hyperconjugation in this case. The reader is referred to Mulliken's paper for a discussion of the other cases.

Raman Spectra [76]

The constituent parts of a molecule are subject to different quantized motions which are involved in absorption of light by the molecule. The vibrations of electrons involve the highest frequencies and hence are called into play when absorption of visible or ultraviolet light is concerned. On the other hand, the vibrational and rotational motions involving the atoms themselves are associated with much lower frequencies and although they are sometimes called into play in the absorption of higher frequencies they are chiefly associated with infrared absorption.

It should be pointed out in passing that not all molecules have infrared spectra.[77] It happens to be a requirement of the electromagnetic theory of light that radiation may be absorbed or emitted only by a system whose electrical configuration, relative to a point in space, is changing. This means that atomic vibration within a molecule will absorb radiation only if the dipole moment changes with the vibration, and rotation results in absorption only if the molecule has a permanent dipole moment. Oxygen, for example, shows no rotation or vibration spectrum.

The apparatus required for the measurement of infrared absorption is costly and rather rare. It was accordingly a matter of no small moment when Sir C. V. Raman discovered in 1928 an effect which made it possible to deduce infrared vibrational frequencies from measurements made in the visible part of the spectrum. He discovered that the scattering of visible light by molecules is accompanied in part by a change in frequency from that of the incident light. The origin of this effect is the interaction of a light quantum ($h\nu$) and a molecule. This may be likened to an inelastic collision between two molecules, since part of the energy of the light quantum is absorbed by the molecule, causing atomic vibration, and the remainder is liberated as light waves of less energy and hence lower frequency. If, however, a molecule in a vibrational or rotational

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[76] For complete reviews of this subject see the following publications of J. H. Hibben: (*a*) *Chem. Rev.*, **13**, 345 (1933); (*b*) *ibid.*, **18**, 1 (1936); (*c*) *The Raman Effect and Its Chemical Applications*, Reinhold Publishing Corp., New York, 1939.

[77] Barnes and Bonner, *J. Chem. Education*, **15**, 25 (1938).

level above the ground level interacts with a quantum of light, the transfer of energy attending the collision is in the reverse direction and the scattered light will have more energy and higher frequency. The lines thus produced are called the anti-Stokes lines. The changes in frequency attending Raman scattering of either kind are identical and are called the "Raman shifts," symbolized by $\Delta\tilde{\nu}$. The value of $\Delta\tilde{\nu}$ is obviously proportional to the difference between the frequency of the exciting light ν_e and that of the Raman line ν_R. Thus

$$h\nu_{\text{abs}} = h\nu_e \pm h\nu_R \tag{10}$$

Since Raman shifts are conventionally expressed in terms of wave numbers or the number of vibrations per centimeter, we may write

$$\Delta\tilde{\nu} = \frac{\nu_e \pm \nu_R}{c} \tag{11}$$

where c is the velocity of light in centimeters per second.

It has been mentioned that Raman shifts are due to light energy absorbed ($h\nu_{\text{abs}}$) in exciting atomic vibrations. It is not, therefore, surprising to find that usually they correspond with the infrared absorption frequencies, and it is to be noticed that no infrared spectrographic equipment is needed for the measurement since both ν_e and ν_R fall in the visible range of the spectrum. The effect is viewed through an ordinary spectrograph at right angles to the direction of the incident light beam.

Raman shifts have the outstanding advantage that they are essentially independent of intermolecular forces and hence of the state of aggregation, in this way differing from visible and ultraviolet absorption spectra; but they have the disadvantage of all spectroscopic measurements, viz., that for polyatomic molecules the spectra are so complicated that it is extremely difficult to interpret them. However, by studying the Raman spectra of a large number of molecules which contain the same functional groups or atomic unions it has been found possible to associate certain shifts with definite groups or linkages. This has resulted in two very important applications of Raman spectra studies to organic chemistry: (1) the determination of the structures of molecules by associating certain of the observed Raman shifts with definite structural units, and (2) studying the effects of substituents on bond strengths, which can be calculated from Raman shifts as explained below.

It will be recalled that from light refraction measurements it is possible to calculate force constants of bonds related to electronic displacements. From Raman shifts it is possible to calculate a different kind of force constant for a bond, one which involves stretching the bond by moving the atoms farther apart. If this bond-stretching force constant is symbolized by f and the reduced mass, M, of two adjacent bound atoms is defined as

$$\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2}$$

where m_1 and m_2 are the masses of the two atoms measured in relative atomic weight units, then it may be shown that

$$\Delta\tilde{\nu} = 4.125\sqrt{\frac{f}{M}} \tag{12}$$

Here f is expressed as the restoring force per unit of displacement expressed in dynes per centimeter. Strictly speaking, this equation only applies accurately to diatomic molecules in which the force is strictly harmonic, but it can be used as a fair approximation even in larger molecules. In polyatomic molecules such as $BrCCl_3$ the reduced mass to be used for calculating the C—Br force constant might, in the limiting case, involve the weight of CCl_3 instead of the atomic weight of carbon. This would correspond to a vibration of the CCl_3 group as a whole. Thus in comparing the Raman shifts due to the stretching of a given bond, say the C—Br bond, in different polyatomic molecules we may not in general assume that the force constants will parallel the Raman shifts unless we can rule out the influence of this "mass effect." However, if the C—H bond was involved instead of the C—Br the reduced mass would depend almost wholly on the light hydrogen atom and the "mass effect" of substitution would be very small.

The phase of Raman spectroscopic studies of most interest to our subject is the effect of constitutive changes in molecules on the bond-stretching force constants. This subject, unfortunately, has been given but scant attention by reviewers, and we must therefore content ourselves with a few fragmentary observations, leaving the critical review to men who are authorities in this field.

In Table VIII are listed such force constants for various bonds. They are expressed in dynes per cm $\times 10^{-5}$. It will be noted that the force constant of the C═C is approximately twice and that of C≡C approximately three times the value for the single C—C bond. This is understandable as is also the trend observed for the series HF > H—O > H—N > H—C. This trend is predictable from a simple viewpoint. If the bonds are stretched slightly the outward movement of the hydrogen atoms must be accompanied to some extent by a movement of the binding electrons. It would require most force to move them away from the highly electronegative fluorine atom. This simple viewpoint also predicts the observed trends as we move down the Mendeleeff columns for the sixth and seventh group elements and also makes clear the trend

TABLE VIII[78]

Force Constants for Bond Stretching

Bond	$f \times 10^{-5}$	Molecule or group
C≡C	15.7	C_2H_2
C≡N	17.9	HCN
	17.5	$(CN)_2$
C=C	8.2–9.8	C_2H_4
C=O	13.4	CH_2O
	14.2	COS
	15.3	CO_2
F—H	8.6	HF
O—H	7.0	H_2O
N—H	6.4	NH_3
C—H	5.9	C_2H_2
	5.8	HCN
	5.0, 4.9	CH_4
	5.0	C_2H_4
	5.0	C_6H_6
H—H	5.1	H_2
S—H	4.0	H_2S
C—C	5.0	C_2H_6
	4.8	$(CN)_2$
	7.6	C_6H_6
C—N	4.9	$MeNH_2$
C—O	4.5	Me_2O
C—S	3.0	Me_2S
C—F	5.8, 5.04	MeF
C—Cl	3.12	MeCl
	2.94	CH_2Cl_2
	2.47	$CHCl_3$
	2.00	CCl_4
C—Br	2.61	MeBr
C—I	2.15	MeI

observed in the Raman shifts for the C—H links given in Table IX. This is a clear indication that the successive substitution of chlorine atoms causes successive increases in the electronegativity of the carbon atom. At first glance, the values of the force constants for the C—Cl bonds in these same compounds (Table VIII) would seem to indicate the opposite effect. This effect, however, is probably due to the increasing mass of the groups CH_3, CH_2Cl, $CHCl_2$, and CCl_3 attached to the C—Cl bonds in question. As previously explained, this mass effect is negligible in the case of C—H bonds since the hydrogen atom is comparatively light (cf. Eq. 12).

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[78] All values except those for C—Hal bonds were taken from Branch and Calvin's *The Theory of Organic Chemistry*, Prentice-Hall, 1941, p. 154. The values for C—Hal were taken from Heller and Polanyi, *Trans. Faraday Soc.*, **32**, 633 (1936).

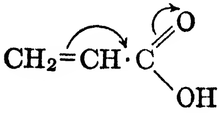
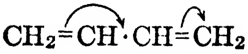
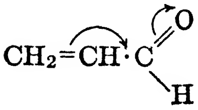
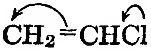
TABLE IX [79]

RAMAN SHIFTS FOR C—H LINKS

Compound	$\Delta\tilde{\nu}$
CH_4	2915
MeCl	2955
CH_2Cl_2	2975
$CHCl_3$	3016

The effect of resonance is illustrated by Table X, which gives the shifts associated with the C=C link. The resonance involving C=C and carboxyl would be expected to be slight and the slight drop in frequency may be caused entirely by the mass effect. But in acrolein and butadiene the effects of the resonance in increasing the polarizability cannot be doubted. A consideration of allyl chloride and vinyl chloride also strongly suggests the effect of resonance in the latter. Prilezhaeva, Syrkin, and Vol'kenshtein [81] have come to similar conclusions. They

TABLE X [80]

Compound	$\Delta\tilde{\nu}$
$CH_2{=}CH\cdot Me$	1647
$CH_2{=}CH\cdot OH$	1646
$CH_2{=}CH\cdot Et$	1642
$CH_2{=}CH\cdot CH_2Cl$	1640
 $CH_2{=}CH\cdot C({=}O)OH$	1638
 $CH_2{=}CH\cdot CH{=}CH_2$	1634
 $CH_2{=}CH\cdot C({=}O)H$	1618
$CH_2{=}CH_2$	1620
 $CH_2{=}CHCl$	1608

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[79] Ref. 76c, p. 136.

[80] Ref. 76c, p. 165.

[81] Prilezhaeva, Syrkin, and Vol'kenshtein, *Acta Physicochim. U.R.S.S.*, **12**, 176 (1940).

point out that successive substitution of chlorine or bromine into ethylene causes successive lowering of the Raman C=C frequencies, and their calculations lead them to the conclusion that the effect must be due not to the increasing masses of the vibrating atoms or groups but to resonance.

Since in these cases we are dealing with the "time variable" polarizability effects it is evident that we have here additional evidence in favor of the electromeric effect of the English school.

Resonance and the Color Theory

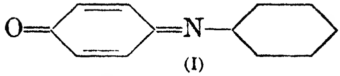
The development of an adequate theory of color production is one of the many cases in which the organic chemists, who were pioneers in the field, ultimately found it necessary to seek the collaboration of workers in the field of chemical physics. At the moment it seems as though the concept of quantum-mechanical resonance is going to solve most of the difficulties which have beset theorists in this field.

The phenomena directly involved in this problem are manifold. Obviously the production of color is only a special case of the absorption of electromagnetic waves, and hence the study of ultraviolet and infrared absorption phenomena should properly be included in a survey of the field. Then, too, considerations of the number, width, and intensities of absorption bands are of equal importance with studies of their wave lengths, which we customarily associate with color. Consideration should also be given to such closely related phenomena as fluorescence and the absorption of polarized light. In view of the enormous field to be covered, the author must once again beg forgiveness for a superficial review.

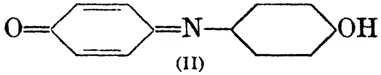
It is generally recognized that the absorption of light in the visible and ultraviolet portions of the spectrum is due to the vibration of electrons. A substance which absorbs in the ultraviolet is, of course, colorless and the electrons exist under relatively high constraints. If the structure of such molecules is altered so as successively to reduce these constraints, the frequencies of light absorbed become smaller and ultimately the absorption bands enter the visible range of the spectrum. The first visible light to be absorbed will, of course, be in the violet, which means that the substance in question will appear yellow to the eye. If the electronic constraints are still further reduced, the absorption bands will shift progressively to regions of lower frequency and we say that "color deepening" is in progress. Thus colors get deeper in the order yellow, orange, red, violet, blue, green. When substitution in a molecule causes color deepening the effect is described by the adjective "bathochromic"; the opposite effect is called "hypsochromic."

The first theory relating color and chemical constitution was developed by Witt.[82] The theory consisted merely in an empirical relation between chemical structure and dyestuff properties. It was pointed out that all colored organic substances then known contained certain unsaturated groups, called chromophores, such as $—N{=}N—$, $>C{=}O$, $>C{=}S$, $>C{=}N$, $—N{=}O$, $—NO_2$, and *o*- or *p*-quinoid structures. However, molecules containing these chromophores are almost always yellow in color and are not dyestuffs. When, however, in addition to a chromophore, an organic molecule also contains groups such as $—NH_2$, $—NHR$, NR_2, or OH (called "auxochromes") the color is deepened and intensified and the molecule becomes a dyestuff. The latter property is bestowed on the molecule in virtue of the fact that the auxochromes are basic or acidic groups capable of direct combination with textile fibers.

Very early in the development of the color theory it was also recognized that salt formation has a profound influence on the production of color, the effect being bathochromic. Thus, in indophenol, I merely contains the chromophore and is yellow; II is produced by the introduction of an auxochrome and the color deepens to red. If now the sodium salt of II is produced, the color is deepened to blue.

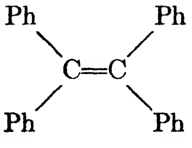


(I)

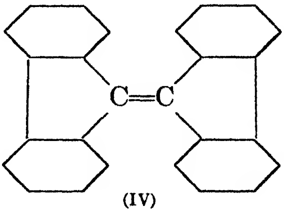


(II)

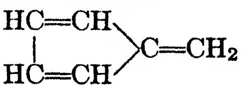
Another early observation of importance was recognition of the fact that increased density of atomic groupings, such as that associated with ring formation, tends to deepen color. For example, compound III is colorless, whereas IV is red. Likewise benzene is colorless, whereas its isomer, fulvene (V) is yellow; this was thought to be due to the more



(III)



(IV)



(V)

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[82] Witt, *Ber.*, **9**, 522 (1876); **21**, 325 (1888); cf. Graebe and Liebermann, *Ber.*, 106 (1868).

dense grouping of the atoms in V. Another well-known example is the fact that whereas azo dyes containing benzene rings are usually yellow, red dyes may be produced if naphthalene rings are involved.

It will be noticed that all the above observations are concerned with the problem of recognizing the structural characteristics which are responsible for the appearance of color. Naturally there were also many attempts to derive theories of color production that would relate the above structural knowledge to vibrating particles of some sort, which were recognized as necessary to the absorption of light. These early theories were reviewed by E. R. Watson[83] in 1918 and by Henrich[84] in 1922.

In 1923 the existing knowledge was welded into a theory by Stieglitz.[85] This theory is chiefly of interest to us because it formed another *chemical* approach to the concept of resonance and in certain respects laid the foundation for the color theory of today. Stieglitz was particularly concerned with the color theory in relation to absorption in the visible spectrum. He wished to ascertain which of the many electrons in the dye molecule are subject to vibrations leading to this particular absorption and to establish the connection between these electron vibrations and the well-known facts relating color to structure and salt formation.

He recognized that the key to the mystery was found in the observation that reduction of a dye to its leuco compound destroys the color and that gentle reoxidation of the reduced form produces color. If the dye is strongly oxidized the color usually reverts to yellow. Thus the dye itself is in an intermediate state of oxidation and must contain both oxidizing and reducing groups. These groups he identified respectively with chromophores and auxochromes. Now the characteristic property of strong reducing groups is that the electrons are to a considerable extent freed from intra-atomic restraint, whereas oxidizing groups are invested with the power to attract and finally absorb electrons from neighboring atoms. With both types of groups in one molecule it would be expected that there would be a tendency to intramolecular electron transfer. Inasmuch as this tendency is definitely related to the freeing of the valence electrons from the ordinary intra-atomic restraints, and since bringing the absorption bands down from the ultraviolet or violet into the lower frequencies of the visible spectrum also involves lessened re-

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[83] E. R. Watson, *Colour in Relation to Chemical Constitution*, Longmans, Green & Co., 1918.

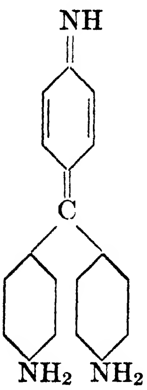
[84] F. Henrich, *Theories of Organic Chemistry*, translated by Johnson and Hahn; John Wiley & Sons, 1922, Chapter XVI.

[85] Stieglitz: (*a*) *Proc. Nat. Acad. Sci.*, **9**, 303 (1923); (*b*) *J. Franklin Inst.*, **200**, 35 (1925).

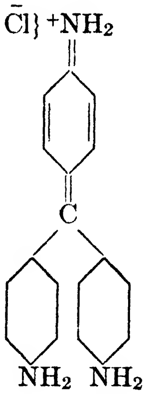
straints, Stieglitz drew the conclusion that color production is due to the oscillation of the electrons which would be involved in such an intramolecular oxidation-reduction process.

The effect of salt formation in causing color deepening fitted naturally into Stieglitz's theory. It is well known that the addition of alkali to hydroquinone or aminophenol makes them more strongly reducing. Hence salt formation at an auxochromic hydroxyl group loosens the electrons responsible for color formation, and color deepening results. Thus with the indophenol mentioned above, such salt formation deepens the color from red to blue, while in phenolphthalein the absorption band is not brought down from the ultraviolet into the visible spectrum until salt formation occurs, not only at the carboxyl group but also at one of the hydroxyl groups.[86]

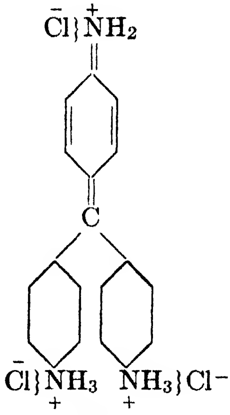
According to Stieglitz, "when salt formation of basic dyes occurs with acids with the production of maximum depth and intensity (of color) the acid is found in the oxidizing component of the dye molecule." [87] On the other hand, salt formation with the basic auxochromic groups destroys their reducing powers and affects their color accordingly. Pararosaniline exemplifies these points of his theory.



Yellow



Red



Yellow

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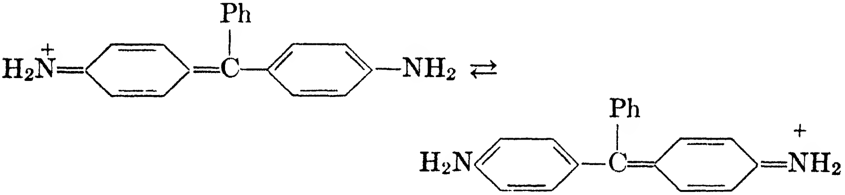
[86] (*a*) Green and Perkin, *J. Chem. Soc.*, **85,** 398 (1904); (*b*) Green and King, *Ber.*, **40,** 3724 (1907); (*c*) Meyer and Spengler, *ibid.*, **38,** 1318 (1905); (*d*) Kober and Marshall, *J. Am. Chem. Soc.*, **33,** 59 (1911).

[87] It is interesting to note that this contention is in accord with the principles of quantum mechanics, for if the unshared electrons of an auxochrome are part of a resonance system, salt formation could only take place by destruction of the resonance. On the other hand, if a fifth or sixth group element is part of a chromophore, its unshared electrons do not contribute to the resonance and hence salt formation should be easier. There is also some chemical evidence in favor of this point of view which has been furnished by Hantzsch and Hilscher, *Ber.*, **41,** 1171 (1908).

Stieglitz held that the electrons do not vibrate "from side to side" of the molecule but merely are freed somewhat from the restraints under which they normally would exist in similar but colorless molecules. There is no need to dwell on this phase of his theory. Subsequent developments have made it clear that the vibrations are of the kind we have considered in resonance phenomena. His contention concerning the fundamental relationship that exists between color production and oxidation-reduction is to be found in the modern theory, in which it is asserted that resonance occurs in dye molecules between the chromophoric (electron sink or acceptor) and the auxochromic (electron source or donor) groups. Usually a conjugated system will serve as an intermediate path over which the electronic resonance is transmitted. His ideas on the effect of salt formation on color have been extended, as we shall soon see.

Let us now examine in more detail the resonance theory of color production.[88] The ion of Dobner's violet may be written in either of the two equivalent forms:



Therefore we should expect complete resonance. It will be observed that the auxochrome (NH_2) is acting as an electron source and the chromophore  as an electron sink. The two are connected by the conjugated system in the benzene ring, which acts as a path for the transmission of the resonance. Similar resonance systems would be expected in the diphenylmethane, indamine, indophenol, auramine, acridine, pyronine, azine, oxazine, thiazine, and cyanine dyes. The very fact that strong resonance would be predicted in all these cases is a strong indication but by no means an overpowering proof of the correctness of this theory of color production. Strong additional support is found in the fact that the predicted influence of symmetry on resonance is readily correlated with its effect on color depth.[88] From the

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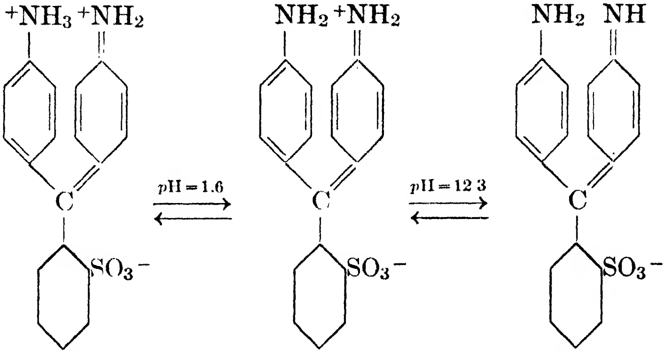
[88] (a) Bury, *J. Am. Chem. Soc.*, **57**, 2115 (1935); (b) Schwarzenbach, Brandenberger, Ott, and Hagger, *Helv. Chim. Acta*, **20**, 490 (1937); (c) Schwarzenbach, Ott, and Hagger, *ibid.*, 498; (d) Schwarzenbach and Ott, *ibid.*, 627; (e) Mohler, Forster, and Schwarzenbach, *ibid.*, 654; (f) Schwarzenbach and Brandenberger, *ibid.*, 1253; (g) Schwarzenbach and Hagger, *ibid.*, 1591.

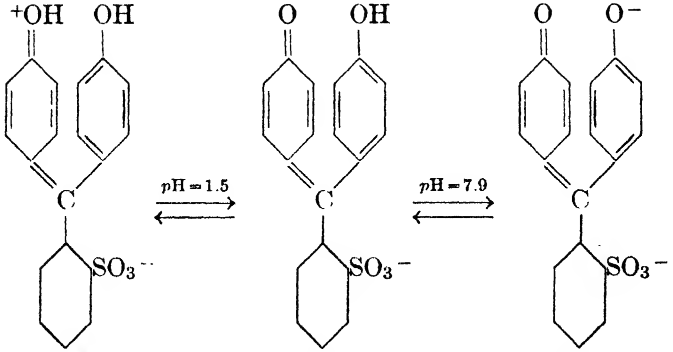
many examples worked out by Schwarzenbach and his collaborators, the following are sufficient to make clear the application of the principle. The values of the pH given are the values at which the respective color changes occur.



VI*A*
Yellow

VI
Violet

VI*B*
Yellow



VII*A*
Red

VII
Yellow

VII*B*
Red

In VI there is a possibility of complete resonance, since the two upper rings are identical except for electron distribution. Accordingly the color is deep. When, however, this symmetry is destroyed either by taking up a proton (VI*A*) or losing one (VI*B*), resonance will be inhibited to a certain extent, with the accompanying change of color to yellow. In VII we have a molecule in which the two main structures contributing to the resonance are not the same and the color is yellow. In both VII*A* and VII*B* symmetry is introduced into the molecule and the color deepens to red.

Recently G. N. Lewis and Calvin[89] have contributed an important discussion of resonance in relation to color. They take the point of view,

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[89] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

at least partially in opposition to Schwarzenbach, that not all types of resonance contribute to the absorption of light. The contributing type of resonance is exclusively that which results in the oscillation of a "formal" electrical charge. Thus in ethane the only resonance forms which contribute to its ultraviolet absorption are $H_3C^{+-}CH_3$ and $H_3C^{-+}CH_3$. In benzene the Kekulé forms do not contribute, but only the minor unperturbed structures involving charge separation, such as .

The nature of chromophores is made clear by a consideration of the effect of conjugation on absorption spectra. This is illustrated in Figure 4 in which the abscissa represents the frequency of radiation and the ordinate is proportional to the extinction coefficient. The molar extinction coefficient ϵ_λ is defined by the equation

$$\epsilon_\lambda = \frac{1}{md} \log \frac{I_{0\lambda}}{I_\lambda} \qquad (13)$$

in which $I_{0\lambda}$ is the intensity of the light of wave length λ which penetrates a layer of pure solvent d cm thick, whereas I_λ is the intensity of light of the same wave length which has penetrated d cm of a solution of molarity m. The two lowest curves are typical of saturated systems. Note, however, that ring formation, which introduces Baeyer strain into a molecule, shifts the absorption band to lower frequencies. In ethylene, where the strain is still greater than that of the six-membered ring, the band is further lowered. There is also introduced a slight change in character of the band, presumably due to the fact that ethylene already has in considerable degree the properties of resonance. The two upper curves are typical of conjugated systems. In these we have, in addition to an absorption suggesting that of ethylene, a new band ("fundamental band") at still lower frequencies, which Lewis attributes to a type of electronic oscillation not found in the other three cases, viz., the type characterized by the electronic coupling or interaction between the conjugated units and resulting in oscillation throughout the whole molecule. Thus we see that a chromophore is nothing but a conjugated framework of atoms which, because it satisfies the requirements for the conjugative type of resonance, already absorbs relatively low frequencies of light. In regard to the frequencies absorbed, it is interesting to remember that we already have learned in our study of refraction phenomena that conjugated systems produce an exaltation of the refraction, which shows the vibration frequencies of the electrons to have been reduced.

Our understanding of the nature of light absorption by conjugated systems will be further increased by a brief consideration of the mathematical aspects of Lewis's theory. When an electron is displaced from its most stable position, the coefficient of restoring force, k, is related to the charge, e, and the polarizability, α, by the equation

$$k = e^2/\alpha \qquad (14)$$

If we now consider a conjugated system made up of n units ("unit oscillators") and consider it placed in an alternating electromagnetic field, the electrons concerned will be displaced the same amount in each unit. This can be conveniently formulated by considering the whole conjugated system as a single oscillator and describing it by the same equations as developed for a unit oscillator with the same coefficient of restoring force but a mass proportional to the number of units, n. Thus if m is the effective mass of electrons displaced in each unit, the total mass of the oscillators in the whole conjugated system will be nm. Now quantum mechanics gives us the relationship

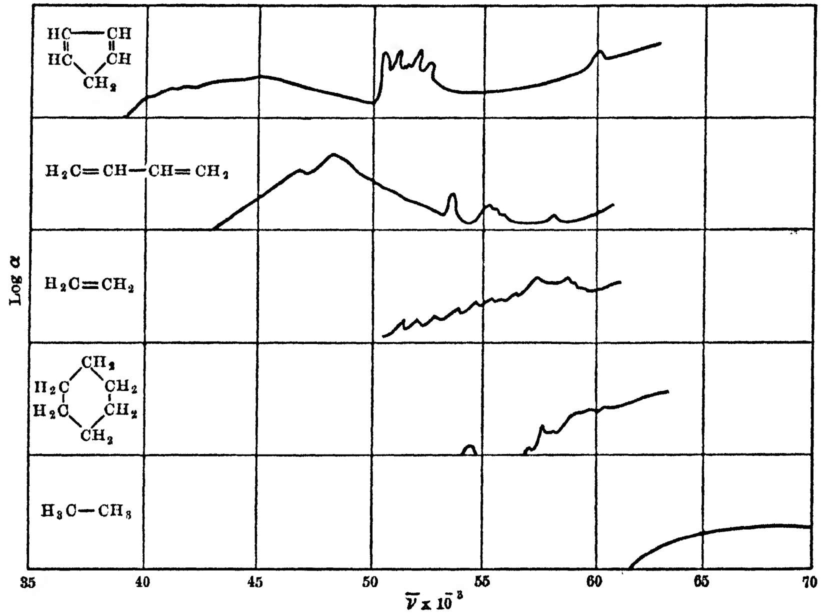


Fig. 4.[89] Absorption spectra of hydrocarbons.

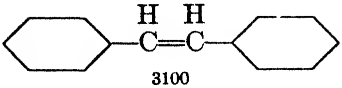
$$2\pi\nu_0 = \sqrt{\frac{k}{nm}} \qquad (15)$$

where ν_0 is the frequency of light which can change the oscillator from quantum number 0 to 1. From this equation it is evident that the frequency of light absorbed by the conjugated system as a result of the resonance along the entire conjugated structure will be less as the number of units increases. This explains at once the fact that conjugated systems absorb at lower frequencies than a simple double bond. It also explains what none of the previous theories explained, i.e., why the color of a dye is deepened by increasing the number and size of the component aromatic rings.

Another long recognized fact which found no explanation in the earlier theories is the one which was expressed earlier in this section by saying that "increased density of atomic groupings, such as that associated with ring formation, tends to deepen color." The explanation is readily found by again considering Equations 14 and 15, from which it is apparent that greater polarizability corresponds to lower frequency of light absorption. Now there is a mass of evidence which shows that the strain introduced by ring formation results in weakening the bonds, i.e., in increasing their polarizabilities. We have already encountered some evidence for this in the data represented in Figure 4. It has also been shown in cyclopropane, as well as in certain other three-ring systems, that the absorption spectra lie between those encountered in single and double bonds.[90] If we grant, in accord with principles established in the last chapter, that polarizabilities of bonds joining atoms of the same period of Mendeleeff's table are proportional to the kernel charges of the atoms involved, then the following double bonds may be arranged in the given order of decreasing polarizabilities:

$$R_2C{=}CR_2 > R_2C{=}NR > R_2C{=}O > RN{=}NR > R_2C{=}S$$

The following three compounds, with their indicated absorption maxima, illustrate the principle.



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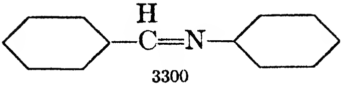
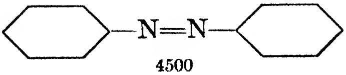


3300



4500

The strongest of these chromophoric groups is C=S, which gives colored compounds even in such simple combinations as thioacetophenone and thiobenzophenone. It is interesting to note that this is another indication that double bond formation with elements of the second period is very difficult, a point which was discussed in the last chapter in relation to **P 3**.

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[90] E. P. Carr and C. P. Burt, *J. Am. Chem. Soc.*, **40**, 1590 (1918).

From the above discussion we now have a clearer understanding of the nature of the chromophore. It is apparent that the frequency of absorption of its fundamental band depends on two factors: (*a*) the "effective mass" of the electrons entering into the conjugative resonance, and (*b*) the polarizabilities of the bonds in question, which can be assigned relative magnitudes in terms of the Baeyer strain concept and Fajan's rules. It is interesting to note that Stieglitz's theory only included consideration of the second of these factors.

The function of the auxochrome is, as previously described, to act as an electron donor to the conjugated chromophore. Under the discussion of acid strength we already have quoted Branch, Yabroff, and Bettman [30] on the great increase in resonance produced by conjugating a group OH with a system like $PhNO_2$. The interaction of a $+T$ group with a $-T$ group always increases the resonance. In general this means the lowering of the frequency of the absorption band (color deepening).

However, Lewis warns us that we must not suppose that high resonance energy implies large absorption of light. In this relation we have already discussed the noncontributing Kekulé forms of benzene. Lewis states: "The (electron) mobility is small in a molecule whose properties correspond to a formula in which all electrons are paired and there is no formal charge on any atom. When such a structure is the major contributing form of a resonating molecule the mobility is still small. When, however, the actual state of a molecule differs considerably from a classical or ideal structure the mobility is greatly increased. In other words, displacement from the ideal structure makes further displacements easier.* Strong color is obtained when two important forms are such that the change from one to the other involves the movement of an electronic charge."

This, then, is one restriction which is put on the relationship of resonance in general to color production. There is also a second restriction which demands a rather lengthy discussion. Let us start by mentioning a theory put forward by Dilthey [91] in 1920. He maintained that ionoid substances are by far the most powerful absorbers of light, although other types of substances might show weak absorption, occasionally even running into the visible region. Lewis points out that this is not necessarily so. For example, many "halochromic" substances become intensely colored upon addition of sufficiently strong acids, taking up protons in the process. "But these same substances absorb with approx-

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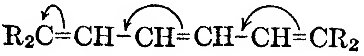
* For example, the operation of the mesomeric effect in *p*-nitrophenol displaces the electrons from the classical structure. This means in turn that further displacements are still easier, i.e., the polarizability is greater.

[91] Dilthey, *Ber.*, **53**, 261 (1920).

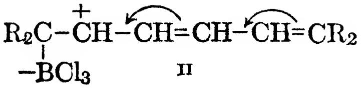
imately the same intensity and at almost the same frequency when neutral substances such as boron trichloride or stannic chloride are added in place of hydrogen ion;[92] yet in these cases the resulting molecules are not ions." He also points out that colored substances such as *p*-nitrophenol absorb lower frequencies of light after they form ions by the addition of a proton.

The way in which the addition of an acid or a substance like boron trichloride (which, like a hydrogen ion, is coordinatively unsaturated) to a chromophore causes color deepening is indicated in the following formulas, where BCl_3 and H^+ have respectively been added to substance I to produce II and III.



$$R_2C{=}CH{-}CH{=}CH{-}CH{=}CR_2$$

I



$$R_2\underset{\substack{| \\ -BCl_3}}{C}-\overset{+}{C}H-CH{=}CH-CH{=}CR_2$$

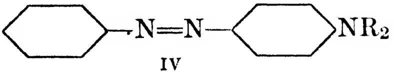
II

$$R_2CH-\overset{+}{C}H-CH{=}CH-CH{=}CR_2$$

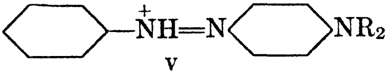
III

Although II is electrically neutral, whereas III is a positive ion, both forms result in greater resonance because a more powerful electron sink (viz., the positively charged β-carbon atom) has been introduced into the resonating system.

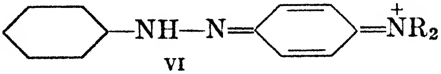
Similar examples are found among azo dyes which are used as acid-base indicators. Thus the addition of a proton to IV increases the resonance, which now involves the oscillation of a positive charge between its positions in V and VI.



IV



V



VI

We may now take another step toward the solution of the problem of the "second restriction" to be placed on the contribution of resonance to color. In formulas VII to XI we find listed the structures and

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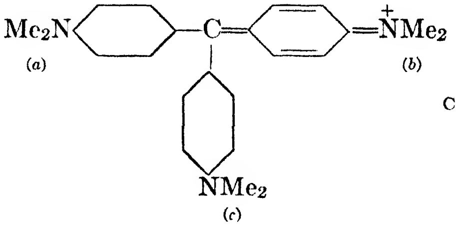
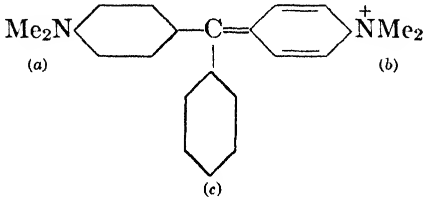
[92] G. N. Lewis and G. T. Seaborg, *J. Am. Chem. Soc.*, **61**, 1886 (1939).

absorption maxima for five colored substances. According to the established principles of quantum mechanics VII should show greater resonance than VIII because there are three equivalent contributing structures in VII but only two in VIII. Despite this fact, however, II is more deeply colored. A similar argument applies to X and XI, which also seem anomalous. Likewise converting VII into IX by the addition of another proton should cut down the resonance, but IX is nevertheless



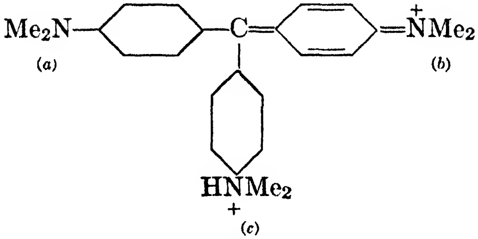
VII

Crystal violet
5900 A°.



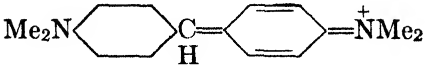
VIII

Malachite green
6230 A°.



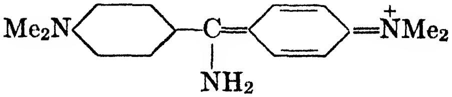
IX

6300 A°.



X

Michler's hydrol
6200 A°.



XI

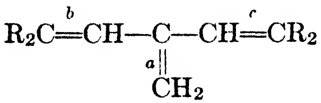
Auramine
4200 A°.

more deeply colored. The first conclusion to be drawn from these data is that changes in total resonance do not necessarily parallel the changes in the resonance responsible for color.

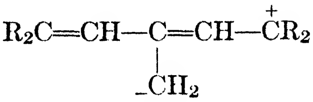
It is desirable also to attempt to draw a second conclusion which will explain why the observed color deepening occurs. Lewis has proposed such an explanation. He assumes that the oscillations responsible for the fundamental absorption band must be in one direction only. Thus in formula VII the positive charge oscillates between all three nitrogen atoms. If this oscillation is only effective in color production when it traverses the horizontal path (*a* to *b*), then we may say that only two-thirds of a charge contributes to color production. In VIII, however, since the charge cannot be effectively relayed to *c*, we may say that a whole charge oscillates horizontally. Thus, according to the principles already established, the effective mass of the oscillator in the horizontal resonance path is greater in VIII than in VII and the color should be deeper in VIII. It is. Much the same argument applies to X and XI. In IX, since positions *a* and *b* are equivalent to each other but not to *c*, the contribution of *c* is diminished and the effective mass of the oscillator transferring electrical charge from *a* to *b* is greater. This means color deepening.

Lewis expresses the principle involved above as follows: "When the color of a substance is associated with an oscillation along a certain path in the molecule, and when it is due to an excess charge (positive or negative) which may be moved toward one or the other ends of this path, then the frequency of absorption will be increased by any influence which diminishes the amount of that charge and decreased by any influence that makes this charge larger." This, then, is the "second restriction" that we must place on the relationship between resonance and color production.

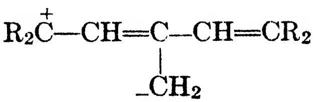
The Lewis theory finds an interesting application in crossed conjugation. In substance XII we would expect a limited resonance to which two alternative paths, *a*-*b* and *a*-*c*, contribute; yet the substance absorbs at a much lower frequency than a straight chain triene. When it is


$R_2C\overset{b}{=}CH{-}\underset{\underset{CH_2}{a\|}}{C}{-}CH\overset{c}{=}CR_2$

XII


$R_2C{=}CH{-}\underset{\underset{{}_{-}CH_2}{|}}{C}{=}CH{-}\overset{+}{C}R_2$

XIII


$R_2\overset{+}{C}{-}CH{=}\underset{\underset{{}_{-}CH_2}{|}}{C}{-}CH{=}CR_2$

XIV

realized, however, that the opening of bond *a* forces a positive charge into the horizontal portion of the molecule which results in resonance between XIII and XIV, we see why the absorbed frequency is so low. In substances of the phorone type, in which the central double bond goes to O instead of to CH_2, the strain is greater and a larger positive charge is forced into the rest of the molecule. The absorption bands extend into the visible. According to the theory we should expect greater strain and deeper color if C=S replaces C=O. This has been found to be the case in substances of the type $(Me_2N \cdot C_6H_4)_2C=X$, where X is CH_2, NH, O, or S.[93] The bathochromic effect increases in this order.

Lewis suggests that the color of the indigoid dyes may be explained on this same basis, the carbonyl group furnishing a positive charge to the resonance system.

The color theory we have been discussing obviously applies to molecules containing only paired electrons. It has long been recognized[94] that, except in nitric oxide, the presence of odd electrons in a molecule also produces color. For further remarks on this subject the reader is referred to Lewis's paper.

Summary of Basic Principles

In the previous chapter an attempt was made to formulate a set of working rules (the "basic principles") which could readily be used by organic chemists in solving practical problems. It was hoped that these rules would augment and to a certain extent replace the empirical, nebulous, and largely unformulated principles which organic chemists customarily use in the solution of their problems. At the end of this chapter it therefore once again becomes of interest to attempt a formulation of those additional basic principles which are of general application and which have emerged from our study of chemical physics.

The basic principle of resonance has already been given in **P 10** of the previous chapter. Also certain deductions concerning the magnitude of resonance may be drawn from **P 3.** The following principles may be added.

P 11. If resonance occurs in any molecular structure, that structure is more stable than any other closely related structure in which resonance is either less or absent.

P 12. Appreciable resonance only occurs between contributing structures having nearly the same energy. Thus resonance reaches a maximum when the contributing forms are identical.

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[93] Burawoy, *Ber.*, **63**, 3155 (1930).

[94] G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

P 13. Other things being equal, the amount of resonance increases with the number of contributing forms.

P 14. Each contributing form must be represented by the same geometrical arrangement of the atomic nuclei and the same number of unpaired electrons.

P 15. With atoms arranged in a ring, only those valence bond structures for which the bonds do not cross need be considered as contributing to the resonance; all others can be represented as resonance combinations of these.

P 16. Unperturbed structures in which adjacent atoms have electrical charges of the same sign contribute much less to resonance than other structures.

P 17. Other things being equal, the most stable resonance form will have the greatest number of covalent bonds.

P 18. Other things being equal, the most stable resonance form will have a formal negative charge on the atom of highest electronegativity.

P 19. Other things being equal, molecules having the least "Baeyer strain" will be most stable.

P 20. An increase in the ionic character of bonds increases the heat of formation of the molecule.

P 21. Coplanarity is demanded of valence bonds entering into conjugative resonance (mesomerism) with each other.

P 22. Carbon-to-hydrogen bonds may enter into hyperconjugative resonance with suitably situated double or triple bonds (first order hyperconjugation) or with other suitably placed carbon to hydrogen bonds (second order hyperconjugation). Both orders of hyperconjugation show the customary effects of resonance, but these effects are stronger in first order hyperconjugation.*

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* Other bonds than C—H bonds may presumably act as donors to hyperconjugation, but probably the effect is strongest with C—H bonds.

CHAPTER VII

SOME CONTRIBUTIONS FROM THE FIELD OF KINETICS

Owing to the fact that relatively few reactions come to equilibrium, the problems of organic chemistry more frequently have their foundations in the field of kinetics than they do in thermodynamics. This is unfortunate since accidental traces of catalytic impurities, although they do not alter the equilibrium point, may completely obscure relationships sought for among reaction velocity data.

The manner in which the English school has qualitatively related reaction velocity to polarization, polarizability, and the electrophilic or nucleophilic properties of reagents has already been presented in detail. It will now be of interest to comb the field of kinetics in search of more exact knowledge with which to test the validity of the English concepts and, if possible, to extend or refine them. As a preliminary to this searching inquiry it will be well to review very briefly the fundamental concepts of the modern theory of reaction velocity.[1]

THE THEORY OF ACTIVATION

The Arrhenius Theory

It has long been known that in nonionic reacting systems in general the rate at which molecules react is less than the rate at which they collide. Arrhenius [2] explained this fact by postulating that molecules cannot react unless at the moment of collision they possess energy in excess of a critical value (E) in which case they are called "active molecules." Furthermore he considered that normal molecules, on the absorption of energy, become active and that a state of equilibrium exists between the normal and active molecules. This equilibrium, of course, should be in accord with the thermodynamic requirements of the van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{1}$$

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[1] (*a*) L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., 1932; (*b*) C. N. Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, Oxford University Press, 3rd ed., 1933; (*c*) E. A. Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, Oxford University Press, 1933.

[2] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

in which K is the equilibrium constant for the reaction

$$\text{normal molecules} \rightleftarrows \text{active molecules} \tag{2}$$

and $-\Delta H$ the accompanying heat of reaction. Since the process of activation is endothermic, an increase in temperature would increase the concentration of active molecules and the speed of the reaction would become greater.

Arrhenius related this concept of activation with an equation he had discovered empirically:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{3}$$

where k is the velocity constant and E a constant whose value is different for each reaction. The relation may be demonstrated as follows: If the speed of any reaction is proportional to the concentration of active molecules we may write $k = c\,[\text{act}]$. Furthermore, the equilibrium constant for Equation 2 is

$$K_{\text{act}} = \frac{[\text{act}]}{[\text{norm}]}$$

Combining these two equations and giving expression to the essentially constant concentration of normal molecules, we get:

$$K_{\text{act}} = \frac{k}{c\,[\text{norm}]} = \frac{k}{C'}$$

therefore

$$d \ln K_{\text{act}} = d \ln k \tag{4}$$

Substitution of $d \ln k$ for $d \ln K_{\text{act}}$ in Equation 1 gives

$$\frac{d \ln k}{dT} = \frac{\Delta H}{RT^2} \tag{5}$$

where ΔH is the heat absorbed in transforming one mole of reactants from the normal to the active condition. It is thus called the heat of activation. If we express it as E, Equations 4 and 5 are seen to be identical and the meaning of the Arrhenius constant becomes evident.

The Collision Theory

Added weight is given to the Arrhenius equation by its derivation from the Maxwell-Boltzmann law for the distribution of molecular speeds. From this law one may first derive an expression for calculating the ratio N_1/N, in which N is the total number of molecules and N_1 is the number of molecules possessing kinetic energies in excess of any given value E. The rigorous derivation made on the basis of a three-dimensional picture may be simplified by considering only two dimensions. This procedure yields the following equation, which is sufficiently accurate for most chemical purposes:

$$N_1/N = e^{-E/RT} \tag{6}$$

Here e is the base of the natural system of logarithms.

If now we let Z equal the number of molecules colliding per second and assume that each collision of activated molecules results in reaction, we get the equation

$$\text{No. of molecules reacting per sec} = Ze^{-E/RT} \qquad (7)^*$$

Since the value of Z is given by the equation

$$Z = \sqrt{2}\pi\sigma^2\bar{\mu}n^2$$

where σ is the molecular diameter, $\bar{\mu}$ the root mean square velocity, and n the number of molecules per cc; and, furthermore, since the variation of $\bar{\mu}$ with the temperature is slight in comparison with that of $e^{-E/RT}$, we may write

$$k = ce^{-E/RT}$$

where c is a constant. If we now take logarithms and differentiate, we get the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

Thus E of the Arrhenius equation is found to be related statistically with the minimum value of the kinetic energy possessed by an "active molecule."

Since E is the heat of activation and since ΔH in general is known to vary with the temperature, it is natural to suspect that E is not strictly a constant. Its variation is slight over the usual small temperature ranges investigated but it has been shown that, for reactions involving ions, E is definitely a function of the temperature.[3]

The nature of the activation process is a problem upon which a huge amount of effort has been expended. Only the high points can be considered here. According to the collision theory of activation, molecules

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[*] Equation 7 must be replaced by a more complex equation in cases where the molecules involve a number of degrees of freedom.

[3] (*a*) Trautz, *Z. anorg. allgem. Chem.*, **102,** 81 (1918); (*b*) Scheffer and Brandsma, *Rec. trav. chim.*, **45,** 522 (1926); (*c*) LaMer, *J. Chem. Phys.*, **1,** 289 (1933); (*d*) LaMer and Miller, *J. Am. Chem. Soc.*, **57,** 2674 (1935); (*e*) Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **164,** 295 (1938).

gain the energy necessary for activation by a process of collision which results in the distribution of molecular speeds according to the probability theory and leads to Equation 7. This equation, however, does not adequately represent the facts, especially for the reactions of more complex molecules, and must be rewritten as

$$k = PZ^{\circ}e^{-E/RT} \tag{8}$$

where Z° is the collision frequency at unit concentrations of all reactants and P is an empirical "probability factor" which measures the probability that activated collisions will result in reaction. It is a measure of conditions other than activated collision which must be fulfilled. It depends in part on the fact that larger molecules must be properly oriented at the moment of impact so that the atoms or groups about to react come into contact with each other. If the proper orientation is not achieved, no reaction occurs, even though the colliding molecules possess the necessary energy of activation. The factor P frequently lies between 1 and 0.1, but in some cases it has been found[4] to be as small as 10^{-8}.

The intramolecular mechanics of the activation process is of particular interest. It is well established that the kinetic energy of molecules is distributed between their various degrees of freedom, which may be classified as translational, rotational, and vibrational. Most diatomic molecules do not show any vibration at ordinary temperatures, but iodine, in which the interatomic constraint is small, is an exception. Vibration is to be expected in more complex molecules. It is therefore of interest to inquire whether, in bimolecular reactions, the activation energy is to be considered as translational, vibrational, or rotational. It is also a matter of interest to ascertain whether the energy of each of a pair of colliding molecules must be greater than a certain critical value or whether it is sufficient that the sum of these energies exceed a critical value. It has been shown that:[5] (1) If the force of impact between two molecules is responsible for activation, then only the "head-on" components of the velocities will be effective. Thus only one degree of freedom will be involved and it can be shown that the requirements of Equation 8 are met if the sum of the two individual energies is equal to E. (2) The requirements are met equally well if the energy is considered to be vibrational and independent critical values of the individual energies are demanded.

Actually, of course, the picture must be more complicated than either of these mechanism-models. When molecules collide there must be a redistribution of the total kinetic energy between all the degrees of

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[4] *(a)* Ref. 1*c*; *(b)* W. E. Vaughan, *J. Am. Chem. Soc.*, **55**, 4115 (1933).

[5] Ref. 1*b*, p. 123.

freedom of both molecules, in accordance with the principles of quantum mechanics.

A closely related question of importance is this: does activation infer dissociation of molecules into either atoms or ions? The answer is a qualified no, as far as gaseous reactions are concerned. While it is true that in some gaseous reactions, especially photochemical reactions, dissociation into neutral atoms occurs, it seems that in most thermal reactions the activation energy is less than the energy corresponding to the dissociation of the reacting molecules. In regard to ionization, Hinshelwood[6] concludes that in ordinary chemical reactions among gases it occurs only as an insignificant side reaction and not as an intermediate reaction.[7] He quotes the work of Brewer who found that on the average one pair of ions was formed for the reaction of about 10^{13} molecules in a number of gas reactions.

The answer to the same question as it relates to reactions taking place in solution is suggested by Hughes and Ingold.[8] Reactions of the type

$$AB \rightarrow A^+ + B^-$$

are highly endothermic in gases, as is evidenced by the fact that thermal ionization does not occur in gases at relatively high temperatures. But in solution, where ionization is common, the above reaction may be coupled with either or both of the following, where S represents a molecule of solvent.

$$A^+ + S \rightarrow SA^+$$

$$B^- + S \rightarrow SB^-$$

These solvolytic reactions, if they occur, are apt to be exothermic to a degree that more than counterbalances the improbability of occurrence of the first reaction. Hence ionization is by no means an improbable mode of activation when reactions occur in solution.

Little or no activation energy is required in reactions between single atoms. In fact we may go farther and state that usually no activation energy is required in any reaction that does not involve the rupture of valence bonds. Thus Lewis[9] has pointed out that reactions consisting solely of the union of an electron donor with an electron acceptor involve no activation energy. This fact is closely connected with the catalytic efficacy of such reactions (acid-base catalysis). Occasionally reactions are found which, although they involve the rupture of linkages, require no

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[6] Ref. 1*b*, p. 152.

[7] Olson and Voge, *J. Am. Chem. Soc.*, **56**, 1294 (1934).

[8] Hughes and Ingold, *J. Chem. Soc.*, 244 (1935).

[9] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

activation energy. This is true of the gaseous reaction $Na + Cl_2 \rightarrow NaCl + Cl$.[10]

Unimolecular Reactions

The aims of this monograph do not justify a discussion of unimolecular gas reactions. Suffice it to say that whereas in bimolecular reactions chemical change results upon the impact of suitably oriented active molecules, in unimolecular reactions the molecules (also activated by collision) have a definite lifetime during which the energy gained by impact is surging back and forth through the various internal degrees of freedom of the molecule in such a way as to produce a succession of stability maxima and minima. If a given active molecule undergoes collision before the stability minimum is reached, it will become deactivated; if the minimum is reached first, it will react.[11]

If unimolecular reactions can only occur among molecules in which the above-mentioned surge of energy is possible, it would be expected that complex molecules containing many degrees of freedom would most frequently decompose by a unimolecular mechanism. Such is, indeed, found to be the case.[12] Thus decompositions of HI, NO_2, and MeCHO are bimolecular, whereas N_2O_5, EtCHO, Et_2O, etc., are unimolecular. These, of course, represent the two extremes and reactions are known which are of a mixed type.

Activation in Displacement Reactions

It was stated above that many reactions are known in which the activation energy is less than the ionization energy or the energy necessary to dissociate the molecule into free radicals or neutral atoms. It is clear, then, that in such cases the activation process is not one of dissociation. The nature of the activation in such cases is pictured plausibly by a widely accepted theory based on an original suggestion by London [13] and later amplified by Polanyi.[14]

Polanyi [14c] restricts his considerations to the reaction type

$$A + BC \rightarrow AB + C \tag{9}$$

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[10] (*a*) Bentler and Polanyi, *Z. physik. Chem.*, **1B**, 3 (1928); (*b*) Bogdandy and Polanyi, *ibid.*, **1B**, 21 (1928); (*c*) Polanyi and Schay, *ibid.*, **1B**, 30 (1928); (*d*) Ootuka and Schay, *ibid.*, **1B**, 62, 68 (1928).

[11] (*a*) Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922); (*b*) Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); (*c*) Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

[12] Hinshelwood, *Proc. Roy. Soc.*, **113A**, 230 (1926); **114A**, 84 (1927).

[13] F. London, *Z. Elektrochem.*, **35**, 552 (1929).

[14] (*a*) Eyring and Polanyi, *Z. physik. Chem.*, **12**, 279 (1931); (*b*) Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 607 (1935); (*c*) M. G. Evans and Polanyi, *ibid.*, **34**, 11 (1938).

which is known as the "three center type" or "displacement reaction." Most organic reactions are of this type.

The mechanism by which a replacement reaction may occur without involving dissociation has been made clear as a result of the mathematical analysis made by the aforementioned scientists and can be pictured as follows: Consider in a reaction represented by Equation 9 that A is initially at a very great distance from BC. Under these circumstances A will make no contribution to the energy of the BC molecule, which may therefore be represented by its normal potential energy curve,

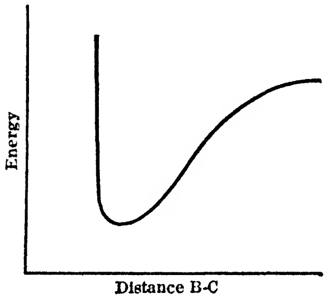


Fig. 1. Potential energy of the molecule BC as a function of internuclear distance.

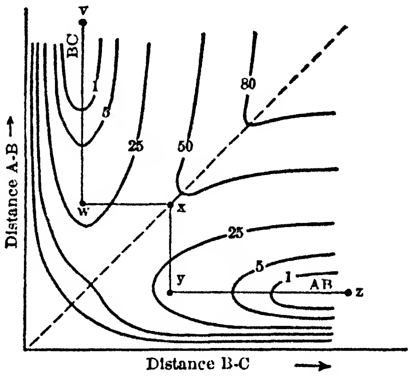


Fig. 2.[14c] Energy contour map for the reaction A + BC → AB + C.

Figure 1. If now A is allowed to approach BC it will be repelled by both B and C, especially by C with which it can form no stable compound. This repulsion increases the potential energy of BC. The minimum increase in energy attending the approach of A and B is that occurring when C is kept as far as possible away from A, i.e., when A, B, and C are in a straight line. Hence this linear configuration of the three nuclei is the only one that need be considered. A three-dimensional diagram is necessary to represent the energy changes taking place as A approaches B, and C recedes. The three variables are the internuclear distances A—B and B—C and the potential energy *E*. If the values of *E* are taken on the vertical axis, we may represent the three-dimensional diagram by an aerial view or contour map (Fig. 2) in which the lines join points for which *E* has a constant value. The numbers associated with the curves are values of *E*. This diagram represents the simplest case possible, viz., the one where A and C are identical from an energy point of view, but the essential relationships are no different in the cases where A and C are different.

Let us now consider Figure 2 in detail. The region marked BC is "a valley" representing the molecule BC. As A approaches B (the distance BC remaining constant) the south side of the valley rises to successively higher altitudes; or, if we keep the distance AB constant and increase the separation of B and C, the east side of the valley gets higher. This last situation is also represented in Figure 1, from which we can incidentally see that at the far eastern edge of the valley (in the neighborhood of $E = 80$) we reach a plateau extending eastward. The set of curves around the region AB represents the reverse of Reaction 9, i.e., the case where C approaches AB. The surfaces of the two valleys intersect along the diagonal dotted line on which the distances AB and BC are equal. If now a vertical plane is erected along the diagonal, it will cut the intersection of the two surfaces in a curve represented in Figure 3. From the fact that the minimum of this curve comes at a value of E slightly less than 50, it is readily seen that this represents a pass between the two valleys which is considerably higher than the bottoms of the valleys (representing the molecules in their normal states) and considerably lower than the plateau (representing complete dissociation).

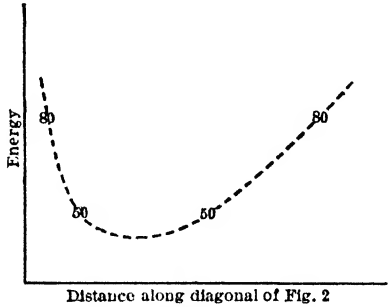


Fig. 3.[11c] Elevation of energy pass between the BC and AB valleys.

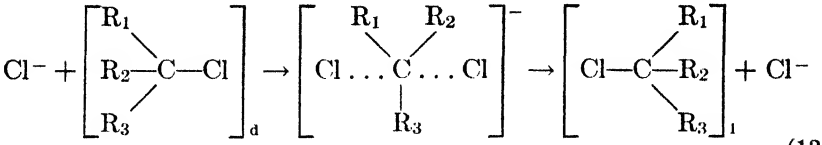
Thus it is seen from considerations of potential energy relationships that as A approaches BC, C receded from B until a condition is reached in which the distances AB and BC are equal. This represents a "transition state" in which neither molecule AB nor BC exists independently, but in which A, B, and C are welded together into an activated complex —"activated" because an amount of energy equal to the height of the pass had to enter the system to get it into that condition. From this activated condition the system can proceed in either direction, producing A + BC or AB + C. Thus the conversion of A + BC into AB + C can take place without ever supplying enough energy to the system to cause dissociation of BC.

The following are examples of the displacement reaction. In each case the intermediate form represents the transition state.

$$OH^- + RI \rightarrow [HO \ldots R \ldots I]^- \rightarrow HOR + I^- \qquad (10)$$

$$CH_3Cl + Na \rightarrow CH_3 \ldots Cl \ldots Na \rightarrow \cdot CH_3 + NaCl \qquad (11)$$

$$H_2O + HOAc \rightarrow H_2O \ldots H \ldots OAc \rightarrow H_3O^+ + OAc^- \qquad (12)$$



(13)

Hammett[15] points out that many reactions which do not appear at first thought to be displacement reactions have been shown by kinetic investigations to involve intermediate steps of this type. "The prevalence of this kind of reaction can mean only that it encounters less resistance than alternative reaction paths."

The Transition State Theory

The picture of the transition state which has just been drawn forms the basis for a theory of chemical activation known as the transition state theory, or the theory of absolute reaction rates.[16] In contrast to the collision theory of activation, which associates activation solely with the kinetic energy of molecules, the transition state theory focuses its attention on the thermodynamic probability of molecules entering the transition state. This leads naturally to the calculation of the free energy of activation ($\Delta F^{\ddagger}$), which is related to the heat of activation ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$) by the well-known thermodynamic equation *

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{14}$$

These two theories may also be contrasted from another point of view. The collision theory, although it only considers the probability of reaction from the standpoint of molecular kinetic energies, by no means insists that other factors fail to contribute to the probability of reaction. But it evades the problem of calculating these other influences by correcting for their omission empirically, i.e., the probability factor P is introduced. Now entropy is itself a measure of probability, but it involves all possible factors without attempting to analyze them. This suggests that there should be a relationship between P and $\Delta S^{\ddagger}$. Such a relationship can be derived mathematically from the transition state theory. It is

$$\Delta S^{\ddagger}{}_{a} - \Delta S^{\ddagger}{}_{b} = R \ln \left[P_a Z_a / P_b Z_b\right] \tag{15}$$

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[15] Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., 1940, p. 131.

[16] (*a*) Pelzer and Wigner, *Z. physik. Chem.*, **B15**, 445 (1932); (*b*) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); (*c*) Evans and Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); (*d*) Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935); (*e*) Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., 1941.

* The symbol ‡ refers to the activation process where all substances involved are in their standard thermodynamic states.

in which the subscripts a and b refer to two different reactions which are being compared.

The term $\Delta F^\ddagger$ measures the work (i.e., "useful work") of reversible transformation of the reactants into the transition state. It can be shown to be related to the velocity constant by the following procedure.

A fundamental equation of the transition state theory is:

$$k = \kappa K^\ddagger \boldsymbol{k}T/h \tag{16}$$

in which $K^\ddagger$ is the equilibrium constant expressed in terms of concentrations rather than activities, $\boldsymbol{k}$ is the Boltzmann constant, h is Planck's constant, and κ is the "transmission coefficient," which represents the probability of the activated complex forming the reaction products after crossing the energy barrier instead of regenerating the initial reactants. The value of κ is frequently close to unity, and it is therefore customary to neglect it. The following well-known thermodynamic equation is considered to apply to the reaction in which the reacting substances pass into the transition state.

$$-\Delta F^\ddagger = RT \ln K^\ddagger \tag{17}$$

Solving for K we get

$$K^\ddagger = e^{-\Delta F^\ddagger/RT}$$

Substitution of this value of K into Equation 16 gives

$$k = \frac{\kappa \boldsymbol{k}T}{h} \cdot e^{-\Delta F^\ddagger/RT} \tag{18}$$

This equation shows that the velocity constant is a function of the work $(-\Delta F^\ddagger)$ necessary to get the reactants into the transition state. The equation applies to reactions of any order in any phase provided that the slow process is the surmounting of a potential energy barrier. In conjunction with Equation 14 it also emphasizes that the speed of reaction depends not on the heat of activation alone but also on the entropy of activation.

ENGLISH ELECTRONIC THEORY FROM VIEWPOINT OF MODERN KINETICS

The foregoing brief review of certain developments in the field of chemical kinetics is adequate to assess the fundamental soundness of the English electronic theory in so far as it relates to reaction velocity. A fundamental assumption of the English theory is this: if electrons are released by a substituent to the reactive point of a molecule, the reaction rate is increased if the attacking reagent is electrophilic and decreased if it is nucleophilic. This hypothesis seems reasonable because of the intuitive conviction that a reaction involving the donation of electrons to an attacking molecule must become "easier" as the *work* of removal of those electrons becomes less—and "easier" was taken to mean faster. However, it was by no means evident from the physical chemistry of 10 years ago that there is any necessary connection between reaction velocity and thermodynamic work terms of any sort. In fact it was repeatedly asserted that there could be no relation between the equilibrium constant (a work term) and the velocity constant of a reaction since

$$K = k_{\text{left}}/k_{\text{right}} \tag{19}$$

and hence the individual values of the velocity constants could be large or small and yet yield the same ratio. However, the transition state theory has shown plainly (Equation 18) that there is a relationship between the over-all rate constant and the work necessary to get the reacting system into the transition state.

Factors Contributing to Reaction Velocity

It has already been seen from Equation 8, $k = PZ°e^{-E/RT}$, that the rate of a reaction at a given temperature depends on three different factors: P, $Z°$, and E. Although the value of $Z°$ changes somewhat with the size of the molecule, its order of magnitude does not vary; hence as a first approximation, differences in reaction velocity may be said to depend on two factors, P and E. This naturally suggests that substitution might affect these two factors differently and that it might be worth while to attack the electronic theory of reaction rates by considering these two factors separately.[17, 18]

Equation 8 may be converted into the following logarithmic form:

$$\ln k = \ln PZ° - \frac{E}{RT} \tag{20}$$

This equation may also be obtained by integration of the Arrhenius Equation 3 if we identify the integration constant with ln PZ. From Equation 20 it is evident that a plot of log k against E at constant temperature can result in a straight line only if $PZ°$ is constant, in which case the slope of the line is $-2.303\ RT$. It is found on making such plots from experimental data that many different series of reactions yield approximately straight lines having the theoretical slope. In this

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[17] Ingold and Nathan, *J. Chem. Soc.*, 222 (1936).

[18] The PZ term is called the "aktionskonstante" by W. Huckel, *Ber.*, **61**, 1517 (1928).

manner it has been shown that the introduction of substituents does not alter the value of PZ° (and hence of P) in the following series: halogenation of phenyl and tolyl ethers,[19] benzoylation of amines,[20] alkaline hydrolysis of benzoic esters,[21] alcoholysis of triarylmethyl chlorides,[22] reaction between substituted dimethylanilines and trinitroanisole,[23] the hydrion catalyzed esterification of aromatic acids with cyclohexanol (slightly doubtful),[24] and the reaction between substituted dimethylanilines and methyl iodide in nitrobenzene solutions.[25] In the following series P tends to increase as E increases: the acid hydrolysis of benzoic esters,[26] the alcoholysis of acyl chlorides,[27] the hydrolysis of aryl sulfuric acids,[28] and the bromination of acetophenones.[29] In these cases the variation of P is never large enough to outweigh changes in E, and Hinshelwood concludes that the changes in reactivity which result from electronic displacements caused by substituents are due primarily to changes in the activation energy.[19, 30] Although this may be a fairly reliable working rule, exceptions to it are known. Thus the sequence of compounds obtained by the comparison of velocity constants is not the same as that obtained from activation energies in the reaction of sodium iodide with substituted dibromides [31] and in the hydrion catalyzed esterification of substituted benzoic acids with methanol.[32]

It has further been demonstrated by Bradfield and Jones [19] in their experiments on the halogenation of aromatic ethers that the total effect of two substituents on E "may be expressed as the sum of the characteristic individual contributions of the groups attached to the benzene nucleus." They encountered an exception to the rule, however, in comparing phenyl and tolyl ethers.[19b] In view of the well-known interactions of groups one might be inclined to doubt the general validity of their rule, but the matter must be decided by further experimentation.

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[19] (*a*) Bradfield and Jones, *J. Chem. Soc.*, 1006 (1928); 2903 (1931); (*b*) B. Spencer and J. Spencer, *ibid.*, 2907 (1931).

[20] Williams and Hinshelwood, *ibid.*, 1079 (1934).

[21] (*a*) Evans, Gordon, and Watson, *ibid.*, 1430 (1937); (*b*) Newling and Hinshelwood, *ibid.*, 1357 (1936).

[22] Nixon and Branch, *J. Am. Chem. Soc.*, **58**, 492 (1936).

[23] Hertel and Dressel, *Z. physik. Chem.*, **B29**, 178 (1935).

[24] Hartman, Storms, and Gassman, *J. Am. Chem. Soc.*, **61**, 2167 (1939).

[25] Laidler, *J. Chem. Soc.*, 1786 (1938).

[26] Timm and Hinshelwood, *ibid.*, 862 (1938).

[27] Branch and Nixon, *J. Am. Chem. Soc.*, **58**, 2499 (1936).

[28] Burkhardt, Horrex, and Jenkins, *J. Chem. Soc.*, 1649 (1936).

[29] Evans, Morgan, and Watson, *ibid.*, **17**, 1167 (1935).

[30] Hinshelwood, Laidler, and Timm, *ibid.*, 848 (1938).

[31] Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937).

[32] Hartman and Borders, *J. Am. Chem. Soc.*, **59**, 2107 (1937).

Contributions from the Transition State Theory

It has recently been emphasized in an important paper by Hinshelwood, Laidler, and Timm[80] that the problem of the influence of substituents on the rates of organic reactions can be attacked from the standpoint of the transition state theory with highly gratifying results. They based their discussion largely on the principles set forth by Evans and Polanyi.[33]

For a working model they chose the typical displacement reaction: $A + BC \rightarrow AB + C$, which can be broken up into four steps involving four energy factors ($E_1 \ldots E_4$) as follows, using Figure 2 and following the line V, W, X, Y, Z.

Step 1 (V to W): $\mathrm{A}\overset{\infty}{\ldots}\mathrm{B}\overset{r_1}{-}\mathrm{C} \rightarrow \mathrm{A}\overset{r_a}{\ldots}\mathrm{B}\overset{r_1}{-}\mathrm{C}$

Step 2 (W to X): $\mathrm{A}\overset{r_a}{\ldots}\mathrm{B}\overset{r_1}{-}\mathrm{C} \rightarrow \mathrm{A}\overset{r_a}{\ldots}\mathrm{B}\overset{r_c}{\ldots}\mathrm{C}$ (transition state)

Step 3 (X to Y): $\mathrm{A}\overset{r_a}{\ldots}\mathrm{B}\overset{r_c}{\ldots}\mathrm{C} \rightarrow \mathrm{A}\overset{r_2}{-}\mathrm{B}\overset{r_c}{\ldots}\mathrm{C}$

Step 4 (Y to Z): $\mathrm{A}\overset{r_2}{-}\mathrm{B}\overset{r_c}{\ldots}\mathrm{C} \rightarrow \mathrm{A}\overset{r_2}{-}\mathrm{B}\overset{\infty}{\ldots}\mathrm{C}$

It is convenient for certain purposes to measure the four energy factors in terms of bond energies and repulsion energies. Thus E_2 and E_3 are functions of the bond energies of BC and AB, respectively, whereas E_1 and E_4 are taken respectively as the repulsion energies of A for BC and AB for C, since two neutral atoms which are not forming a bond repel each other.

Since the transition state is reached at the end of the second step, it is apparent that

$$E = E_1 + E_2 \tag{21}$$

This equation should not be interpreted to mean that E_3 and E_4 are without effect on the activation energy, since all four energy factors are not independent variables. It must be remembered that the height of the "pass" (the transition state) depends on where one valley intersects the other and hence depends on each valley. Evans and Polanyi explain the relationships as follows: "One might say that the bond to be formed begins to pull at a stage where the original binding is not yet broken." They incidentally point out that, if the activation process consists in complete dissociation of BC, the activation energy is merely the energy of dissociation of BC.

The dependency of E on the four energy factors may be shown neatly as follows[30] by the use of Figure 4. In this figure curve I is a normal attraction curve for BC under the influence of the repulsive force of A.

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[33] Evans and Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

When A is removed to infinity, curve I becomes curve III, only part of which is shown. Curve II is the repulsive curve for AB and C (it may be visualized as the intersection of the west side of the AB valley shown in Figure 2 with a vertical plane parallel to the BC axis and passing through the bottom of the valley). The intersection of the two curves, slightly rounded off to allow for the effect of resonance between the two states (i.e., A + BC and AB + C) represents a condition where the two states have equal energies. This is the transition state, and E is the amount of energy necessary to carry the system into this state from its normal state. The latter is represented by the minimum of curve III.

We may now trace the influence of positive increments in each of the four energy factors on E (see Fig. 4).

E_1 would increase E by raising curve I without affecting curve III.

E_2 would increase E by lowering the minimum of III.

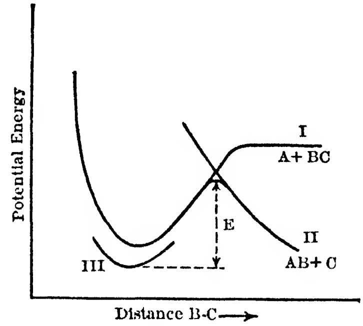


FIG. 4.[30]

E_3 would decrease E by lowering II because higher bond energy results in lower potential energy of the system AB + C.

E_4 would increase E since greater repulsion raises the potential energy of the system AB + C and hence raises II.

It is of interest to note that three of these energy factors raise and only one lowers the activation energy. Evans and Polanyi speak of the former as sources of inertia and the latter as chemical driving force.

The problem of the influence of substituents on reaction rates can be successfully attacked by considering the influence on the contributing energy factors if two simplifying assumptions are made:[30] (1) Changes in reactivity which result from electrostatic displacements caused by substituents are due primarily to changes in the activation energy (not in the PZ term). (2) The additional charges appearing on given atoms as a result of electron displacements introduce an extra electrostatic term into the energy of the bond between a given atom and its neighbor, and this term can be calculated as though it were entirely a classical coulombic one.

It is recognized, of course, that the main part of both the bond energy and the energy of repulsion are nonclassical; it is only the variations produced by substituents that are considered to be coulombic.

If now e_A, e_B, and e_C represent the effective charges on the atoms A, B, and C, respectively, if x represents interatomic distances in general, and if W represents the resonance contribution to any particular energy value, then we may write

$$E_1 = W_1 - \int_{\infty}^{r_a} \frac{e_A e_B}{x^2}\, dx = W_1 + \frac{e_A e_B}{r_a} \tag{22}$$

$$E_2 = W_2 - \int_{r_1}^{r_c} \frac{e_B e_C}{x^2}\, dx = W_2 - \frac{e_B e_C}{r_c}\left(\frac{r_c}{r_1} - 1\right) \tag{23}$$

Strictly speaking, the dielectric constant of the medium should be included in the coulombic terms, but inasmuch as it becomes small at small interatomic distances and is thus an unknown function of the distance x, it is convenient to consider it unity. Certainly very few of the interatomic lines of force pass through the medium when the atoms concerned are in the transition complex.

Equation 21 should be kept in mind. E_3 and E_4 contribute to the activation energy only as they affect r_a and r_c in Equations 22 and 23.

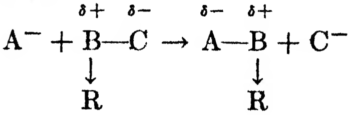
If now a hydrogen atom in the group B is considered to be substituted by R, the English theory maintains that the effective charge on B is changed. Let this change be represented by δe_B. Then the corresponding changes produced in E_1 and E_2 will be

$$\Delta E_1 = \frac{e_A \delta e_B}{r_a} \tag{24}$$

$$\Delta E_2 = \frac{-e_C \delta e_B}{r_c}\left(\frac{r_c}{r_1} - 1\right) \tag{25}$$

Note that the two effects operate in opposite directions.

Since the bond B—C is mainly covalent and will be disrupted by a slight extension, and since the extension experienced in passing into the transition state is considerably less than that corresponding to actual disruption, it is apparent that r_c/r_1 will not exceed unity very greatly and will probably be much less than 2. Furthermore r_a and r_c will be of the same order of magnitude. If, then, we may further assume that e_A and e_C are of the same order of magnitude, the conclusion follows that ΔE_1 will in general be greater than ΔE_2. This is equivalent to stating that in general a substituent increases E if it increases the repulsion between the attacking reagent and the seat of reaction in the molecule attacked, and vice versa. This statement is entirely equivalent to **P 2** of the original English theory. To make clear this important concordance, consider the following case:



$$\mathrm{A}^- + \underset{\substack{\downarrow\\ \mathrm{R}}}{\overset{\delta+}{\mathrm{B}}}—\overset{\delta-}{\mathrm{C}} \rightarrow \overset{\delta-}{\mathrm{A}}—\underset{\substack{\downarrow\\ \mathrm{R}}}{\overset{\delta+}{\mathrm{B}}} + \mathrm{C}^-$$

The electron-attracting substituent makes e_B more positive. Hence δe_B (Equation 24) is positive. However, e_A is negative. Thus ΔE_1 is negative, and since ΔE_2 contributes but little, ΔE is also negative. This corresponds to a faster reaction. From the standpoint of **P 2** the electron density at the seat of reaction is decreased by electron displacement toward R. This results in a faster reaction with the nucleophilic attacking reagent A^- since the electron-deficient B exerts a stronger pull on the electrons of the donor reagent.

It is gratifying to find that this rather elaborate analysis of the factors affecting the energy of activation leads to the same principle that the English theorists deduced from quite another point of view. It must not be forgotten, however, that this accord was achieved on the basis of four simplifying assumptions: (1) The reaction is of the displacement type. (2) The substituent influences the reaction rate by changing E much more than PZ. (3) The substituent influences the "energy factors" through alteration of coulombic forces only. (4) The effective charges on A and C are roughly equal.

Judging from the large number of cases in which the correct predictions are given by **P 2,** it must be that actual conditions are frequently in accord with these assumptions. The explanation of exceptions is accordingly to be sought in the nonfulfillment of these conditions, and the strength of the Hinshelwood viewpoint lies in its ability to bring many of these exceptions into line.

Of the four assumptions in question, Hinshelwood considers only variations in the last. If e_A should become sufficiently small, it is evident from Equations 24 and 25 that ΔE_2 will become the predominant factor. He thus arrives at a second conclusion:

P 23. The normal tendency for a substituent to alter the activation energy in accord with its effect on the attraction between the attacking reagent and the active center of a molecule will be weakened with the weakening or removal of any well-defined positive or negative center in the attacking reagent. When such a center has become weak enough there will be a reversal of the effect, and the influence of the substituent will then be determined by its effect on the bond energy.

As a corollary to this principle might be added the obvious fact that an increase in e_C will also increase the importance of the bond strength of B—C relative to the repulsion between A and BC.

In addition to the problem of the influence of substituents on the reaction rate, another related problem of equal importance exists, viz., the prediction of the change of rate produced by changing from one kind of an attacking reagent to another, i.e., by changing the functional group or the reacting atom of the attacking reagent in contrast to the changes discussed above, which involved the changes induced in a given functional group by various substituents. The two problems would be the same if it were not for the fact that W, which is of more importance than the coulombic term in Equation 23, may be very different for two different kinds of attacking molecules while it is assumed here to be the same for a given molecule and its substitution products.

Hinshelwood et al. argue as follows in relation to this problem: "Suppose we change from a given attacking reagent to another, the permanent repulsion (W_1) of which by BC is much greater. Activation being a compromise between the two processes of forcing up the reagent and stretching the bond, the most economical reaction route will now be that involving a greater stretching of BC and a less intimate approach of A." Thus r_c and r_a both become greater. "In the limit of extreme repulsion, the most economical mode of reaction would be by the complete disruption of BC. As we move in the direction of this limiting case the relative importance of the repulsion energy diminishes and that of the bond energy increases. This is reflected in an increase of $\Delta E_2/\Delta E_1$ as r_a and r_c increase, the charges being assumed to remain the same. Thus we arrive at another principle."

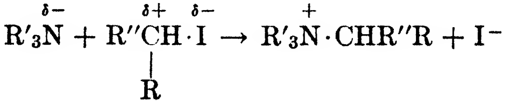
P 24. "If the same molecule is attacked by two different reagents whose charges do not differ greatly, then as the total activation energy increases, it is influenced by substituents in the attacked molecule less and less in the sense predicted from the change in the repulsion of the reagent and may, for very large activation energies, become subject to influences parallel with those of the substituent on bond strength."

A similar principle may be easily deduced where A is constant and the reacting atom or group in BC is changed.

These rules do not allow absolute predictions to be made but they do explain some experimentally observed trends. A few examples will suffice to show the value of these new principles.

The formation of quaternary ammonium salts may be represented as follows.

$$A + B\text{—}C \rightarrow A\text{—}B + C$$



$$\overset{\delta-}{R'_3N} + R''\underset{\displaystyle\mid \atop \displaystyle R}{C}\overset{\delta+}{H}\cdot\overset{\delta-}{I} \rightarrow R'_3\overset{+}{N}\cdot CHR''R + I^-$$

Electron release from R and R″ cause e_B to become smaller; therefore e_B decreases in the order $MeI > EtI > Pr^{\beta}I$, E_1 (repulsion) becomes greater in the order $MeI < EtI < Pr^{\beta}I$, and E becomes greater in the same order since it depends chiefly on E_1 (**P 2**). These are the experimentally observed facts.

If now B is kept constant and A is changed from pyridine (weak base) to triethyl amine (stronger base), then $-e_A$ becomes greater in the order $C_5H_5N < Et_3N$ since the stronger base has the greater electron density at the point of reaction (**P 2**), and E_1 and E therefore become less in the order $C_5H_5N > Et_3N$. This is in accord with the experimental facts.

If now Table I is examined it will be noticed that the increase in E produced by changing from methyl to isopropyl iodide is greater for triethyl amine than for pyridine. This is readily explained by reference to Equation 24: for a given value of δe_B, which is negative in this case, ΔE_1 becomes larger as e_A becomes more negative, as it does on passing from pyridine to triethylamine. Furthermore ΔE will vary in the same direction as ΔE_1 (**P 2**); this explains the observed trend.

TABLE I

Activation Energies in the Formation of Quaternary Ammonium Salts [30]

Solvent	$E_{pyr} - E_{Et_3N}$		$E_{PrI} - E_{MeI}$	
	MeI	$Pr^\beta I$	Et_3N	C_5H_5N
Benzene	4600	900	7400	3700
Nitrobenzene	3900	700	6300	3100

Likewise for a given change of base, ΔE is greater for methyl iodide than for isopropyl iodide since $+e_B$ is larger for methyl iodide.

These considerations make it clear that the formation of quaternary ammonium salts may be placed in that larger class of reactions in which E depends largely on repulsion energy (E_1) and only slightly on bond energy (E_2). In this class also may be placed the benzoylation of amines,[30] the acid and alkaline hydrolysis of benzoic esters,[30] and the acid or base catalyzed prototropic changes.[34]

A comparison of the alcoholysis of acyl chlorides [27] with the alcoholysis of triarylmethyl chlorides in ether-alcohol solution [22] is offered by Hinshelwood et al.[30] as an illustration of the application of **P 23**, although at first sight they appear to be four-center reactions. It has already been remarked, however, that many complex reactions seem to function as three-center reactions as far as the activation process is concerned. It is by no means impossible that the three-center character of these particu-

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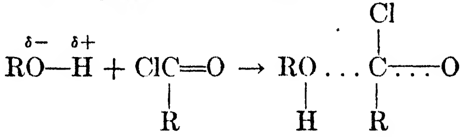
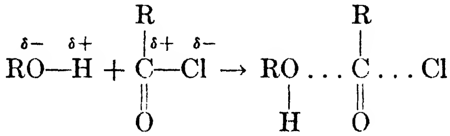
[34] (*a*) Ref. 29; (*b*) Shoppee, *J. Chem. Soc.*, 1117 (1933).

lar reactions is to be explained on the basis of some such formulation of the rate-controlling step as the following:



$$\overset{\delta-}{\mathrm{RO}}-\overset{\delta+}{\mathrm{H}} + \mathrm{Cl}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}{=}\mathrm{O} \rightarrow \underset{\mathrm{H}}{\underset{|}{\mathrm{RO}}}\ldots\overset{\mathrm{Cl}}{\overset{|}{\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}}}\cdots\mathrm{O}$$

or



$$\overset{\delta-}{\mathrm{RO}}-\overset{\delta+}{\mathrm{H}} + \overset{\mathrm{R}}{\overset{|}{\underset{\mathrm{O}}{\underset{\|}{\overset{\delta+}{\mathrm{C}}}}}}-\overset{\delta-}{\mathrm{Cl}} \rightarrow \underset{\mathrm{H}}{\underset{|}{\mathrm{RO}}}\ldots\overset{\mathrm{R}}{\overset{|}{\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}}}\ldots\mathrm{Cl}$$

The experimental values are given in Table II. It is seen in benzoyl chlorides that the introduction of negative groups decreases the activation energy, as would be expected if the repulsive term (E_1) were predominant. But just the reverse effect is found with the triarylmethyl chlorides, indicating that the C—Cl bond strength is the predominant factor. Hinshelwood's interpretation of these facts starts with a recognition that e_B would be smaller in the triarylmethyl halides than in the benzoyl halides, since in the latter case both Cl and O are attracting electrons away from B. Thus in the latter case there is a more powerful attraction of the alcohol molecule, and in the transition state there would be a relatively close approach and relatively smaller bond stretching, resulting in the greater importance of the repulsion term. In triarylmethyl halides the reverse situation would occur because of the small charge on B, and the bond strength would be the preponderant factor. Thus again the trends observed line up with the theory.

TABLE II

ACTIVATION ENERGIES FOR THE ALCOHOLYSIS OF SOME ORGANIC HALIDES [36]

	(cal)
p-Nitrobenzoyl chloride	11,100
p-Chlorobenzoyl chloride	13,850
Benzoyl chloride	14,400
p-Methoxybenzoyl chloride	18,650
Diphenyl-*p*-tolylmethyl chloride	12,450
Triphenylmethyl chloride	13,420
p-Chlorotriphenylmethyl chloride	13,480
p-Nitrophenylmethyl chloride	16,710

The Importance of the Probability (or Entropy) Factor

Hinshelwood's simplified treatment of reaction velocity was based on the four assumptions given on page 203. The first and fourth of these assumptions have already been discussed with the result that it was found necessary to expand **P 2** of the older theory. This led to **P 23** and **P 24.** Let us now further our avowed intention of extending or refining the older theory by studying the third assumption and hence finding out to what extent and under what conditions the reaction velocity depends primarily on the activation energy and only secondarily on the *PZ* factor.

In very many cases substitution or a change of solvent exerts a negligible influence on the *PZ* factor of the Arrhenius equation while altering *E* significantly, but only too frequently cases are encountered in which changes in *PZ* are definitely preponderant. Thus when the solvent used in the hydrolysis of *tert.*-butyl bromide is changed from 80% ethanol to 95% acetone,[35] *E* changes insignificantly while *PZ* changes from 2.0×10^{13} to 9.2×10^{10}. Likewise the velocity differences observed between the hydrolyses of the different ethyl halides appear to be mainly due to changes in *PZ*.[36] In other cases already mentioned changes in the *PZ* factor, although not predominant, are by no means negligible.

Grant and Hinshelwood [37] have pointed out that reactions between organic molecules and ions usually give *P* a value close to unity. In such cases the value of *PZ* would not be expected to change much with substitution, since usually a substituent would not alter the collision frequency (*Z*) profoundly. Unfortunately this rule encounters frequent exceptions; e.g., the reaction of iodide ions with aliphatic dibromides,[38] the hydrolysis of esters [37] and *tert.*-butyl halides [35] by hydroxyl ions, the hydrogen ion catalyzed esterification of benzoic acids,[39] and the hydrogen ion catalyzed bromination of acetophenones.[29] It may well be that some reactions which appear *prima facie* to involve ions as reactants may be found to have quite other mechanisms; but if this is true in many cases the rule will be of little practical use.

When a reaction is varied only by the introduction of a substituent, there is some tendency for the velocity of the reaction to be governed largely by changes in *E*. On the other hand, the *PZ* factor is apt to be predominant when the solvent is varied, when the nature of the catalyst is changed, or when the nature of the reaction of a given substance is changed completely, as where an alkyl halide is hydrolyzed or converted into a quaternary ammonium salt.[40]

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[35] Cooper and Hughes, *J. Chem. Soc.*, 1183 (1937).

[36] Hughes and Shapiro, *ibid.*, 1177 (1937).

[37] Grant and Hinshelwood, *ibid.*, 258 (1933).

[38] Davis and Heggie, *J. Org. Chem.*, **2,** 470 (1937).

[39] Hartman and Borders, *J. Am. Chem. Soc.*, **59,** 2107 (1937).

[40] Hinshelwood, *Trans. Faraday Soc.*, **34,** 138 (1938).

It is also of no little practical value to know that in reactions involving the substitution of benzene in the *meta* and *para* positions, PZ is essentially constant.[40] Quite the contrary is true, however, of *ortho* substitutions in general.

These vague generalizations, although better than nothing, are highly inadequate. We must remember that reaction rates depend jointly on the $\Delta H^\ddagger$ (or E) and $\Delta S^\ddagger$ (or PZ) factors, and since the qualitative electronic theory of the English school has so far been able to deal only with the former factor, it is obviously a matter of great practical importance to develop a theory which will make possible the *a priori* estimation of the entropy terms. Only a crude beginning has been made in the solution of this problem. The remainder of this section will be devoted to a review of what little has been done in this direction.

Let us start by transferring our attention from problems of kinetics to those of ordinary thermodynamics. If we consider a system undergoing an isothermal change, we may properly say that the increase in entropy attending that change represents the increase in the randomness of the molecules; or, since energy becomes more unavailable by becoming more random, we may say that the capacity of the system for isothermally unavailable energy is increasing.[41] It follows that entropy is in a sense a measure of the freedom of a system—its freedom to move in a random fashion or to absorb more random kinetic energy. This suggests a close relationship between entropy and heat capacity; indeed thermodynamics makes the relationship clear by the well-known equation

$$S = \int_0^T C_P \, d \ln T \tag{26}$$

On the theoretical side it should be clear that the same considerations of degrees of freedom which are used to explain heat capacity must also serve to explain entropy. It follows that the introduction of new degrees of freedom or the lessening of forces constraining rotation and vibration should increase the entropy. For example, the transformation of a double bond into a single bond should result in an entropy increase because free rotation is possible only around the latter, and steric hindrance of free rotation around a single bond should decrease the entropy. Likewise, it seems to be a rather general rule that reactions like $2H_2 + O_2 \rightarrow 2H_2O$, in which more molecules are consumed than produced, are accompanied by an entropy decrease. This is due to the large decrease of translational freedom.

The problem of developing the theory of heat capacity to the point where an *a priori* estimation of entropy changes is possible is a difficult

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[41] Roseveare, *J. Chem. Education*, **15**, 214 (1938).

problem even when it involves stable molecules which can be thoroughly studied; but when it involves such a nebulous state of aggregation as the transition complex, with which we must deal if we are to make predictions of the entropy of activation, mere contemplation of the difficulties of the problem is staggering.

Since the entropy of activation seems to be so closely bound up with kinetic energy, and the activation energy is pictured (Fig. 4) as being a potential energy term, it will be worth our while to consider a little more thoroughly the relationships of potential and kinetic energies to chemical reactivity.

Potential energy is, by definition, that part of the total energy of a system which is due to forces "acting at a distance." It must, then, consist of the various attractive and repulsive forces outlined above in discussing the paper of Evans and Polanyi.[16c] It is evident that these forces, and hence the potential energy, will be profoundly altered by electronic displacements produced, e.g., by substitution. In addition to the potential energy, the molecular system also contains kinetic energy, compounded of translational, vibrational, and rotational energies. The kinetic energy of the system is a function of temperature, mass, and molecular rigidity, and therefore also of electronic displacements.

Hammett [15] discusses in considerable detail the general question of the relation of potential and kinetic energy terms to problems of equilibria and rates of reaction. He considers a reaction of the type: A $\rightleftarrows$ B, and shows how, using the Boltzmann distribution equation and the quantum theory, it is possible to develop the equations

$$\Delta F^\circ = F^\circ_B - F^\circ_A = \Delta E_P + \Delta E_Z - RT \ln (f_B/f_A) \qquad (27)$$

$$\Delta H = H_B - H_A = \Delta E_P + \Delta E_Z + RT^2 \frac{d \ln (f_B/f_A)}{dT} \qquad (28)$$

In these equations ΔE_P and ΔE_Z refer respectively to the changes in potential and kinetic energy per mole occurring when the molecules are all in their lowest quantum states and f is the so-called partition function which shows the distribution of energy between the various quantum states describing vibrational and rotational energies.

For our immediate purpose the importance of these equations lies in the fact that they show that ΔH and ΔF° (and hence K) depend in general both on kinetic and potential energy terms, and hence that even these thermodynamic functions are not simply related to electron displacements because of the presence of the kinetic energy terms. Furthermore, if we accept the transition state theory, there is an equilibrium between the reactants and the transition state and hence B in the above equation may be taken as the transition state and Equations 27 and 28 become

$$\Delta F^{\ddagger} = \Delta E^{\ddagger}{}_P + \Delta E^{\ddagger}{}_Z - RT \ln (f^{\ddagger}/f_A) \tag{29}$$

$$\Delta H^{\ddagger} = \Delta E^{\ddagger}{}_P + \Delta E^{\ddagger}{}_Z + RT^2 \frac{d \ln (f^{\ddagger}/f_A)}{dT} \tag{30}$$

Since $\Delta F^{\ddagger}$ determines the value of k and $\Delta H^{\ddagger} \sim E$, it is apparent that both activation energy and velocity constant share in the disturbing influence of the kinetic energy terms.

It thus becomes apparent that if the kinetic energy term is in general large enough roughly to equal or exceed the potential energy term, and if furthermore the value of this kinetic energy term is either more subject to mass or temperature effects than to electron displacement effects, or is influenced by electron displacement effects oppositely to ΔE_P, then we need expect no simple relation between equilibrium and reaction speeds on the one hand with electron displacement effects, bond energies, or dipole moments on the other. Such thoughts suggest the importance of attacking certain problems. However, pending the solution of these problems, it is of interest to note that there is one condition under which $\Delta F°$, ΔH, $\Delta F^{\ddagger}$, and $\Delta H^{\ddagger}$ depend on ΔE_P alone, viz., when the corresponding entropy change is zero. This conclusion may be deduced from the following considerations:[15] If $\Delta S° = 0$, then in view of the relationship

$$\Delta F = \Delta H - T\Delta S \tag{31}$$

it follows that $\Delta F = \Delta H$. Thus Equations 27 and 28 (or 29 and 30) may be equated and it follows that

$$-\ln (f_B/f_A) = T \frac{d \ln (f_B/f_A)}{dT}$$

This could only be true if

$$\ln (f_B/f_A) = 0 = \frac{d \ln (f_B/f_A)}{dT}$$

Thus $f_B/f_A = 1$ at all temperatures. This could be true only if the energy-level spacings of the reactants and products are identical, which in turn demands also that $\Delta E_Z = 0$. It then follows from Equations 27 and 28 that if $\Delta S = 0$,

$$\Delta H = \Delta F° = \Delta E_P \tag{32}$$

and from Equations 29 and 30 that, if $\Delta S^{\ddagger} = 0$,

$$\Delta H^{\ddagger} = \Delta F^{\ddagger} = \Delta E^{\ddagger}{}_P$$

It is of incidental interest that ΔE_P is temperature-independent.

If we wish to predict the effect of electron displacements on the rate of a reaction we become concerned with the difference in the activation energies for two reactions, *a* and *b*, which differ in regard to solvent or substituent. Equation 30 then becomes [15]

$$\Delta H^{\ddagger}_a - \Delta H^{\ddagger}_b = (\Delta E^{\ddagger}_{Pa} - \Delta E^{\ddagger}_{Pb}) + (\Delta E^{\ddagger}_{Za} - \Delta E^{\ddagger}_{Zb}) + RT^2 \frac{d}{dT}\left(\ln \frac{f^{\ddagger}_a f_b}{f^{\ddagger}_b f_a}\right) \tag{33}$$

If

$$\Delta F^{\ddagger}_a - \Delta F^{\ddagger}_b = \Delta H^{\ddagger}_a - \Delta H^{\ddagger}_b \tag{34}$$

then

$$\Delta S^{\ddagger}_a - \Delta S^{\ddagger}_b = 0 \tag{35}$$

Hammett points out that here, too, these conditions can only occur if the last term in Equation 33 becomes zero, and this implies a large probability that $\Delta E^{\ddagger}_{Za} - \Delta E^{\ddagger}_{Zb} = 0$. If this is so,

$$\Delta H^{\ddagger}_a - \Delta H^{\ddagger}_b = \Delta E^{\ddagger}_{Pa} - \Delta E^{\ddagger}_{Pb} \tag{36}$$

A convenient test for the actual existence, in any given case, of the condition expressed by Equation 35 is that the following relationship hold true:

$$\Delta S^{\ddagger}_a - \Delta S^{\ddagger}_b = 0 = \frac{d}{dT}\left(RT \ln \frac{k_a}{k_b}\right) \tag{37}$$

This equation follows readily by the combination of Equations 18 and 35 with the following equation, whose equivalent in terms of ordinary thermodynamic quantities is well known.

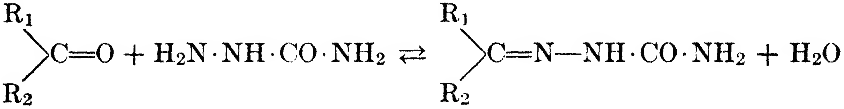
$$\Delta S^{\ddagger} = -\frac{d\Delta F^{\ddagger}}{dT} \tag{38}$$

It also follows from Equation 15 that if the entropy of activation is constant, then $P_aZ_a = P_bZ_b$. We thus finally arrive at the following important conclusion.

P 25. If the value of the *PZ* term (or $\Delta S^{\ddagger}$) for a given reaction is not altered by substitution or by a change of solvent then the activation energy and the velocity constant become functions of potential energy changes alone and, at constant temperature, the velocity constant is a function of the activation energy only (cf. Eq. 8).

The problem of the electronic interpretation of reaction rates thus becomes much simplified when *PZ* is constant or essentially constant, and it is only under this condition that we may with confidence apply those principles of the English theory which have to do with activation energy Incidentally, it should now be apparent that Hinshelwood et al. were justified in interpreting E in terms of potential energy alone, as was done in Figure 4, since they assumed the PZ term to be essentially constant.

Qualitatively, the influences which have just been set forth as regulating the entropy of activation are rather well illustrated in a recent paper by Price and Hammett.[42] A kinetic study was made of the well-known reaction of semicarbazone formation,



$$\underset{R_2}{\overset{R_1}{>}}C{=}O + H_2N\cdot NH\cdot CO\cdot NH_2 \rightleftarrows \underset{R_2}{\overset{R_1}{>}}C{=}N{-}NH\cdot CO\cdot NH_2 + H_2O$$

and its reverse, the hydrolysis. Their experimental results are listed in Tables III and IV. The subscript 0 refers to acetone, which was taken as a standard of comparison. If we apply our qualitative theory to the prediction of activation energies of semicarbazone formation we observe that the values given in Table III for the open chain compounds are not altogether what we would have predicted in view of the fact that the ketones exhibit electrophilic properties in carbonyl addition reactions and hence should experience an increase in $\Delta H^\ddagger$ when electron-releasing alkyl groups are substituted on the α-carbon atoms as well as when the

TABLE III [42]

Relative Entropies, Heats, and Free Energies of Activation for Semicarbazone Formation at 12.5° ($\Delta H^\ddagger_0 = 2000$ cal)

	$\Delta S^\ddagger - \Delta S^\ddagger_0$ (cal/deg)	$\Delta H^\ddagger - \Delta H^\ddagger_0$ (cal)	$\Delta F^\ddagger - \Delta F^\ddagger_0$ (cal)
Acetone	0.00	0	0
Diethyl ketone	−6.50	−600	1300
Pinacolone	−9.70	−200	2500
Cyclopentanone	3.30	2000	1100
Cyclohexanone	0.40	−900	−1100
Furfural	3.20	2100	1200
Acetophenone	−1.90	2600	3200

TABLE IV [42]

Relative Entropies, Heats, and Free Energies of Activation for Semicarbazone Hydrolysis at 12.5° ($\Delta H^\ddagger_0 = 1100$ cal)

	$\Delta S^\ddagger - \Delta S^\ddagger_0$ (cal/deg)	$\Delta H^\ddagger - \Delta H^\ddagger_0$ (cal)	$\Delta F^\ddagger - \Delta F^\ddagger_0$ (cal)
Acetone	0.00	0	0
Diethyl ketone	−8.70	−2500	0
Cyclopentanone	−3.20	600	1500
Cyclohexanone	−0.40	−900	−800

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[42] F. P. Price, Jr., and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).

carbonyl group enters into resonance with conjugated aromatic nuclei, as in furfural and acetophenone. That ring closure would have the effect of increasing $\Delta H^{\ddagger}$ in cyclopentanone and decreasing it in cyclohexanone we could hardly have predicted. Even more interesting is the fact that the values of $\Delta F^{\ddagger}$ (and hence of k) exhibit a decided lack of parallelism with those of $\Delta H^{\ddagger}$, a fact which is easily traced to the entropy terms, which are far from constant and, in fact, quite overpowering in their influence. Much the same may be said for the hydrolytic experiments (Table IV).

The entropy differences listed in Table III show a marked tendency to parallel the rigidity of the carbonyl compounds involved. The most rigid molecules must be cyclopentanone with its planar ring structure and slightly strained bond angles and furfural with its rigid ring and the partial double bond character of the link between the carbonyl group and the ring. These two substances show the highest values of $\Delta S^{\ddagger}$. In regard to the aliphatic compounds, it is also to be noted that as the ketones become more highly substituted with methyl groups and hence as more bonds are introduced, the activation entropies become successively lower. Since the latter group of molecules, owing to their many internal degrees of freedom, must have relatively higher entropies in their normal states, it suggests that the transition state in this particular reaction possesses a relatively rigid structure and that less constrained compounds undergo a larger increase in rigidity and therefore a larger decrease in entropy on entering the transition state than the more rigid compounds. The low entropy value for acetophenone is, however, surprising, since it would be expected to be a relatively rigid molecule in virtue of the partial double bond character of the link between the carbonyl and the phenyl groups.

In seeking an explanation as to why the compounds having the most degrees of freedom lose them to a greater extent on entering the transition state than do the more rigid compounds, Kirkwood[43] has pointed out that a charged body (the carbonyl group) immersed in a medium of high dielectric constant (the solvent) repels a body of low dielectric constant (methyl groups, etc.). If this influence causes the repulsion of the methyl groups in diethyl ketone and pinacolone to occur to such an extent in the transition state that they interfere with each other's free rotation, then the observed low entropies of activation are accounted for. Such an effect would be impossible with the cyclic compounds. One might add to Kirkwood's suggestion that since the reaction is acid catalyzed, the likelihood of a sizeable positive charge near the carbonyl group in the critical complex is fairly certain.

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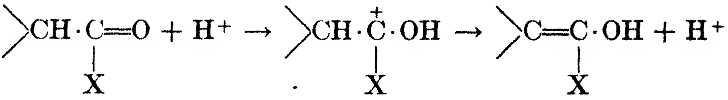
[43] Reported in Ref. 42.

Except for the conclusion that attempts to interpret the effects of structure on reactivity are apt to be dangerous if consideration is given to potential energy terms alone, the above discussion leaves us with no definitely established generalization. It strongly suggests, however, that there is a relationship between the entropy of activation and the rigidity of the reactant molecules. Among the factors which might contribute to rigidity is bond strength, and since the strength of bonds at reactive centers also helps determine the activation energy, we should be prepared to find at least a tendency for parallelism between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (or E and PZ). Such a tendency has, indeed, frequently been observed, especially where PZ changes significantly, but the conditions under which this occurs have not yet been fully worked out.[44] Fairclough and Hinshelwood[45] have suggested that the greater bond strength associated with the more rigid molecules is associated with a greater frequency of molecular vibration and therefore might result in decreasing the time necessary for the activated complex to complete its rearrangement. Under certain conditions this might well be reflected in a greater probability of reaction and hence P would increase with E.

Some substantiation is found for this point of view in studies on the rates of decarboxylation of carboxylic acids.[46] These decompositions are unimolecular and hence their rates are clearly dependent on intramolecular distribution of energy, according to the Lindemann theory. It is found that on passing from trichloro- to tribromoacetic acid the activation energy decreases by 12,500 cal and PZ is decreased more than a million times. Since the C—C bond in trichloroacetic acid is the stronger (the polarizability becomes less, owing to the constraining influence of the more electronegative chlorine atoms) it is supposed that it would have a greater activation energy and a greater frequency of vibration. The latter would result in a smaller time lag between activation and reaction and the probability (P) that an activated molecule will decompose would be enhanced.

Another explanation of the variation of the PZ term has been advanced by Evans, Morgan, and Watson[29] for a catalyzed reaction which takes place in several steps, e.g., the acid catalyzed bromination of substituted acetophenones. If in this case the rate-controlling enolization is considered to occur in two steps,



$$>\mathrm{CH}\cdot\underset{\overset{|}{\mathrm{X}}}{\mathrm{C}}{=}\mathrm{O} + \mathrm{H}^+ \rightarrow >\mathrm{CH}\cdot\underset{\overset{|}{\mathrm{X}}}{\overset{+}{\mathrm{C}}}\cdot\mathrm{OH} \rightarrow >\mathrm{C}{=}\underset{\overset{|}{\mathrm{X}}}{\mathrm{C}}\cdot\mathrm{OH} + \mathrm{H}^+$$

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[44] Raine and Hinshelwood, *Trans. Faraday Soc.*, **34**, 138 (1938).

[45] Fairclough and Hinshelwood, *J. Chem. Soc.*, 538, 1573 (1937).

[46] Fairclough, *ibid.*, 1186 (1938).

it is apparent that if X aids the addition of H^+ in the first step, it would impede its removal in the second. They show that the trend of the data away from a constant P factor can be interpreted on this basis. This work has been criticized by Ingold and Nathan,[17] who claim that the range of velocities covered was too small to justify the conclusions drawn.

Hammett [47] has warned that the supposed parallelism between E and PZ might erroneously appear to hold if the data used involved only small variations in k. This follows from Equation 20, from which it is apparent that if k were constant log PZ would necessarily be linear in E.

A discussion of the influence of the solvent on the PZ factor will be postponed until Chapter X.

A Further Contribution from the Transition State Theory

Recently Ri and Eyring [48] have shown that it is possible to calculate the rate of nitration of monosubstituted benzenes with fair precision by combining the English theory with the transition state theory and certain simplifying assumptions. The calculation makes use of dipole moment data and the rate constant for the nitration of unsubstituted benzene. Since this is the first successful attempt to put the English theory of reaction velocity on a quantitative basis, it merits detailed consideration.

Their initial assumption is much like that used in developing Equation 23, viz., that the *change* in $\Delta F^\ddagger$ of nitration produced by substitution may be considered as due entirely to coulombic factors, whereas the value of $\Delta F^\ddagger$ of nitraton for benzene itself is considered as being essentially nonclassical. Accordingly (see Eq. 23) the value of the activation free energy $\Delta F^\ddagger{}_s$ for the substituted compound becomes

$$\Delta F^\ddagger{}_s = \Delta F^\ddagger + \frac{\epsilon_y \epsilon_n N}{rD} \tag{39}$$

where $\Delta F^\ddagger$ refers to the unsubstituted benzene, N is Avogadro's number, and ϵ_y and ϵ_n are the charges on the reacting carbon atom and the attacking reagent, respectively. If this value of $\Delta F^\ddagger{}_s$ is substituted for $\Delta F^\ddagger$ in Equation 18, we get

$$k_y = \kappa \frac{kT}{h} e^{-[\Delta F^\ddagger + N\epsilon_y\epsilon_n/rD]/RT} \tag{40}$$

If k_H is the rate constant at a carbon atom of benzene (o, m, or p), it follows that

$$\frac{k_y}{k_H} = e^{-[\epsilon_y\epsilon_n/(rD)]/kT} \tag{41}$$

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[47] Ref. 15, p. 123.

[48] Ri and Eyring, *J. Chem. Phys.*, 8, 433 (1940).

The distance r_1 between the carbon atom and NO_2^+ in the transition state is taken as 1.6 A°. This value is taken as 10% larger than the normal distance, 1.46 A°, since calculations of potential surfaces for activated complexes indicate that the interatomic distances which are changing are often about 10% larger than the normal distances. The dielectric constant is taken as unity, for the reasons discussed in relation to Equation 23.

In order to use Equation 41 it is necessary to evaluate ϵ_y and ϵ_n. The authors assume that the nitrating agent is ionized into a negative OH^- ion and a positive NO_2^+ ion, and hence take ϵ_n as equal to one elementary electrostatic charge, viz., 4.80×10^{-10} esu. The calculation of ϵ_y at the various positions in the benzene ring is made as follows: The charges on the carbon atoms of the ring are considered to be wholly due to the I_s and M effects, all polarizability influences being neglected. The I_s effect is considered, as a first approximation, to induce equal charges ϵ_i on the six carbon atoms of the benzene ring and a charge of $-6\epsilon_i$ on the substituent group X. The M effect is considered to contribute the charge ϵ_r to each *ortho* and *para* carbon atom. These charges are counterbalanced by two charges of $-\frac{3}{2}\epsilon_r$ each, located respectively on X and on the carbon atom attached to X. Accordingly, the charge distribution in the molecule can be represented by the following equations:

$$\begin{aligned}
&(a)\quad \epsilon_m = \epsilon_i \\
&(b)\quad \epsilon_p = \epsilon_o = \epsilon_m + \epsilon_r \\
&(c)\quad \epsilon_1 = \epsilon_m - \tfrac{3}{2}\epsilon_r = \epsilon_m - \tfrac{3}{2}(\epsilon_p - \epsilon_m) \\
&(d)\quad \epsilon_x = -6\epsilon_i - \tfrac{3}{2}\epsilon_r = -6\epsilon_m - \tfrac{3}{2}(\epsilon_p - \epsilon_m)
\end{aligned} \tag{42}$$

where ϵ_1 is the charge on the carbon atom attached to X.

If now it is assumed that the inductive part of the dipole moment of Ph—X is equal to the moment μ_{ali} of the compound Aliph—X, then, since the center of gravity of the six charges $6\epsilon_i$ is at the center of the hexagon and the distance from C_1 to the center is r_b and is equal to the bond length of C—C, it follows that

$$\mu_{\text{ali}} = -6\epsilon_m(r_b + r_x) \tag{43}$$

where r_x is the bond length of C—X. From this equation ϵ_m may be calculated. If furthermore $\mu_{\text{aro}} - \mu_{\text{ali}}$ is taken equal to the resonance part of μ_{aro}, it follows that

$$\mu_{\text{aro}} - \mu_{\text{ali}} = -\tfrac{3}{2}(\epsilon_p - \epsilon_m)(r_x + 2r_b) \tag{44}$$

from which ϵ_p, and hence ϵ_o, may be calculated. Finally, any one of the values of ϵ_p, ϵ_o, and ϵ_m may be substituted for ϵ_y in Equation 41 and the rate of nitration at any nuclear position may be calculated relative to the rate of nitration of benzene. Obviously this method can be used to calculate the fraction of nitration at each nuclear position. The authors show how this calculation may be refined to take into account the expected difference between ϵ_o and ϵ_p, using the Lapworth-Robinson theory[48a] of the *ortho-para* ratio. The results of their refined calculations are compared with the experimentally determined values in Table V, from which it is apparent that the theory is successful to a degree which is highly gratifying. Incidentally, these calculations form the best evidence yet adduced in favor of the English concept of the relation between electron density and reaction velocity (**P 2**), and it is particularly to be noted that it was not found necessary to assume the existence of a field effect.

TABLE V[48]

NITRATION OF MONOSUBSTITUTED BENZENES AT 25°

	Position	Calculated	Observed
Chlorobenzene	*o*	39.8%	31.0%
	m	0.2	....
	p	60.0	69.0
Bromobenzene	*o*	39.8	41.4
	m	0.2	....
	p	60.0	58.6
Iodobenzene	*o*	40.0	43.7
	m	0.2	...
	p	59.8	56.3
Nitrobenzene	*o*	0.7	7.9
	m	94.7	91.6
	p	4.6	0.5

The authors also have shown that esterification, hydrolysis, benzoylation, and quaternary salt formation may be treated in the same way from the study of side chain reactivities.

Recently Price[48b] has reviewed certain experimental evidence in which the electrostatic polarizing forces for a large variety of substituents are calculated from dipole moment data and interatomic distances. These calculations show a decided parallelism between the calculated electrostatic forces and the observed directive influences of the groups in question, strongly indicating that these forces are largely responsible for orientation, as Ri and Eyring assumed.

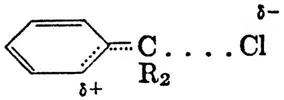
[48a] Chap. V, p. 102.

[48b] C. C. Price, *Chem. Rev.*, **29**, 37 (1941).

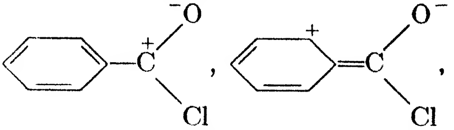
Resonance and Reactivity

If the postulated relationship between reactivity and the T effects of the English theory is combined with the quantum-mechanical concepts of stabilization by resonance and the dependence of resonance on the number of possible unperturbed forms, and if to this combination of ideas is added the concept of the transition state, we arrive at a rather satisfactory method of dealing with rate problems.

Nixon and Branch [22] have illustrated the application of such a method in the alcoholysis of triarylmethyl chlorides. Since this reaction involves the separation of a chloride ion and since the positive ion so produced would allow of more resonance forms (+$=CR_2$, etc.) than the initial chloride, it is apparent that if we consider the positive ion as the activated state, any influence which will aid resonance will increase the stability of the positive ion and hence decrease the work ($\Delta F^{\ddagger}$) necessary to get the system into the activated state. However, here as in other cases, our knowledge of the transition state theory does not permit us to envision the activated state as the free ion. Hence the following guess may be added to the exposition of Nixon and Branch to bring these different concepts into accord. Just as the approach of A to $B—C$ results in a condition which we may picture as $A \ldots B \ldots C$, so resonance might be considered to produce the following transition state:



The activation energy for the reaction of ethanol with diphenylmethyl chloride is much greater than with triphenylmethyl chloride. This is interpreted as due to the greater number of unperturbed forms made possible by the additional phenyl group, thus stabilizing the transition state of the triphenyl compound relative to that of the diphenyl compound. In general it would be expected that resonance, and hence reaction rate, would be increased by any continuation of the conjugate system of a phenyl group by unsaturated groups in the *ortho* or *para* positions or by atoms having unshared electrons. The reaction rate would also be increased by $+I$ groups because they would lessen the electronic constraints in the phenyl nuclei and hence aid the resonance. Groups having a $-I$ effect would have the opposite influence. The rates of alcoholysis of the substituted-triphenylmethyl chlorides are in essential agreement with these principles; they decrease in the order p-OMe > p-Me > H > p-F > p-I > p-Cl > p-Br > p-NO_2. It will be observed that the usual trouble with the order of the halogens among themselves is in evidence.

In the alcoholysis of benzoyl chloride[27] the situation in regard to resonance is reversed, since resonance is present in the initial compound,  etc., and presumably is destroyed when the addition complex is formed. Thus in this case groups that augment the resonance decrease the reaction rate. The success of this interpretation is indicated by the following comparison:

k (predicted): OMe < Me < H < Halogens < NO_2

k (found): OMe < Me < H < F < Cl < I < Br < NO_2

E (found): OMe > Me > F > H > Cl > Br = I > NO_2

In making the prediction it was assumed as usual that $-I > +M$ for the halogens and that it is impossible to predict with accuracy the way that these two effects will sum up for the individual halogens.

A Reinterpretation of Nucleophilic and Electrophilic Reactivity[49]

The Lapworth theory classifies reactive centers in molecules as nucleophilic or electrophilic, depending on their states of electron possession. Furthermore it postulates that these reactive centers manifest different tendencies to react, i.e., they possess different degrees of nucleophilic or electrophilic reactivity, which are measured by their "tendencies," respectively, to give up or take up electrons.

We might justly inquire whether these "tendencies" are to be judged by thermodynamic or kinetic criteria. Certainly they have never been quantitatively defined, and this difficulty is emphasized when one attempts to decide whether one center in a molecule is more electrophilic than another center is nucleophilic. Their qualitative method has been rather successful, however, and one is tempted to hope that it can lead the way to more quantitative formulations. With this hope in mind, let us attempt to analyze and reinterpret their method of measuring the above-mentioned "tendencies."

As a first approximation it is common practice to neglect polarizability effects and to judge nucleophilic reactivity by comparing the ionization constants of acids. Thus the CN^- ion is more nucleophilic than the chloride ion. This procedure really consists in selecting the hydrogen

[49] Remick, *J. Org. Chem.*, **7**, 534 (1942).

ion as an arbitrary standard in reference to which nucleophilic tendencies are measured by a thermodynamic criterion, viz., the ionization constant. The procedure of measuring electrophilic reactivity is not so well standardized. Sometimes it is measured in terms of reduction potentials, sometimes by electronegativity differences deduced from the periodic table, sometimes by observing the speed of reaction with a nucleophilic reagent, etc. The methods are obviously a hodge-podge of thermodynamics, kinetics, and general theory. One cannot help but notice, however, that thermodynamic relationships are very frequently used. Hence, if the theory is leading us anywhere it seems to be pointing out that the speed of the initial, presumably rate-controlling, step of a reaction is greater when the ΔF or ΔH of bond formation is less, and hence of several centers in one molecule, the first to react, statistically speaking, will be the one which liberates the most energy when it forms a bond with the attacking reagent. Since the attacking reagent has nucleophilic and electrophilic centers which may be varied from one extreme of reactivity to another, it is obvious that either center of the original molecule might be the more reactive, depending on the nature of the attacking reagent, and hence the hope of cataloguing each compound as to the amount and kind of its reactivity is a vain one. It would seem preferable to calculate the amount of energy which would be liberated with the formation of each bond in each conceivable reaction and judge the point of initial reaction (the rate-controlling step) and the speed in this manner.

Such a procedure would be only a first approximation, however, as polarizability factors are assumed to affect the velocity of reactions. Since these become effective by altering the electron density at the reactive center on demand of the attacking reagent and in proportion to its electrical field (a function of its dipole moment) it seems that their effect must be to increase the energy of the bond about to be formed. When bond formation is complete and the polarizability demand thus ceases to exist, the resultant relaxation will allow the bond energy to drop to its normal value. Thus the polarizability effects furnish energy to help the reaction over the familiar energy hump, or pass.

This is as far as the qualitative theory of the English school can lead us in our search for a reliable quantitative or semi-quantitative measure of electrophilic and nucleophilic reaction tendencies. It is significant, however, that it has led us right to the door of the transition state theory, and it is apparent that if we add to the qualitative picture just outlined the concept of quantum-mechanical interaction, by which the bond being formed can contribute energy to the bond being broken, we will have at our disposal a means of calculating which pair of centers, in a given pair of molecules, will react with each other. This amounts to an *a priori* determination of mechanism and classification according to types *A* and *B*. This being accomplished, we might then predict qualitatively the effect of substituents on the reaction without first establishing by experiment whether it falls in class *A* or *B*, as was previously necessary.

However, there are difficulties with this procedure. In the first place no adequate mathematical procedure has yet been devised by which polarizability effects may be taken into account in applying the equations of the transition state theory. Furthermore, the calculation of quantum-mechanical interaction is difficult. It would, therefore, seem preferable to refine the qualitative theory by making a semi-quantitative extension along the lines indicated above.

As a first step in this procedure we might clearly redefine certain terms. We may now say that a molecule exhibits nucleophilic properties in a given reaction if it contains an electron-rich center whose union with the attacking molecule would involve a smaller value of ΔF than any of its electron-poor centers. Moreover, if two such molecules are being compared in relation to their reaction with a given attacking reagent, then the one involving the smaller ΔF may be said to have the higher nucleophilic reactivity.

As a second step, let us consider the possibility of making some sort of rough calculations of the relative activation energies which would be involved when various alternative reaction centers interact. If the problem is simplified by considering only reactions which can be correctly formulated as follows:

$$A + B\text{—}C \rightleftarrows A \ldots B \ldots C \rightarrow A\text{—}B + C \tag{45}$$

and

$$D\text{—}E + F\text{—}G \rightleftarrows D \ldots E \ldots F \ldots G \rightarrow D + E\text{—}F + G \tag{46}$$

and if we remember that the activation energy is essentially ΔH for the rate-controlling step, then it is apparent that the activation energy for Equation 45 would be

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}_{AB} - \Delta H^{\ddagger}_{BC} \tag{47}$$

where $\Delta H^{\ddagger}_{AB}$ and $\Delta H^{\ddagger}_{BC}$ represent the amount of energy absorbed, respectively, on the formation of the bonds A . . . B and B . . . C (as they are in the transition state) from gaseous A, B, and C. Similarly we may write for Equation 46

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}_{EF} - \Delta H^{\ddagger}_{DE} - \Delta H^{\ddagger}_{FG} \tag{48}$$

Now it appears that all bonds in the transition state are formed to about the same extent (Ri and Eyring[48] state that they are usually about 10% longer than normal bonds) so for rough comparative purposes it seems justified to write

$$\Delta H^{\ddagger}_{*} = \Delta H_{AB} - \Delta H_{BC} \tag{49}$$

where ΔH_{AB} and ΔH_{BC} represent respectively the amount of heat absorbed in forming the normal bonds A—B and B—C from their gaseous atoms, and $\Delta H^{\ddagger}_{*}$ is a sort of limiting value of the activation energy. A comparison of $\Delta H^{\ddagger}_{*}$ for different pairs of reactive centers should enable us to pick out the pair whose interaction would involve the least activation energy. Fortunately the calculation is very simple if polarizability factors and the effects of substitution are neglected. These neglected factors are very important, of course, but very frequently it happens that qualitative considerations involving the customary methods of the English theory show that the neglected factors could only serve to increase the difference between the values of $\Delta H^{\ddagger}_{*}$ calculated for two different pairs of reaction centers. In such cases the method leaves little to be desired except quantitative refinements. But when this is not the case we are sorely in need of some adequate semi-quantitative method of approximating the influence of these effects.

A few examples will serve to demonstrate the method and its validity. In all cases the labor of calculation will be minimized by neglecting all factors which will cancel out in the final comparison. When this is done the final value will be called the "comparative heat of activation" and will be symbolized by $\Delta H^{\ddagger}_{\text{com}}$. It must, of course, be remembered that the probability of reaction does not depend on $\Delta H^{\ddagger}$ alone but involves $\Delta S^{\ddagger}$ also.

Ethylene + *Chlorine.* It has been established by experiment that ethylene is the nucleophilic reagent in this reaction. The proposed method of calculation readily leads to the same conclusion. There are two possible ways in which the reaction might proceed in the gaseous phase (corrections for solvent influence will be considered in Chapter X):

(*A*) $$\mathrm{H_2C{=}\!\!-\overset{+}{C}H_2(g) + Cl^-(g) \rightarrow H_2C{=}\!\!-CH_2Cl(g)}$$

(*B*) $$\mathrm{H_2C{=}\!\!-\overset{+}{C}H_2(g) + Cl^+(g) \rightarrow CH_2Cl\cdot\overset{+}{C}H_2(g)}$$

As agreed, no account is here taken of the reactions $\mathrm{CH_2{=}CH_2} \rightarrow \mathrm{\overset{-}{C}H_2{-}\overset{+}{C}H_2}$ and $\mathrm{Cl_2} \rightarrow \mathrm{Cl^-} + \mathrm{Cl^+}$ since they occur in each case and hence cancel out in the final comparison.

The values of $\Delta H^{\ddagger}_{\text{com}}$ for reactions A and B can readily be calculated from tables of bond energies (Chapter VI, Table I), electron affinities (Table VI), and ionization potentials (Table VII) as illustrated below.

$$\begin{array}{lllrr}
(A) & C^+ + e \rightarrow C & \text{(ioniz. pot.)} & \Delta H = & -258.5 \text{ kcal} \\
 & Cl^- \rightarrow Cl + e & \text{(electron aff.)} & & 85.3 \\
 & C + Cl \rightarrow C{-}Cl & \text{(bond energy)} & & -66.5 \\
\hline
 & C^+ + Cl^- \rightarrow C{-}Cl & & \Delta H^{\ddagger}_{\text{com}} = & -239.7 \text{ kcal} \\
 & & & & \\
(B) & C^- \rightarrow C + e & \text{(elec. aff.)} & \Delta H = & 31.6 \text{ kcal} \\
 & Cl^+ + e \rightarrow Cl & \text{(ioniz. pot.)} & & -298.5 \\
 & C + Cl \rightarrow C{-}Cl & \text{(bond energy)} & & -66.5 \\
\hline
 & C^- + Cl^+ \rightarrow C{-}Cl & & \Delta H^{\ddagger}_{\text{com}} = & -333.4 \text{ kcal}
\end{array}$$

These computed values, which serve as $\Delta H^{\ddagger}_{\text{com}}$ in this particular problem, are in reality what we might call "ionic bond energies" with their signs reversed; i.e., we may define "ionic bond energy" as the amount of heat liberated in the formation of a gaseous molecule or radical from its elementary gaseous ions. Table VIII records the negative values of a number of "ionic bond energies" (i.e., values of $\Delta H_{A^+B^-}$) * calculated as above.

Returning now to our immediate problem, it is obvious from our calculations that reaction B would demand the least activation energy and hence that ethylene should exhibit nucleophilic character in this reaction unless the entropy of activation turned out to be an overpowering influence. Owing to the great similarity of reactions A and B, one might reasonably hope that there would be little if any difference in their entropies of activation, and since ethylene is symmetrical and unsubstituted it seems likely that all polarizability influences should also cancel out. There is, then, no need of refining the calculations, and the demonstration that ethylene should exhibit nucleophilic character when attacked by chlorine is complete. It is of interest to note that this conclusion was achieved without the use of any reaction velocity data and thus stands in contrast to the methods used in Chapter V to establish the same conclusion.

Ethylene + Halogens. The next check on our method will be to see if it is capable of predicting the well-established order of velocities of halogen addition to ethylene, viz., $Cl_2 > Br_2 > I_2$. Perusal of Table

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* The symbol $\Delta H_{A^+B^-}$ refers to the formation of AB from A^+ and B^- and carries no insinuation as to the polar character of AB.

VIII shows that in all three cases ethylene would be nucleophilic. Thus we may proceed as follows:

$$\Delta H^{\ddagger}{}_{*} = \Delta H_{\mathrm{C^-—Cl^+}} - \Delta H_{\mathrm{C=C}} - \Delta H_{\mathrm{Cl^+—Cl^-}}$$

$$\Delta H^{\ddagger}{}_{\mathrm{com}} = \Delta H_{\mathrm{C^-—Cl^+}} - \Delta H_{\mathrm{Cl^+—Cl^-}}$$

$$\begin{array}{ll}
\mathrm{C^- + Cl^+ \rightarrow C—Cl} & \Delta H = \Delta H_{\mathrm{C^-—Cl^+}} = -333.4 \text{ kcal} \\
\underline{\mathrm{Cl_2 \rightarrow Cl^- + Cl^+}} & \underline{\Delta H = \Delta H_{\mathrm{Cl^-—Cl^+}} = 271} \\
\mathrm{C^- + Cl_2 \rightarrow CCl + Cl^-} & \qquad\qquad\quad \Delta H = -62.4
\end{array}$$

$$\mathrm{H_2C{=}CH_2 + Cl_2 \rightarrow \overset{+}{C}H_2{\cdot}CH_2Cl + Cl^-}; \quad \Delta \mathrm{H}^{\ddagger}{}_{\mathrm{com}} = -62.4 \text{ kcal}$$

Similar calculations for bromine and iodine give respectively −57.8 and −50.3 kcal. These figures give the correct order of velocities. It is unfortunate, however, that the value of the electron affinity of bromine is in grave doubt.[50] If, as a first approximation, we assume that the polarizability effects of ethylene are brought into play in proportion to the dipole moments of the attacking reagents, then, since all three halogens are nonpolar, these effects would not be brought into play at all and hence need not enter our calculations.

Hydrolysis of Alkyl Halides. The three following mechanisms are conceivable if the hydrolysis takes place in basic solutions in which, of course, the hydronium ion concentration is very low.

(I) A nucleophilic attack by hydroxyl ion on carbon:

$$\mathrm{CH_3X + OH^-{\cdot}Aq \rightleftarrows HO \ldots CH_3 \ldots X + Aq \rightarrow CH_3OH + X^- + Aq}$$

Aq stands for water of hydration which is presumably lost on entering the transition state.

(II) An electrophilic attack by hydrogen on halogen.

$$\mathrm{CH_3X + HOH \rightleftarrows HO \ldots H \ldots X \ldots CH_3 \rightarrow OH^- + HX + CH_3{}^+}$$

(III) An electrophilic attack by hydrogen on carbon.

$$\mathrm{CH_3X + HOH \rightleftarrows HO \ldots H \ldots CH_3 \ldots X \rightarrow OH^- + CH_4 + X^+}$$

The corresponding values for $\Delta H^{\ddagger}{}_{*}$ may now be calculated for the case where X = Cl.

$$(\Delta H^{\ddagger}{}_{*})_{\mathrm{I}} = \Delta H_{\mathrm{C^+O^-}} - \Delta H_{\mathrm{C^+Cl^-}} - \Delta H_{\mathrm{AqOH^-}} = -\Delta H_{\mathrm{AqOH}} - 1 \text{ kcal}$$

$$(\Delta H^{\ddagger}{}_{*})_{\mathrm{II}} = \Delta H_{\mathrm{H^+Cl^-}} - \Delta H_{\mathrm{C^+Cl^-}} - \Delta H_{\mathrm{H^+O^-}} = 245 \text{ kcal}$$

$$(\Delta H^{\ddagger}{}_{*})_{\mathrm{III}} = \Delta H_{\mathrm{C^-H^+}} - \Delta H_{\mathrm{H^+O^-}} - \Delta H_{\mathrm{C^-Cl^+}} = 300 \text{ kcal}$$

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[50] Mayer and Helmholz, *Z. Physik*, **75**, 19 (1932). Glockler and Calvin, *J. Phys. Chem.*, **4**, 492 (1936), report 88 ± 3.4 kcal, whereas Piccardi, *Atti. acad. Lincei* [6], **3**, 566 (1926) reports 86.7 kcal.

TABLE VI

ELECTRON AFFINITIES OF ATOMS[51]

Atom	Elec. volts	Kcal/mole	Atom	Elec. volts	Kcal/mole
H	0.76	17.5	Si	0.60	13.8
Li	0.34	7.8	P	0.15	3.4
B	0.12	2.8	S	2.06	47.5
C	1.37	31.6	Cl	3.70	85.3
N	0.04	0.9	Br[50]		81.5
O	3.80	87.6	Ag	0.95	21.9
F	3.94	91.2	I[52]		72.6
Na	0.08	1.8			

TABLE VII

IONIZATION POTENTIALS AND ENERGIES[53]

Atom	Elec. volts	Kcal/mole	Atom	Elec. volts	Kcal/mole
H	13.572	311.8	Na	5.12	118.0
Li	5.363	123.5	Si	8.12	187.1
B	8.257	190.3	P	10.9	251.2
C	11.217	258.5	S	10.30	237.4
N	14.48	333.7	Cl	12.952	298.5
O	13.550	312.3	Br	11.80	272.0
F	17.34	399.7	I	10.6	244.3

TABLE VIII[49]

Bond	Ions	$\Delta H_{A^+B^-}$-(kcal/mole)	Bond	Ions	$\Delta H_{A^+B^-}$-(kcal/mole)
H—C	H^+,C^-	−367.5	C—I	C^-,I^+	−258.2
H—N	H^+,N^-	−394.6	N—Cl	N^-,Cl^+	−336.0
H—O	H^+,O^-	−334.4	N—Cl	N^+,Cl^-	−286.8
H—Cl	H^+,Cl^-	−329.2	O—Cl	O^-,Cl^+	−260.2
H—Br	H^+,Br^-	−317.6	Cl—Cl	Cl^-,Cl^+	−271.0
H—I	H^+,I^-	−310.6	Br—Br	Br^-,Br^+	−236.6
C—C	C^+,C^-	−285.5	I—I	I^-,I^+	−207.9
C—N	C^+,N^-	−306.2	C═C	C^+—C^-	(−268.3)
C—O	C^+,O^-	−240.9	C═N	C^+—N^-	+2.3
C—Cl	C^+,Cl^-	−239.7	C═O	C^+—O^-	(−249.9)
C—Cl	C^-,Cl^+	−333.4	P—Cl	P^+,Cl^-	−228.7
C—Br	C^+,Br^-	−231.0	P—Cl	P^-,Cl^+	−357.9
C—Br	C^-,Br^+	−294.4	P—H	P^-,H^+	−371.4
C—I	C^+,I^-	−231.4			

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[51] Unless otherwise designated, these values were taken from Glockler and Lind, *Electrochemistry of Gases and Other Dielectrics*, John Wiley & Sons, 1939. The factor 23.05 was used to convert electron volts into kcal/mole.

[52] Mayer, *Z. Physik*, **61**, 798 (1930).

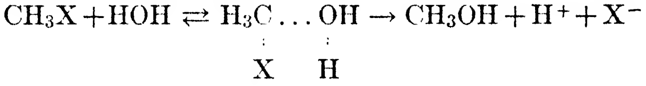
[53] Latimer, *Oxidation Potentials*, Prentice Hall, 1938.

Obviously there is no chance of a hydrocarbon being formed (III). The value for the heat of hydration of the hydroxyl ion is not known, but it could hardly be much more than 100 kcal.[54] Thus mechanism I is clearly favored, which is in accord with experiment, as we have already learned.

Having thus established the mechanism, we may now calculate $\Delta H^{\ddagger}{}_{\text{com}}$ for RCl and RBr. Taking $\Delta H^{\ddagger}{}_{\text{com}} = \Delta H_{\text{C}^+\text{X}^-}$, we get the values 239 and 231 kcal for chlorides and bromides respectively. The experimental activation energies for the hydrolysis of ethyl chloride and ethyl bromide fall in the same order, viz., 23 and 21 kcal, respectively.[55]

If the hydrolysis is carried out in an acid solution, the above three mechanisms become respectively

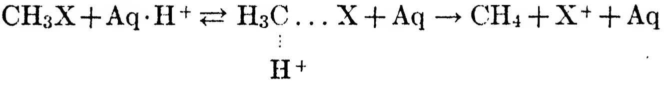
(I)



$$\text{CH}_3\text{X} + \text{HOH} \rightleftarrows \underset{\text{X}}{\overset{}{\text{H}_3\text{C}}}\ldots\underset{\text{H}}{\text{OH}} \rightarrow \text{CH}_3\text{OH} + \text{H}^+ + \text{X}^-$$

(II) $\text{CH}_3\text{X} + \text{Aq}\cdot\text{H}^+ \rightleftarrows \text{H}_3\text{C}\ldots\text{X}\ldots\text{H}^+ + \text{Aq} \rightarrow \text{CH}_3{}^+ + \text{HX} + \text{Aq}$

(III)



$$\text{CH}_3\text{X} + \text{Aq}\cdot\text{H}^+ \rightleftarrows \underset{\text{H}^+}{\text{H}_3\text{C}}\ldots\text{X} + \text{Aq} \rightarrow \text{CH}_4 + \text{X}^+ + \text{Aq}$$

$$(\Delta H^{\ddagger}{}_*)_{\text{I}} = \Delta H_{\text{C}^+\text{O}^-} - \Delta H_{\text{C}^+\text{Cl}^-} - \Delta H_{\text{H}^+\text{O}^-} = 333 \text{ kcal}$$

$$(\Delta H^{\ddagger}{}_*)_{\text{II}} = \Delta H_{\text{H}^+\text{Cl}^-} - \Delta H_{\text{C}^+\text{Cl}^-} - \Delta H_{\text{AqH}^+} = 164 \text{ kcal}$$

$$(\Delta H^{\ddagger}{}_*)_{\text{III}} = \Delta H_{\text{H}^+\text{C}} - \Delta H_{\text{C}^-\text{Cl}^+} - \Delta H_{\text{Aq}\cdot\text{H}^+} = 219 \text{ kcal}$$

These figures show mechanism II to be the favored mechanism. This is at least in accord with the trend experimentally observed in acid solutions.

The Hydrolysis of the Chlorides of Nitrogen and Phosphorus. The hydrolysis of NCl_3 yields HOCl, whereas that of PCl_3 yields HCl. This perplexing difference in behavior between two sister elements has been a standing challenge to theorists and it is interesting to discover to what extent our method of calculation is able to meet the challenge.

We may simplify the problem by making the calculations on the basis of pure water as the reactant. Then, since the concentration of H_3O^+ and OH^- ions are very low, we may assume water as the most probable attacking reagent. Now regardless of whether the attack is made by hydrogen or oxygen atoms of water the H—OH bond must become ruptured and hence this energy factor will cancel out. We may then consider H^+ and OH^- as the attacking reagents for purposes of comparison.

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[54] Rice, *Electronic Structure and Chemical Binding,* McGraw-Hill Book Co., New York, 1940, p. 402.

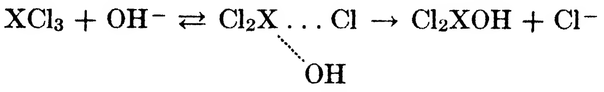
[55] Grant and Hinshelwood, *J. Chem. Soc.*, 258 (1933).

There are four possible modes of attack since there are two possible attacking ions and two possible points of attack, viz., P or Cl. These four possibilities may be formulated as follows, using X to represent either P or N:

$$\text{(I)}\qquad XCl_3 + H^+ \rightleftarrows H \ldots XCl_2 \ldots Cl \rightarrow HXCl_2 + Cl^+$$

$$\text{(II)}\qquad XCl_3 + H^+ \rightleftarrows Cl_2X \ldots Cl \ldots H \rightarrow Cl_2X^+ + HCl$$

(III)



$$XCl_3 + OH^- \rightleftarrows \underset{\ddots\, OH}{Cl_2X} \ldots Cl \rightarrow Cl_2XOH + Cl^-$$

$$\text{(IV)}\qquad XCl_3 + OH^- \rightleftarrows Cl_2X \ldots Cl \ldots OH \rightarrow Cl_2X^- + HOCl$$

The calculations of the corresponding values of $\Delta H^{\ddagger}_{com}$ may now easily be made from the data in Table VIII. If X is taken to be phosphorus, then

$$\begin{array}{llrr}
\text{(I)} & P^- + H^+ \rightarrow P\text{—}H; & \Delta H = & -371.4\text{ kcal} \\
 & P\text{—}Cl \rightarrow P^- + Cl^+; & \Delta H = & 357.9 \\
\cline{3-4}
 & & \Delta H^{\ddagger}_{com} = & -13.5\text{ kcal} \\
\text{(II)} & H^+ + Cl^- \rightarrow H\text{—}Cl; & \Delta H = & -329.2\text{ kcal} \\
 & P\text{—}Cl \rightarrow P^+ + Cl^-; & \Delta H = & 228.7 \\
\cline{3-4}
 & & \Delta H^{\ddagger}_{com} = & -100.5\text{ kcal}
\end{array}$$

(III) Data unavailable.

$$\begin{array}{llrr}
\text{(IV)} & O^- + Cl^+ \rightarrow O\text{—}Cl; & \Delta H = & -260.2\text{ kcal} \\
 & P\text{—}Cl \rightarrow P^- + Cl^+; & \Delta H = & 357.9 \\
\cline{3-4}
 & & \Delta H^{\ddagger}_{com} = & 97.7\text{ kcal}
\end{array}$$

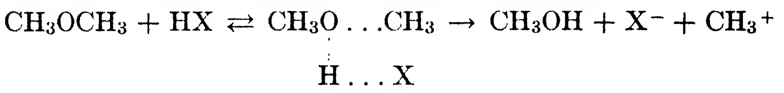
Thus the relative probabilities of the three mechanisms for which data are available turn out to be II > I > IV. If we may assume that all three chlorine atoms are removed by the same mechanism, we are thus led to the result that PCl_3 should yield $H_3PO_3 + HCl$ on hydrolysis.

If the corresponding calculations are made for NCl_3, the values of ΔH_{com} for cases I, II, and IV are found respectively to be -58.6, -43.4, and $+76.8$. Thus mechanism I is most probable in this case, and we would predict that NCl_3 would yield $HOCl + NH_3$ on hydrolysis.

Our assumption that all three chlorine atoms are removed by the same mechanism is justified by qualitative considerations. Thus if the first chlorine atom is replaced by hydrogen the lone pair of the resulting $HXCl_2$ is all the more available for coordination with another proton (mechanism I), and XH_3 will ultimately result. But if mechanism II results in the replacement of Cl^- by OH^-, the resultant $HO \cdot XCl_2$ will be only slightly more basic than XCl_3, since the $-I_s$ effect of hydroxyl is only slightly less than that of chlorine. In view of the large difference in $\Delta H^{\ddagger}_{\text{com}}$ (-13.5 compared to -100.5 kcal) which is found between mechanisms I and II in this case, it is hardly likely that this slight alteration would cause an inversion of mechanism in the second or third step.

Reactions of Ethers with Halogen Hydrides, etc. Three possible mechanisms may be considered.

(I) An electrophilic attack by hydrogen ion on oxygen:

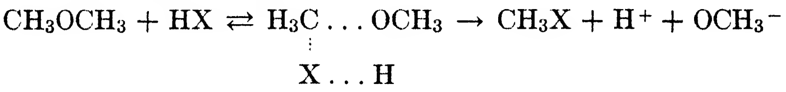


$$CH_3OCH_3 + HX \rightleftarrows \underset{\underset{\textstyle H \ldots X}{\vdots}}{CH_3O} \ldots CH_3 \rightarrow CH_3OH + X^- + CH_3^+$$

(II) An electrophilic attack by hydrogen ion on carbon:

$$CH_3OCH_3 + HX \rightleftarrows X \ldots H \ldots CH_3 \ldots OCH_3 \rightarrow CH_4 + X^- + OCH_3^+$$

(III) A nucleophilic attack by X^- on carbon:



$$CH_3OCH_3 + HX \rightleftarrows \underset{\underset{\textstyle X \ldots H}{\vdots}}{H_3C} \ldots OCH_3 \rightarrow CH_3X + H^+ + OCH_3^-$$

The most probable mechanism may now be predicted by calculating the corresponding values of $\Delta H^{\ddagger}{}_{*}$ for the case in which HX is HI.

$$(\Delta H^{\ddagger}{}_{*})_{\text{I}} = \Delta H_{\text{H}^+\text{O}^-} - \Delta H_{\text{C}^+\text{O}^-} - \Delta H_{\text{H}^+\text{I}^-} = 218 \text{ kcal}$$

$$(\Delta H^{\ddagger}{}_{*})_{\text{II}} = \Delta H_{\text{H}^+\text{C}^-} - \Delta H_{\text{C}^-\text{O}^+} - \Delta H_{\text{H}^+\text{I}^-} = 295$$

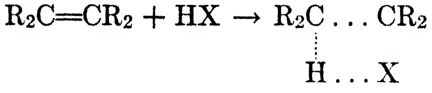
$$(\Delta H^{\ddagger}{}_{*})_{\text{III}} = \Delta H_{\text{C}^+\text{I}^-} - \Delta H_{\text{C}^+\text{O}^-} - \Delta H_{\text{H}^+\text{I}^-} = 321$$

Similar calculations made for HBr and HCl show that in all cases mechanism I is the most probable. Incidentally, the calculations make it amply clear why the reaction cannot lead to the formation of a hydrocarbon and an alkyl hypochlorite (II).

The next step is to decide which of the halogen hydrides should be most reactive. For this purpose we may calculate $\Delta H^{\ddagger}_{\text{com}} = -\Delta H_{\text{H}^+\text{X}^-}$. We thus get the following values for ΔH_{com}: 311 for HI, 318 for HBr, 329 for HCl, 334 for water, and 334 for ROH. It is thus predicted that HI is the most reactive, which is in accord with experience, although concentrated aqueous solutions are used experimentally, whereas our calculations were made for the gas phase reaction. It is well known that ethers are practically unreactive with water and alcohols at room temperature. Furthermore the hydrolysis is said to be accelerated by hydrogen ions and not by hydroxyl ions, which is in accord with the nucleophilic properties established for the ethers by our rough calculations.

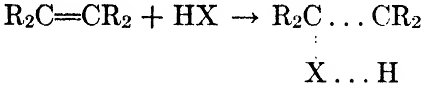
The Addition of Hydrogen Halides to Olefins. First it must be determined whether the rate-controlling step is an electrophilic attack by the hydrogen ion or a nucleophilic attack by the halide ion on the carbon atom of the olefin.

(I)



$$\mathrm{R_2C{=}CR_2 + HX \rightarrow \underset{\overset{\vdots}{H}\ldots X}{R_2C}\ldots CR_2}$$

(II)



$$\mathrm{R_2C{=}CR_2 + HX \rightarrow \underset{\overset{\vdots}{X}\ldots H}{R_2C}\ldots CR_2}$$

$$\text{(I)}\qquad \Delta H^{\ddagger}_{*} = \Delta H_{\mathrm{C^-H^+}} - \Delta H_{\mathrm{H^+X^-}} - \Delta H_{\mathrm{\underset{+}{C}=\underset{-}{C}}} \qquad (50)$$

$$\text{(II)}\qquad \Delta H^{\ddagger}_{*} = \Delta H_{\mathrm{C^+X^-}} - \Delta H_{\mathrm{H^+X^-}} - \Delta H_{\mathrm{\underset{+}{C}=\underset{-}{C}}}$$

therefore

$$\text{(I)}\qquad \Delta H^{\ddagger}_{\mathrm{com}} = \Delta H_{\mathrm{C^-H^+}} = -367.5$$

$$\text{(II)}\qquad \Delta H^{\ddagger}_{\mathrm{com}} = \Delta H_{\mathrm{C^+X^-}} = -239.7 \text{ for HCl}$$

$$-231.0 \text{ for HBr}$$

$$-231.4 \text{ for HI}$$

It is concluded, therefore, that reaction I represents the rate-controlling step. The next problem is to make a comparison of the relative speeds of addition of the different hydrogen halides. From Equation 50 it is evident that $\Delta H^{\ddagger}_{\mathrm{com}} = -\Delta H_{\mathrm{H^+X^-}}$ for this purpose.

$$\text{For HCl:}\quad \Delta H^{\ddagger}_{\mathrm{com}} = -\Delta H_{\mathrm{H^+Cl^-}} = 329.2$$

$$\text{For HBr:}\quad \Delta H^{\ddagger}_{\mathrm{com}} = -\Delta H_{\mathrm{H^+Br^-}} = 317.6$$

$$\text{For HI:}\quad \Delta H^{\ddagger}_{\mathrm{com}} = -\Delta H_{\mathrm{H^+I^-}} = 310.6$$

The predicted order of velocity (neglecting entropy factors) thus turns out to be HI > HBr > HCl, which is in complete accord with the well-known facts.

CHAPTER VIII

ELECTROCHEMICAL STUDIES OF ORGANIC OXIDATION-REDUCTION REACTIONS

REVERSIBLE REACTIONS

General Theory

There is no field in the realm of organic chemistry which has been more successfully placed on a firm foundation of fundamental physicochemical law than the one dealing with those systems capable of forming thermodynamically reversible voltaic cells. They represent one extreme of the generalized definition of oxidation-reduction or redox reactions—that extreme in which electron transfer is complete.

In this field it is customary to use the "European convention" in regard to the sign of the half-cell potential. By international accord it has been agreed that the electrons travel through the external circuit from the negative to the positive pole of a voltaic cell. Thus the negative pole of a cell will be the one immersed in the solution whose electron-escaping tendency is the larger. Half-cell potentials are always measured relative to the normal hydrogen electrode whose potential is the zero point of the potential scale. According to the European convention, the potential of a given half-cell is positive if it takes up electrons more readily than the normal hydrogen half-cell. This is equivalent to saying that the sign of an electrode is assigned to the half-cell of which it is a part when the other half-cell is a normal hydrogen electrode.

Since by thermodynamic convention the potential (E) of a reaction is always positive when the reaction proceeds spontaneously from left to right and since in writing half-cell reactions to accompany half-cell potentials a positive sign means that the given half-cell is taking up electrons from the hydrogen cell, then to be completely consistent, half-cell reactions must be written with the electrons on the left. Thus we have:

$$Cl_2(1\text{ atm.}) + 2e \rightarrow 2Cl^- \ (a = 1); \quad E = \quad 1.360 \tag{1}$$

$$Zn^{++} \ (a = 1) + 2e \rightarrow Zn(s); \quad E = -0.758 \tag{2}$$

Thus the positive sign in Equation 1 means that electrons are taken up spontaneously from a normal hydrogen electrode, whereas the negative sign in Equation 2 means that reduction of the zinc ion by the normal hydrogen electrode is not thermodynamically possible. Thus if we are using European conventions the half-cell potentials all correspond to reduction reactions, i.e., they are "reduction potentials." They should not be referred to as "oxidation potentials" unless the American convention is being used and never should the term "oxidation-reduction potential" be employed to describe definite quantitative data although it is commonly employed in referring to this field in general when no implications concerning conventions are involved.

Usually organic redox systems involve hydrogen ions and thus the simple Nernst equation of the type used for metal-metal ion systems is inadequate. The Peters' equation [1] is used instead. Its general form for reactions involving two electrons per mole is [2]

$$E_h = E_0 - \frac{RT}{2F} \ln \left(\frac{S_R}{S_O}\right) + \frac{RT}{2F} \ln f(K_1, K_2, [\mathrm{H}^+]) \tag{3}$$

in which E_h is the potential relative to the normal hydrogen system, R is the molar gas constant, T the absolute temperature, $[S_R]$ and $[S_O]$ the stoichiometric concentrations of the reduced and oxidized components of the system, respectively, and the last term indicates some function of the hydrogen ion concentration and the first and second ionization constants of the acids formed by reduction. The exact form of the last term varies according to the type of system involved. If the measurements are made in a buffer solution, the last term of Equation 3 becomes constant and the equation reduces to the form:

$$E_h = E'_0 - \frac{RT}{2F} \ln \left(\frac{S_R}{S_O}\right) \tag{4}$$

From this equation it is evident that E'_0 is the potential at the point of half reduction. In the range of half reduction small additions of oxidizing or reducing agents change the potential very little, and hence we have here an analogy with buffer solutions. Just as an acid-base system becomes "buffered" at a certain pH, so an oxidation-reduction system may become "poised" at a given value of E_h. No word has been coined to express the redox equivalent of a buffer solution, but the term "poising solution" seems to be a logical extension of the above terminology.

Let us now return to the motif introduced in the opening paragraph. The reduction potentials of these reversible redox systems may easily

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[1] R. Peters, *Z. physik. Chem.*, **26**, 193 (1898).

[2] W. M. Clark, *The Determination of Hydrogen Ions*, 3rd ed., Williams & Wilkins, 1928.

and accurately be measured, although liquid junction potentials introduce an element of uncertainty; the activity coefficients, free energy changes, and heats of reaction may be calculated readily from the electrochemical data; and best of all, two such systems mixed together practically always react in strict accord with thermodynamic predictions. The reactions are very rapid, which means that we are not harassed with kinetic considerations, and hence we may say for such reactions that if they are thermodynamically possible they will actually occur. Furthermore, these paragons of amenability allow their potentials to be influenced by chemical substitution in a completely consistent manner: they are always raised by electronegative substituents (electronegative, of course, meaning that the sum of the I_s and M effects operates to draw electrons away from the rest of the molecule when the group in question is substituted for hydrogen) and the order of relative electronegativities is always the same,* notwithstanding that in most cases substitutions must be *ortho* to the group involved in the redox process. No disturbing "*ortho* effects" have, to my knowledge, been discovered.

According to Equation 3 a pure oxidant will have an infinitely high potential and a pure reductant an infinitely low one. Thus on mixing any pure oxidant with any pure reductant, there is bound to be some reaction if they are of the reversible type. However, by the time 1% of the reaction has taken place, the potential of the reducing system, if it involves a two-electron change, may be calculated from Equation 4 to be

$$E_h = E'_0 - \frac{0.059}{2} \log \frac{99}{1}$$

which approximately makes $E_h = E'_0 - 0.059$, that is to say, about 0.06 volt below the normal potential. Thus for all practical purposes we can consider the working range of such a substance as $E'_0 \pm 0.06$ volt. This means that, if a pure oxidant is mixed with a pure reductant, there will not be an appreciable reaction if E'_0 for the reductant lies above $E'_0 + 0.12$ volt for the oxidant.

If it may be assumed that the reader can handle thermodynamics with reasonable facility, then there is certainly no need for further discussion of reversible redox systems, for he is already in full possession of all the knowledge requisite for predicting the direction and extent of all such reactions. However, any satisfaction which he derives from this thought must be tempered with the realization that very few organic redox systems are thermodynamically reversible. With the exception of several systems which are chiefly of biological interest, the only ones

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* I know of only one exception, in which case the order of Cl and Br is reversed.

which have so far been shown to be thermodynamically reversible are those given in Table I. To this list we will later add several systems involving free radicals. Dyestuffs of the azo and triphenyl methane classes have definitely been shown not to be reversibly reduced. All other common organic compounds may safely be considered to undergo irreversible oxidation or reduction or both, except perhaps some dyestuffs belonging to families which have not yet been potentiometrically investigated.

TABLE I

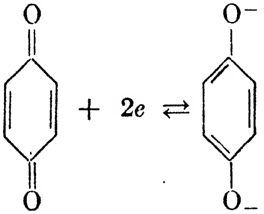
REVERSIBLE ORGANIC REDOX SYSTEMS

OXIDANT	REDUCTANT
Quinones	Hydroquinones
Quinone-imines	Aminophenols, etc.
Quinone-diamines	Phenylenediamines, etc.
Azo-benzenes	Hydrazobenzenes
Nitrosobenzenes	Phenylhydroxylamines
Indophenol dyes[3]	Leuco compounds
Indamine dyes	" "
Azine dyes	" "
Oxazine dyes	" "
Thiazine dyes	" "
Indigoid dyes	" "
Flavin dyes	" "
Arylarsonic acids	Arylarsenoxides
Nitroguanidine	Nitrosoguanidine

The intramolecular conditions which regulate reversibility have not been completely worked out, but some insight into the problem may be gained by consideration of the following cases: In reactions involving only metals and their ions we may write the half-cell reactions as follows if we ignore solvation effects:

$$M^{n+} + ne \rightleftarrows M \tag{5}$$

Such systems are reversible and involve complete electron transfer from one metal to the ion of the other metal. In the quinhydrone electrode, however, the half-cell reaction is more complicated:



(6a)

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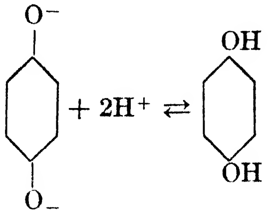
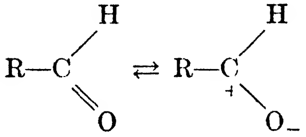
[3] Under this heading may also be included the pyrazine derivative, murexide. Kuhn and Lyman, *Ber.*, **69B**, 1547 (1936).

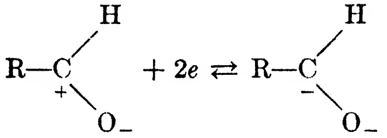


(6*b*)

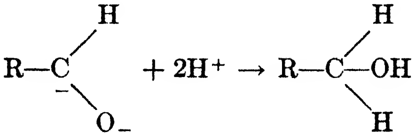
Here the organic molecule first gains two electrons from the reducing agent and then partially gives them up again to the hydrogen ions (Eq. 6*b*). Without stressing the implied relations to the generalized redox concept, the important thing is that the half-cell reaction involves not only electron transfer, which in itself is presumably always reversible, but also a step (6*b*) in which a covalent linkage is formed. It happens that this step is reversible in this case, but the opposite situation is readily seen to be a general possibility. Thus we might guess that the reduction of an aldehyde proceeds as follows:



(7*a*)



(7*b*)



(7*c*)

The sluggishness of the last step, involving as it does a C—H link, is a reasonable explanation of the fact that aldehydes are not reduced reversibly.

The Ion-Free Radical Equilibrium

Some years ago Conant, Small, and Taylor[4] pointed out that there is a formal analogy between the redox systems:

$$M^+ + e \rightarrow M \tag{8}$$

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[4] Conant, Small, and Taylor, *J. Am. Chem. Soc.*, **47**, 1959 (1925).

where M stands for a metal, and

$$Ph_3C^+ + e \rightarrow Ph_3C \qquad (9)$$

They found that the reduction potential of the second system could be measured by either of two methods, although the results were rather rough, owing to the rapid irreversible secondary reactions of the free radicals. The first method was the method of mixtures, in which one half-cell consisted of known concentrations of triphenylmethyl sulfate and triphenylmethyl in a solvent consisting of glacial acetic acid, bromobenzene, and sulfuric acid. The second method consisted in titrating the carbinol with aqueous solutions of vanadous salts, which are strong reducing agents. The solvent was glacial acetic acid to which had been added a strong mineral acid to assure the conversion of the carbinol to the positive carbonium ion. Their work established semi-quantitatively the thermodynamic reversibility of the reaction represented by Equation 9 and showed incidentally that free radicals can be produced in a polar environment. Similar conclusions were reached in experiments on phenylxanthenol and its dimethoxy derivative, which also yield dissociable ethanes. However, when substances like diphenyl carbinol were used, the reaction was irreversible, since the tetraphenylethane produced was not dissociated.

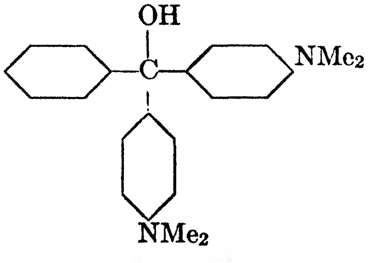
It seems safe to conclude from this series of experiments that dimolecular reductions of this type have a free radical mechanism. Thus the preparation of tetraphenylethane by the reduction of diphenyl carbinol with vanadous chloride may be represented by the equations

$$Ph_2CHOH + HX \rightleftarrows Ph_2\overset{+}{C}H + X^- + HOH$$

$$Ph_2\overset{+}{C}H + V^{++} \rightleftarrows Ph_2\overset{\bullet}{C}H + V^{+++}$$

$$2Ph_2\overset{\bullet}{C}H \rightleftarrows Ph_2CH \cdot CHPh_2$$

Similar dimolecular reductions were shown to occur with salts of *p*-dimethylaminotriphenylcarbinol and malachite green,[5] the dye base of which is



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[5] Conant and Bigelow, *J. Am. Chem. Soc.*, **53**, 676 (1931).

Semiquinones and the Theory of the Reversible Two-Step Oxidation

The reduction of quinones clearly involves two electrons per mole. From the standpoint of mechanism it is a matter of some importance to discover whether these two electrons are added stepwise or not. Before examining the related experimental evidence it will be well to consider the general theory of electron interchange reactions as described by Michaelis and Schubert.[6]

If the substance B is capable of reversible stepwise reduction we may write:

$$B + e \rightleftarrows B^- \qquad (10)$$

$$B^- + e \rightleftarrows B^= \qquad (11)$$

In favorable cases all three molecular species B, B^-, and $B^=$ will coexist in solution, the relative amounts of each found at equilibrium being, of course, a function of the two equilibrium constants concerned. If it were possible to add B^- to the equilibrium mixture dismutation would occur according to the equation

$$2B^- \rightleftarrows B + B^= \qquad (12)$$

The equilibrium constant for Equation 12 is called the dismutation constant. If this constant were sufficiently large in any case it is apparent that the intermediate form B^- would not exist in appreciable quantities. This presumably describes the case of benzoquinone.

Both of the ions are capable of combining with protons and hence on the above equilibria we have superimposed the following:

$$B^- + H^+ \rightleftarrows BH \qquad (13)$$

$$B^= + 2H^+ \rightleftarrows BH_2 \qquad (14)$$

As a result of these relationships it is evident that the over-all equilibrium will be a function of the *p*H of the solution. One further equilibrium may yet be involved, viz.,

$$2BH \rightleftarrows B_2H_2 \qquad (15)$$

The possibility of dimerization is a consequence of the unpaired electron possessed by BH.

It is customary to refer to compounds of the type B_2H_2 as meriquinones, to the B type as quinones or holoquinones, and to the BH or B^- type as semiquinones. Meriquinones are usually dissociated in solution although they frequently exist in the solid state.

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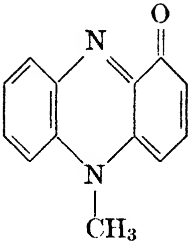
[6] Michaelis and Schubert, *Chem. Rev.*, **22**, 437 (1938).

The first experimental detection of semiquinones was accomplished by Friedheim and Michaelis [7] and independently by Elema.[8] In the following years examples of semiquinone formation multiplied rapidly, chiefly as the result of the work of Michaelis and his collaborators.[9] The properties of semiquinones are all much alike and hence the description of any one of them will suffice to elucidate their redox behavior. Pyocyanine has been chosen for this purpose. It has the formula



A potentiometric study showed that from pH 6 to 10 its reduction took place in one step, involving two electrons per molecule, but below pH 6 it took place in two steps, as evidenced by the accompanying change of color from red to green to colorless and by the shape of the curves obtained by plotting the potential against the per cent reduction. The curves obtained for reductions in very acid solutions correspond with the thermodynamic equations for semiquinone formation. Figure 1 illustrates the effect of pH on the value of E'_0. The green color is due to the semiquinone, and it is to be noted that as the pH rises the potentials of the first and second steps approach each other until at pH 5 they are identical. Beyond that value of the pH any reductant which is strong enough to produce the semiquinone is more than strong enough to complete the reduction. Thus, from the thermodynamic viewpoint, the one-electron change is impossible above pH 5.

The same phenomenon is presented from a different viewpoint in Figure 2, which shows all possible cases. The curves are not experimental curves but are merely graphical representations of the thermodynamic equations. The number attached to each curve is the "semiquinone formation constant" (i.e., the reciprocal of the dismutation constant); each one obtains at a different value of the pH. The circles represent the points on the curves where $E = E'_0$ for the first step (white circles) and the second step (black circles) of the oxidation. It is particularly to be noticed that when the semiquinones are stable the

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[7] Friedheim and Michaelis, *J. Biol. Chem.*, **91**, 355 (1931).

[8] Elema, *Rec. trav. chim.*, **50**, 907 (1931).

[9] Michaelis, *Chem. Rev.*, **16**, 243 (1935).

two halves of the curve are clearly distinguishable and that the curves gradually approach the one-step two-electron type as the stability of the semiquinones becomes less.

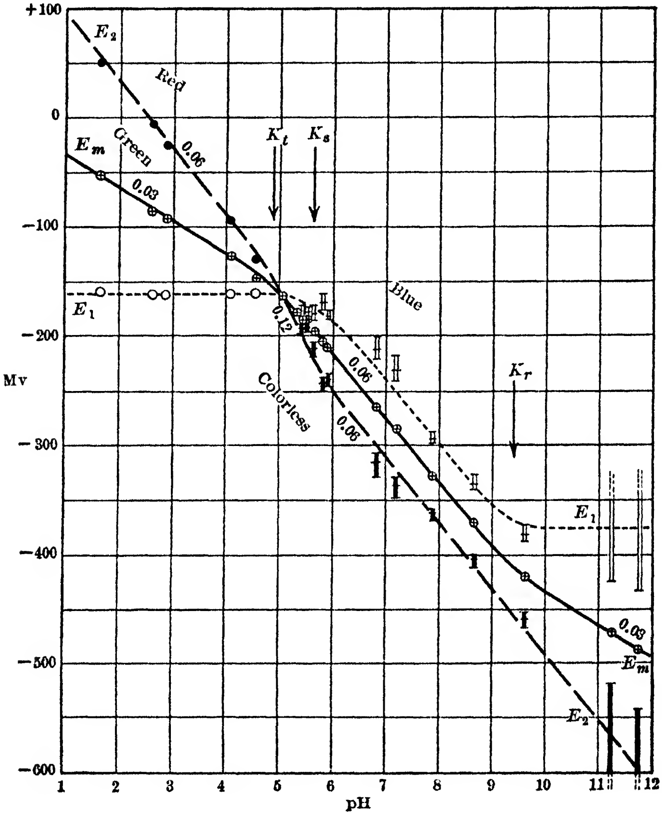


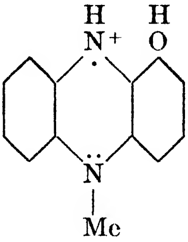
FIG. 1. The three normal potentials E_1, E_m, E_2, of pyocyanin plotted against *p*H. K_t, K_s, K_r are acidic ionization constants of the oxidized, semiquinone, and reduced forms. (*Taken from:* Michaelis, *Biochem. Z.*, **255**, 65, 1932.)

In addition to the potentiometric proof of the existence of semiquinones there was eventually added spectroscopic [10] and magnetometric [11] evidence. In regard to the latter it will be remembered that the existence of paramagnetic properties is the proof *par excellence* of the presence of unpaired electrons in molecules. It has been shown by actual experiment that quinhydrone is diamagnetic.[11]

[10] (*a*) Schwarzenbach and Michaelis, *J. Am. Chem. Soc.*, **60**, 1667 (1938); (*b*) Michaelis and Granick, *ibid.*, **62**, 204 (1940); (*c*) Granick, Michaelis, and Schubert, *ibid.*, **62**, 1802 (1940).

[11] Michaelis, Schubert, Reber, Kuck, and Granick, *ibid.*, **60**, 1678 (1938).

Michaelis considers that the structure of the semiquinone of pyocyanine, which exists only in acid solution and hence only as a salt, is given by the formula



and that its stability is due to resonance of essentially the same type postulated for other stable free radicals. All semiquinones are stabilized the same way and are formed by the addition of an electron to one end of a system of conjugated double bonds. The atoms at the end of such systems are usually oxygen or nitrogen. If oxygen, the semiquinone level is favored in alkaline solutions; if nitrogen, in acid solutions. Semiquinones differ from other free radicals in several important respects. They are stable in aqueous solutions, whereas free radicals of the triphenylmethyl type are not. This is probably related to the fact that they are ions as well as free radicals. Secondly, they seem to have very little tendency to dimerize, although recently several cases of dimeriza-

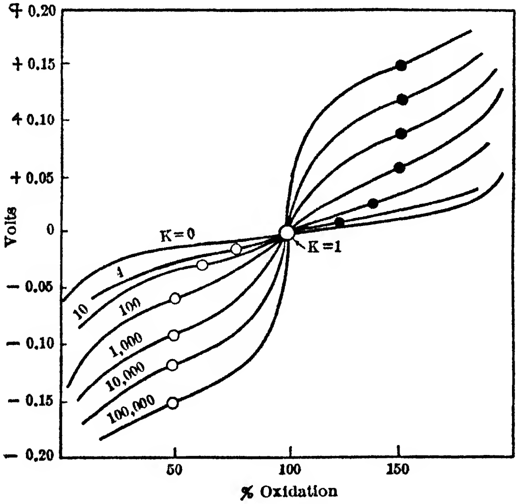


Fig. 2.[9] Relation between reduction potential and % oxidation at different values of the semiquinone formation constant (K).

tion have been detected.[12] This trait is also to be ascribed to the circumstance that they are ions, for the like charges would repel each other. Finally, there is the very fundamental difference that they undergo reversible dismutation. Irreversible dismutation, of course, is common enough among free radicals. For example, ethyl radicals irreversibly yield ethane and ethylene.

SEMI-REVERSIBLE AND IRREVERSIBLE REACTIONS

Apparent Oxidation and Reduction Potentials

For years most physical chemists have maintained that there is no general relationship between the free energy change attending a chemical reaction and the speed with which that reaction takes place. A favorite example for illustrating the reasonableness of this contention is the electrochemical reaction whose speed may be varied between wide limits by the introduction of resistance in the external circuit without changing the potential and hence without changing the molal free energy. It was at one time suggested [13] that the speeds of reactions taking place in the ordinary way are similarly related to their free energy changes by the "chemical resistance" of the system. The analogy bore no fruit, however, and one rarely hears of it any more. Although empirical relationships are frequently found between ΔF and reaction speed for a given reaction of a given compound and its derivatives, it is safe to say that no general relationship of this kind has ever been found.

Despite the lack of any such general relationship it was pointed out by Conant and Cutter [14] that the speeds with which many organic compounds are irreversibly oxidized or reduced qualitatively parallel the potentials of the oxidizing or reducing agents used, and they illustrated it by their own study of the homogeneous reductions of maleic acid and dibenzoylethylene. In the same year Holluta [15] showed in his studies on the oxidation of formates that there seemed to be a relation between the potential of the oxidizing agent and the speed of the reaction. The relationship was later explained in an orthodox way by Conant and Lutz [16] and developed by Conant and other collaborators.[17]

According to these investigators there is one set of conditions under which the speed of a reaction must be governed by a free energy change,

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[12] (*a*) Michaelis and Fetcher, *ibid.*, **59**, 2460 (1937); (*b*) Michaelis and Schubert, *J. Biol. Chem.*, **119**, 133 (1937).

[13] Nernst, *Z. Elektrochem.*, **7**, 1005 (1901); Jouguet, *Annales phys.*, **5**, 5, 470 (1926).

[14] Conant and Cutter, *J. Am. Chem. Soc.*, **44**, 2651 (1922).

[15] Holluta, *Z. physik. Chem.*, **102**, 276 (1922).

[16] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1047 (1923).

[17] See Conant, *Chem. Rev.*, **3**, 1 (1927) for references.

i.e., where some equilibrium process controls the amount of material undergoing a subsequent irreversible transformation. Thus if a reaction may be correctly formulated as follows

$$AH_2 + B \underset{}{\overset{\text{fast}}{\rightleftarrows}} A + BH_2 \tag{16}$$

$$A \xrightarrow{\text{slow}} P \tag{17}$$

it is clear that the speed of reaction (17) depends on the concentration of AH_2, which in turn depends on the equilibrium constant of the reversible step (16). This equilibrium constant is, of course, a function of the potentials of the two systems interacting, viz., (*a*) A, AH_2 and (*b*) B, BH_2. Thus if, in two different experiments, the substance AH_2 is treated respectively with B_1 and B_2 and if $(E'_0)_{b_1} < (E'_0)_{b_2}$, then a greater equilibrium concentration of A will exist when B_2 is the oxidizing agent and hence the more rapidly will the slow transformation into P proceed.

The quantitative formulation of the problem demands (1) that the equilibrium concentration of A be expressed, by the use of Equation 4, in terms of the concentrations of the other substances involved in the first step together with the normal potentials (E'_0) of the two systems *a* and *b*, and (2) that the speed of the second step be expressed by means of the ordinary equation for the velocity of a first order reaction. Since the equilibrium concentration of A occurs in both equations, there is thus achieved a relationship between the two. For the case in which *n* is the same for both b_1 and b_2, the following equation can be derived:

$$(E'_0)_{b_1} - (E'_0)_{b_2} = 0.03 \log \frac{k_1}{k_2} \tag{18}$$

where *k* is the over-all velocity constant of the reaction. In deriving this equation it was stipulated (1) that the initial concentrations of B and BH_2 must be equal, (2) that there must initially be one mole of AH_2 per oxidizing equivalent of B, and (3) that *n* must be the same for both b_1 and b_2 (another equation was given for use when this is not the case). As a final step in the development, the "apparent oxidation potential" (A.O.P.) of AH_2 is defined as the potential (E'_0) of a hypothetical oxidizing system (B, BH) of the type in which $n = 1$, which will give a value of $k = 0.01$ in its reaction with AH_2. Practically, this means that a system whose (reversible) reduction potential is equal to the A.O.P. of AH_2 will cause 20% to 30% oxidation of AH_2 in 30 minutes. The "apparent reduction potential" (A.R.P.) is similarly defined.

With the introduction of this definition, Equation 18 takes the form

$$\text{A.O.P.} = (E'_0)_{b_2} + 0.03 \log \frac{0.01}{k_2} \qquad (19)$$

The values of $(E'_0)_{b_2}$ and k_2 are experimentally determined by the following method. A buffer solution containing equivalent concentrations of B and BH_2 forms one half-cell. Its potential $(E'_0)_{b_2}$ is measured potentiometrically. The proper quantity of AH_2 is now introduced, a stop watch is started, and the reaction speed is measured by following the drop in potential with time.

Table II gives the data for a typical series of experiments. From these data the A.O.P. of 1,4-aminonaphthol was calculated to be 0.480 volt. In Table III are collected representative results of experiments made in Conant's laboratory.

TABLE II[17a]

POTENTIAL DATA FOR THE OXIDATION OF 1,4-AMINONAPHTHOL IN 0.2N HCl AT 23°

Poising system ($S_R = S_O$)	$(E'_0)_b$	Change in potential (mv)		
		5 min	15 min	30 min
Ferric chloride	0.726	250	270	280
p-Benzoquinone	0.656	185	198	. . .
Potassium ferricyanide	0.631	170	180	185
p-Xyloquinone	0.549	70	88	95
1,2-Naphthoquinone	0.506	17	36	50
2,6-Dimethoxyquinone	0.471	3	7	12
1,4-Naphthoquinone	0.426	0	0	0

A.O.P. = 0.480 volt

pH = 0.76

The influence of substituents on these apparent oxidation or reduction potentials is difficult to interpret theoretically because the influence is exerted both on the potential of the reversible step and on the velocity constant of the irreversible step. It is, of course, conceivable that sometimes one, sometimes the other factor will be the predominant influence. As a matter of experimental fact, however, the influence of substituents on A.O.P.'s or A.R.P.'s seems to be much the same as on reversible potentials. Thus the values of E'_0 for naphthoquinones are lower than for benzoquinone while the values of A.O.P. for the naphthols are lower than those for phenol. For phenol and its derivatives, the decreasing order of A.O.P. produced by substituents is H > *m*-OH > *p*-OMe > *p*-NH_2. The successive introduction of nitro groups into nitrobenzene

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[17a] Conant and Pratt, *J. Am. Chem. Soc.*, **48**, 3178 (1926).

TABLE III

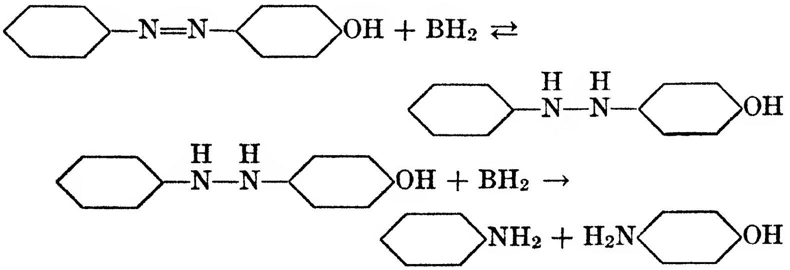
Substance	pH	A.O.P.	A.R.P.
Maleic acid	0.76		−0.25
m-Nitrobenzoic acid	6.77		−0.14
Orange II	6.77		−0.14
Benzoyl acrylic acid	6.77		−0.13
m-Nitrophenol	6.77		−0.10
Phenylnitromethane	0.76 *		−0.08
Nitrobenzene	0.76 *		+0.06
Benzoylacrylic acid	0.76		+0.06
m-Nitrobenzoic acid	0.76		+0.06
m-Dinitrobenzene	0.76		+0.16
1,3,5-Trinitrobenzene	0.76 *		+0.26
Phenol	5.0	+0.780	
Resorcinol	5.0	+0.775	
Hydroquinone monomethylether	5.7	+0.480	
β-Naphthol	8.9	+0.460	
Resorcinol	8.5	+0.415	
α-Naphthol	6.9	+0.393	

* 75% acetone, 25% aqueous HCl, total acidity 0.2*N*.

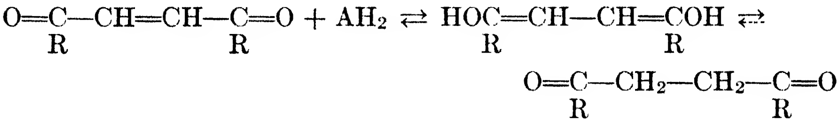
increases the A.R.P., although the introduction of a carboxyl group in the *m*-position has no influence at all.

A fact of great theoretical importance emerges from this work when one recognizes that quantitative or even semi-quantitative concordance between experimental values for any redox system and Conant's equations is a strong indication that a thermodynamically reversible redox step precedes an irreversible rate-controlling step. The latter need not, of course, be a first order reaction, but if it is, the A.O.P. or A.R.P. will be essentially independent of the total concentration. Where this is not the case, the situation is more complicated and the A.O.P. is a less satisfactory concept, necessarily varying with the concentration.

In many cases it has been found possible to establish chemical equations for each step of irreversible redox reactions. For example, the first step in the reduction of azo dyes is the reversible azo-hydrazo transformation, the second step the cleavage of the molecule which is characteristic of *ortho* and *para* hydroxy and amino derivatives of hydrazobenzene.



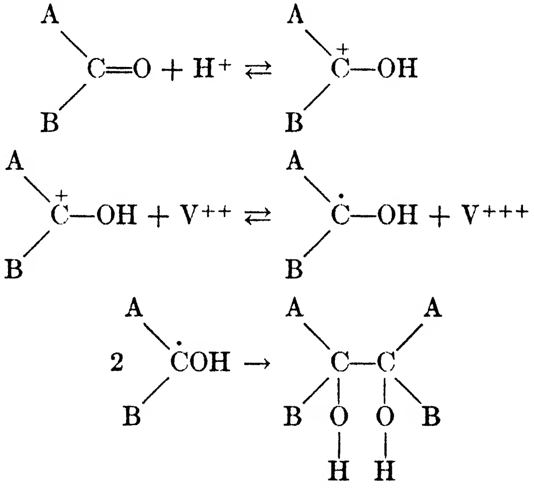
Unsaturated 1,4-diketones are irreversibly reduced despite the formal identity of their common conjugated system $O{=}C{-}C{=}C{-}C{=}O$ with that found in the reversibly reduced quinones. In the former case, however, the enolic form is not stable and slowly tautomerizes to the keto form.



$$O{=}\underset{R}{C}{-}CH{=}CH{-}\underset{R}{C}{=}O + AH_2 \rightleftarrows HO\underset{R}{C}{=}CH{-}CH{=}\underset{R}{C}OH \rightleftarrows O{=}\underset{R}{C}{-}CH_2{-}CH_2{-}\underset{R}{C}{=}O$$

The dotted arrow used in the equation for the keto-enol change is meant to indicate that although the reaction can be reversed, it is not sufficiently mobile to be classed as thermodynamically reversible. This is equivalent to saying that it is a slow change.

Conant and Cutter [17b] presented arguments in favor of the following mechanism for the dimolecular reduction of carbonyl compounds by vanadous chloride.



where A is C_6H_5 or an α,β-unsaturated group and B is H or C_6H_5. It will be noted that the second step is analogous to the proved reversible reduction of Ph_3C^+ to $Ph_3C\cdot$.[18]

Conant and Pratt [16] demonstrated conclusively that the mechanism of the oxidation of amino-phenols and amino-naphthols proceeds as follows:

$$HO\cdot R\cdot NH_2 + B \rightleftarrows O{=}R{=}NH + BH_2$$

$$O{=}R{=}NH + H_2O \rightarrow O{=}R{=}O + NH_3$$

[17b] Conant and Cutter, *J. Am. Chem. Soc.*, **48**, 1016 (1926).

[18] See p. 235, this chapter.

The first step is of the aminophenol-quinoneimine type which has been proved reversible[19] (cf. Table I).

The same authors[20] pointed out that since the oxidation of phenols and naphthols proved to be amenable to electrochemical formulation there must be involved a reversible redox step. The fact that dimolecular oxidation products of these substances had been found by others led them to suggest that the reversible step involved the formation of a free radical.

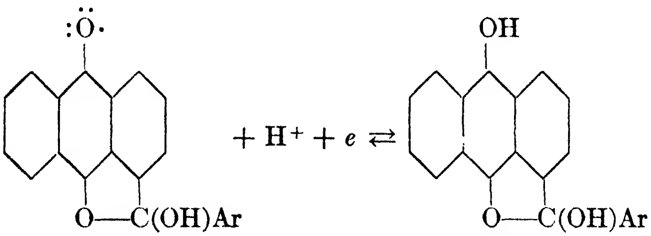
$$\mathrm{ROH} + \mathrm{B} \rightleftarrows \mathrm{RO}\cdot + \mathrm{BH} \tag{20}$$

$$\mathrm{RO}\cdot \rightarrow \cdot\mathrm{RO} \tag{21}$$

$$\cdot\mathrm{RO} \rightarrow \text{dimolecular products and further oxidation} \tag{22}$$

$$\cdot\mathrm{RO} + \mathrm{RO}\cdot \rightarrow \text{dimolecular products and further oxidation} \tag{23}$$

Further evidence that free radicals of this type are intermediate products in these reactions comes from the work of Pummerer and Goldschmidt and their collaborators,[21] who isolated several bivalent nitrogen radicals and aroxyls, some of which were produced by the direct oxidation of the corresponding amine or phenol. Finally it was shown by Fieser and Young[22] that Scholl's[23] stable free anthroxyl radical (I) forms a reversible redox system with its reduction product II, and they measured the potential of the reaction



(I) (II)

This seems to prove that reactions of the type of Equation 20 really are mobile and reversible.

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[19] (a) Fieser, *J. Am. Chem. Soc.*, **52,** 4915 (1930); (b) Bagdanov, *J. Phys. Chem.* (U.S.S.R.), **7,** 733 (1936); (c) Cameron, *J. Phys. Chem.*, **42,** 1217 (1938).

[20] Conant and Pratt, *J. Am. Chem. Soc.*, **48,** 3220 (1926).

[21] (a) Goldschmidt and collaborators, *Ber.*, **53,** 44 (1920); **55,** 616, 628, 3197, 3216 (1922); *Ann.*, **437,** 194 (1924); **438,** 202 (1924); **445,** 123 (1925); **478,** 1 (1930); (b) Pummerer and collaborators, *Ber.*, **47,** 1472 (1914); **59,** 2161 (1926).

[22] Fieser and Young, *J. Am. Chem. Soc.*, **54,** 4095 (1932).

[23] Scholl, *Ber.*, **64,** 1158 (1931).

Conant, Aston, and Tongberg[24] demonstrated that the oxidation of aldehydes lends itself to formulation by Conant's method. The oxidation of aliphatic aldehydes at 80° by complex cyanides in basic solutions and by ceric salts in acidic solutions were studied and both were shown to involve oxidation at the *alpha* carbon atom. The complete mechanisms for the reaction could not be established, but again it was suggested that the reversible step probably consists of the formation of a free radical or peroxide.

Critical Potentials

It has been emphasized that the A.O.P. and A.R.P., although they are called potentials, are in reality not purely thermodynamic constants but are compounded of the velocity constant for the slow step and the E'_0 value for the reversible transformation of the organic compound into its unstable intermediate oxidized or reduced form. Neither of these component constants can be determined separately from the customary data. In certain cases, however, the E'_0 value in question can be determined by a special technique if the intermediate product is not too unstable.[25] A number of cases exist, however, in which this instability is so high that the technique in question cannot be employed. For such cases Fieser[26] devised a method based on the following reasoning. As the potentials of the poising systems used become progressively less, the velocity of the reaction approaches zero. "Under these conditions the velocities of reaction for a series of compounds all approach the limiting value of zero and hence they are all very nearly the same at some point representing a small percentage of oxidation in a brief period of time." Bearing in mind, then, that the rate factors may influence the values of the A.O.P. for two different reactions in very different relative amounts when they are progressing at the speeds used for A.O.P. determinations, when the speed approaches zero the relative influences of these rate factors approach the same value. Hence a comparison of A.O.P.'s at the point of zero velocity should be closely comparable to a comparison of the corresponding values of E'_0 for the system involving the unstable oxidant.

Actually the method used by Fieser consists in plotting the initial potential of the poising system used against the per cent oxidation and extrapolating to zero per cent oxidation. The value of the potential thus obtained he calls the critical potential (E_c).

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[24] (*a*) Conant and Aston, *J. Am. Chem. Soc.*, **50**, 2783 (1928); (*b*) Conant, Aston, and Tongberg, *ibid.*, **52**, 407 (1930).

[25] Fieser, *J. Am. Chem. Soc.*, **52**, 4915 (1930).

[26] Idem, *ibid.*, **52**, 5204 (1930).

The values of E'_0 and E_c have both been determined for only a few systems. Table IV gives such a comparison. The essentially constant difference is to be expected for similar systems, i.e., for systems of the same oxidizing equivalence.

TABLE IV

SYSTEM, NAMED AS REDUCTANT	E'_0	E_c	DIFFERENCE
p,p'-Dihydroxydiphenyl	0.954	0.882	0.072
p,p'-Dihydroxystilbene	0.854	0.786	0.068
p-Phenylenediamine	0.783	0.710	0.073
p-Aminophenol	0.733	0.673	0.060

Semi-Reversible Systems

The thermodynamic approach to problems involving the electron escaping tendency is necessarily limited to reversible changes. This is readily seen from the statistical point of view. The molal ΔF involved in the conversion of A into B depends on the concentration (activity) of both A and B because the probability of the reaction proceeding to the right is proportional to the concentration of A and the probability of the reverse reaction is proportional to the concentration of B. The net probability of the reaction going to the right is the factor upon which the value of ΔF depends, and this obviously depends in turn on the assumption of reversibility. Thermodynamically minded chemists have usually assumed that any process for which ΔF is negative will occur in the course of time, that is to say, they assume that the difference between reversible and irreversible reactions is one of degree rather than of kind. Let us, however, brave an excursion into the dank shadows of unorthodoxy along with such revolutionary companions as Bancroft and Magoffin [27] and suggest that after all, in view of the lack of any experimental foundation for such an assumption, it is surprising to find it accepted with open arms in to the society of such preeminently respectable laws as those of thermodynamics.

Let us, then, for the sake of argument, suppose that A can pass into B but that the reverse process is impossible. Obviously the probability of the change can have no relationship to the concentration of B. Suppose, furthermore, that A gives up electrons in the process. Will there not be a definite electron-escaping tendency * regardless of the inapplicability of the thermodynamic measuring stick? If such were the case the potential would not be the same as that for other like substances nor would it depend on the ratio of the concentrations of A and B. Rather it would

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[27] Bancroft and Magoffin, *J. Am. Chem. Soc.*, **57**, 2561 (1935).

* To avoid clashes of definition, the term "electron escaping tendency" is not being used here with its customary thermodynamic implications.

depend on the concentration of A alone and on the undefined normal potential of that one substance.

An electrode which seems to meet the requirements of this frankly hypothetical case is the sulfite-sulfate electrode which has been discussed by Bancroft and Magoffin.[27, 28] It is not reversible since, although sulfite is easily oxidized electrolytically to sulfate, the reverse process cannot be carried out electrolytically at any concentration using temperatures that can be reached in open vessels. It has been established that the potential of the sulfite-sulfate electrode depends upon the concentration of the sulfite but not upon that of the sulfate. Yet the electrode so nearly exhibits the behavior of truly reversible electrodes that it was originally mistaken for one. Equilibrium conditions "were not reached with great rapidity; but, upon standing, steady values were obtained reproducible to within about a millivolt."[29] This electrode may then be classed as semi-reversible since the oxidation reaction is reversible and the reduction reaction irreversible.

Another much investigated redox system which forms a semi-reversible electrode, at least under certain conditions, is the system cysteine-cystine. The two components of this system are mutually interconvertible. These reactions may be most simply represented by the equation

$$2RSH \rightleftarrows RSSR + 2H^+ + 2e \tag{24}$$

In this form it represents equally well other sulfhydryl-disulfide systems which behave similarly, such as glutathione[30] and thioglycollic acid.[31] It has been reliably shown[30a, 32] that mixtures of cysteine and cystine establish fairly reproducible potentials, the values of which are given by the equation

$$E_h = E_0 - \frac{RT}{F}\,p\text{H} - \frac{RT}{F}\ln\,[\text{RSH}] \tag{25}$$

Note that here again the concentration of the oxidant is conspicuously absent from the equation. When an oxidimetric titration of cysteine was attempted,[33] the potentials obtained varied with the oxidizing agent used. When cystine was reduced electrolytically at the same mercury

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[28] Bancroft and Magoffin: (*a*) *J. Am. Chem. Soc.*, **58**, 2187 (1936); (*b*) *J. Franklin Inst.*, **224**, 283 (1937).

[29] Lewis, Randall, and Bichowsky, *J. Am. Chem. Soc.*, **40**, 356 (1918).

[30] (*a*) Dixon and Quastel, *J. Chem. Soc.*, **123**, 2943 (1923); (*b*) D. E. Green, *Biochem. J.*, **27**, 678 (1933); (*c*) Ghosh and Ganguli, *Biochem. Z.*, **279**, 296 (1935).

[31] (*a*) E. K. Fischer, *J. Biol. Chem.*, **89**, 753 (1930); (*b*) E. Larsson, *Svensk Kem. Tids.*, **45**, 65 (1933).

[32] Michaelis and Flexner, *J. Biol. Chem.*, **79**, 689 (1928).

[33] Williams and Drissen, *J. Biol. Chem.*, **87**, 441 (1930).

cathode which was to be used for the voltaic measurements it was found by Ghosh and his collaborators[34] that the orthodox thermodynamic equation involving the concentrations of both oxidant and reductant was followed. They ascribed the failures of previous investigators to a film of oxygen which is so firmly bound to the mercury electrodes that it can be removed only by electrolysis. As pointed out by Green,[30b] however, there seems to be the possibility that the electrolytic reduction of cystine produces a reductant with which cystine is in mobile equilibrium, yet this reductant is not cysteine.

A colorimetric method was used by Fruton and Clarke.[35] They measured the equilibrium degree of reduction by cysteine of dyes having known reduction potentials, using different concentrations of the former and different *p*H values. They found also that the thermodynamic equation was followed.

Whatever is the correct explanation of these curiously conflicting results and of others not mentioned,[36] one thing is certain, viz., that none of these measured potentials is thermodynamically related to the reaction of Equation 24. This fact was established by the very careful work of Borsook, Ellis, and Huffman,[37] who made the thermal measurements necessary to calculate the true thermodynamic potential of the reaction of Equation 24. Their value of the potential did not accord with those of any previous investigators. Table V compares these conflicting values. The extreme possible error in the thermal data is 43 mv.

TABLE V[37]

POTENTIAL MEASUREMENTS ON THE CYSTEINE-CYSTINE SYSTEM

INVESTIGATOR	METHOD	E'_0
Williams and Drissen	Potentiometric; oxidation of cysteine with:	
	KIO_3	+0.06
	$K_2Cr_2O_7$	+0.13
	I_2	+0.13
Ghosh et al.	Potentiometric; electrolytic reduction of cystine	−0.329
Fruton and Clarke	Colorimetric; oxidation of cysteine, reduction of cystine by dyes.	−0.222
Borsook, Ellis, and Huffman	Thermal method.	−0.390

It seems almost certain that it will ultimately be found that there are several different intermediate products in the reaction, some of which

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[34] (*a*) Ghosh, Raychaudhuri, and Ganguli, *J. Indian Chem. Soc.*, **9**, 43 (1934); (*b*) Ghosh and Ganguli, *Biochem. J.*, **28**, 381 (1934).

[35] Fruton and Clarke, *J. Biol. Chem.*, **106**, 667 (1934).

[36] See Ref. 30 for a complete discussion.

[37] Borsook, Ellis, and Huffman, *J. Biol. Chem.*, **117**, 281 (1937).

are in mobile equilibrium with cystine, some with cysteine, and probably none with both. Hence we tentatively conclude that under certain conditions, at least, there actually obtains a semi-reversible electrode system whose potential depends on the concentration of cysteine and not on that of cystine. It will be noticed that here, as in the sulfite-sulfate case, we experimentally encounter that condition which we predicted would occur if one-way reactions were possible. Of course, we need not insist that the reactions be 100% one-way reactions; the same experimental results would be obtained if the reverse reactions were very slow.

Some experiments by Preisler [38] are particularly significant. He undertook to study the rate of reduction of cystine and several other dithio acids by vanadous chloride and chromous chloride, using Conant's method. He found that chromous chloride resulted in a more rapid reduction than vanadous chloride, which would be expected in view of the greater reducing power of the former. But when the potential of the poising system was changed as much as 70 mv by altering the ratio of oxidant to reductant, the reaction rate was not affected!

Preisler also points out that the potentials of reversible redox systems which cause measurable reduction of cystine may be as much as 400 mv more negative than systems which cause oxidation of cysteine. This contrasts strongly with completely reversible systems in which very small changes in potential, either up or down from the equilibrium value, will cause "measurable" oxidation or reduction, respectively. He also points out that this difference becomes very much enhanced for still more irreversible cases, such as the alcohol-aldehyde system, in which oxidation of the alcohol can only be effected by very powerful oxidizing agents such as dichromic acid, while reduction of the aldehyde requires very powerful reducing agents such as sodium amalgam in dilute acid solution or zinc dust in glacial acetic acid. The gap between the potentials of dichromic acid and these metals almost spans the entire range of potentials known for chemical systems. Apparently neither the forward nor backward reaction of this system is mobile.

In the aldehyde-acid system we find another variation of the same idea. Weak oxidizing agents will oxidize aldehyde (e.g., silver salts in alkaline solution), but most of the strong reducing agents are unable to reduce the acids. Again there is a potential gap not explained by thermodynamics.

The necessity, in cases such as these, for employing an excess of potential to force the reaction is explained by Bancroft's theory of the "energy hump." [27, 28] This energy hump, according to Bancroft, is essentially the same thing as activation energy, except that he insists on tying it up

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[38] Preisler, *J. Biol. Chem.*, **87**, 767 (1930).

with the idea that certain reactions may be 100% irreversible. In reversible systems where no activation energy is required, no energy hump occurs between a reductant and its conjugate oxidant. In cases where the oxidation or reduction or both are slow, there must be enough energy or, better, enough potential to get the molecules over the hump. The height of the hump is the difference between the potential which would be required if the system were thermodynamically reversible and the potential actually required to produce the reaction. Bancroft ties the concept up with overvoltage in the following words:[28b] "When a reaction can be made to take place electrolytically, the height of the energy hump is defined as the difference of the free energy of the system and the voltage energy necessary to produce the reaction."

If I may risk interpreting Bancroft, I would add that there seems to be a very important difference between his energy hump and the activation energy, inasmuch as the latter involves random heat energy, whereas his hump involves high grade energy. It reminds one strongly of the free energy of activation. If he is right, the height of the energy hump measured electrolytically should accord with the potential of a reversible oxidizing agent just large enough to cause appreciable reaction. We will see later, in studying polarographic research, that something of this nature seems to be the case.

The evidence reviewed thus far indicates that there are three different types of redox reactions: (1) thermodynamically reversible reactions, (2) slow reactions in which the rate-controlling step is preceded by a reversible step, and (3) reactions in which the first redox step involves a potential hump which renders them essentially one-way processes. In this third type the reactions may be rapid, in which case we may call them semi-reversible; or they may be slow. In either case they tend to set up with an inert electrode a definite potential which is independent of the concentration of the products of the redox reaction and hence is incapable of thermodynamic formulation; furthermore, they are characterized by the fact that they will not proceed at a measurable rate unless their co-reactants are capable of exerting a potential which is in excess of that which would be involved in their reversible transformation. The magnitude of this excess may be said to be conditioned by the height of the potential hump. Our knowledge of this third type is very incomplete at the present time, and it is inevitable that future research will modify the remarks which have just been made concerning it.

Irreversible Electrodes and Catalysis

In the final analysis, the difference between reversible and irreversible systems may well be merely a matter of reaction velocity. This naturally suggests that by the use of proper catalysts many irreversible systems could be induced to yield reversible electrodes.

An example of such a case is the succinate-fumarate system which is not electromotively labile. Borsook and Schott [39] improved on the earlier work of Thunberg [40] and Lehmann [41] by showing that the succinate-fumarate system could be induced to come to a true equilibrium with methylene blue or indigo-tetrasulfonate if an enzyme from beef heart was used as a catalyst. A noble metal electrode immersed in such a solution behaved in all respects like a reversible electrode. If the dyestuff were omitted, however, no significant potential could be obtained. The explanation is probably as follows. In order for a redox system to behave in an electromotively reversible fashion when in contact with an electrode it must be so mobile that when electrons are drawn from the cell by momentarily closing the switch connecting it with the potentiometer, they will be immediately replenished. Now whereas the succinate-fumarate system is sufficiently activated by the enzyme so that it can slowly come to equilibrium with the dye-leuco compound system, it is not rendered sufficiently mobile to maintain the electrical double layer at the electrode during potentiometric adjustments. This latter function is performed, however, by the highly mobile dyestuff system which has already come to equilibrium with the succinate-fumarate system and hence is at the same potential. Dyestuffs or other reversible redox systems used in this way are termed "mediators."

These investigators showed that the potential measured by this method corresponded closely with that calculated from thermal data, and that hence the enzyme acted as a true catalyst.

The lactate-pyruvate system also yields a reversible electrode under similar conditions.[42]

Heyrovský's Polarographic Method

The polarographic method, originally developed by Heyrovský,[43] has in recent years attracted much attention as a method of analysis. Its importance to theoretical organic chemistry, however, lies not in the empirical relationships which have been applied by the analysts but in

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[39] Borsook and Schott, *J. Biol. Chem.*, **92**, 535 (1931).

[40] Thunberg, *Skand. Arch. Physiol.*, **46**, 339 (1925).

[41] Lehmann, *ibid.*, **58**, 173 (1929).

[42] (*a*) Wurmser and DeBoe, *Compt. rend.*, **194**, 2139 (1932); (*b*) Baumberger, Jurgensen, and Bardwell, *J. Gen. Physiol.*, **16**, 961 (1933); (*c*) Barron and Hastings, *J. Biol. Chem.*, **107**, 567 (1934); (*d*) Ganguli, *J. Indian Chem. Soc.*, **14**, 656 (1937).

[43] Heyrovský, *Chem. Listy*, **16**, 256 (1922); *Phil. Mag.*, **45**, 303 (1923).

the theoretical significance of the so-called half-wave potentials and decomposition potentials determined for irreversible systems.[44]

In principle the apparatus used in polarographic measurements consists of an electrochemical cell containing the solution to be investigated and equipped with a dropping mercury electrode. In the bottom of the cell a pool of mercury forms the other electrode. The cell is connected to a variable source of e.m.f., which is measured with a potentiometer or a slide wire and the current is measured with a suitable galvanometer connected in series with the cell. Current-voltage curves are obtained by gradually increasing the e.m.f. A typical example of such a curve is given in Figure 3. It was obtained by electrolyzing an air-free solution of $0.0013M$ zinc sulfate in $0.1N$ potassium chloride.[44a, 45] A very small "residual current" flows through the cell until the decomposition potential is reached at an applied e.m.f. of about 1 volt. Just beyond this point continuous electrolysis begins. As the applied e.m.f. is increased the current increases very rapidly until a "limiting current" has been reached. "Under optimum conditions, and with all other factors constant, the limiting current is directly proportional to the concentration of the electro-reducible substance . . . The decomposition potential of a given solution is characteristic of the particular electro-reducible substance present. Even more characteristic is the so-called half-wave potential, which, as its name implies, is the value of the applied e.m.f., or, better, the potential of the dropping electrode against an external reference electrode, at that point on a current voltage curve where the current is equal to one-half of its limiting value (see Fig. 3). In contradistinction to the decomposition potential, which depends to some extent

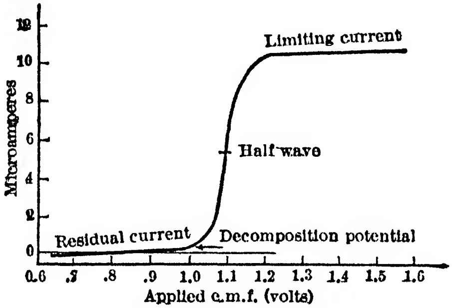

FIG. 3.[44a] Polarographic current-voltage curve.

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[44] For a review of the field see (*a*) Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939); (*b*) O. H. Müller, *ibid.*, 95; (*c*) Heyrovský, *ibid.*, 125.

[45] Knoke, *Angew. Chem.*, **50**, 728 (1937).

on the concentration of the reducible substance, the half-wave potential is, in general, entirely independent of the concentration of the reducible substance, provided that the composition of the solution with respect to foreign salts is kept constant. The half-wave potential is also independent of the particular capillary used and of its drop time."[46] Strictly speaking, the half-wave potentials expressed in terms of the total applied e.m.f. are not characteristic of the reducible substances present. If, however, they are expressed in terms of the potential of the dropping electrode against an external reference electrode, they do become characteristic of the reducible substance present.

If the dropping mercury electrode is connected to the negative pole of the polarizing e.m.f. reduction of the substance in contact with the mercury drops ensues. The curves thus obtained are called cathodic current-voltage curves and are the ones usually measured. In certain cases, however, the connections may be reversed, yielding anodic current-voltage curves which are related to the oxidation of the cell material.

If the polarographic method is applied to a well-buffered solution of a reversible system such as quinone-hydroquinone, the half-wave potential is found to be the same as the E'_0 value for the system.[47] Moreover, the astounding observation was made that the half-wave potentials have the same value when either the quinone or hydroquinone is present alone in the solution. This fact gives us an interesting insight into the mechanism of the process. It must mean that "one-half of all the molecules of quinone which diffuse to the cathode in unit time must have been instantly reduced at the half-wave potential, and the hydroquinone formed must have remained at the electrode surface long enough to produce the potential. Similarly, one-half of all the hydroquinone ions which diffuse to the anode in unit time are oxidized to quinone and remain at the electrode surface long enough to establish the condition of E'_0."

This suggests that, if we were using instead some irreversibly reducible substance, the half-wave potential would be the E'_0 corresponding to the reversible reduction of this substance into some unstable intermediate reduction product. It would be required, however, that this intermediate product have sufficient stability so that it would not undergo appreciable secondary change during the very short time that the mercury drop was being formed and was breaking away from the tip. It would also be required that the reduction process take place with extreme rapidity. These conditions would undoubtedly be fulfilled in varying degrees by different substances and hence the interpretation of the half-wave poten-

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[46] Ref. 44a, pp. 5 and 7.

[47] Müller and Baumberger, *Trans. Electrochem. Soc.*, **71**, 181 (1937).

tial would be expected to depend upon the degree to which these conditions are met.

Regardless of the amount of truth contained in these conjectures, the facts of the case are that in many such "irreversible" reductions a smooth *S*-curve is obtained on the polarogram and a regular shift of the reduction potential is observed. This strongly suggests that the reduction step actually being measured is a reversible one. It is a common and unfortunate habit among polarographers to refer to such reductions as reversible. The polarographic method does, however, furnish a good method of showing whether or not a given redox reaction is truly reversible.[48] The method depends on the observation made in the study of the quinone-hydroquinone system [47] that when the dropping mercury electrode was first used as a cathode in a solution of quinone, and then used as an anode in a solution of hydroquinone, the two half-wave potentials were identical. This behavior may serve as a very convenient criterion to determine the reversibility of a redox system. If the two steps do not yield the same half-wave potentials, then the reaction must be thermodynamically irreversible. This test is unfortunately limited by the fact that the highest potential available at the mercury electrode is E_h = 0.65 volt.

Since the polarograph is proving to be such a powerful tool in the investigation of irreversible redox reactions, it is naturally a matter of great interest to compare the polarographic results with those of Conant and his collaborators. Unfortunately very few of the compounds used by Conant have been subjected to polarographic measurement. However, Müller [44b] has obtained polarograms for nitrobenzene, dinitrobenzene, and azobenzene, from which it is evident that Conant's A.R.P. values differ from the half-wave potentials but "coincide with the beginning of a rise in current due to the onset of reduction," which is to say that they are slightly more negative on the scale of reduction potentials than the polarographic "decomposition potential." This is precisely what we would have expected, since the A.R.P., defined as it was in a highly arbitrary manner, corresponds to that potential which would cause a rather rapid reaction, whereas the decomposition potential corresponds to a slower "detectable" reaction. The lack of correspondence between the half-wave potential and the A.R.P. also follows if we assume that the former corresponds to the E'_0 value of the reversible step, since the A.R.P. was itself compounded of this same E'_0 and the velocity constant of the irreversible step, neither of which could in general be determined separately.

Finally let us return to the more indefinite picture of the "energy

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[48] Müller and Baumberger, *J. Am. Chem. Soc.*, 61, 590 (1939).

hump" or the "potential hump," as it should have been called. It was previously remarked that "the height of the energy hump measured electrolytically should accord with the potential of a reversible oxidizing agent just large enough to cause appreciable reaction." It is obvious that the polarographic work just described shows this to be true for the only systems so far investigated from this point of view.

Theories Concerning the Relationship between One-Electron and Two-Electron Redox Reactions

If a redox system is sufficiently mobile to impress a measurable and reproducible potential on a noble metal electrode and if the magnitude of that potential is quantitatively expressed by thermodynamic equations, then it might naturally be expected that such a system would react rapidly with a second system having the same properties. That this is not always so has been known for a long time.[49] Comparatively recently a theory to explain certain of these anomalies was put forward by Shaffer.[50] He pointed out that Ce^{++++} oxidizes Tl^{+} only very slowly despite the fact that the potential of the ceric-cerous system is much higher than that of the thalic-thalous system; and similarly that iodine reacts very slowly with Ti^{+++}. Both of these reactions, however, are catalyzed by manganese salts or by certain dyestuffs which are capable of forming semiquinones. Shaffer points out that a probable explanation lies in the possibility that Tl^{+} cannot lose one electron at a time but must lose two at once if it is to react at all. Since the ceric-cerous system involves only a one-electron change, it would follow that reaction could only take place between the two by a three-body collision. Such collisions are improbable, and hence the speed of such reactions would be cut down enormously. If, however, there is present also some substance like manganous ion, which can lose either one or two electrons at a time (three ions of manganese are possible: Mn^{++}, Mn^{+++}, and Mn^{++++}) then the reaction should be and is strongly catalyzed, the manganese ions acting as carriers. The same would be true of dyestuffs which form semiquinones, since their redox reactions may involve either one or two electrons.

Since the advent of Shaffer's theory there has appeared another of somewhat similar character which is called "the principle of compulsory univalent oxidation" by its author, Michaelis.[51] According to this prin-

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[49] Knecht and Hibbert, *New Volumetric Reduction Methods in Quantitative Analysis*, Longmans, 1925, pp. 6, 7.

[50] Shaffer, *J. Am. Chem. Soc.*, **55**, 2169 (1933); *J. Phys. Chem.*, **40**, 1021 (1936).

[51] (*a*) Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); (*b*) Michaelis and Fetcher, *J. Am. Chem. Soc.*, **59**, 1246 (1937); (*c*) Michaelis, *Ann. Rev. Biochem.*, **7**, 1 (1938).

ciple oxidations of organic compounds can proceed at a measurable speed only in steps of one electron each. In amplification of this principle we cannot do better than to reproduce Michaelis's own remarks.[51a] "Whenever this bivalent oxidation can be brought about by two successive univalent oxidations, then the kinetics of such a reaction will be greatly enhanced. The thermodynamic possibility of the univalent oxidation, and the existence of the radical as an intermediate step of the complete bivalent oxidation, will depend on the dismutation constant. If this constant is very large, it is equivalent to saying: The formation of the radical involves a very high step in energy. Only if, due to resonance, the formation of the radical requires relatively little energy, will the bivalent oxidation run smoothly. The reason why the oxidation of organic compounds is frequently very sluggish, even when an oxidant of thermodynamically sufficient oxidative power is applied, is that the oxidation has probably, as a rule, to go through two univalent steps; and to go through the intermediate step means, in general, climbing over a large energy hill, except in those cases described above in which the semiquinone formation constant is relatively large. It is the task of all catalysts and enzymes concerned with oxidation-reduction processes to ease the climb over this energy hill, or to convert the substance to be oxidized into some form, or into some compound, in which the intermediate radical will have a stronger resonance and so a greater stability than it has in the original form."

In support of this theory Michaelis and Fetcher [51b] have shown that the oxidation of benzoin to benzil on adding an oxidizing agent such as oxygen or iodine proceeds in two successive univalent steps and that the oxidation does not proceed at all unless the solution is alkaline enough to allow the existence of the intermediate semiquinone in equilibrium with benzoin and benzil.

Further support is found in the demonstration that although 1,4-diaminodurene yields a semiquinone on oxidation, methylation of the amino groups prevents the formation of a semiquinone because steric hindrance prevents a planar configuration, and thus the resonance necessary for stabilization of the semiquinone is impossible.[52] Now the point relevant to the present discussion is that the unmethylated compound acts as an oxidation catalyst in increasing respiration of erythrocytes but the methylated compound has no catalytic effect.

Although, as stated by its author, the principle of compulsory univalent oxidation applies only to organic compounds, the restriction is undoubtedly meant to apply to redox reactions involving the rupture and

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[52] (*a*) Granick, Michaelis, and Schubert, *Science*, **90**, 422 (1939); (*b*) Michaelis, Schubert, and Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

formation of covalent linkages. If this is true, some studies on inorganic redox reactions made by Kirk and Browne[53] seem to have a significant bearing on the validity of the principle. They pointed out that certain oxidizing agents oxidize hydrazine to a mixture of nitrogen, ammonia, and water, whereas another group of oxidizing agents produce hydronitric acid also. Since substances of widely different reduction potentials fall in each group, they were forced to look elsewhere for an explanation and eventually decided that the oxidizing agents of the first group are mono-delectronators and those of the second group are di-delectronators. Certain oxidizing agents were found to react both ways at once. Mono-delectronators were defined as oxidizing agents which accept one electron only per active unit (atom, ion, or molecule) and di-delectronators those which accept two electrons. The terminology, which is convenient, can, of course, be extended to reducing agents which may be classified as mono- or di-electronators. This work certainly seems to show that in the case of hydrazine, at any rate, either one or two electrons at a time may be taken up.

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[53] R. E. Kirk and A. W. Browne, *J. Am. Chem. Soc.*, **50**, 337 (1928).

CHAPTER IX

ELECTRON-PAIRING REACTIONS

EVIDENCE FOR MECHANISMS

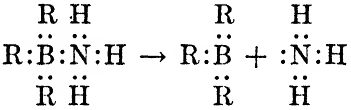
General Remarks

We have previously distinguished between two types of decomposition:

$$\text{Ionic}\quad \mathrm{A{:}B \rightarrow A{:}^- + B^+} \qquad (1)$$

$$\text{Nonionic}\quad \mathrm{A{:}B \rightarrow A\cdot + \cdot B} \qquad (2)$$

The reverse reactions involving bond formation could be similarly catalogued. The fundamental distinction between the two types is not, however, the formation of ions and "nonions"; it is that in type 1 a process of electron sharing or "unsharing" is involved, whereas in type 2 the process involves a pairing or "unpairing" of electrons. Thus the terminology "ionic" and "nonionic" is misleading, because dissociations such as



$$\mathrm{R{:}\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{B}}}}{:}\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{N}}}}{:}H \rightarrow R{:}\overset{R}{\underset{R}{\ddot{\underset{\cdot\cdot}{B}}}} + {:}\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{N}}}}{:}H} \qquad (3)$$

are of the "ionic type" (1) but yet involve no ions. Reactions of type 1 have been called "acid-base reactions" in terms of the generalized theory of acids and bases,[1] whereas reactions of type 2 are widely referred to as "atom and radical reactions."

"Displacement reactions," which we studied in conjunction with the transition state theory, may be of either type. If they are of type 1 they may involve the simultaneous sharing of one electron pair and "unsharing" of another, e.g.,

$$\left[{:}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{H}\right]^- + \mathrm{R}{:}\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}{:} \rightarrow \mathrm{H}{:}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{R} + \left[{:}\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}{:}\right]^- \qquad (4)$$

If they are of type 2, e.g.,

$$\mathrm{R\cdot + R'{:}H \rightarrow R{:}H + R\cdot'} \qquad (5)$$

they may involve the simultaneous pairing and "unpairing" of electrons. In principle, Equation 5 seems to be no different from Equation 6:

$$\mathrm{Na\cdot + {:}\ddot{\underset{\cdot\cdot}{Cl}}{:}R \rightarrow Na^+ + {:}\ddot{\underset{\cdot\cdot}{Cl}}{:}^- + \cdot R} \qquad (6)$$

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[1] See the Lewis theory of acids and bases, Appendix IV.

in which, presumably, the sodium electron becomes paired with one of the chlorine's electrons, forcing the disruption of the covalent electron pair. However, the reaction

$$R_3C^+ + V^{++} \rightarrow R_3C\cdot + V^{+++} \tag{7}$$

seems to be fundamentally different, since no pairing or unpairing can possibly be involved. Yet it is a "radical reaction" in the sense that a free radical is formed.

The general confusion of nomenclature is apparent and seems to justify the following pair of new definitions: (1) An electron-sharing reaction is one involving the sharing and/or "unsharing" of electron pairs. (2) An electron-pairing reaction is one involving the pairing and/or "unpairing" of electrons.

Obviously one step of a reaction may be of the first and another step of the second type. If so, they are apt to be regulated by fundamentally different laws. Furthermore, a given bond may be activated by either mechanism, depending on the environment. As an example we may take the well-known case of hexaphenyl ethane which dissociates into ions in liquid sulfur dioxide but into free radicals when dissolved in a nonpolar solvent.

Dissociation reactions involving the "unsharing" of electrons are brought about by such agencies as polar catalysts (including cases such as the glass walls of the reaction vessel), polar solvents, acids, bases, etc. —in brief, by generalized acids and bases.[1] In the gaseous state they may also be produced by electron impact methods or *alpha* particles. Dissociation reactions involving the unpairing of electrons are commonly photochemical or thermal decompositions.

Our chief interest in this chapter will be electron-pairing displacement reactions. A unique characteristic of reactions of this kind is that they may give rise to "chain reactions." Thus if $R_3C\cdot$ is highly reactive, which is usually the case, it will attack another molecule, producing thereby another free radical or an atom containing an unpaired electron. This in turn will attack another molecule, and so on, setting up a reaction chain which will be terminated when two particles having unpaired electrons meet and combine. In gaseous reactions these chains are apt to become very long, resulting in such rapid reactions that explosions frequently result.

When free radicals of short life are produced in solution, let us say by photochemical decomposition, they are so thoroughly encased by the solvent that either they will recombine with each other quickly after deactivating collisions with the solvent molecules, or they will decompose, or they will react with the solvent molecules. In practice it is found that the reaction with the solvent is the path usually followed. Reaction with some other solute is possible but unlikely in dilute solutions.

The picture just given of a free radical enclosed in a "cage" of solvent molecules is an essential part of the Franck-Rabinowitsch principle of primary recombination.[2] The kinetic significance of the principle lies in the fact that the distribution of free radicals or atoms in, let us say, a strongly illuminated solution is not entirely random, but there is a tendency for the fragments produced by the dissociation of a molecule to be more closely clustered than would correspond to random distribution. "Thus in addition to the 'normal' probability of recombination governed by the law of mass action there will be an additional probability of 'primary recombination' of two particles which have been parts of the same molecule before dissociation."

When an electron-pairing type of reaction results in the production of a stable free radical, it is, of course, not difficult to demonstrate the presence of the free radical and hence the type of rupture. But when the free radical has only a transient existence in the course of a reaction, it is frequently no small task to establish the activation mechanism.

The evidence which has so far been accumulated in favor of the existence of electron-pairing mechanisms will be carefully reviewed in the following sections of this chapter. Later we will discuss the advances which have been made by investigators seeking to establish the fundamental laws which regulate electron-pairing reactions.

Photochemical Reactions

In the field of photochemistry it has been found that electron-pairing mechanisms are most readily reconciled with experimental data on reaction rates. The most extensively investigated case is the photochemical interaction of hydrogen and chlorine. It is generally conceded that the chlorine molecule is first split into atoms by the absorption of a quantum of light energy

$$Cl_2 + h\nu \rightarrow 2Cl$$

and that the reaction then proceeds by a chain mechanism:[3]

$$Cl + H_2 \rightarrow HCl + H$$

$$H + Cl_2 \rightarrow HCl + Cl$$

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[2] Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[3] (*a*) Bodenstein, *Z. physik. Chem.*, **85**, 346 (1913); (*b*) Nernst, *Z. Elektrochem.*, **24**, 335 (1918).

The fact that the rate of formation of HCl is proportional to the square root of the chlorine concentration [4] is in keeping with the first step of the reaction, since each chlorine molecule is there pictured as giving rise to two identical atoms which would have identical reactivities. This would hardly be the case if the activation produced two oppositely charged ions. A similar situation is encountered in the photochemical interaction of chlorine with carbon monoxide.[5]

Aside from the kinetic evidence, there is also chemical evidence that photochemical activation is of the electron-pairing type. For example, the photochemical decomposition of methyl iodide gives a 35% yield of ethane,[6] which could hardly result from an ionic decomposition unless both positive and negative alkyl ions were produced—an unlikely occurrence. Further evidence of the nonpolar photochemical dissociation of alkyl halides is furnished by spectroscopic investigations [7] and by a study of methyl iodide.[8]

The above evidence may be taken as typical. An exhaustive survey of all such evidence from the field of photochemistry would be out of place in a book like this one.[9]

Thermal Decomposition

The interpretation of pyrolytic reactions as electron-pairing reactions is richly substantiated by a variety of experimental evidence. In the first place, decompositions of organic molecules to give stable free radicals such as triphenylmethyl are pyrolytic in the broad sense although they occur at room temperature or below. Other compounds have to be heated to higher temperatures in order to be decomposed into free radicals.

There is evidence that as the number of aryl groups in these substituted ethanes is reduced the dissociation tendency of the ethane C—C bond gradually diminishes. Thus penta-arylethanes when heated to temperatures ranging from 71° to 105° become colored owing to the formation of free triaryl radicals.[10] The diaryl radicals simultaneously

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[4] (*a*) Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913); (*b*) Thon, *ibid.*, **124**, 327 (1926).

[5] (*a*) Bodenstein, *ibid.*, **130**, 422 (1927); (*b*) Bodenstein and Onoda, *ibid.*, **131**, 153 (1928); (*c*) Bodenstein, Lenher, and Wagner, *ibid.*, **B3**, 459 (1929); (*d*) Lenher and Rollefson, *J. Am. Chem. Soc.*, **52**, 500 (1930).

[6] Job and Emschwiller, *Compt. rend.*, **179**, 52 (1924).

[7] (*a*) Herzberg and Scheibe, *ibid.*, **25**, 716 (1929); (*b*) Iredale, *Nature*, **604** (1930); (*c*) Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

[8] Bates and Spence, *J. Am. Chem. Soc.*, **53**, 1689 (1931).

[9] For recent reviews see (*a*) Hey, *Chem. Soc. Ann. Repts.*, **37**, 272 (1940); (*b*) H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

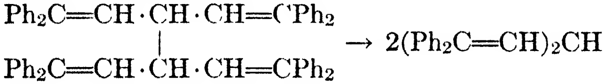
[10] W. E. Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936).

produced associate to form tetra-aryl ethanes.[10] Moreover, solutions of penta-arylethanes absorb oxygen at 80–105°, forming the unsymmetrical peroxides $R_3COOCHR_2$, which must have been formed from the corresponding free radicals. Cleavage of the C—C bond in these compounds may also be effected by the action of sodium amalgam.

Turning next to the tetra-arylethanes, we find that *s*-tetra-α-naphthylethane develops no color when heated in benzene solution.[11] Likewise *s*-tetra-*p*-methoxyphenylethane develops no color when heated alone or in xylene solution.[12] The distillation of *s*-tetraphenylethane proceeds at 280° without decomposition, but the incipient weakening of the C—C bond is indicated by its cleavage with potassium:

$$Ph_2CH \cdot CHPh_2 + 2K \rightarrow 2Ph_2CHK$$

Evidence for the existence of a free radical of this general type, however, seems to have been discovered in the case of *s*-tetra (ββ-diphenylvinyl) ethane,[13] which presumably dissociates as follows:



$$\begin{array}{c} Ph_2C{=}CH \cdot CH \cdot CH{=}CPh_2 \\ | \\ Ph_2C{=}CH \cdot CH \cdot CH{=}CPh_2 \end{array} \rightarrow 2(Ph_2C{=}CH)_2CH$$

When finally we turn to less highly aryl-substituted ethanes, such as α,α,β-triphenylethane, α,β-diphenylethane, and phenylethane, no evidence of weakness of the C—C bonds can be found.[14]

Interesting light is thrown on the subject by a comparison of the activation energies for C—C cleavage in these compounds.[15] They are: 19 kcal for hexaphenylethane, 27.6 kcal for pentaphenylethane, and 80 kcal for ethane itself.

Another closely related example is 9,10-diphenylanthracene, which is colorless at room temperature and becomes colored when it is heated. This is interpreted as an intramolecular nonpolar dissociation.[16]

In a similar category fall the famous experiments of Paneth, Hofeditz, and Lautsch,[17] in which they succeeded in demonstrating that free methyl and ethyl radicals are produced when $PbMe_4$ and $PbEt_4$ are heated to high temperatures. Their method consists in carrying the tetra-alkyl lead compound in a stream of pure hydrogen at pressures of 1 to 2 mm through a heating unit. The gases issuing from this hot zone

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[11] Wuis and Mulder, *Rec. trav. chim.*, **57**, 1385 (1938).

[12] Nauta and Mulder, *Rec. trav. chim.*, **58**, 1062 (1939).

[13] Wittig and Obermann, *Ber.*, **68**, 2214 (1935).

[14] Hey, *Ann. Repts. Chem. Soc.*, **37**, 260 (1940).

[15] Ref. 14 and Bachmann and G. Osborn, *J. Org. Chem.*, **5**, 29 (1940).

[16] Ingold and Marshall, *J. Chem. Soc.*, 3080 (1926).

[17] (*a*) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (*b*) Paneth and Lautsch, *ibid.*, **64**, 2702 (1931).

are led at a carefully controlled rate over thin metallic mirrors produced by distillation of various metals onto the walls of the cold portion of the tube. These mirrors are removed by the highly reactive gas passing over them, producing products which are identified as the corresponding metallic alkyls. The only tenable theory seems to be that the tetra-alkyl lead compound is initially decomposed into lead and free alkyl radicals, the latter combining with the metallic mirrors in the cooler portion of the tube. They determined from these experiments that the half-life period of the free methyl and ethyl radicals is about 0.006 sec. The short half-life period is due to the very great tendency of the free methyl and ethyl radicals to combine with themselves to produce, respectively, ethane and butane. Thus one can say with considerable assurance that the pyrolytic production of ethane and butane from the corresponding lead alkyls has an electron-pairing mechanism.

Rice and his coworkers,[18] using a modification of the original Paneth method, showed that free radicals, most frequently methyl radicals, can be produced by the pyrolysis of a variety of organic compounds such as hydrocarbons, ketones, ethers, and aldehydes.

Free radicals have the ability to induce chain reactions in the decomposition or polymerization of organic compounds. Thus when butane containing only 1 per cent of dimethyl mercury was heated at a temperature which was too low to cause the decomposition of pure butane in the allotted time, it decomposed into the usual pyrolytic products, plus an additional quantity of methane equivalent to the methyl group of the dimethyl mercury.[19] This experiment may reasonably be interpreted as a pyrolytic decomposition of dimethyl mercury into free methyl radicals which initiate reaction chains by the abstraction of hydrogen atoms from the butane. A similar experiment [20] was made on acetaldehyde containing a few per cent of azomethane; similar results were obtained.

Of related interest is the fact that Ogg and Polanyi [21] have demonstrated that stereochemical inversion results when an optically active halide like *sec.*-butyl iodide undergoes a homogeneous decomposition in the gas phase at 238° to 276°. The first step is a unimolecular decomposition of the butyl iodide into an iodine atom and a free radical. A Walden inversion then occurs when the iodine atom attacks another molecule of butyl iodide. At first thought it seems strange that an inversion would result from an attack by an electrically neutral particle, since some orienting influence must be at work to force the iodine atom to

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[18] For a review see F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, The Johns Hopkins Press, 1935.

[19] Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

[20] Sickman and Allen, *J. Am. Chem. Soc.*, **56**, 1251 (1934).

[21] Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

attack the butyl iodide molecule from the side opposite the attached iodine atom. However, it has been shown that if a free monovalent atom reacts with a diatomic molecule composed of two monovalent atoms the activation energy resulting from interchange forces is a minimum when the three atomic nuclei lie on a straight line.[22] Probably the same principles apply when more complicated molecules are involved.

The production of free radicals by the thermal decomposition of metallo-organic compounds in the liquid phase also has been inferred from such reactions as:

(1) Refluxing $PbPh_4$ with mercury yields some Ph_2Hg.[23]

(2) $PbPh_4$, $SnPh_4$, and $HgPh_2$ when heated in paraffin oil containing sulfur yield PhSSPh.[24]

(3) Ph_2Hg heated with alcohols yields benzene, an aldehyde, and an ester.[25]

$$HgPh_2 \rightarrow Hg + 2Ph\cdot$$

$$2Ph\cdot + RCH_2OH \rightarrow RCHO + 2C_6H_6$$

$$2RCHO \rightarrow RCO_2\cdot CH_2R$$

Reactions of Azo and Diazo Compounds and of Nitrosoacylarylamines[26]

Among the many compounds which pyrolyze to yield gaseous free radicals are the azo compounds. Thus azo methane, MeN═NMe, decomposes at 400° to give free methyl radicals and nitrogen.[27] Benzene diazonium chloride has been shown to decompose under acetone, attacking the metals Sb, Bi, Pb, Sn, Ni, Fe, Cu, Ag, and Hg even though the mixture is kept neutral with calcium carbonate.[28] In view of the well-known tendency of free radicals to form compounds with metals, these experiments strongly indicate that free phenyl radicals are produced by the decomposition. Likewise benzenediazonium chloride under acetone reacts with sulfur, selenium, and tellurium to give Ph_2S, Ph_2Se, and Ph_2TeCl_2, respectively.[29] Curiously enough, however, it does not react with boron, silicon, or phosphorus.[29]

[22] (*a*) London, *Sommerfeld Festband*, **104** (1928); (*b*) Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

[23] Dull and Simons, *J. Am. Chem. Soc.*, **55**, 3898 (1933).

[24] Razuviev and Koton, *J. Gen. Chem.* (U.S.S.R.), **5**, 361 (1935).

[25] Idem, **1**, 864 (1931).

[26] (*a*) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937); (*b*) Hey, *Ann. Repts. Chem. Soc.*, 275–290 (1940); (*c*) Hey and Waters, *Nature*, **140**, 934 (1937).

[27] (*a*) Leermakers, *J. Am. Chem. Soc.*, **55**, 3499 (1933); (*b*) Rice and Evering, *ibid.*, **55**, 3898 (1933).

[28] (*a*) Waters, *Nature*, **140**, 466 (1937); *J. Chem. Soc.*, 2007 (1937); 864 (1939); (*b*) Makin and Waters, *ibid.*, 843 (1938).

[29] Waters, *ibid.*, 1077 (1938).

Pray [30] found that the rates of decomposition of benzenediazonium chloride in a series of aliphatic alcohols were all of the same order and in the lower members of the series were practically identical. He obtained similar results when the decomposition proceeded in a series of aliphatic acids. It had previously been shown by Hantzsch and Jochem [31] that the reactions with methyl and ethyl alcohols take different paths:

$$PhN_2Cl + MeOH \rightarrow PhOMe + N_2 + HCl$$

$$PhN_2Cl + CH_3CH_2OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

This fact makes it all the more remarkable that the rates were identical for these two reactions and strongly indicates that the rate-determining step in each is the same, viz., the formation of free phenyl radicals.

Similar reactions have also been carried out between aromatic diazonium chlorides (or nitrosoacylarylamines) and pyridine.[32] The earliest work [32a] indicates the formation of α and γ-arylpyridines, whereas the later work indicates the formation of α, β, and γ isomers. Since electrophilic reagents (note that the benzenediazonium ion would be an example) attack pyridine in the *beta* position, it appears that here we have evidence that free radicals do not follow the usual laws of directive influence. This was also evidenced by the earlier work of Gomberg and his collaborators,[33] who found that when a cold moderately concentrated aqueous solution of sodium aryldiazotate is vigorously stirred with an aromatic liquid the following reaction ensues:

$$ArN_2OH + PhR \rightarrow ArC_6H_4R + N_2 + H_2O$$

They considered that the ArN_2OH was produced by hydrolysis of the diazotate and dissolved by the aromatic liquid layer in which the reaction took place. They found that *ortho-para* substitution resulted regardless of the nature of the group already present. R, for example, might be CH_3, Br, CN, or NO_2.[34]

In general diazobenzene hydroxides and cyanides [35] react with aliphatic C—H linkages according to the equation [26b]

$$R\cdot + R'H \rightarrow RH + \cdot R' \qquad (8)$$

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[30] Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

[31] Hantzsch and Jochem, *Ber.*, **34**, 3337 (1901).

[32] (*a*) Mohlau and Berger, *Ber.*, **26**, 1994 (1893); (*b*) Haworth, Heilbron, and Hey, *J. Chem. Soc.*, 349, 358, 372 (1940); (*c*) Butterworth, Heilbron, and Hey, *ibid.*, 355 (1940); (*d*) Heilbron, Hey, and Lambert, *ibid.*, 1279 (1940).

[33] (*a*) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924); (*b*) Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

[34] For further examples see Ref. 26*a*, p. 179.

[35] Stephenson and Waters, *J. Chem. Soc.*, 1796 (1939).

and with aromatic C—H linkages as follows:

$$R\cdot + R''H \rightarrow RR'' + H\cdot \tag{9}$$

A similar series of reactions is evidenced by N-nitrosoacetanilide. Thus Bamberger [36] established the following reaction:

$$PhN(NO)COMe + C_6H_6 \rightarrow Ph_2 + N_2 + MeCO_2H$$

N-nitrosoacetanilide is considered to be tautomeric with benzene antidiazoacetate since the former can be obtained by acetylating sodium benzenediazotate with acetic anhydride.[37] Thus the free radical mechanism proposed for the reaction on the basis of experiments by Grieve and Hey [38] seems less surprising than it otherwise would be. The proposed mechanism is as follows:

$$PhN(NO)COMe \rightarrow Ph\cdot + N_2 + MeCOO\cdot \tag{10a}$$

$$Ph\cdot + PhR \rightarrow p\text{-}PhC_6H_4R + \cdot H \tag{10b}$$

$$MeCOO\cdot + H\cdot \rightarrow MeCO_2H \tag{10c}$$

If, as in the case of the diazohydroxide reactions, step *a* is the rate-controlling step, then the rate of evolution of nitrogen should be independent of R. This was found to be essentially the case, and good unimolecular velocity constants were obtained.[38] The production of the neutral acetate radical in step *a* was demonstrated by Waters,[39] who pointed out that the amount of acetic acid produced is always less than would correspond to the amount of nitrogen liberated. This is related to the fact that in many cases carbon dioxide is also evolved. This could very well be due to the decomposition of the free acetate radical,

$$MeCOO\cdot \rightarrow CO_2 + Me\cdot$$

$$2Me\cdot \rightarrow C_2H_6$$

since in the electrolysis of acetates in aqueous solution carbon dioxide is liberated at the anode, where presumably the primary production of acetate radicals takes place:

$$MeCOO^- \rightarrow e + MeCOO\cdot$$

It is also a matter of much interest that in these reactions of nitrosoacetanilide with PhR, *para*-substitution always resulted even though R was represented by such different groups as CH_3, Cl, NO_2, and CHO.[38]

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[36] Bamberger, *Ber.*, **30**, 366 (1897).

[37] (*a*) Bamberger, *Ber.*, **27**, 914 (1894); (*b*) von Pechmann and Frobenius, *ibid.*, **27**, 651 (1894); (*c*) Hantzsch and Wechsler, *Ann.*, **325**, 226 (1902).

[38] (*a*) Grieve and Hey, *J. Chem. Soc.*, 1797 (1934); (*b*) Butterworth and Hey, *ibid.*, 116 (1938).

[39] Waters, *ibid.*, 113 (1937).

From these facts and the ones previously presented in relation to the reactions of benzenediazo hydroxides it is clear that when free radicals are the reactants we may expect directive influences on the entering substituent to be different from those encountered in either electrophilic or nucleophilic substitutions by ions.

The behavior of diazobenzene hydroxides and cyanides summarized by Equations 8 and 9 above is also evidenced by nitrosoacylarylamines and by arylazotriarylmethanes.[40]

Diacyl Peroxides [26]

The following reaction occurs when a benzene solution of dibenzoyl peroxide is heated:

$$\text{PhCOO}\cdot\text{OOCPh} + C_6H_6 \rightarrow \text{Ph}_2 + CO_2 + \text{PhCO}_2\text{H}$$

The participation of the solvent in the reaction was proved by experiments in which di-*p*-chlorobenzoyl peroxide was heated with benzene producing 4-chlorodiphenyl and not the 4,4′-dichlorodiphenyl. Similarly di-*m*-nitrobenzoyl peroxide with benzene yields 3-nitrodiphenyl.[40]

The mechanism of these and similar reactions has been a matter of considerable dispute, but Hey and Waters [26a] feel that a free radical mechanism is most consistent with the known facts. They represent the initial decomposition as

$$\text{PhCOO}\cdot\text{OOCR} \rightarrow \text{Ph}\cdot + \text{RCOO}\cdot + CO_2$$

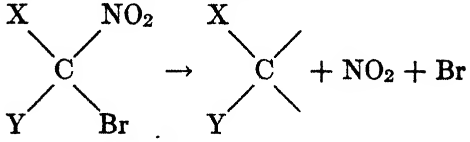
or

$$\text{PhCOO}\cdot\text{OOCR} \rightarrow \text{R}\cdot + \text{PhCOO}\cdot + CO_2$$

and the subsequent reaction of these free radicals with the solvent (as in the previous section of this chapter) accounts for the diverse products of reaction.

Bromonitro Compounds

These compounds readily undergo thermal decomposition to yield a variety of products, usually, if not always, including nitrogen dioxide. Allen and Wilson [41] have shown that in many such cases the formation of the observed end products can readily be explained on the assumption of the primary formation of a free diradical, thus:



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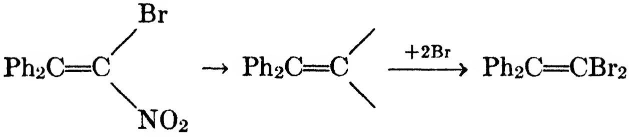
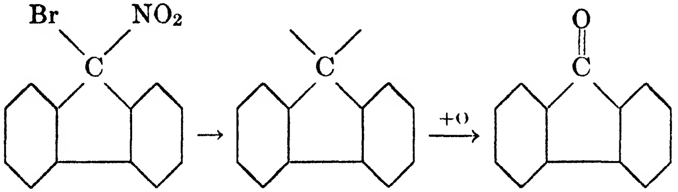
[40] Gelissen and Hermans, *Ber.*, **58**, 285 (1925).

[41] C. F. H. Allen and C. V. Wilson, *J. Org. Chem.*, **5**, 146 (1940).

A few of their examples are given below. They are all readily understood if one bears in mind that the diradical may combine either with bromine or oxygen, the latter apparently coming from the NO_2 and resulting in NO as a final product.[42]

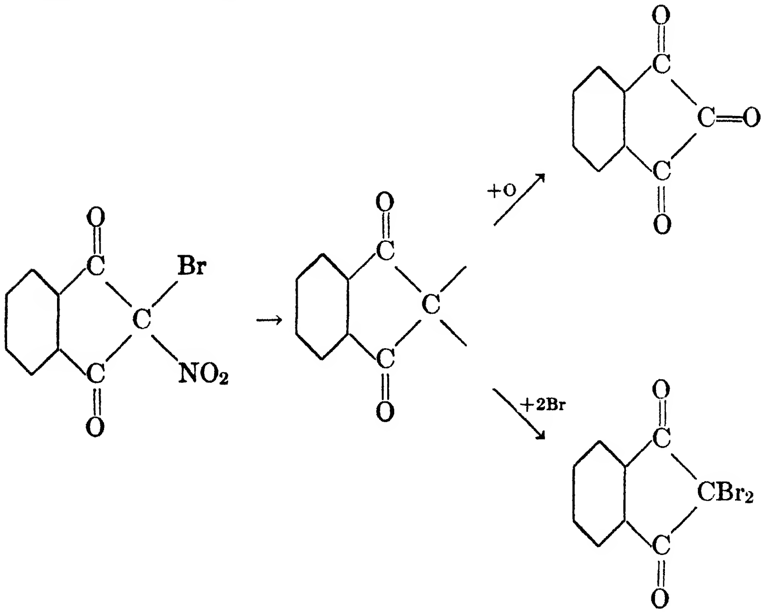


(11)



(12)

In the following reaction, which was carried out in nitrobenzene solution, both products are obtained and the combined yields account for nearly all of the starting material.[43] This is a strong argument in favor of the diradical mechanism.



(13)

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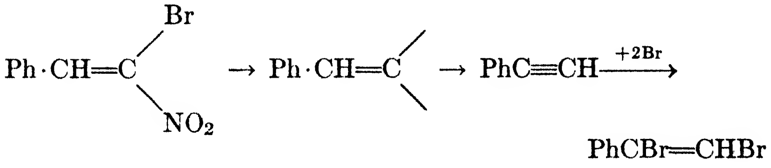
[42] **Wislicenus and Waldmuller, *Ber.*, 41, 3340 (1908).**

[43] **Wanag and Lode, *Ber.*, 71, 1267 (1938).**

In the following case the diradical could easily rearrange, as indicated, in virtue of the presence of a mobile hydrogen atom adjacent to the double bond.



$$\mathrm{Ph\cdot CH{=}C(Br)(NO_2)} \rightarrow \mathrm{Ph\cdot CH{=}C\langle} \rightarrow \mathrm{PhC{\equiv}CH} \xrightarrow{+2\mathrm{Br}} \mathrm{PhCBr{=}CHBr} \quad (14)$$

Reactions Initiated by Reducing Atoms

We may next consider the evidence for another type of electron-pairing reaction in which metals of low electron affinity react with neutral molecules. Such a reaction is the one between sodium and alkyl halides. It was shown by von Hartel and Polanyi[44] that, if sodium vapor carried in a stream of hydrogen is allowed to pass through an aperture into a chamber containing the vapor of an alkyl halide, a reaction ensues which can best be represented by the following equations involving the formation of a free methyl radical:

$$\mathrm{Na + MeCl \rightarrow NaCl + Me\cdot}$$

$$\mathrm{2Me\cdot \rightarrow C_2H_6 \rightarrow C_2H_4 + H_2}$$

$$\mathrm{2Me\cdot + H_2 \rightarrow 2CH_4}$$

In order to demonstrate that free radicals were actually formed, experiments were performed in a modified apparatus[45] in which methane was used as a carrier gas for the sodium vapor. The mixture of sodium vapor and methane then passed through a nozzle into the alkyl halide vapor as before; then, before the free methyl radicals so produced had a chance to react completely, the gas streamed through a second nozzle into iodine vapor, where the free alkyl radical (methyl or ethyl) reacted with the iodine to produce the corresponding alkyl iodide. In other experiments chlorine or hydrogen was used in place of the iodine.[46]

Additional evidence that free radicals are produced by this method has recently been furnished by Allen and Bawn,[47] who employed the Paneth technique with antimony and tellurium mirrors.

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[44] von Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930).

[45] Horn, Polanyi, and Style, *Trans. Faraday Soc.*, **30**, 189 (1934).

[46] (*a*) Horn and Polanyi, *Z. physik. Chem.*, **25B**, 151 (1934); (*b*) von Hartel, *Trans. Faraday Soc.*, **30**, 187 (1934).

[47] A. O. Allen and Bawn, *ibid.*, **34**, 463 (1938).

For the corresponding reaction in solution, the Wurtz-Fittig reaction, it is more difficult to present a convincing argument in favor of a nonionic mechanism. Two mechanisms have been proposed and supported:

$$(1) \qquad RI + Na \rightarrow R\cdot + NaI$$

$$2R\cdot \rightarrow R_2$$

$$(2) \qquad RI + 2Na \rightarrow Na^+R^- + NaI$$

$$NaR + RI \rightarrow NaI + R_2$$

Recently strong support for the first mechanism has been found.[48] It was repeatedly observed in studies on the Fittig, Ullmann, and related reactions that one of the products formed on treating aryl halides in ether solution with sodium or copper was the corresponding aryl hydrogen compound. Since free radicals always seem to abstract hydrogen from aliphatic solvents, this fact strongly suggests the initial production of free aryl radicals. In order to obtain confirmation of this view, iodobenzene was caused to react with copper bronze in a sealed tube in the presence of an excess of ethyl benzoate. This time, since the solvent was aromatic, it would be expected that if free phenyl radicals were formed they would substitute in the *ortho* and *para* positions of ethyl benzoate (it should be remembered that when free radicals attack benzene derivatives they enter the *ortho* and *para* positions irrespective of the substituent group already present). Such was found to be the case, no other reaction products being observed.

The classical example of the formation of triphenylmethyl and hexaphenyl ethane by the action of silver and other metals on triphenylmethyl chloride also falls in the category under discussion. The electron-pairing mechanism of such dimolecular reductions may be considered as established by the work of Gomberg and others. In the closely related tetra-arylethanes, although they do not in general dissociate on heating in benzene, xylene, etc., colorations are frequently observed during the reaction of the diarylmethyl halides with silver.[14, 49] Although only dimolecular reduction products can be detected, the coloration is taken as evidence of the momentary existence of free diarylmethyl radicals. Further evidence for this contention is found in the fact that if the reaction with diphenylchloromethane is carried out in an atmosphere of oxygen or nitrous oxide, the yield of *s*-tetraphenylethane is reduced from 100 to 2 to 8% presumably because the free radicals are removed as a peroxide or a nitrous oxide addition compound.[50]

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[48] Rapson and Shuttleworth, *Nature*, **147**, 675 (1941).

[49] Nauta and Mulder, *Rec. trav. chim.*, **58**, 514 (1939).

[50] Idem, **58**, 1070 (1939).

The formation of Grignard compounds presumably involves an electron-pairing mechanism, at least it may be said that such has been shown to be the case in the formation of triphenylmethyl magnesium bromide. Gomberg and Bachmann [51] showed that when one mole of triphenylmethyl bromide reacted with a half gram-atom of magnesium only triphenylmethyl and magnesium bromide were present at the end of the reaction.

$$\mathrm{Mg} + 2\mathrm{Ph_3CBr} \rightarrow 2\mathrm{Ph_3C\cdot} + \mathrm{MgBr_2} \qquad (15)$$

When an additional half gram-atom of magnesium was added at this stage there resulted quantitative conversion into triphenylmethyl magnesium bromide.

$$2\mathrm{Ph_3C\cdot} + \mathrm{MgBr_2} + \mathrm{Mg} \rightarrow 2\mathrm{Ph_3CMgBr} \qquad (16)$$

To check Equation 16 they showed that pure triphenylmethyl reacts with magnesium bromide and magnesium to yield triphenylmethyl magnesium bromide.

On the basis of this work it seems very likely that the formation of Grignard reagents in general proceeds by the same mechanism. The frequent formation of bimolecular reaction products (R_2 from RCl) during Grignard reactions is easily explained on this basis. Other workers also have interpreted the formation of Grignard compounds by a free-radical mechanism.[52]

Oxygen Induced Chain Reactions

Since oxygen gas is paramagnetic it is considered to contain two electrons whose spins are not paired and its formula is frequently written as $:\underset{\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot}{\ddot{\mathrm{O}}}:$, which makes it a free radical of the diradical type. Its well-known reaction with triphenylmethyl to form the corresponding peroxide is a natural consequence of the pairing of the odd electrons of these two reactants. Kinetic investigations of the reaction show, however, that the reaction is in reality a chain reaction.[53] The following equations represent the probable steps in the reaction:

$$\mathrm{Ph_3C{-}CPh_3} \rightleftarrows 2\mathrm{Ph_2C\cdot}$$

$$\mathrm{Ph_3C\cdot} + :\underset{\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot}{\ddot{\mathrm{O}}}: \rightarrow \mathrm{Ph_3COO\cdot}$$

$$\mathrm{Ph_3COO\cdot} + \mathrm{Ph_3C{-}CPh_3} \rightarrow \mathrm{Ph_2COOCPh_3} + \mathrm{Ph_3C\cdot}$$

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[51] Gomberg and Bachmann, *J. Am. Chem. Soc.*, **52**, 2455 (1930).

[52] (*a*) Gilman and Fothergill, *J. Am. Chem. Soc.*, **50**, 3334 (1928); (*b*) Gilman and Kirby, *ibid.*, **51**, 1572 (1929).

[53] (*a*) Ziegler, Ewald, and Orth, *Ann.*, **479**, 277 (1930); (*b*) Ziegler and Orth, *Ber.*, **65**, 628 (1932); (*c*) Ziegler and Ewald, *Ann.*, **504**, 162 (1933).

Many other chain reactions are induced by oxygen as a result of its diradical properties. Thus the following mechanism[54] has been suggested for the "autoxidation" of benzaldehyde by ferric salts in the presence of oxygen.[55]

$$\mathrm{PhCHO} + \mathrm{Fe}^{+++} \rightarrow \mathrm{Ph}\underset{\bullet}{\mathrm{C}}{=}\mathrm{O} + \mathrm{Fe}^{++} + \mathrm{H}^{+}$$

$$\mathrm{Ph}\underset{\bullet}{\mathrm{C}}{=}\mathrm{O} + \mathrm{O}_2 \rightarrow \mathrm{PhCO{\cdot}OO\cdot}$$

$$\mathrm{PhCO{\cdot}OO\cdot} + \mathrm{PhCHO} \rightarrow \mathrm{PhCO{\cdot}OOH} + \mathrm{Ph}\underset{\bullet}{\mathrm{C}}{=}\mathrm{O}$$

The reaction chains can be effectively broken by certain substances, among them dibiphenyleneethylene, which becomes oxidized to fluorenone in the process.[56]

These examples are sufficient to indicate the possibilities of oxygen-induced chain reactions; a number of others are known.

The Peroxide Effect

General Theory. The peroxide effect in the addition of hydrogen bromide to alkenes, which was discovered and extensively investigated by Kharasch and his collaborators, has already been partially discussed in an earlier chapter. An extension of that discussion in the present chapter is justified by the fact that it is now believed that the "abnormal addition" involves an electron-pairing mechanism, whereas the "normal addition" is electron sharing in character. These conclusions were reached only after a vast amount of painstaking research, which has recently been critically reviewed by Mayo and Walling.[57] The following discussion is taken largely from their review, which the reader should consult for the bibliography as well as for the related polemics.

The normal and abnormal reactions are apparently independent and competing. This conclusion is based on experiments which show that compounds having a low rate of normal addition (this is ideally determined by using HCl or HI which are not subject to the peroxide effect) are most influenced by traces of oxygen or peroxides which catalyze the competing abnormal addition. When the normal addition is somewhat faster (e.g., vinyl bromide) it is capable of overpowering the abnormal reaction only when the latter is inhibited by an antioxidant. In the case of allyl bromide the normal addition reaction is still faster and ordinary purification of materials and exclusion of air during the addition reaction result in complete victory for the normal reaction. Finally we

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[54] See Ref. 18, p. 179.

[55] Wieland and Richter, *Ann.*, **486**, 226 (1931).

[56] Wittig and Lange, *ibid.*, **536**, 266 (1938).

[57] Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

encounter a group of alkenes, including styrene, in which the normal reaction is so fast that the abnormal addition product may be obtained only by using a solvent to cut down the rate of the normal reaction. This dilution effect is a natural consequence of the fact that the normal reaction is largely, if not entirely, of an order higher than the second. The abnormal reaction shows no large dilution effect.

The chief arguments advanced in favor of the electron-pairing mechanism for the abnormal reaction and the details of its operation are as follows:

(1) The abnormal addition is caused by small amounts of oxygen and peroxides and inhibited by small amounts of antioxidants. Therefore it must be a chain reaction. This strongly suggests an electron-pairing mechanism.

(2) The oxygen or peroxides must alter the mechanism through action on the hydrogen bromide, not the alkene, since hydrogen chloride is not subject to the peroxide effect. Bromine should result from such an interaction, but molecular bromine has no effect on the reaction in the dark. However, if bromine atoms were produced by the oxidation a chain reaction would inevitably follow if the energy requirements were met.

$$\mathrm{HBr} + \mathrm{O_2} \xrightarrow{\text{alkene}} \mathrm{HOO\cdot} + \mathrm{Br\cdot} \tag{17}$$

$$\mathrm{RCH{=}CH_2} + \mathrm{Br\cdot} \longrightarrow \mathrm{R}\underset{\bullet}{\mathrm{C}}\mathrm{HCH_2Br} \tag{18}$$

$$\mathrm{R}\underset{\bullet}{\mathrm{C}}\mathrm{HCH_2Br} + \mathrm{HBr} \longrightarrow \mathrm{RCH_2CH_2Br} + \mathrm{Br\cdot} \tag{19}$$

Equation 17 attempts to indicate that the oxygen reacts with the hydrogen bromide through the agency of the alkene. The reaction in the absence of the alkene is very slow, but it has been shown that, in the presence of the alkene, peroxides are quickly formed which react slowly with the hydrogen bromide.

(3) The abnormal orientation usually observed in peroxide-catalyzed additions is not surprising in view of the similar behavior of other electron-pairing reactions, but an explanation is desirable. Kharasch, Engleman, and Mayo[58] at one time suggested that since bromine atoms are electrophilic they would attack the carbon atom with the higher electron density. In the normal ionic reaction the hydrogen ion is the electrophilic atom; hence the two mechanisms would give opposite orientation. It is, of course, also conceivable that the bromine could gain electrophilic properties by becoming a positively charged ion as a result of oxidation by the peroxide. However, the above authors prefer to explain the abnormal addition on the basis of the production of bromine

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[58] Kharasch, Engleman, and Mayo, *J. Org. Chem.*, **2**, 288, 400, 577 (1937).

atoms because more energy would be required to separate charged particles in nonpolar solvents. There are objections, however, to the theory that the orientation results from the bromine atom seeking the center of highest electron density. In the first place we have already seen in the electron-pairing reactions of free radicals produced from diazotates that *ortho-para* orientation results even when the attack is made on nitrobenzene in which the point of highest electron density is the *meta* position. Furthermore it has been found that no reversal of normal orientation is observed in the abnormal addition of hydrogen bromide to α,β-unsaturated acids and esters. Mayo and Walling[57] have come to the conclusion that a more satisfactory theory of the orientation phenomena is the one which maintains that "the point of attack by the bromine atom is little affected by the polarity of the double bond, but depends upon the relative stability of the two bromoalkyl radicals which may be formed." Radical stability is here intended in the sense of higher heat of formation. In order that this theory explain the observed phenomena, it is necessary, for example, that the following decreasing stabilities of free radicals obtain:

$$\mathrm{R\underset{\bullet}{CH}\cdot CH_2Br} > \mathrm{RCHBr\cdot \underset{\bullet}{CH_2}}$$

$$\mathrm{RCHBr\cdot \underset{\bullet}{CH}X} > \mathrm{R\underset{\bullet}{CH}\cdot CHXBr}$$

$$\mathrm{RCHBr\cdot \underset{\bullet}{CH}\cdot CO_2R'} > \mathrm{R\underset{\bullet}{CH}\cdot CHBr\cdot CO_2R'}$$

The first of these pairs derives from the fact that *n*-propyl bromide results from the abnormal addition of hydrogen bromide to propylene, the second from the fact that abnormal addition to vinyl halides produces the 1,2-dihalide, and the third from the fact that peroxide-catalyzed addition to α,β-unsaturated acids yields the normal product, as predicted by either the Lucas or the English electronic theory. The authors of the theory leave these predictions for future verification.

(4) The abnormal reactions are very rapid and presumably involve long chains. The authors argue, therefore, that the energy of activation must be very small and hence that the probability of reaction is governed by the value of ΔH for bond formation. Hence a rapid chain reaction is held to be impossible when any step is appreciably endothermic. The values of ΔH for reactions 18 and 19 are given in Table I with the understanding that the hydrogen bromide may be replaced by any other halogen hydride. When two values are given for ΔH the first is based on the bond energies of Sherman and Ewell[59] and the second on those

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[59] See Groggins, *Unit Processes in Organic Syntheses*, McGraw-Hill Book Co., 1938, p. 160.

TABLE I[57]

Reaction No.	ΔH (kcal/mole)			
	HF	HCl	HBr	HI
Eq. 18	−64; −66	−27; −25	−13	+1; −4
Eq. 19	+60	+15	0	−16

of Pauling.[60] The estimates are, of course, rough but they seem to indicate that rapid atom reactions involving HF and HCl are unlikely because in those cases reaction 19 is endothermic. Furthermore they claim that reaction 17 is slow for HBr and may be negligible with HCl and HF. For HI, reactions 17 and 19 should proceed easily but reaction 18 may not; furthermore the normal reaction is very rapid and is further catalyzed by molecular iodine, which is surely present as a result of the oxidation of HI. These considerations leave HBr as the only halogen hydride which may reasonably be expected to fulfill the conditions for an abnormal addition. Thus in a rough way, at least, their theory explains why only HBr, of all the halogen hydrides, is subject to the peroxide effect.

Mercaptan Additions. Mercaptans resemble halogen hydrides in their ability to add to alkenes with the production of isomeric products.

$$RCH{=}CH_2 + R'SH \rightarrow RCH_2CH_2SR' \quad \text{(abnormal addition)}$$

$$RCH{=}CH_2 + R'SH \rightarrow RCH(SR')CH_3 \quad \text{(normal addition)}$$

Like HBr, their abnormal additions are accelerated by oxygen and peroxides but they differ in that the abnormal product is the one usually formed when no catalysts for the normal addition are used.

Bisulfite Additions. Another reagent which is apparently capable of adding to double bonds by an electron-pairing chain mechanism is sodium bisulfite. When it adds to aldehydes, ketones, or α,β-unsaturated acids the products correspond with the normal products of hydrogen halide addition. However, alkenes do not react with bisulfite even under gas pressures of 15 to 40 lb per sq in. unless oxygen is admitted, under which conditions the products isolated were exclusively the primary sulfonates, corresponding to abnormal additions as judged by the orientation observed upon addition of hydrogen bromide or mercaptan.

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[60] See Chapter V.

Mayo and Walling comment as follows on the probable mechanism of the reaction: "It has already been shown by Franck and Haber[61] and by Bäckström[62] that the oxidation of sulfite to bisulfite are chain reactions involving the $\cdot SO_3^-$ ion-radical and the $\cdot HSO_3$ radical. The necessity for using oxygen or other oxidizing agents in the addition reaction, the small proportion of agent required, and the advantage of introducing this agent gradually, as well as the inhibition of the reaction by hydroquinone, and the fact that the product corresponds to an abnormal addition, all suggest a chain reaction involving free radicals."[63]

$$\mathrm{SO_3^{=}} + \text{oxidant} \rightarrow (\cdot\mathrm{SO_3})^- + \text{oxidant}^-$$

$$(\cdot\mathrm{SO_3})^- + \mathrm{RCH{=}CH_2} \rightarrow (\mathrm{R\underset{\bullet}{C}H\cdot CH_2SO_3})^-$$

$$(\mathrm{R\underset{\bullet}{C}H\cdot CH_2SO_3})^- + \mathrm{HSO_3^-} \rightarrow \mathrm{RCH_2\cdot CH_2SO_3^-} + (\cdot\mathrm{SO_3})^-$$

The extent to which the sulfite ion-radical and the sulfonate ion-radical may be associated with a proton is not known. The range of pH over which addition can take place suggests that either or both charged and uncharged radicals may participate.

Chlorinations. In the presence of small amounts of organic peroxides, sulfuryl chloride reacts with organic substances to yield chlorinated derivatives.[64] The following equations typify the reactions.

$$\mathrm{RH} + \mathrm{SO_2Cl_2} \rightarrow \mathrm{RCl} + \mathrm{SO_2} + \mathrm{HCl}$$

$$\mathrm{R_2C{=}CR_2} + \mathrm{SO_2Cl_2} \rightarrow \mathrm{R_2CCl\cdot CR_2Cl} + \mathrm{SO_2}$$

These reactions are thought to be chain reactions involving the production of free radicals and chlorine atoms. Apparently these reactions are less facile in the neighborhood of groups or atoms having strong $-I$ effects, since (1) in the reaction with alkyl halides the chlorine atom enters the molecule as far as possible from the halogen atom already present; (2) in reactions with compounds such as toluene the side chain becomes halogenated, the second chlorine atom entering with difficulty, while a third one cannot be introduced; (3) the nitrotoluenes, acetyl chloride, and methylchloroform cannot be chlorinated under these conditions; (4) the reaction with acetic acid is difficult, whereas the higher acids readily react, chiefly in the *beta* and *gamma* positions, not the α.

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[61] J. Franck and F. Haber, *Sitzber. preuss. Akad. Wiss. Physik. math. Klasse*, 250 (1931).

[62] Bäckström, *Z. physik. Chem.*, **25B**, 122 (1934).

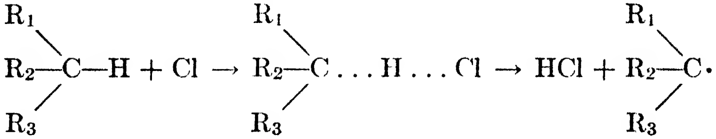
[63] Kharasch, May, and Mayo, *J. Org. Chem.*, **3**, 175 (1938).

[64] (*a*) Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142, 3432 (1939); **62**, 925 (1940); (*b*) Kharasch and Alice T. Read, *ibid.*, **61**, 3089 (1939); (*c*) Kharasch, Chao, and H. C. Brown, *ibid.*, **62**, 2393 (1940).

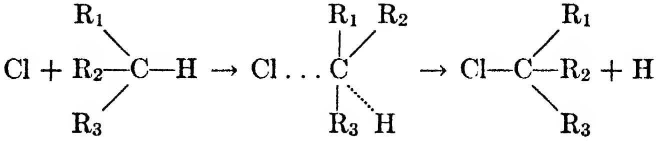
It is an interesting fact that if, instead of peroxides, a halogen carrier such as iodine is used, sulfuryl chloride introduces a chlorine atom in the *alpha* position of aliphatic acids. It is also of interest that ethyl and isopropyl benzenes are chlorinated in the *alpha* position as a result of the peroxide-catalyzed reaction.

If light is used as an activating agency sulfuryl chloride causes sulfonation, especially in the presence of aromatic compounds containing nitrogen in the ring. These too are chain reactions involving chlorine atoms and free radicals.

Since it has been shown in the hydrogen-chlorine reaction that chlorine atoms are produced photochemically, it is reasonable to explain the photochemical chlorination of methane, which proceeds with the explosive violence characteristic of gaseous chain reactions, and the photochemically activated side-chain chlorination of toluene as due to free chlorine atoms. Support for this idea is found in recent work from Kharasch's laboratory[65] in which it was shown that primary active amyl chloride, $ClCH_2 \cdot CH_2(CH_3)CH_2 \cdot CH_3$, could be converted into the optically inactive $CH_2Cl \cdot CCl(CH_3)CH_2 \cdot CH_3$ (and other products) either by photochemical chlorination or by the peroxide-catalyzed reaction with sulfuryl chloride. Since the latter reagent had been shown in a number of cases to react by the production of free chlorine atoms, the identity of the reaction products strongly suggest that free chlorine atoms are also the reactive reagent in the photochemical reaction. The chief significance of the work under discussion, however, is that the production of an inactive form of 1,2-dichloro-2-methylbutane (which contains an asymmetric carbon atom) shows clearly that the mechanism accords with Equation 20, not Equation 21,



$$R_2{-}\overset{R_1}{\underset{R_3}{C}}{-}H + Cl \rightarrow R_2{-}\overset{R_1}{\underset{R_3}{C}} \ldots H \ldots Cl \rightarrow HCl + R_2{-}\overset{R_1}{\underset{R_3}{C}}\cdot \qquad (20)$$



$$Cl + R_2{-}\overset{R_1}{\underset{R_3}{C}}{-}H \rightarrow Cl \ldots \overset{R_1\ R_2}{\underset{R_3\ H}{C}} \rightarrow Cl{-}\overset{R_1}{\underset{R_3}{C}}{-}R_2 + H \qquad (21)$$

since the latter would require stereochemical inversion and hence the retention of optical activity, whereas the former would result in racemization if the free radical had an appreciable half-life period.

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[65] H. C. Brown, Kharasch, and Chao, *J. Am. Chem. Soc.*, **62**, **3435** **(1940)**.

Intramolecular Rearrangements

It will no doubt be found, when the mechanism of intramolecular rearrangements has been more exhaustively studied, that many of them, involving as they frequently do the unstable union of two electronegative elements, involve the pyrolytic formation of free radicals. One such case in which there can no longer be much doubt as to the mechanism is the rearrangement in certain phenyl ethers at their boiling points.[66] In these reactions the nonaromatic group, such as allyl, benzyl, and *tert.*-butyl, migrate from the oxygen to the benzene nucleus. If such rearrangements are allowed to proceed in suitable solvents the free radicals produced by the thermal dissociation attack the solvent. Thus on heating benzyl phenyl ether in quinoline, benzyl quinoline is formed in addition to the usual products of the rearrangement. Toluene is also formed. Both of these facts clearly indicate the primary formation of free benzyl radicals.

The following allylic rearrangement has been shown to be catalyzed by the simultaneous presence of hydrogen bromide and peroxides:[67]

$$BrCH_2\cdot CH{=}CH\cdot CH_3 \rightarrow CH_2{=}CH\cdot CHBr\cdot CH_3$$

Since allyl-type chlorides are not susceptible to corresponding influences, the presumption is strong that an electron-pairing mechanism is involved. The rearrangement of α-bromoacetoacetic ester to the γ-bromo compound is also catalyzed by hydrogen bromide in the presence of air, peroxide, or light.[68] Again, hydrogen chloride has no such influence and the mechanism is probably of an electron-pairing character.

Electrolytic Reactions

When hydrogen ions are electrolytically discharged at the cathode it seems inevitable that free hydrogen atoms must first be formed; these then combine to form molecular hydrogen. When the solution around the cathode contains nonionized solutes they are frequently reduced. One would suspect that this reduction is brought about by the free hydrogen atoms, and some support for this idea exists. Thus the electrolytic reduction of ketones and aldehydes yields the dimolecular products.[69] These reactions are most easily explained by equations like the following:

$$2Me_2CO + 2H\cdot \rightarrow 2Me_2\underset{\bullet}{C}OH \rightarrow Me_2C(OH)C(OH)Me_2$$

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[66] Hickinbottom, *Nature*, **142**, 830 (1938). See also Mumm and Diedrichsen, *Ber.*, **72B**, 1523 (1939).

[67] Kharasch, Margolis, and Mayo, *J. Org. Chem.*, **1**, 393 (1936).

[68] Kharasch, Sternfeld, and Mayo, *J. Am. Chem. Soc.*, **59**, 1655 (1937).

[69] (*a*) Willstatter and Verauguth, *Ber.*, **38**, 1985 (1905); (*b*) Tafel, *ibid.*, **42**, 3146 (1909); (*c*) Schepss, *ibid.*, **46**, 2564 (1913); (*d*) see also Ref. 26.

Hey and Waters [26a] point out that the free radical mechanism of such reactions receives confirmation from the fact that in warm acid solutions the electrolytic reactions of ketones with mercury cathodes yield mercury dialkyls and with lead cathodes yield lead tetra-alkyls. We have already learned that such reactions are typical of free radicals.

It is customary to represent the anodic discharge of ions also as involving the preliminary production of atoms or free radicals, thus:

$$2Cl^- \rightleftarrows 2e + 2Cl\cdot \rightarrow Cl_2 \tag{22}$$

and

$$CH_3COO^- \rightleftarrows e + CH_3COO\cdot \tag{23a}$$

$$CH_3COO\cdot \rightarrow CO_2 + \cdot CH_3 \tag{23b}$$

$$2\cdot CH_3 \rightarrow C_2H_6 \tag{23c}$$

This mechanism for the electrolysis of acetates was proposed by Crum, Brown, and Walker,[70] but Glasstone and Hickling [71] prefer to explain the reaction in another way on the basis of their "hydrogen peroxide theory of electrolytic oxidations." According to this theory the electrolysis of water solutions involves the reversible anodic discharge of hydroxyl ions with the formation of free hydroxyl radicals which then combine irreversibly to form hydrogen peroxide.

$$OH^- \rightleftarrows \cdot OH + e \tag{24}$$

$$2\cdot OH \rightarrow H_2O_2 \tag{25}$$

Since the second step is irreversible and fast, the concentration of hydroxyl radicals is reduced to a small value and hence, according to the electrochemical equation for the first step,

$$E_h = E'_0 + \frac{RT}{F} \ln \frac{(\cdot OH)}{(OH^-)} \tag{26}$$

the reduction potential will be very low and this particular oxidation "will take precedence over, or will accompany to some extent, nearly all other anodic reactions. Under most conditions, therefore, it is to be expected that hydrogen peroxide will be formed, even at relatively low anode potentials, probably as a thin concentrated layer over the electrode surface. In the absence of a depolarizer capable of being oxidized, the hydrogen peroxide will decompose to give oxygen and water, but if a suitable depolarizer is present, it will bring about oxidation in its own

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[70] Crum, Brown, and Walker, *Ann.*, **261**, 107 (1891).

[71] Glasstone and Hickling: (*a*) *J. Chem. Soc.*, 1878 (1934); (*b*) *Electrolytic Oxidation and Reduction*, Chapman & Hall, London (1935); (*c*) *Chem. Rev.*, **25**, 407 (1939).

characteristic manner; this may be accompanied by oxidation due to the nascent oxygen arising from the decomposition of the peroxide and possibly by evolution of oxygen gas. The extent to which oxidation by hydrogen peroxide takes place will depend on the stability of the latter under the conditions of the electrolysis, and all factors capable of affecting the decomposition of the peroxide may be expected to have some influence on the electrolytic oxidation."[71c]

It should be pointed out that the same arguments which were used to show that hydroxyl ions should be discharged at low potentials could be applied equally well to show that organic ions, as in Equation 23, should also be discharged at very low potentials if their irreversible steps are rapid. Hence it seems by no means impossible that at least occasionally organic ions might be electrolytically oxidized by mechanisms such as that of Equation 23.

However, Glasstone and Hickling conclude from their experiments that in aqueous solution the hydroxyl ions are discharged in preference to the acetate ions, forming hydrogen peroxide in high local concentration. They then react as follows:

$$2CH_3COO^- + H_2O_2 \rightarrow C_2H_6 + 2CO_2 + 2OH^-$$

However, in nonaqueous solutions in which hydrogen peroxide cannot be formed the Crum-Brown-Walker mechanism probably operates. Thus when benzoic acid is electrolyzed in pyridine solution, γ-phenyl pyridine (and possibly some of the α-isomer) and diphenyl-4-carboxylic acid are formed in addition to diphenyl.[72] A reasonable mechanism would be the following:[26b]

$$\begin{aligned} PhCO_2H &\rightarrow PhCO_2^- + H^+ \\ PhCO_2^- &\rightarrow PhCOO\cdot + e \\ PhCOO\cdot &\rightarrow Ph\cdot + CO_2 \\ Ph\cdot + C_5H_5N &\rightarrow PhC_5H_4N + H\cdot \\ Ph\cdot + PhCO_2H &\rightarrow PhC_6H_4\cdot CO_2H + H\cdot \end{aligned}$$

THE BASIC THEORY OF ELECTRON-PAIRING REACTIONS

The evidence establishing the occurrence of electron-pairing displacement reactions has been presented and a number of examples have been given. If now we wish to equip ourselves to make predictions concerning electron-pairing reactions it is evident that we must first dig

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[72] Fichter and Stenzl, *Helv. chim. Acta*, **22**, 970 (1939).

still more deeply into the fundamental electronic laws which regulate their behavior. Among the questions we would like answered are the following: How are we to know whether or not a given mixture of substances under specified conditions is going to react by an electron-pairing mechanism? What role will be played in these reactions by influences such as electronegativity, electron affinity, bond energies, polarizability, resonance, and other electron displacements? How are these influences altered by the thermodynamic environment? In the following pages an attempt will be made to answer some of these questions as well as the present paucity of experimental data and published theories will permit.

Conditions Favoring the Occurrence of Electron-Pairing Reactions

There are three possible modes of dissociation of normal covalent linkages:

$$\mathrm{A{:}B} \rightarrow \mathrm{A{:}^-} + \mathrm{B^+} \tag{27}$$

$$\mathrm{A{:}B} \rightarrow \mathrm{A\cdot} + \mathrm{\cdot B} \tag{28}$$

$$\mathrm{A{:}B} + \mathrm{S} \rightarrow \mathrm{{:}A^-} + \mathrm{SB^+} \tag{29}$$

The third type, in which S stands for a solvent molecule, could also conceivably include the cases

$$\mathrm{AB} + \mathrm{S} \rightarrow \mathrm{SA^-} + \mathrm{B^+} \tag{29a}$$

and

$$\mathrm{AB} + 2\mathrm{S} \rightarrow \mathrm{SA^-} + \mathrm{SB^+}\ \text{etc.} \tag{29b}$$

The first type involves such a high energy of dissociation that it probably never occurs in ordinary chemical reactions. The second type involves much smaller dissociation energies, corresponding to Pauling's bond energies. The following simple calculation makes the relationship clear.

$$\begin{array}{llll}
\mathrm{C} \rightarrow \mathrm{C^+} + e; & \Delta H = 258.5\ \text{kcal} & \text{(ionization potential)} & (30a) \\
\mathrm{Cl} + e \rightarrow \mathrm{Cl^-}; & \Delta H = -85.3 & \text{(electron affinity)} & (30b) \\
\mathrm{C{-}Cl} \rightarrow \mathrm{C} + \mathrm{Cl}; & \Delta H = 66.5 & \text{(bond energy)} & (30c) \\
\hline
\mathrm{C{-}Cl} \rightarrow \mathrm{C^+} + \mathrm{Cl^-}; & \Delta H = 239.7\ \text{kcal} & & (30d)
\end{array}$$

The last two equations represent respectively the electron-pairing and electron-sharing dissociations. The third type, Equation 29, normally involves the least energy of dissociation because the ionization is thermodynamically coupled with the highly exothermic solvation process.

Solvation requires the presence of unshared electron pairs or coordinative unsaturation in the solvent, which means in general a polar solvent. However, lacking a polar environment, which is the case in the gaseous phase or in solutions in nonpolar solvents, it is evident from the above thermodynamic considerations that an "unpairing" of electrons is the favored mode of dissociation.

It must be remembered that the above considerations apply only to normal covalences. If coordinate covalences are involved, as in Equation 3, the picture may be very different indeed, since then the "unsharing" process does not involve the work of separating unlike charges.

In addition to dissociation reactions and their reverse (association) we have the displacement type in which the joint operation of association and dissociation reduces the activation energy to a value below the dissociation energy, as we learned in studying the transition state theory. In such cases, if the attacking reagent is an ion or one end of a dipolar molecule, an electron-sharing reaction ensues. If, however, the attacking particle—charged or uncharged—contains an unpaired electron and if the molecule attacked contains none (which is characteristic of most stable substances) the reaction, if any, will be of the electron-pairing type.

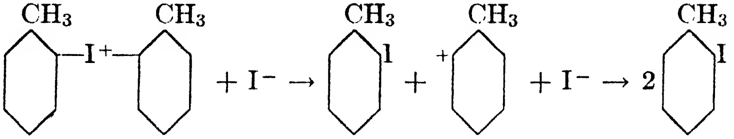
Although electron-sharing displacement reactions may take place between un-ionized compounds I know of no case where electron-pairing displacement reactions have been shown to occur between two molecules neither of which has any unpaired electrons. Thus it appears that an electron-pairing type of dissociation is prerequisite to this latter type of reaction. This simplifies the problem of predicting when such reactions are apt to occur and reduces it to the problem of predicting the conditions under which free radicals or atoms containing unpaired electrons can be formed. We are thus led to the following principle.

P 26. Displacement reactions of the electron-pairing type may only occur (1) in a nonpolar environment as the result of primary photochemical or thermal dissociation or (2) in any environment in the presence of a sufficiently powerful monoelectronator or monodelectronator.

It must be realized in applying this principle that an electrode may act as a monoelectronator or monodelectronator and the thermal decomposition of catalysts, such as peroxides, produces free radicals which may induce chain reactions. Both possibilities are covered by the wording of the principle.

The greatest difficulty in applying the principle lies in the fact that all of the conditions of the principle may be fulfilled and yet no reaction will take place unless the free energy and activation energy requirements are met. This difficulty is not new to us, and the problem is by no means solved. However, a little progress has been made in this direction and some of the more significant developments will be described later in this chapter.

It must not be thought that thermal decomposition always produces a symmetrical rupture of an electron-pair bond. Indeed it would be difficult to formulate a reasonable electron-pairing mechanism for the decomposition of most ions. For example, consider the decomposition of di-*o*-tolyliodonium iodide. In this case it is definitely known that the I—I bond is an ionic bond [73] and the production of pure *o*-iodotoluene by decomposition of the dry salt at 155° is thought to proceed by the following mechanism:



In view of the free positive pole initially present on the bound iodine atom, it would be hard indeed to believe that on breaking a C—I bond one electron would be attracted and the other repelled by this positive pole.

The Influence of Polarizability

In discussing the reaction between sodium atoms and organic halide vapors, Heller and Polanyi [74] have remarked, "It seems reasonable that the force which counteracts an elongation of the halogen bond should also be responsible for the chemical inertia of such reactions which lead to the splitting up of the bond." As a measure of these counteracting forces, or bond strengths, they chose the restoring force constants, f, as derived from Raman spectra and compared them with their own values of velocity constants, k, or collision numbers, S, where the latter is defined by the equation

$$S = 6.3 \times \frac{10^{14}}{k}$$

Some of their values are given in Table II. The values given show the predicted relationship between the velocity and the force constant, although the parallelism is not equally evident for some of their data on inorganic chlorides.

A similar relationship was observed by Ogg [75] who found the activation energies for the bimolecular reactions of hydrogen iodide with

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[73] Medlin, *J. Am. Chem. Soc.*, **57,** 1026 (1935).

[74] Heller and Polanyi, *Trans. Faraday Soc.*, **32,** 633 (1936).

[75] Ogg, *J. Am. Chem. Soc.*, **56,** 534 (1934).

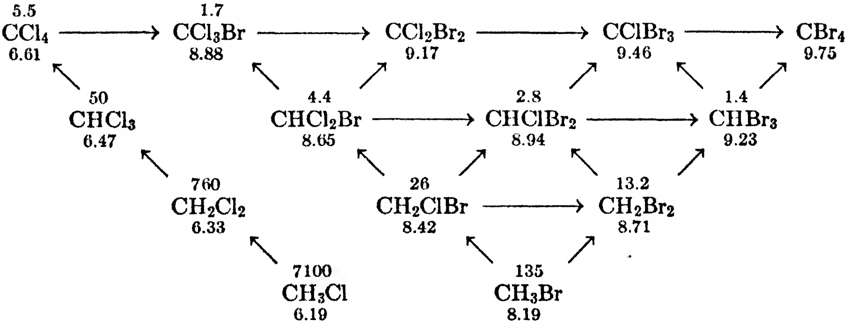
TABLE II

COMPOUND	S	$f \times 10^{-5}$
CH_3Cl	7100	3.12
CH_2Cl_2	310	2.94
$CHCl_3$	22	2.47
CCl_4	2	2.00
CH_3Cl	7100	3.12
CH_3Br	75	2.61
CH_3I	1	2.15

methyl, ethyl, and *n*-propyl iodides to be respectively 33.4, 29.8, and 29.2 kcal. It is to be observed that the second and third values are about 10 per cent lower than the first. A parallel relationship exists among the Raman frequencies associated with the stretching of the carbon-halogen bond in homologous alkyl halides, those for the methyl halides being about 10 per cent greater than for the ethyl halides.

Another closely related study was made on the reaction between sodium atoms and polyhalogenated methane derivatives by Haresnape, Stevels, and Warhurst.[76] In this case the authors chose to compare the velocity data with "atomic refractions" instead of Raman force constants. The "atomic refractions" of the reacting halogen atoms were calculated by a method devised by Stevels.[77] By this method he claimed to be able to calculate the alteration in the atomic refraction of an atom in a molecule produced by further substitution. This method was discussed and criticized in Chapter V.[78] The data for the comparison in question are given in Table III. The figures above each formula are the "collision yields," i.e., the average number of collisions per effective col-

TABLE III[76]



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[76] Haresnape, Stevels, and Warhurst, *Trans. Faraday Soc.*, **36,** 465 (1940).

[77] Stevels, *ibid.*, **33,** 1381 (1937); **34,** 429 (1938).

[78] This text, p. 81.

lision of the reacting particles, whereas the figures under the formulas are the atomic refractions of the reacting halogen atoms. In each molecule containing both chlorine and bromine, the figure given refers to the bromine atom since it is the one to react.

From the data in Table III we may draw the following conclusions concerning the halide molecules listed and their reactions with sodium atoms:

(1) An increase in the electronic polarizability of the carbon-halogen bond which reacts, results in an increased reaction rate.

(2) The substitution of a hydrogen by a halogen atom increases the electronic polarizability of a given carbon-halogen bond already in the same molecule.

(3) The replacement of a chlorine by a bromine atom increases the electronic polarizability of a given carbon-halogen bond.

The second of these conclusions is contrary to the English theory, as was pointed out before.[78] If, however, an improvement of Stevel's mathematical method should bring it into line, conclusion 1 would no longer be valid. For the time being, this discrepancy must remain a moot point. The best that we can do is to conclude tentatively that polarizability influences alter the probability of chemical reaction by an electron-pairing mechanism in the same way as for an electron-sharing mechanism, viz., greater polarizability means greater reactivity.

The *PZ* Factor in Electron-Pairing Reactions

The work of Norrish and his collaborators[79] gives us some insight into the problem of explaining why the probability factor P is unchanged for one group of reactions as we pass from the gas phase to solution or from solvent to solvent, and may for simple reactions be of the order of unity ("normal reactions"), whereas for another group of reactions in solution, P not only has a small value but varies widely from solvent to solvent, becoming smaller as the polarity of the solvent decreases ("abnormal reactions").

These workers studied the photochemical decomposition of ketones. In the gas phase, reactions of the type of Equation 31 preponderated with ketones having short hydrocarbon chains, whereas those involving long chains reacted according to Equation 32.

$$\mathrm{MeCOEt} \rightarrow \cdot\mathrm{COMe} + \mathrm{Et}\cdot \rightarrow \mathrm{CO} + \mathrm{Me}\cdot + \mathrm{Et}\cdot \rightarrow \mathrm{CO} + (\mathrm{C_2H_6} + \mathrm{C_3H_8} + \mathrm{C_4H_{10}}) \quad (31)$$

$$\mathrm{MeCO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3} \rightarrow \mathrm{Me_2CO} + \mathrm{CH_2{=}CH\cdot CH_3} \quad (32)$$

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[79] Reviewed by Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937).

When these reactions are carried out in saturated hydrocarbon solvents the free radicals produced in Equation 31, instead of combining with each other, abstract hydrogen from the solvent molecules, thus producing methane, ethane, acetaldehyde, and carbon monoxide and producing unsaturation in the solvent

$$\cdot CH_3 + C_nH_{2n+2} \rightarrow CH_4 + C_nH_{2n+1} \quad \text{etc.}$$

Reaction 32 is unchanged in solution since the net effect is the same as though no free radicals were produced. (This will be discussed below.)

Di-*n*-propyl ketone decomposes by both mechanisms. On studying the quantum yields for each of these concurrent reactions it was found that they were essentially constant over a temperature range of 20° to 100° in the gas reaction. In solution, however, the quantum yield in the reaction typified by Equation 31 is markedly influenced by temperature and reduced to an extremely small value, whereas in the other reaction the quantum yield is about the same as in the gaseous reaction and is only slightly affected by temperature. The explanation offered is that the first reaction, when occurring in solution, consists almost completely of a reaction of the free radicals with the solvent. This reaction is temperature dependent and at low temperatures it is so slow that much primary recombination of the free radicals occurs (Franck-Rabinowitsch principle) and the net effect of the light absorption is largely the dissipation of the light energy as heat. This results in a low quantum yield and a low probability factor, *P*.

The reaction resembling Equation 32 presents a sharp contrast in that it proceeds just about as fast in solution as in the gas phase and is nearly temperature independent. The same thing is true of aldehydes which decompose photochemically according to the equation [80]

$$RCHO \rightarrow RH + CO$$

producing little or no R_2 or H_2, and react only slightly with the solvent. In explanation of this behavior Norrish [81] has suggested that the two stages of the photochemical decomposition process

$$RCHO + h\nu \rightarrow R\cdot + H\underset{\bullet}{C}{=}O \quad -89.5 \text{ cal}$$

$$H\underset{\bullet}{C}{=}O \rightarrow H\cdot + CO \quad \text{(thermoneutral)}$$

occur in such rapid succession that the two fragments R· and H· rarely get free from one another and hence combine before they have a chance

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[80] (*a*) Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931); (*b*) M. Burton and G. K. Rollefson, *J. Chem. Phys.*, **6**, 416 (1938).

[81] Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).

to react with the solvent. It seems strange, however, that in the similar decomposition of such compounds as methyl ethyl ketone, the two free radicals which break away from the carbonyl group do manage to evade each other's influence long enough to form ethane and butane in the gas phase reaction and to react with the solvent when the decomposition occurs in solution. I see no reason to believe that the second step of this decomposition is any slower than that of the aldehyde, especially since, as we shall see, the former is exothermic. Therefore I prefer the explanation suggested by Griffiths,[82] that the difference between the aldehyde and ketone lies not in the activation energy of the second step of the dissociation but rather in the probable fact that correct orientation of two alkyl radicals may have to occur before mutual collision can produce union, whereas no such orientation would be required for the hydrogen atom.

In reactions like that of Equation 32 the nonpolar dissociation of one linkage necessarily produces at the same moment two free radicals which are so close to each other that, if facile disproportionation between them happens to be possible, the chances are that they will react with each other before they have a chance to react with the solvent. If this is so, it should be equally true that in reactions like that of Equation 31, in which two free radicals separate from a third fragment which happens to be stable, there should be a greater probability that reaction with the solvent will preponderate since the dissociation may occur in steps. It may also be significant that here the two free radicals are farther apart than if they had been produced by the dissociation of one bond only.

In support of this idea we might first mention that the above principle ought to apply to thermal as well as to photochemical decompositions [79] and then recall that in the thermal decompositions of diazonium compounds, diacyl peroxides and nitrosoacylarylamines in solution, reaction with the solvent is always the chief reaction. In all these cases the free radicals which reacted with the solvent were produced by the rupture of separate bonds. Even in the *syn*-diazocyanides, in which the aryl and cyano radicals are very close to each other, treatment with copper results in the interaction of the radicals with the solvent and not in their union with each other.[35] Aldehydes form the sole exception to this rule, and Griffiths' explanation seems to account for the anomaly.

We may tentatively conclude that when thermal or photochemical decompositions in solution result in the rupture of two bonds in the same molecule (neither one being a bond to a hydrogen atom) with the production of one fragment which, like CO or N_2, is stable, the operation of the Franck-Rabinowitsch principle of primary recombination will result in a

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[82] J. G. A. Griffiths, *Trans. Faraday Soc.*, **30**, 117 (1934).

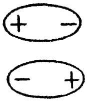
lowering of the probability factor, P, and the chief reaction will be with the solvent; and that when the decomposition results in the primary rupture of only one linkage, if the two radicals so produced can be stabilized by mutual disproportionation, reaction with the solvent molecules is slight and the probability factor, P, will not vary much on passing from the gas phase to solution or from one solvent to another.

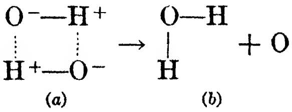
An entirely different influence affecting the probability factor P is the purely steric effect of vicinal atoms. Thus if a free methyl radical attacks a saturated hydrocarbon it will break a C—H bond rather than a C—C bond despite the fact that more energy is required to break the C—H. Thus, for example,[83]

$$\cdot CH_3 + CH_3\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow CH_4 + CH_3\underset{\bullet}{C}H\cdot CH_2\cdot CH_3$$

The explanation is that the carbon atoms of the hydrocarbon are so thoroughly encased by surrounding hydrogen atoms that the attacking methyl group cannot get close enough to them to rupture a C—C bond.

The Influence of Dipole Moments in Free Radicals

Joseph Weiss[84] has pointed out that when free radicals have dipole moments, such as in the hydroxyl radical, the electrostatic interaction between two such radicals makes it much more probable that orientation will occur during their mutual approach, with the result that at the moment of impact there will be a very high probability that a positive center and a negative center will come together. Of the two ways in which this can happen,  and , the first will preponderate because it represents a condition of lower potential energy. In hydroxyl radicals this means that there is a very small probability of hydrogen peroxide being formed, since this would necessitate the union of the two negatively charged oxygen atoms. Rather, one would expect that they would approach each other in the favored orientation (*a*)



$$\underset{(a)}{\begin{matrix} O^{-}\text{—}H^{+} \\ \vdots \qquad \vdots \\ H^{+}\text{—}O^{-} \end{matrix}} \rightarrow \underset{(b)}{\begin{matrix} O\text{—}H \\ | \\ H \end{matrix}} + O$$

and then disproportionate, if the energy relationships favor such a change.

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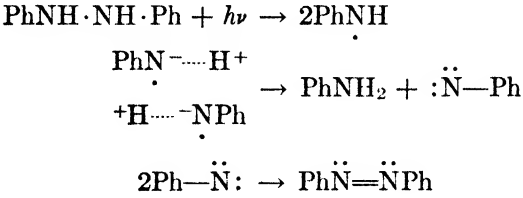
[83] (*a*) Frey, *Ind. Eng. Chem.*, **26**, 198 (1934); (*b*) Sickman and Allen, *J. Am. Chem. Soc.*, **56**, 1251 (1934).

[84] Weiss, *Trans. Faraday Soc.*, **36**, 856 (1940).

As a matter of fact hydrogen peroxide is thermally decomposed with great ease and would be expected to yield free hydroxyl radicals on so doing. As is well known, the decomposition products are water and oxygen.

It should be evident from the above that disproportionation should be favored in the case of radicals having dipole moments. Experience bears this out in general.

An example from the realm of organic chemistry was supplied by Weiss.[84] Irradiation of an alcoholic solution of hydrazobenzene with light in the region between 2300 and 2700 A° in the absence of oxygen yielded aniline and azobenzene. The following mechanism was suggested:



$$PhNH\cdot NH\cdot Ph + h\nu \rightarrow 2Ph\underset{\bullet}{N}H$$

$$\begin{array}{l} Ph\underset{\bullet}{N}^{-}\cdots H^{+} \\ {}^{+}H\cdots {}^{-}\underset{\bullet}{N}Ph \end{array} \rightarrow PhNH_2 + :\ddot{N}—Ph$$

$$2Ph—\ddot{N}: \rightarrow Ph\ddot{N}{=}\ddot{N}Ph$$

In conclusion we must recognize that the probability factor P, being much dependent on orientation influences in general, would naturally be much affected by the presence of dipole moments in free radicals.

Bond Energies in Relation to Electron-Pairing Reactions

General Remarks. The term "bond energy" has already been defined as the amount of energy which must be absorbed to break a bond of a gaseous molecule with the production of neutral gaseous atoms or radicals and is customarily expressed in kcal/mole. The definition itself suggests that bond energies are ideally suited to the measurement of the heat of formation of free radicals from neutral molecules. This would be true if it were not for the fact that tables of bond energies are based on the assumption that, for example, the rupture of each successive bond of methane involves the same amount of energy. We have already seen that this is probably far from true and although such errors would cancel each other in all calculations involving the rupture of all four bonds, this would not be the case for a reaction such as

$$CH_4 \rightarrow H\cdot + \cdot CH_3 \qquad (33)$$

and this happens to be just the type of reaction in which we are interested at the moment.

If, however, we are to avoid entangling ourselves with certain very questionable complications of chemical physics, the best we can do is to use bond energies for the estimation of the heats of such reactions as that of Equation 33.

It happens, however, that Pauling's values for the energies of bonds involving carbon must be corrected before they may be used even for such a rough calculation.[85, 86] This correction arises from the fact that gaseous elementary carbon may exist in two forms—chemically divalent and tetravalent—which are referred to respectively as the ^3P and ^5S states. The energy difference between these two forms has been estimated spectroscopically [87] to be 37 kcal. It happens that gaseous carbon exists in the ^3P (divalent) state, whereas the imaginary dissociation of organic molecules into atoms produces carbon atoms in the ^5S (tetravalent) state. Thus the above correction must be applied to the ordinary bond energy values if we are to use them in calculations involving the production of free radicals rather than atoms.[86] The application of this correction to the bond energies of Sidgwick and Bowen [88] give the values listed in Table IV.

It will be noticed that the value of 103 kcal for the C—H bond energy is considerably higher than Pauling's value of 87.3, as would be expected. It is significant that all estimates of the energy required to break the first C—H bond in methane place it at or above 95 kcal.[89] It has been calculated from the reaction of deuterium atoms with methane to be 108 ± 5 kcal,[89b] from *ortho-para* hydrogen conversion by methyl radicals to be about 103 kcal,[90] from the thermal decomposition of methane to be 100 ± 6 kcal,[91] and from the homogeneous thermal decomposition of alkyl iodides together with some thermochemical data to be 103.6 kcal.[89d] These values accord well with Norrish's value of 103 kcal (Table IV) and strongly hint at the correctness of his underlying premises.

The use of Table IV for calculating the heats of reactions such as that of Equation 33 should be obvious. Thus for Equation 33, $\Delta H = 103$ kcal, while the production of free methyl radicals from ethane should absorb 89.5 kcal/mole.

If we are to consider the relation between bond energies and the course of electron-pairing reactions, it is immediately obvious that we are once

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[85] Norrish, *Trans. Faraday Soc.*, **30,** 103 (1934).

[86] Mecke, *Z. Elektrochem.*, **36,** 589 (1930).

[87] Heitler and Herzberg, *Z. Physik*, **53,** 52 (1929).

[88] Sidgwick and Bowen, *Ann. Repts. Chem. Soc.*, 367 (1931).

[89] (*a*) Hartel and Polanyi, *Z. physik. Chem.*, **11,** 97 (1931); (*b*) Trenner, Morikawa, and H. S. Taylor, *J. Chem. Phys.*, **5,** 203 (1937); (*c*) Burton, *ibid.*, **7,** 1072 (1939); (*d*) Butler and Polanyi, *Nature*, **146,** 129 (1940); (*e*) H. A. Taylor and Burton, *J. Chem. Phys.*, **7,** 572 (1939).

[90] Patat, *Z. physik. Chem.*, **32B,** 274 (1936).

[91] Rice and Dooley, *J. Am. Chem. Soc.*, **56,** 2747 (1934).

TABLE IV

SUBSTANCE	LINK	BOND ENERGY (kcal)
CH_4	H—C	103
C_2H_6	C—C	89.5
CH_3NH_2	C—N	64.2
CH_3NCO	C=N	129.5
C_2H_4	C=C	162
H_2CO	C=O	178
Me_2CO	C=O	183.5
CO	C≡O	235.5 *
C_2H_2	C≡C	220.5
HCN	C≡N	207.5
N_2	N≡N	210

* No correction was necessary for this value since in CO the carbon is already in the divalent condition.

more face to face with the problem of relating thermal data to reaction rates. We have learned that, in general, there seems to be no necessary relationship between the height of an energy hump and the difference in levels between two adjacent energy valleys. But if a reaction consists merely in the breaking of one bond, then it would seem inevitable that the energy of activation should equal the ΔH for the dissociation. Thus if the primary rate-determining step of an electron-pairing reaction is the symmetrical rupture of an electron pair bond, the activation energy should equal the bond energy.

When we turn to experimental work in search of corroboration of this idea we find that it is frequently difficult to demonstrate that the rate-determining process is a unimolecular decomposition involving the rupture of one bond;[92] in fact, it sometimes happens that it is not. Thus Jones and Ogg[93] decided that the main mechanism of the thermal decomposition of *n*-propyl iodide is as follows:

$$n\text{-}C_3H_7I \rightleftarrows n\text{-}C_3H_7 + \tfrac{1}{2}I_2 \quad \text{(equilibrium)}$$

$$n\text{-}C_3H_7 + I_2 \rightarrow iso\text{-}C_3H_7I + I \quad \text{(slow)}$$

$$iso\text{-}C_3H_7I \rightarrow \tfrac{1}{2}C_3H_8 + \tfrac{1}{2}C_3H_6 + \tfrac{1}{2}I_2 \quad \text{(rapid)}$$

Even the mechanism of the thermal decomposition of methane is in doubt. Thus Rice and Dooley[91] claim that the primary rate-controlling step is

$$CH_4 \rightarrow CH_3 + H \tag{34}$$

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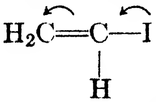
[92] See, for example, J. L. Jones and Ogg, *J. Am. Chem. Soc.*, **59**, 1939 (1937).

[93] Jones and Ogg, *ibid.*, **59**, 1931 (1937).

with an activation energy of 100 kcal while Belchetz[94] presents good evidence that it is

$$CH_4 \rightarrow CH_2 + H_2 \qquad (35)$$

Kassel[95] presents arguments against Rice and Dooley and in favor of Belchetz and calculates the activation energy to be 79.0 kcal.

Turning next to the thermal decomposition of organic iodides we find that Ogg[96] studied the thermal reactions of methyl, ethyl, and *n*-propyl iodides with hydrogen iodide and concluded that the reaction is complex, involving two rate-controlling steps: (1) a bimolecular reaction of alkyl iodide and hydrogen iodide, and (2) a unimolecular dissociation of the alkyl iodide into an alkyl radical and an iodine atom. He calculated the energy of activation for the unimolecular reactions to be 43 kcal in each case. He also studied the thermal dissociation of *s*-butyl iodide and found it also to be of a complex mechanism involving a unimolecular decomposition of the iodide into a free alkyl radical and an iodine atom, the energy of activation for which he found to be 39.42 kcal.[97] The corresponding value for *iso*-propyl iodide[92] was found to be 42.9 and for acetyl iodide[98] to be 43.1 kcal. It is to be noted that all these values fall rather close to Pauling's value for the C—I bond energy, 45.5 kcal, which value, however, is based on that of 87 kcal for the C—H bond. But we have seen that at least 95 kcal is required to rupture the first C—H bond in methane, and if this value is used in estimating the bond strength of C—I in alkyl halides a new value of at least 53 kcal is obtained for the C—I bond.[89d] This happens to correspond very well with the activation energy for the thermal decomposition of ethyl iodide, which was shown by Butler and Polanyi[89d] to involve a unimolecular disruption of the C—I bond as the rate-determining process. They obtained the value of 52.5 kcal for ethyl iodide. A summary of their results is given in Table V. The bond energies there given were calculated from the approximate relationship log $k = -Q/RT + 13$. In the cases of the phenyl and vinyl iodides it is apparent that resonance of the type  $H_2C{=}\underset{\displaystyle H}{\underset{|}{C}}{-}I$ would strengthen the C—I bond. This accounts for the higher bond energies (activation energies) in these two cases. The lower bond energies for the allyl, benzyl, and acetonyl iodides are

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[94] Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

[95] Kassel: (*a*) *J. Am. Chem. Soc.*, **54**, 3949 (1932); (*b*) *ibid.*, **57**, 833 (1935).

[96] Ogg, *J. Am. Chem. Soc.*, **56**, 526 (1934).

[97] Ogg, *Trans. Faraday Soc.*, **31**, 482 (1934).

[98] J. L. Jones, *J. Am. Chem. Soc.*, **61**, 3284 (1939).

TABLE V

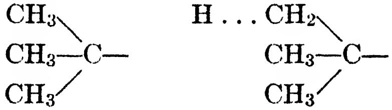
Iodide	Suggested Bond Energy (kcal)	
Ethyl	52.5	
Vinyl	56.6	Partial double bond character.
Phenyl	54.0	
Allyl	39.0	Radical degeneracy.
Benzyl	44.0	
Acetonyl	45.5	
t-Butyl	45.1	
Benzoyl	44.5	
Acetyl	(50.7)	

interpreted as due to a degeneracy of the free radicals which stabilizes them relative to the undissociated iodide:

$$H_2C{=}CH{-}CH_2I \leftrightarrows H_2C{=}CH{-}\underset{\bullet}{C}H_2 + \cdot I: \qquad (36a)$$

$$H_2C{=}CH{-}\underset{\bullet}{C}H_2 \rightleftarrows H_2\underset{\bullet}{C}{-}CH{=}CH_2 \qquad (36b)$$

The strong reduction of bond strength of the *t*-butyl iodide they explain as due to a free radical degeneracy of the type



(37)

in which the right-hand form may be present in nine different forms as compared with only three in the ethyl radical (**P 13**).

It is obvious from the cases just cited that there is considerable experimental support for the theoretically reasonable idea that a reaction in which the primary step is merely the unimolecular symmetrical disruption of a valence bond involves an activation energy equal to the energy of the bond disrupted. It is disheartening, however, to find discrepancies as large as those between Ogg and Polanyi amounting to 10 to 13 kcal and to find that thermal decompositions of relatively simple saturated molecules are not always unimolecular. Indeed the difficulties do not stop here. Baughan and Polanyi,[99] from thermochemical data and from the value of 103.6 kcal for the heat of rupture of the first bond in methane, calculate that the C—C bond strength in ethane is 88.2 kcal. This is vastly different from Pauling's value of 58.6 kcal. Baughan[100] has recently pointed out that if we take the value of 104 kcal for the strength of the first bond to be broken in methane and assume Pauling's

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[99] Baughan and Polanyi, *Nature*, **146**, 685 (1940).

[100] Baughan, *ibid.*, **147**, 542 (1941).

average value for all four bonds, the average of the other three C—H bonds would be only 82 kcal. This would indicate that Pauling's value for the C—C in ethane would be too low and hence seems at first thought to be a reasonable explanation of the observed discrepancy. However, Baughan rejects this explanation because Voge's quantum mechanical calculations [101] indicate no such large differences for the energies involved in successively rupturing the bonds of methane and because the heat of successive substitution of hydrogens in methane by a halogen varies but little along the series. He calculated these from thermal data for the respective successive steps and found them to be: −21.1, −21.4, −21.1, and −20.7 for substitution by Cl; −35.0, −32.5, −32.0, and −31.0 by Br; −49.0, −46.8, and −45.3 (fourth step unknown) by I. These results indicate rather small differences between the strengths of successive C—H bonds.

If, then, the above explanation of the discrepancy cannot be accepted, Pauling's table of carbon bond strengths must involve some systematic error and Baughan suggests that it is probably in the value of the heat of formation of carbon as monatomic vapor from carbon in the standard state. Goldfinger and Jeunnehomme [102] concluded that spectroscopic measurements leave three possible values for this quantity: −168.8, −123.6, and −107 kcal. Baughan showed that if the value −168.8 were used, Pauling's value for C—H changes from 87.3 to 98.6, for C—C from 58.6 to 81.2, and for C═C from 100 to 145 kcal. A similar correction to the "average" bond strengths of Sidgwick,[103] who took the value of 150 as the heat of formation of atomic carbon, gives for the aliphatic series C—H 98.4, C—C 81.1, C═C 143. These values agree well with those derived by Polanyi et al.[89d, 99] from consideration of the decomposition kinetics of alkyl iodides. Baughan finally concludes: "The single assumption, therefore, that the heat of vaporization of graphite to monatomic carbon vapor is 168.8 or thereabouts is sufficient to reconcile the serious discrepancies between 'kinetic' and 'thermochemical' values for carbon bond strengths. In view of this fact it would be of interest if further spectroscopic research could give a definitive answer to this question of the heat of dissociation of carbon monoxide."

Thermodynamic Coupling. Considerations such as those of Equations 36*b* and 37 lead us into the second phase of our subject. In the early part of our discussion we explored the possibility that a reaction in which the rate-controlling step is merely the rupture of a bond involves

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[101] Voge, *J. Chem. Phys.*, **4**, 581 (1936).

[102] Goldfinger and Jeunnehomme, *Trans. Faraday Soc.*, **32**, 1591 (1936).

[103] Sidgwick, *The Covalent Link in Chemistry*, Cornell University Press, 1933, Chapter IV.

an activation energy which is equal to the energy of the bond suffering rupture. In the explanation of Equations 36, however, we find the idea that if the initial endothermic step is followed by an exothermic step, the two somehow become thermodynamically coupled with the result that the activation energy is decreased. In terms of the transition state theory we might express the idea by saying that the onset of resonance pictured in Equation 36*b* starts to take effect before the initial rupture (36*a*) is complete and hence there is an intersection of the two energy valleys with a resultant transition state or energy pass lower than the plateau of complete dissociation.

The possibility of such an energy coupling was recognized to have an important bearing on reaction velocity problems even before it was possible to picture the relationships involved in terms of potential energy diagrams. Thus, for example, Rice[104] in 1931 explained the disproportionation reactions of free hydrocarbon radicals by pointing out that such a reaction really involves two steps,

$$\mathrm{RCH_2\cdot\underset{\bullet}{C}H_2 \rightarrow R\underset{\bullet}{C}H\cdot\underset{\bullet}{C}H_2 + \cdot H} \tag{38a}$$

$$\mathrm{R\underset{\bullet}{C}H\cdot\underset{\bullet}{C}H_2 \rightarrow RCH{=}CH_2} \tag{38b}$$

the first of which is highly endothermic and the second exothermic. The net result is that "the formation of the double bond contributes to the activation energy necessary to decompose the radical and thus permits the separation of a free hydrogen atom."

Another example of this energy coupling is to be found in the photochemical decomposition of methyl ethyl ketone studied extensively by Norrish and his collaborators.[85] They found that irradiation of this ketone by light of 2800 A° produced, in addition to carbon monoxide, comparable quantities of ethane, propane, and butane. The reaction is not a chain reaction. The amount of carbon monoxide produced is closely equivalent to the total hydrocarbon yield. This is consistent with the fact that no appreciable quantity of diketone is detectable and undoubtedly means that the primary dissociation of one bond, e.g.,

$$h\nu + \mathrm{MeCOEt \rightarrow Me\cdot + \cdot CO\cdot Et} \tag{39a}$$

is immediately followed by the *spontaneous* decomposition of the larger radical:

$$\mathrm{O{=}\underset{\bullet}{C}{-}Et \rightarrow Et\cdot + CO} \tag{39b}$$

The free alkyl radicals thus formed may then combine together to form the three different hydrocarbons found experimentally.

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[104] (*a*) F. O. Rice, *J. Am. Chem. Soc.*, **53**, 1962 (1931); (*b*) F. O. Rice and W. R. Johnston, *ibid.*, **56**, 214 (1934).

The first step (39*a*) is obviously endothermic and the activation energy is supplied by the light. If the second step is to be "spontaneous" it must be exothermic.* In so far as it involves the rupture of a C—C bond it is obviously endothermic to the extent of 89.5 kcal (Table IV). Thus we must look for a "driving force" to overcome this "chemical inertia." It is found at once in what Norrish calls the "reorganization" of the CO radical into a stable CO molecule. The "energy of reorganization" comes from the pairing of the odd electrons

$$\dot{\underset{\cdot}{\mathrm{C}}}::\ddot{\mathrm{O}}: \rightarrow :\mathrm{C}::\ddot{\mathrm{O}}:$$

and the onset of resonance and would be very difficult to calculate where the necessary thermal data do not exist. Fortunately they do exist in this case, and they were applied by Norrish as follows:

$$
\begin{array}{rll}
\mathrm{H_2CO} \rightarrow \mathrm{H_2} + \mathrm{CO}; & \Delta H_1 = 2 \text{ kcal} & (40a) \\
2\mathrm{H}\cdot + \dot{\underset{\cdot}{\mathrm{C}}}\mathrm{O} \rightarrow \mathrm{H_2CO}; & \Delta H_2 = -206 & (40b) \\
\mathrm{H_2} \rightarrow 2\mathrm{H}\cdot; & \Delta H_3 = 103 & (40c) \\
\hline
\dot{\underset{\cdot}{\mathrm{C}}}\mathrm{O} \rightarrow \mathrm{CO}; & \Delta H = -101 \text{ kcal} & (40d)
\end{array}
$$

The value of ΔH_1 was taken from the International Critical Tables, ΔH_2 is the heat of formation for two C—H bonds (cf. Table IV), while ΔH_3 is the heat of dissociation of hydrogen (cf. Table I, Chapter VI). It is thus clear from Equation 40*d* that the transformation of a CO radical into carbon monoxide is exothermic.

We may now make the desired calculation for Equation 39*b* by splitting it up into two thermodynamic steps.

$$
\begin{array}{rll}
\mathrm{O{=}\underset{\cdot}{C}{-}Et} \rightarrow \dot{\underset{\cdot}{\mathrm{C}}}\mathrm{O} + \cdot\mathrm{Et}; & \Delta H = 89.5 \text{ kcal} & (41a) \\
\dot{\underset{\cdot}{\mathrm{C}}}\mathrm{O} \rightarrow \mathrm{CO}; & \Delta H = -101 & (41b) \\
\hline
\mathrm{O{=}\underset{\cdot}{C}{-}Et} \rightarrow \mathrm{CO} + \cdot\mathrm{Et}; & \Delta H = -11.5 \text{ kcal} & (41c)
\end{array}
$$

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* Strictly speaking, it is not a negative ΔH but a negative ΔF which determines the spontaneity of a reaction. However, values of ΔF are rarely available, whereas values of ΔH may be estimated from tables of bond energies with ease and with fair accuracy. This fact has apparently given rise to much wishful thinking on the part of many chemists who use ΔH as a criterion for determining the direction of a chemical reaction. The relationship between the two is given by the equation: $\Delta F = \Delta H - T\Delta S$ and it so happens that ΔS and ΔH usually have the same sign except in cases where ΔS is small. Thus it is unsafe to take the sign of ΔH as a criterion of spontaneity except where the $T\Delta S$ term is relatively small.

Thus the calculation shows that the decomposition of $O{=}\underset{\bullet}{C}{-}Et$, Equations 39*b* and 41*c*, is exothermic. We are thus enabled to predict that no diketones should be formed, that primary recombination should not preclude the formation of hydrocarbons, that three hydrocarbons should be formed in comparable quantities by the combination of the ethyl and methyl radicals (since all three should involve about the same amount of energy, viz., 89.5 kcal), and that carbon monoxide should be a product of the reaction.

We have now discussed three examples of energy coupling. In each case the rupture of a bond (endothermic) was coupled with an exothermic step involving electron pairing and/or the onset of resonance. The nature of this coupling seems to be adequately described by the transition state theory; its extent determines the height of the energy hump. We have seen that Norrish, in the case of the photochemical decomposition of methyl ethyl ketone, considered the coupling between reactions 41*a* and 41*b* to be complete, i.e., he assumed that all the "reorganization energy" found its way into the C—Et bond and aided in breaking it. In general, however, we are not justified in assuming that the coupling is complete, i.e., we are not justified in adding together the heats of reaction for an endothermic step and the exothermic steps coupled with it and calling the sum the energy of activation. In reality such a sum represents the height of the energy hump which would result from complete coupling, and hence it is the minimum activation energy conceivable. The actual extent of the coupling may sometimes be calculated with fair accuracy by means of quantum-mechanical methods. For the ordinary purposes of the organic chemist, however, a less exact and more easily applied generalization would be helpful. Judging from the calculations of Rice and Norrish the following rule will be found helpful in making semi-quantitative predictions.

P 27. If a reaction is considered to occur in a logical succession of unit steps, then the minimum activation energy for the reaction may be calculated by adding together the ΔH values of the first endothermic step and those of any succeeding steps which, on the basis of the transition state theory, could be coupled with it.*

If a given reaction includes two or more uncoupled endothermic steps it must be treated mathematically by the rate equations developed for "successive reactions." In such cases the application of **P 27** would give the minimum activation energy for each of the successive reactions. It is well to remember, as pointed out by Eyring,[105] that if an energy

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* The essential identity of this rule with the ideas introduced in the last section of Chapter VII is easily recognized.

[105] Eyring, *J. Am. Chem. Soc.*, **54**, 3191 (1932).

hump amounts to much less than 20 kcal/mole, "the rate at which molecules accumulate sufficient energy to pass over the barrier, even at ordinary temperatures, makes it impossible to isolate any but the molecular species of lowest energy."

The practical value of **P 27** lies in the fortunate fact that, at least for similar reactions, the use of the minimum values of activation energies leads to the proper prediction of the main course of a reaction and even of the relative amounts of different end products formed. The rest of this section will be devoted to examples of applications of this principle made as indicated above.

The photochemical decompositions of ketene [106] and diazomethane [107] have been discussed by Norrish [86] from the viewpoint of bond energies (Table IV). Ketene decomposes photochemically into carbon monoxide and ethylene, indicating the liberation of CH_2 radicals, whereas the decomposition of diazomethane, although more complex, is only satisfactorily accounted for by the primary liberation of CH_2 radicals. The ketene decomposition may be formulated as follows, using a bracket to indicate the coupled steps.

$$\left[\begin{array}{llll} H_2C{=}C{=}O \rightarrow \dot{\underset{\cdot}{C}}H_2 + \dot{\underset{\cdot}{C}}O; & \Delta H_1 = & 162 \text{ kcal} & (42a) \\ \qquad\qquad \dot{\underset{\cdot}{C}}O \rightarrow CO; & \Delta H_2 = & -101 & (42b) \end{array}\right.$$

$$\begin{array}{llll} \qquad 2\,\dot{\underset{\cdot}{C}}H_2 \rightarrow CH_2{=}CH_2; & \Delta H_3 = & -162 & (42c) \\ \hline CH_2{=}C{=}O \rightarrow CO + C_2H_4; & \Delta H_4 = & -101 \text{ kcal} & (42d) \end{array}$$

This over-all reaction is seen to be exothermic, but the minimum activation energy is seen to be 162 − 101 = 61 kcal if we follow Norrish in assuming that the reorganization energy of step 42*c* is not coupled with the first two unit steps. The threshold value for the photochemically active light is 77 kcal, which makes the above value seem reasonable.

In the case of diazomethane the rate-controlling process is

$$\left[\begin{array}{llll} CH_2{=}N_2 \rightarrow \dot{\underset{\cdot}{C}}H_2 + \dot{\underset{\cdot}{N}}_2; & \Delta H_5 = & 129.5 \text{ kcal} & (43a) \\ \qquad\qquad \dot{\underset{\cdot}{N}}_2 \rightarrow N_2; & \Delta H_6 = & -121.2 & (43b) \end{array}\right.$$

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[106] Norrish, Crane, and Saltmarsh, *J. Chem. Soc.*, 1533 (1933). Cf. Ross and Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 1112 (1934), and Norrish, Crane, and Saltmarsh, *ibid.*, **56**, 1644 (1934).

[107] Kirkbride and Norrish, *J. Chem. Soc.*, 119 (1933).

The value of ΔH_6 is calculated as the difference in the heats of formation from their gaseous atoms of the N═N link in gaseous azobenzene and the N≡N link, 208 − 86.8 = 121.2 kcal.[108] By combining ΔH_5 and ΔH_6 we get a value of only 8.3 kcal for the minimum activation energy. The threshold value for the photochemically active light is 60 kcal, again obviously adequate.

From the standpoint of thermal decomposition both compounds are thermodynamically unstable since the over-all reactions involve negative values of ΔH and presumably of ΔF. But from Norrish's kinetic viewpoint it is obvious that diazomethane should be easily decomposed, whereas ketene would require at least 61 kcal to activate it and hence should be rather stable. The experimental facts are that diazomethane is notoriously unstable,[109] whereas ketene is very stable, being formed as an end product of the thermal decomposition of acetone.[110]

The Reactions of Free Alkyl Radicals with Organic Compounds

Smith and Taylor [111] measured the activation energies of the reaction between various hydrocarbons and the methyl radicals produced by the photodecomposition of dimethyl mercury. The reactions for which the activation energies were measured may be represented by the equation

$$\cdot CH_3 + RH \rightarrow CH_4 + \cdot R$$

Their results are as follows:

Ethane and neopentane, $E = 8.3$ kcal
n-Butane, $E = 5.5$ kcal
iso-Butane, $E = 4.2$ kcal

They consider that these differences in activation energies are due to differences in the bond energies of primary, secondary, and tertiary C—H bonds and on the basis of their own work as well as that of Kistiakowsky and his collaborators [112] suggest that a primary C—H bond has 2.5 kcal more energy than a secondary C—H bond, which in turn has 4 kcal more than a tertiary C—H bond. A similar conclusion was reached some years earlier by Rice [113] on the basis of a study of the products of thermal

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[108] Sidgwick, Sutton, and Thomas, *J. Chem. Soc.*, 406 (1933).

[109] Rice and Glasebrook, *J. Am. Chem. Soc.*, **55**, 4329 (1933).

[110] Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, **A111**, 245 (1926).

[111] J. O. Smith, Jr., and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

[112] (*a*) Kistiakowsky, Ruhoff, H. A. Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 137 (1936); (*b*) Dolliver, Gresham, Kistiakowsky, and Vaughan, *ibid.*, **59**, 831 (1937); (*c*) Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan, *ibid.*, **60**, 440 (1938).

[113] F. O. Rice, *ibid.*, **55**, 3035 (1933).

decomposition of hydrocarbons. He placed the two figures respectively at 1.2 and 4.0 kcal.

If we attempt to apply **P 27** to these reactions, we are led to conclude that the minimum activation energy for the reaction involving the rupture of a primary C—H link is zero, since one primary bond is broken and another formed. For the reactions involving secondary and tertiary bonds the values of ΔH would then be -2.5 and -4 kcal respectively. While negative activation energies are meaningless, negative values of minimum activation energies no doubt have significance for purposes of comparison as long as they have small values. These three values, therefore, give the right order of reactivities, although the minimum activation energy is in each case about 8 kcal below the actual value.

The reaction of methyl radicals with hydrogen,

$$\cdot CH_3 + H_2 \rightarrow CH_4 + \cdot H \tag{44}$$

was found to have an activation energy of 9 ± 2 kcal.[114] If we wish to apply **P 27,** we must first know the bond energy of the primary C—H link. We have already seen that such estimates range from 95 to 103 kcal and that the value of 95 gave good concordance between the bond energy of C—I and the activation energy of reactions involving its rupture. We may therefore calculate the minimum activation energy as follows:

$$\begin{array}{lr}
H_2 \rightarrow 2H\cdot; & \Delta H = \ \ 103 \text{ kcal} \\
\cdot CH_3 + \cdot H \rightarrow CH_4; & \Delta H = -95 \text{ kcal} \\
\hline
\cdot CH_3 + H_2 \rightarrow CH_4 + \cdot H; & \Delta H = \ \ 8 \text{ kcal}
\end{array}$$

The agreement is good but it should be mentioned that there is some small doubt as to whether Equation 44 correctly represents the reaction whose activation energy was measured.[115]

It is generally conceded that the collision of two methyl radicals with each other does not result in their combination, since the resulting molecule would then contain enough energy to disrupt the new bond formed; but if two such radicals undergo a ternary collision with some other molecule M

$$2\cdot CH_3 + M \rightarrow C_2H_6 + M \tag{45}$$

then M may take up the excess energy, allowing the two radicals to combine. It has frequently been assumed that such a reaction would involve no energy of activation, but Taylor and Burton [115a] made certain

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[114] Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

[115] (*a*) H. A. Taylor and Burton, *ibid.*, **7**, 675 (1939); (*b*) H. A. Taylor, *ibid.*, **7**, 679 (1939).

measurements which indicate strongly that an activation energy of about 22 kcal is involved in the reaction. Rice[116] had previously decided from empirical considerations of the known products of pyrolysis of many substances that all reactions involving the combination of free alkyl radicals involve an activation energy of about 8 kcal and in addition a steric factor of about 0.1. We can only conclude that the mechanism by which M takes up the excess energy involves an energy hump.

The Thermal Decomposition of Hydrocarbons

The thermal decomposition reactions of organic compounds differ from their reactions with pre-formed radicals in that the primary rate-controlling step is the formation of free radicals. Usually this step is incapable of being coupled and hence involves a high activation energy. The secondary reactions involve these free radicals. They may (1) attack neutral molecules, usually abstracting hydrogen for steric reasons already discussed, e.g.,

$$\cdot CH_3 + C_2H_6 \rightarrow CH_4 + \cdot C_2H_5 \tag{46}$$

(2) they may disproportionate, e.g.,

$$\cdot CH_2 \cdot CH_2 \cdot CH_3 \rightarrow \cdot CH_3 + CH_2{=}CH_2 \tag{47}$$

or (3) they may recombine as in Equation 45. Obviously reactions 46 and 47 may be chain-initiating reactions. When reaction chains occur the relative proportions of end products depend on the relative activation energies of the rate-controlling secondary steps by which the respective chains are propagated. It has been found that when free hydrocarbon radicals involving three or more carbon atoms are produced by the Paneth method they are unstable and decompose into smaller radicals and olefin molecules. In such cases it is obvious that the "reorganization" involved in the formation of the olefins is the chemical driving force. This reorganization energy may be roughly calculated from the data in Table IV as follows:

$$\begin{array}{lllr}
2\overset{\bullet}{\underset{\bullet}{C}}H_2 \rightarrow CH_2{=}CH_2; & \Delta H = & -162 \quad \text{kcal} & (48a) \\
\underset{\bullet}{C}H_2{-}\underset{\bullet}{C}H_2 \rightarrow 2\overset{\bullet}{\underset{\bullet}{C}}H_2; & \Delta H = & 89.5 & (48b) \\
\hline
\underset{\bullet}{C}H_2{-}\underset{\bullet}{C}H_2 \rightarrow CH_2{=}CH_2; & \Delta H = & -72.5 \text{ kcal} & (48c)
\end{array}$$

[116] Rice, Ref. 18, p. 191.

Such a reorganization in methyl radicals is, of course, impossible and in ethyl radicals it could only occur if a C—H bond were first ruptured,

$$\begin{array}{lrl}
\cdot\mathrm{CH_2}\cdot\mathrm{CH_3} \rightarrow \underset{\bullet}{\mathrm{CH_2}}\text{—}\underset{\bullet}{\mathrm{CH_2}} + \cdot\mathrm{H}; & \Delta H = & 103 \quad \text{kcal} \\
\underset{\bullet}{\mathrm{CH_2}}\cdot\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{CH_2{=}CH_2}; & \Delta H = & -72.5 \\
\hline
 & E_{\min} = & 30.5 \text{ kcal}
\end{array}$$

whereas for the hydrocarbon radicals the reorganization may be coupled with the breaking of the weaker C—C link:

$$\begin{array}{lrl}
\mathrm{RCH_2}\cdot\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{R}\cdot + \underset{\bullet}{\mathrm{CH_2}}\cdot\underset{\bullet}{\mathrm{CH_2}}; & \Delta H = & 89.5 \text{ kcal} \\
\underset{\bullet}{\mathrm{CH_2}}\cdot\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{CH_2{=}CH_2}; & \Delta H = & -72.5 \\
\hline
 & E_{\min} = & 17.0 \text{ kcal}
\end{array}$$

Thus the relative instability of the higher alkyl radicals is readily explained.

The decomposition of di-*n*-butyl mercury at 490° yields the following products:[117] 75% C_2H_4, 27% C_4H_{10} (*n*), 14.1% C_6H_{14}, 8.35% C_2H_6, 2.8% C_8H_{18}, 1.8% (C_5H_{10} + C_5H_{12}), 1.32% C_4H_8 (*n*), 0.58% C_3H_8, 0.35% CH_4.

Let us now attempt an analysis of the problem by the use of **P 27.** The primary decomposition produces *n*-butyl radicals which then may conceivably undergo the following secondary reactions. The numbers at the right are minimum activation energies in kcal/mole.

$$\text{I. } \mathrm{CH_3}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{\bullet}{\mathrm{CH_2}} \rightarrow \underset{\bullet}{\mathrm{CH_3}} + \underset{\bullet}{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\underset{\bullet}{\mathrm{CH_2}} \qquad +89.5$$

$$\text{II. } 2\mathrm{CH_3}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{\bullet}{\mathrm{CH_2}} + \mathrm{M} \rightarrow \mathrm{C_8H_{18}} + \mathrm{M} \qquad (+22)$$

$$\left.\begin{array}{lr}
\text{III. } \mathrm{CH_3CH_2CH_2}\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{H}\cdot + \mathrm{CH_3CH_2}\underset{\bullet}{\mathrm{CH}}\underset{\bullet}{\mathrm{CH_2}} & +92.5 \\
\mathrm{CH_3CH_2}\underset{\bullet}{\mathrm{CH}}\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{CH_3CH_2CH{=}CH_2} & -72.5
\end{array}\right\} +20$$

$$\left.\begin{array}{lr}
\text{IV. } \mathrm{CH_3CH_2CH_2}\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{CH_3}\underset{\bullet}{\mathrm{CH_2}} + \underset{\bullet}{\mathrm{CH_2}}\underset{\bullet}{\mathrm{CH_2}} & +89.5 \\
\underset{\bullet}{\mathrm{CH_2}}\underset{\bullet}{\mathrm{CH_2}} \rightarrow \mathrm{CH_2{=}CH_2} & -72.5
\end{array}\right\} +17$$

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[117] Frey and Hepp, *J. Am. Chem. Soc.*, **55**, 3357 (1933).

$$\left.\begin{array}{llr} \text{V.} & CH_3CH_2CH_2\underset{\bullet}{C}H_2 \rightarrow CH_3CH_2\underset{\bullet}{C}H\underset{\bullet}{C}H_2 + H\cdot & +92.5 \\ & CH_3CH_2CH_2\underset{\bullet}{C}H_2 + H\cdot \rightarrow C_4H_{10} & -95 \\ & CH_3CH_2\underset{\bullet}{C}H\underset{\bullet}{C}H_2 \rightarrow C_4H_8 & -72.5 \end{array}\right\} -75$$

$$\left.\begin{array}{llr} \text{VI.} & CH_3CH_2CH_2\underset{\bullet}{C}H_2 \rightarrow CH_3\underset{\bullet}{C}H_2 + \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 & +89.5 \\ & CH_3\underset{\bullet}{C}H_2 + CH_3CH_2CH_2\underset{\bullet}{C}H_2 \rightarrow C_6H_{14} & -89.5 \\ & \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 \rightarrow C_2H_4 & -72.5 \end{array}\right\} -72.5$$

Reaction VI is not ruled out by steric considerations since one radical can attack another at its trivalent carbon atom, which is not completely shielded from attack by attached atoms. The energy liberated is then passed along to the weakest C—C bond, which dissociates.

The relative probabilities of the primary reactions, assuming the *PZ* factor the same in all cases, is therefore VI = V ≫ IV > III ≧ II ≫ I. Remembering that ethylene is produced in both IV and VI and that butene is produced in both III and V we would predict the following relative amounts of products:

$$C_2H_4 > C_4H_8 > C_4H_{10} = C_6H_{14} > C_8H_{18} \qquad (49)$$

The products of the secondary reactions are most apt to react with butyl radicals since they are present in the greatest concentration. We may list the subsequent reactions of the products of reaction VI as VI*a*, VI*b*, etc.

$$\left.\begin{array}{llr} \text{VI}a. & C_2H_4 \rightarrow \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 & +72.5 \\ & CH_3CH_2CH_2\underset{\bullet}{C}H_2 + \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 \rightarrow CH_3(CH_2)_4\underset{\bullet}{C}H_2 & -89.5 \end{array}\right\} -17$$

$$\left.\begin{array}{llr} \text{VI}b. & C_2H_4 \rightarrow CH_2{=}\underset{\bullet}{C}H + H\cdot & +95 \\ & CH_3CH_2CH_2\underset{\bullet}{C}H_2 + CH_2{=}\underset{\bullet}{C}H \rightarrow & \\ & \qquad\qquad CH_2{=}CH(CH_2)_3CH_3 & -89.5 \end{array}\right\} +5.5$$

Low *P* factor.

$$\left.\begin{array}{llr} \text{VI}c. & C_2H_4 \rightarrow CH_2{=}\underset{\bullet}{C}H + H\cdot & +95 \\ & CH_3CH_2CH_2\underset{\bullet}{C}H_2 + H\cdot \rightarrow C_4H_{10} & -95 \end{array}\right\} 0$$

$$\left.\begin{array}{lr} \text{VI}d.\ C_6H_{14} \rightarrow CH_3(CH_2)_3\underset{\bullet}{C}HCH_3 + H\cdot & +92.5 \\ CH_3CH_2CH_2\underset{\bullet}{C}H_2 + H\cdot \rightarrow C_4H_{10} & -95 \end{array}\right\} -2.5$$

$$\left.\begin{array}{lr} \text{VI}e.\ C_6H_{14} \rightarrow CH_3(CH_2)_3\underset{\bullet}{C}HCH_3 + H & +92.5 \\ CH_3(CH_2)_3\underset{\bullet}{C}HCH_3 + CH_3CH_2CH_2\underset{\bullet}{C}H_2 \rightarrow C_{10}H_{22} & -89.5 \end{array}\right\} +3$$

Very low *P* factor.

Of these reactions VI*a* seems to be the most probable, but it is not a finished reaction; VI*d* seems to rank next, its net result being the transformation of hexane into butane, which will alter the relations in sequence 49 to $C_4H_{10} > C_6H_{14}$ in accord with experiment. Furthermore, the hydrogen atom produced in VI*d* will unite with free butyl radicals to increase further the yield of butane and, since ethylene is present in high concentration, it will to some extent combine with the hydrogen atoms to form ethane. It would be difficult, however, to fit ethane accurately into sequence 49. The free hexyl radicals produced in large amounts in VI*a* together with those produced in VI*d* may occasionally collide with hydrogen atoms or free butyl radicals with resultant combination, but the following disproportionation seems much more probable:

$$\left.\begin{array}{lr} C_6H_{13} \rightarrow CH_3CH_2CH_2\underset{\bullet}{C}H_2 + \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 & +89.5 \\ \underset{\bullet}{C}H_2\underset{\bullet}{C}H_2 \rightarrow CH_2{=}CH_2 & -72.5 \end{array}\right\} +17$$

Even at room temperature this small activation energy would be furnished very readily so that the disproportionation must be practically, if not completely, spontaneous at 490°. VI*a* would therefore result in still more ethylene.

We may summarize the predictions of **P 27** thus far as follows:

$$C_2H_4 \gg C_4H_8 > C_4H_{10} > C_6H_{14} > C_8H_{18}$$

and an appreciable quantity of C_2H_6.

Reaction V has already been shown to be highly probable, so it is now necessary to analyze the subsequent reactions of its products, C_4H_8 and C_4H_{10}, as we did with reaction VI. Such an analysis leads to the conclusion that more C_4H_{10}, C_2H_4 and C_6H_{18} will be formed. Examination of the possible products of the less important reactions I to IV makes clear how the remaining products found experimentally could have been formed. Thus the small amount of methane found is presumably the result of the high activation energy of reactions of type I.

Admittedly the analysis of so complicated a reaction is beset by uncertainties, but the predictions line up remarkably well with the experimental data. That more octane was produced than predicted may indicate that the surprising value of 22 kcal for reaction II is not correct, or that at 490° this reaction becomes practically instantaneous and thus competes successfully with reactions V and VI, whose activation energies must be close to zero even at room temperature.

If a similar analysis be made of the products to be expected from the thermal decomposition of diisobutyl mercury, the following sequence is predicted for the main products:

$$n\mathrm{C_4H_8} = n\mathrm{C_4H_{10}} \geqq \mathrm{C_8H_{18}} > \mathrm{C_3H_6}$$

The assumption was here made that the union of two isobutyl radicals is practically instantaneous. The experimental results are as follows:[117] 22.6% C_8H_{18}, 16.2% nC_4H_8, 15.8% nC_4H_{10}, 10.7% C_3H_6, 8.5% C_5H_{12}, 1.7% CH_4, 1.08% ($C_6H_{12} + C_6H_{14}$), 0.63% C_2H_4, 0.62% C_3H_8, 0.59% C_7H_{16}, 0.32% C_5H_{10}.

Rice[113] has successfully attempted a more quantitative prediction of the products of thermal decomposition of hydrocarbons at temperatures of 500° to 800°. He used four basic assumptions, all of which are in qualitative accord with the above principles. They are as follows:

(1) The only stable alkyl radicals are methyl and ethyl. The others decompose into olefins and either methyl or ethyl groups or atomic hydrogen.

(2) When a free radical attacks a hydrocarbon molecule steric considerations favor its attack on hydrogen atoms.

(3) The relative chances of reaction of primary, secondary, and tertiary hydrogen atoms are in the ratio of 1 : 2 : 10 respectively.

(4) Thermal decomposition of a hydrocarbon results in the primary rupture of a C—C bond.

The initial rupture of the hydrocarbon will produce a pair of free radicals (R in the example below) which will then induce chain reactions by abstracting hydrogen atoms from hydrocarbon molecules. The main products of reaction will then be the ones resulting from these chain reactions. The quantitative composition is found by assigning to each chain cycle a number determined by the number of primary, secondary, or tertiary hydrogen atoms associated with the cycle in question, each multiplied by their relative chance of reaction (1 : 2 : 10). As an example we may study 2,3-dimethylpentane, for which the following chain cycles would seem to be possible.

I. $CH_3\cdot CHMe\cdot CHMe\cdot CH_3 + R\cdot \rightarrow RH + CH_3\cdot CHMe\cdot CHMe\cdot$
$CH_2\cdot \underset{\bullet}{C}H_2 \rightarrow RH + CH_2{=}CH_2 + CH_3\cdot CHMe\cdot \underset{\bullet}{C}H\cdot CH_3 \rightarrow$
$RH + CH_2{=}CH_2 + CH_3CH{=}CHCH_3 + \cdot CH_3$

II. $CH_3\cdot CHMe\cdot CHMe\cdot CH_2\cdot CH_3 + R\cdot \rightarrow RH + \underset{\bullet}{C}H_2\cdot CHMe\cdot$
$CHMe\cdot CH_2\cdot CH_3 \rightarrow RH + CH_3CH_2{=}CH_2 + CH_3\underset{\bullet}{C}HCH_2CH_3$
$\rightarrow RH + CH_3CH_2{=}CH_2 + CH_3CH{=}CH_2 + \cdot CH_3$

III. $CH_3\cdot CHMe\cdot CHMe\cdot CH_2\cdot CH_3 + R\cdot \rightarrow RH + CH_3\cdot CHMe\cdot$
$CHMe\cdot \underset{\bullet}{C}H\cdot CH_3 \rightarrow RH + CH_3\cdot CH{=}CH\cdot CH_3 + CH_3\underset{\bullet}{C}HCH_3$
$\rightarrow RH + CH_3CH{=}CHCH_3 + CH_3CH{=}CH_2 + H\cdot$

IV. $CH_3\cdot CHMe\cdot CHMe\cdot CH_2\cdot CH_3 + R\cdot \rightarrow RH + CH_3\cdot \underset{\bullet}{C}Me\cdot$
$CHMe\cdot CH_2\cdot CH_3 \rightarrow RH + CH_3\cdot CH{=}CHCH_3 + CH_3\underset{\bullet}{C}H_2$
or $RH + CH_3CMe{=}CH\cdot CH_2\cdot CH_3$

V. $CH_3\cdot CHMe\cdot CHMe\cdot CH_2CH_3 + R\cdot \rightarrow RH + CH_3\cdot CHMe\cdot$
$\underset{\bullet}{C}Me\cdot CH_2CH_3 \rightarrow RH + CH_3\cdot CH{=}CMe\cdot CH_2\cdot CH_3 + \cdot CH_3$
or $RH + CH_3\cdot CHMe\cdot CMe{=}CH_2 + \cdot CH_3$

VI. $CH_3\cdot CHMe\cdot CHMe\cdot CH_2\cdot CH_3 + R\cdot \rightarrow RH + CH_3\cdot CHMe\cdot$
$\underset{\underset{\bullet}{CH_2}}{CH}\ CH_2CH_3 \rightarrow RH + CH_3CH_2CH{=}\underset{\bullet}{C}H + CH_3CH{=}CH_2$
or $RH + CH_3CH\cdot CH{=}CH_2$

Proceeding in the manner indicated, he predicted quantitatively the products of decomposition of the hydrocarbons indicated in Figures 1 and 2. These figures also indicate the high success of his predictions.

Benzene and ethylene are thermodynamically unstable, their free energies of formation being respectively 30.6 and 12.3 kcal at 298° K for the gases.[118] Their actual stabilities are very high, however, as shown by the fact that they are commonly formed in high temperature pyrolytic reactions. Our theory would suggest that in these cases there must occur as a first step either the rupture of a C—H bond (ΔH = 95 kcal) or in ethylene the complete or partial rupture of C=C (ΔH = about 22 if only one bond is broken) all of which are highly endothermic and incapable of being coupled except, possibly, through chain reactions which would not lead to the final production of the elements but to products such as diphenyl and hydrogen, which actually result from the pyrolysis of benzene. In benzene there exists also the possibility of the rupture of a C—C bond which would involve the destruction of most of the resonance of the conjugated system of double bonds in benzene. Thus the answer to the anomalous actual stabilities of these compounds is to be ascribed to the circumstance that the rupture of some one bond must precede the eventual decomposition into atoms and that the primary step is in each case highly endothermic because it cannot be coupled with any subsequent exothermic step. That some of the subsequent steps must be exothermic (in relation to ΔF) is, of course, definitely established by the negative value of ΔF for the over-all reactions. It is particularly to be noted that the actual stabilities of these

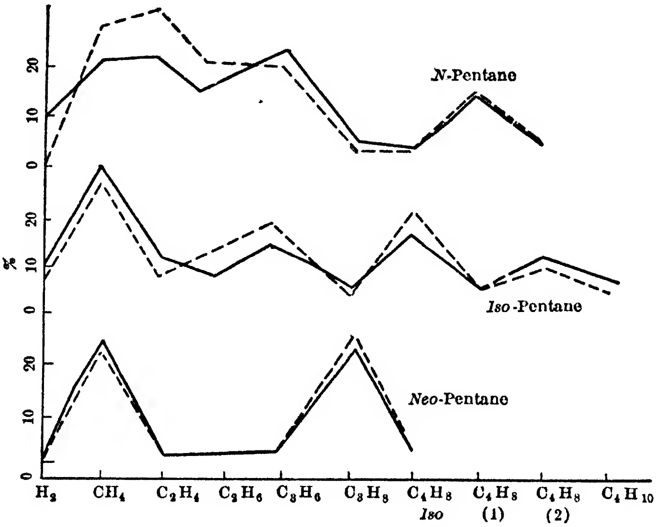

Fig. 1.[113] Observed (—) and calculated (——) products in the thermal decomposition of pentanes.

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[118] Parks and Huffman, *The Free Energies of Some Organic Compounds*, The Chemical Catalog Co., 1932.

compounds are not anomalous in the light of our theory but are definitely predictable.

A similar case is that of acetylene and its derivatives, which readily polymerize at high temperatures to yield respectively benzene and its derivatives. Ethylene apparently has much less tendency to form cyclic hydrocarbons, judging from the very careful work of Storch[119] which was carried out at 377° and 393° under practically oxygen-free conditions. Although in his first paper he reported the possible presence of cyclic hydrocarbons in rather small amounts, in his later work he reported none. As compared to ethylene, acetylene would be expected to have more tendency to cyclize since the benzene formed in the latter case should be able to throw its resonance energy into a "reorganization" step and hence favor reaction in its direction.

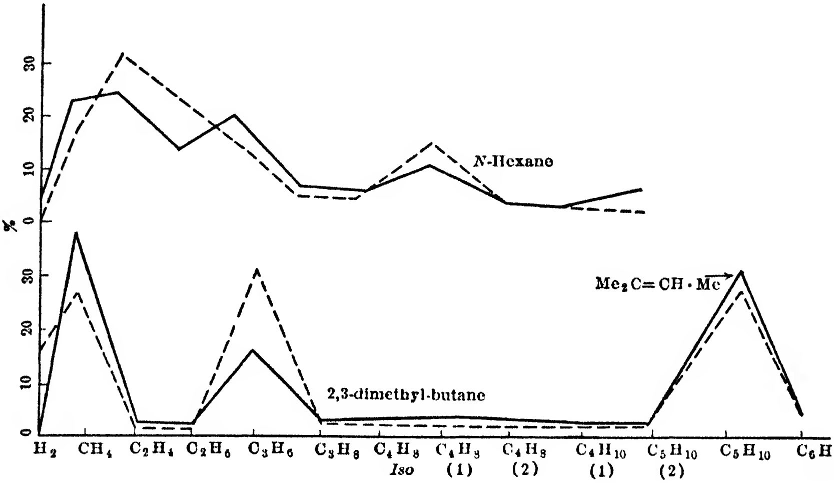

FIG. 2.[113] Observed (—) and calculated (——) products in the thermal decomposition of hexanes.

In conclusion it may be said that a knowledge of bond energies used in accordance with **P 27** seems to furnish a fairly reliable guide in attempting to predict the products of thermal decomposition. It must be remembered, however, that although **P 27** gives us a rough measure of relative activation energies, the speed of reactions depends also on the probability factor, *P*, and hence the consideration of influences affecting the value of *P* are of equal importance. The peculiar ability of reaction chains to pass along the activation energy from molecule to molecule is also an independent factor of importance. Finally it must

[119] Storch, *J. Am. Chem. Soc.*, **56**, 374 (1934); **57**, 2598 (1935).

be remembered that bond energy values may be altered by resonance and by substituents. These combined considerations, although frequently difficult to apply because of quantitative uncertainties, should at least give the organic chemist a better working tool than any nonelectronic method could do and a more convenient tool than quantum mechanics.

CHAPTER X

THE ROLE OF THE SOLVENT

[NOTE: If the reader is unfamiliar with the earlier history of the chemistry of nonaqueous solutions he is urged to read Appendix IV before attempting this chapter.]

The choice of proper solvents for use in organic syntheses is a matter of great practical importance to the organic chemist, who characteristically solves such problems by the application of his empirical knowledge and his "instinct." Since we have addressed ourselves to the problem of improving his methods of attack, it is plainly our duty to examine modern physicochemical research and to find out to what extent it has solved the problem of the role played by the solvent in altering the equilibrium, speed, and course of reactions. Incidentally we shall be interested in discovering, if we can, the alteration produced in the inductive and tautomeric effects and the electrophilic and nucleophilic reaction tendencies by solvent influence. Finally, since we have relied somewhat on ionization constants as a measure of relative electronegativities, we will wish to reexamine the validity of this relation in the light of studies made on nonaqueous solutions.

DEFINITIONS OF ACIDS AND BASES

Generalized Concepts

Opinion among chemists seems to be divided at the moment on the question of defining acids and bases. To some, the Brönsted-Lowry definition [1] seems to be too broad to be practical. Others [2] consider that it is not broad enough to give a fundamental distinction and many prefer the Lewis definition.[1] Personally I wish that these innovators had coined new words for their new generalizations and left the old words, acid and base, to be relegated to the glossary of the decadent but not forgotten past—"not forgotten," because our well-established nomenclature of compounds is and will continue to be based on the classical concepts.

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[1] See Appendix IV.

[2] (*a*) Germann, *J. Am. Chem. Soc.*, **47**, 2461 (1925); (*b*) Usanovich, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 182 (1939); (*c*) N. F. Hall, *J. Chem. Education*, **17**, 124 (1940); (*d*) Luder, *Chem. Rev.*, **27**, 547 (1940).

Of the two new systems, the one of Brönsted and Lowry does least violence to our nomenclature and is becoming widely accepted. It has also the incidental advantage that it is more convenient to use, for the present, in the discussion of most modern exact work on acidity, since hydrogen electrode potentials have been taken as the measure of acidity. Hence I shall adopt the Brönsted-Lowry definitions for general use in the remainder of this book. When it becomes necessary to refer to acids in the Lewis sense, I shall use the term "electron acceptor" or simply "acceptor." In such discussions bases may be referred to either as such or as "donors." The corresponding adjectives are the familiar words "electrophilic" and "nucleophilic."

Whatever one may think about the relative merits of the Brönsted-Lowry and the Lewis definitions, there can no longer be any doubt that the truly fundamental characteristics of acids and bases are their donor and acceptor properties. "A base is a base because it can donate an electron pair to form a coordinate bond. An acid is an acid because it can accept an electron pair to form a coordinate bond. Neutralization is the formation of the covalent bond between the acid and the base. . . . The formation of the covalent bond . . . destroys the distinctive properties of both the acid and the base."[2d] Brönsted's former opinion that protons alone among electron acceptors have the properties we customarily ascribe to acids (mobility in particular) is an opinion which recent research has rendered untenable.

Lewis[3] has recently discussed the merits of his own viewpoint. He listed the following properties as being the distinguishing properties of acids and bases.

(1) When an acid and base can combine, the process of combination, or neutralization, is a rapid one.

(2) An acid or base will replace a weaker acid or base from its compounds.

(3) Acids or bases may be titrated against one another by the use of substances, usually colored, known as indicators.

(4) Both acids and bases play an extremely important part in promoting chemical processes through their action as catalysts.

A few representative examples will make clear the justification of Lewis's concept of generalized acids and bases. He carried out titrations in dioxane and acetone as solvents, using as bases pyridine and triethyl amine and as acids (acceptors) SO_2, BCl_3, $SnCl_4$, and $AgClO_4$. In all these cases neutralization was rapid, the color changes observed with a given indicator were independent of the acids and bases used (although

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[3] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

in certain other cases he found a high specificity in this regard), and they could be titrated back and forth, showing their complete reversibility. The use of HCl gave identical results. Sulfur dioxide and boron chloride are "acidic" (electrophilic) because they contain only electron sextets, whereas $SnCl_4$ and $AgClO_4$ are acceptors in virtue of the ability of the metals to hold more than eight electrons in their valence shells.

Leveling effects are also commonly noted among generalized acids and bases. Thus a strong acid like sulfur trioxide or a strong base like sodium nitride is almost completely hydrolyzed by water.

Boron chloride and stannic chloride are stronger acids than carbon dioxide. Accordingly when sodium carbonate suspended in an acetone-carbon tetrachloride mixture is treated with boron chloride or stannic chloride, carbon dioxide is displaced. This fact is of particular importance since, in the days when the Arrhenius theory led the field, the fact that dry HCl dissolved in benzene had almost no effect on carbonates was taken as strong support for the theory. It now becomes apparent that this support rested on the fortuitous circumstance that too weak an acid was used.

In regard to catalytic effects, the Friedel-Crafts reaction seems to be an example. That the $AlCl_3$ does act as an acid in such cases is indicated by the fact that $AlCl_3$ and $AlBr_3$ give conducting solutions when dissolved in ethyl chloride.[4] Transference experiments show that the anion contains the aluminum, and the following equation represents the mobile equilibrium which obtains.

$$EtCl + AlCl_3 \rightleftarrows Et^+ + AlCl_4^-$$

It seems likely, therefore, that $AlCl_3$ catalyzes the Friedel-Crafts reactions by exercising its electrophilic (acidic) properties in taking up the base, Cl^- ion, and thus producing a highly reactive carbonium ion.

Studies of reactions in liquid sulfur dioxide [5] furnish particularly good examples of the generalized acid-base reactions. The self-ionization of liquid sulfur dioxide is represented by the equation

$$2SO_2 \rightleftarrows SO_3^{=} + SO^{++}$$

[4] (*a*) Wertyporoch et al., *Z. physik. Chem.*, **A162,** 398 (1932); **A168,** 31, 124 (1934); (*b*) Wohl and Wertyporoch, *Ber.*, **64B,** 1357 (1931).

[5] (*a*) Walden and Centnerszwer, *Ber.*, **32,** 2862 (1899); (*b*) Jander and Wickert, *Z. physik. Chem.*, **A178,** 57 (1936); *Ber.*, **70B,** 251 (1937); (*c*) Jander and Ullman, *Z. anorg. allgem. Chem.*, **230,** 405 (1937); (*d*) Jander, Kroll, and Immig, *ibid.*, **232,** 229 (1937); (*e*) Jander and Ruppolt, *Z. physik. Chem.*, **A179,** 43 (1937); (*f*) Jander and Immig, *Z. anorg. allgem. Chem.*, **233,** 295 (1937); (*g*) Wickert, *Z. Elektrochem.*, **44,** 410 (1938).

Since sulfite and thionyl ions are capable of existence in these solutions, reactions in which sulfites are neutralized by thionyl compounds are to be expected, as[6]

$$K_2SO_3 + SOCl_2 \rightleftarrows 2KCl + 2SO_2$$

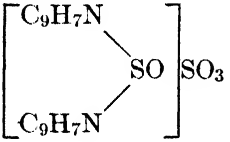
It is found also that ammonia solvates in liquid sulfur dioxide much as it does in water.

$$NH_3 + H_2O \rightarrow (H \cdot NH_3)OH$$

$$2NH_3 + 2SO_2 \rightarrow [(SO \cdot (NH_3)_2]SO_3$$

The thionyldiammonium sulfite may be neutralized by $SOCl_2$.

Quinoline and triethylamine yield the onium compounds I and II when dissolved in liquid sulfur dioxide, the thionyl ion playing the same role customarily played by the proton.



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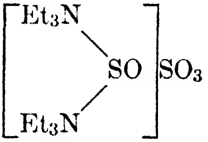

II

These and many other similar observations[7] make it evident that the interactions of acids and bases, in the classical sense, are only special cases of the generalized theory.

Secondary Acids and Bases

In a recent paper[8a] Lewis modernizes his definition of acids as follows: An acid is "any substance one of whose atoms is capable of receiving into its valence or coordination shell the basic electron pair of another atom." It is obvious that all substances would be acids or bases or both according to this definition, but in view of the fact that the facility of interaction of acids and bases is a time-honored criterion for the classification, Lewis found it convenient to subdivide each of these groups of substances further on the basis of their reactivity.[3,8] The combination of certain acids or bases involves no energy of activation. These are called "primary" acids and bases. Others, called "secondary" acids and bases, require energy of activation when they react with each other or with primary bases and acids, respectively.

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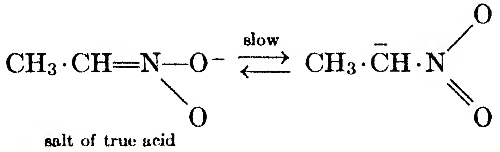
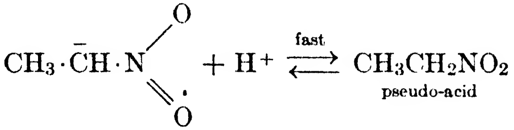
[6] Ref. 5*b*. The correctness of this formulation has been disputed by Cornog and Lamb, *Proc. Iowa Acad. Sci.*, **40**, 97 (1933).

[7] (*a*) See, e.g., Cady and Elsey, *J. Chem. Education*, **5**, 1425 (1928); (*b*) G. B. L. Smith, *Chem. Rev.*, **23**, 165 (1938).

[8] G. N. Lewis and Seaborg: (*a*) *J. Am. Chem. Soc.*, **61**, 1886 (1939); (*b*) *ibid.*, **61**, 1894 (1939).

Lewis's secondary acids naturally call to mind the pseudo-acids of Hantzsch.[9] For example, Hantzsch found that nitroethane reacts only slowly with alkalies to form salts, and that if the sodium salt is neutralized with hydrochloric acid the electrical conductivity of the solution falls slowly to that of the sodium chloride solution. The interpretation is evident from the following equations.





It is clear that pseudo-acids qualify as secondary acids according to Lewis's definition, but the new term goes much farther than the old one which, of course, applied only to hydrogen acids. The important question, however, is whether we are going to be able to explain the behavior of all secondary acids and bases by generalizing Hantzsch's tautomeric theory of pseudo-acids and bases. The answer seems to be a qualified "yes." A few examples will make this clear.

If a carbon dioxide molecule contains two double bonds it is not an acid (acceptor) because it cannot take up any more electrons as long as the double bonds remain intact. If, however, activation energy is supplied to open one double bond it will then be able to exercise acceptor properties. Some doubt remains, of course, as to the extent to which the double bond character is maintained in the normal molecule, but experiment shows that carbon dioxide is neutralized only slowly and hence that it is a secondary acid. The following experiment is illuminating.[8a] "If at −60° we dissolve carbon dioxide in alcohol and divide the solution equally between two tubes, A and A′, and if at the same temperature we have an alcohol solution containing dilute sodium ethylate and a little indicator . . . divided between the two tubes, B and B′, then if A is added to B at once there is no immediate change of color. However, on standing for some 15 minutes the carbon dioxide neutralizes the ethylate ion and the indicator passes slowly through its color changes. If now, having stood for half an hour or so, the contents of A′ are added to B′, the indicator goes at once to the acid color." It

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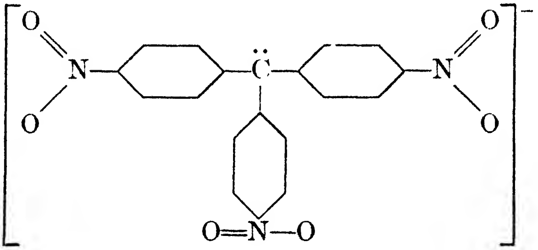
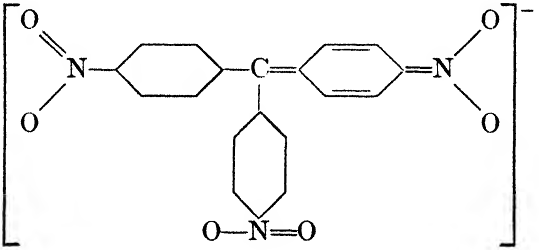
[9] Hantzsch, *Ber.*, **32**, 575 (1899).

appears, then, that carbon dioxide is not an acid in its normal state of lowest energy but becomes one slowly through some internal excitation. This is closely similar to the tautomerism observed in pseudo-acids, except that it appears to be a kind of electromerism. Organic acid chlorides and anhydrides and the Ph_3C^+ ion also show the characteristics of secondary acids.

The studies made on the trinitrotriphenylmethide ion are particularly illuminating. When 4,4′,4″-trinitrotriphenylmethane is dissolved in an alkaline alcoholic solution it loses a proton, giving the intensely blue trinitrotriphenylmethide ion. When this solution is acidified at −30° to −80°, the color fades slowly and more slowly, the lower the temperature, showing that a typical activated slow reaction is taking place, viz., the transformation of the blue secondary base into a primary base. The structures of these two substances are not known with certainty, but Lewis and Seaborg suggest that perhaps the primary base may be represented by formula I and the secondary base by formula II.



I



II

If this were true, the secondary base should be able to act as a primary base with respect to the addition of an acid to an oxygen atom but not to the central carbon atom. Although oxygen is much less basic than $>$C:, one would expect that a sufficiently strong acid would cause the immediate addition of a proton to the oxygen atom. The prediction was verified to the extent that it was shown that hydrogen chloride reacted immediately with the blue ion. Thus it is seen that a substance may act as a secondary acid or base with respect to neutralization at one point of a molecule and at the same time behave as a primary acid or base with respect to some other point.

A peculiar difficulty is encountered in this theory, however, for both forms I and the three modifications of form II are commonly considered to be structures which contribute to resonance of the ion. Lewis and Seaborg [8a] pointed out in this regard, generalizing the formulas I and II as S_1 and S_2, that "If we take this view we have to consider, not only what fraction of the time the molecule can react as though it were in the form S_1, but also how frequently this state or phase recurs, or, in other words, the resonance frequency. In the case of a gaseous collision the duration of the collision is presumably of the same order of magnitude as the resonance time. In such a case the chance of an effective collision might depend very greatly upon whether the reacting form is a major or minor constituent of the resonating molecule. On the other hand, in a liquid, if two molecules come together, they possibly remain together for a considerable time, during which a resonating molecule may pass many times through its various phases. In such a case it would appear that the probability of effective collision would not depend very greatly upon the extent to which the reacting form contributes to the resonance state." He then goes on to say, "When one of the contributing structures of a resonating substance, no matter how small the contribution may be, has the form of an acid or base, the substance will behave as a primary acid or base, and when it combines with any primary base or acid it will do so without activation."

If this is the case, and if forms I and II are contributing structures, then it is obvious that I and II cannot represent the structures of the primary and secondary bases. Furthermore, the same difficulty would arise if we attempted to replace I and II by any other reasonable electronic modifications. Lewis and Seaborg consider several possible explanations of this difficulty and finally conclude tentatively that the most likely explanation is that there is no resonance between the formulas corresponding to a primary and those corresponding to a secondary acid. This conclusion, if it is verified, will merely constitute another of the selection rules which restrict resonance [10] and will furnish strong evidence in favor of the idea that the primary and secondary forms of an acid or base are electromers in the sense in which that term was originally used, i.e., electronic tautomers which should be capable of isolation. It is in this sense that Lewis's concept can be said to be a generalization of Hantzsch's theory.

Lewis also points out that a second type of secondary behavior is evident when acids or bases are neutralized wholly or in part with the sol-

[10] See Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).

vent. Thus if an acid is dissolved in a basic solvent a covalence is formed, $A + S \rightarrow A{-}S$, which must be broken if a stronger base than the solvent is to replace the solvent:

$$AS + B \rightarrow AB + S$$

Such reactions usually require activation energy, but in many cases it is small enough to be ignored.

Closely related to this last point is the behavior of hydrogen acids. According to the Lewis definition such substances as HCl or H_3O^+ are acids because they are coordinatively unsaturated, i.e., because the hydrogen atoms can form hydrogen bonds. In a reaction like

$$H_2O + HCl \rightarrow H_2O \ldots H \ldots Cl \rightarrow H_3O^+ + Cl^-$$

no activation energy is required for the first step since no bond is being broken. But it also happens that the chemical driving force furnished by the formation of a bond between H and H_2O is more than sufficient to break the HCl bond, so the second step also proceeds without activation energy. The acidic properties of HCl do not, of course, rest in any way upon the circumstance that this second step happens to take place, i.e., HCl is not a primary acid because it can *give up a proton.* In cases where stable hydrogen bonds are formed, the first step is presumably instantaneous and the second thermodynamically improbable.

THE MEASUREMENT OF ACIDITY AND BASICITY

Acidity

When an acid is dissolved in a basic solvent, or a base in an acidic solvent, the following reaction takes place.

$$HB_1 + B_2 \rightleftarrows HB_2 + B_1 \quad (1)$$

Obviously this equation will represent equally well the reaction of an acid and a base in an aprotic solvent, or the self-ionization of an amphiprotic solvent. If B_2 represents the solvent, the extent to which this reaction takes place at a given temperature is determined not alone by the intrinsic strength of the acid (i.e., its intrinsic proton donating tendency independent of the environment) but it also depends on the base strength of the solvent as well as on other solvent properties, such as the dielectric constant; it will also depend on the charge types of acids and bases involved because the dielectric constant of the medium will affect the work of proton transfer (and thus ΔF and the equilibrium conversion) differently for acids of different charge types. The equilibrium conversion in Equation 1 will also depend on the degree of association of the acid (or base) and finally on the concentration of all molecular and ionic species present, partly because these species may be involved directly in the equilibrium (1) and partly because the activity coefficients of those involved in the equilibrium will be affected by the concentration of everything involved in the solution.

It is obvious that the availability or escaping tendency of protons from a given solution will depend on the equilibrium conversion in Equation 1. If other acids are also present, they will not only affect this equilibrium conversion but will also alter the average proton escaping tendency of the whole solution in proportion to their own intrinsic acidities and equilibrium concentrations. The "acidity" of any solution may logically be taken to mean the escaping tendency of protons from that solution and may be measured by the partial molal free energy change involved in transferring protons from that solution to some standard state. Since [11]

$$\bar{F} - \bar{F}^\circ = RT \ln (\mathrm{H}^+)$$

it is obvious that the hydrogen ion activity or, better, its logarithm measures the "acidity" of a solution.[12] As a consequence of the well-known equation for the hydrogen electrode

$$E_h = -\frac{RT}{F} \ln (\mathrm{H}^+) \tag{2}$$

an alternative measure of "acidity" is to be found in the potential of the cell: [12] H_2(1 atm.), H^+ ($a = 1$), H^+($a = x$), H_2(1 atm.), if we neglect the liquid junction potential or correct for it. Obviously colorimetric determinations with indicators may be substituted for the electrometric method.[13]

In the above discussion it was insinuated that measurements in all solvents should be referred to a single standard state. This may most conveniently be chosen as an aqueous solution in which has been retained the customary convention of making a/m approach unity as m approaches zero.[14]

We see then that a logical definition of acidity can be set up in terms of individual hydrogen ion activities. Unfortunately this is not as

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[11] Activities will be indicated by parentheses, concentrations by square brackets; $\bar{F}$ indicates the partial molal free energy.

[12] Brönsted, *Chem. Rev.*, **5**, 291 (1928).

[13] (*a*) Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); (*b*) Brönsted, *Ber.*, **61B**, 2049 (1928); (*c*) Hammett, *J. Am. Chem. Soc.*, **50**, 2666 (1928).

[14] Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925).

convenient as using the mean ion activity ($a_{\pm}$) but we must realize that using the latter is not strictly equivalent. However, in solutions weaker than 0.01 molal the difference is apt to be very slight.[15]

Acid Strength

Let us now turn to the problem of measuring the change in the strength of an acid caused by variation of the solvent and the related problem of determining the relative strengths of two acids either in the same or in different solvents. This concept of "acid strength" seems simple enough until we try to fashion an adequate definition for it. In the first place, it is apparent from the way in which we have just used the term that it is different from "intrinsic acid strength" because it varies with the solvent. Furthermore, it carries the insinuation that high "acid strength" should result in high "acidity," other things being equal; and if "acid strength" is to be a property of an acid in a given medium, it should be defined in such a way that it is independent of the concentration of the acid.

This last stipulation suggests that the activity constant, defined for an acid HB as follows

$$K^*_a = \frac{(\mathrm{H}^+)(\mathrm{B})}{(\mathrm{HB})} \tag{3}$$

would be a satisfactory measure of "acid strength," since it is a true thermodynamic constant and hence completely independent of the concentration. Unfortunately, however, K^*_a is quite.independent of the solvent medium if a single standard state is chosen. Moreover, it is useless if the comparison is to be made between two acids, even in the same solvent, since different negative ions are involved.[16] Such a comparison would involve the apparently impossible problem of picking two standard states, one for each negative ion, which would be thermodynamically equivalent.

Brönsted[12] has suggested that acid strength be measured by an "acidity constant" which he defined as

$$K_{\mathrm{acid}} = \frac{[\mathrm{B}](\mathrm{H}^+)}{[\mathrm{HB}]} \tag{4}$$

According to this definition K_{acid} measures the proton activity of a solution in which [B] = [HB]. Its value obviously depends on the solvent, as desired, and Brönsted contended that it would measure the

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[15] See, for example, Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., 1923, table 8, p. 382.

[16] Brönsted, Ref. 12, p. 294.

"acidity" of binary solutions under comparable conditions. Furthermore, if it is a constant, as its name implies, it should be independent of the concentration of the acid and hence satisfy the three requirements we set up for any function which would adequately measure acid strength. Unfortunately, however, these acidity constants are found frequently to be far from constant.[17]

For the measurement of base strength Brönsted similarly defined the basicity constant.

$$K_{\text{bas}} = \frac{[\text{HB}]}{[\text{B}](\text{H}^+)} \tag{5}$$

This constant is meant to measure the base strength of B and, since the strength of a base is obviously inversely proportional to the strength of its conjugate acid, it is taken as the reciprocal of the acidity constant of HB.

These Brönsted constants have the advantage that, in so far as they are constant and in so far as the half dissociation points of acids truly represent comparable conditions, they are equally valid for comparing the acid strengths of the same acid in different solvents or of different acids either in the same or in different solvents.

The classical dissociation constant, K_a, although it gives a fairly satisfactory measure of the relative strengths of two acids in the same solvent, is absolutely useless for the comparison of the strength of one acid in different solvents. This may be readily understood by examination of the equation

$$\text{HB} + \text{S} \rightarrow \text{HS}^+ + \text{B}$$

in which S represents a molecule of the solvent and the charge type of B is not stipulated. Since

$$K_a = \frac{[\text{SH}^+][\text{B}]}{[\text{HB}]} \tag{6}$$

it is apparent that the value of K_a depends on the extent to which the solvent removes protons from the acid. A strongly basic solvent will do this very effectively, and the more effectively it is done the more firmly will the protons be held and hence the less will be the acidity of the solution.[18] Thus if K_a were used as a measure of acid strength, an acid would appear to be much stronger in a liquid ammonia than in a water solution, but as a matter of fact the proton-escaping tendency is less in the ammonia solution.

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[17] Hall, *J. Am. Chem. Soc.*, **52**, 5120 (1930).

[18] Kolthoff, *Rec. trav. chim.*, **49**, 413 (1930).

It is apparent from the above discussion that acid strength, as we have defined it, cannot be measured by K_a or K^*_a. It may be measured by K_{acid}, but even this function is not entirely satisfactory.

The Acidity Function

Hammett [13c] pointed out that when it is attempted to determine the acidity of a solution colorimetrically by using a simple basic indicator, one actually succeeds only in measuring the tendency of the acids, in their particular environment, to transfer protons to the indicator base. Thus, if *In* represent the indicator base, we have

$$\mathrm{HB} + In \rightleftarrows \mathrm{B}^- + \mathrm{H}In^+$$

Furthermore, he showed that such a measure of acidity is not in general the same as that given by an acid indicator, and neither one is identical with the hydrogen ion activity, which has been shown previously to be a logical measure of acidity. However, despite the fact that the indicator method does not measure acidity, as previously defined, it does measure something closely akin to it and of perhaps even greater importance in organic chemistry, viz., the tendency of an acid solution to transfer a proton to a base.[19] This is of importance not only in ordinary protolytic equilibria but also in acid catalysis where the active intermediate complex is formed in this way.

As an aid in using the indicator method for the determination of acidity, Hammett and Deyrup [19] defined an "acidity function," symbolized by H_0 or H_-, the subscripts indicating the charge type of the indicator base involved. The defining equations are:

$$\mathrm{H}_0 = -\log\left(\frac{(\mathrm{H}^+)f_{\mathrm{B}}}{f_{\mathrm{BH}^+}}\right) \tag{7}$$

$$\mathrm{H}_- = -\log\left(\frac{(\mathrm{H}^+)f_{\mathrm{B}}}{f_{\mathrm{HB}^+}}\right) \tag{8}$$

in which the f's are the activity coefficients. As a definition of the base strength of an indicator they chose pK^*_a of the conjugate acid. Note that this definition makes "base strength" independent of the solvent, unlike Brönsted's definition.

$$pK^*_a = -\log\left(\frac{(\mathrm{H}^+)(\mathrm{B})}{(\mathrm{BH}^+)}\right) = -\log\left(\frac{[\mathrm{H}^+][\mathrm{B}]}{[\mathrm{BH}^+]}\right) - \log\left(\frac{f_{\mathrm{H}^+}f_{\mathrm{B}}}{f_{\mathrm{BH}^+}}\right) \tag{9}$$

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[19] Hammett and Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

Owing to the inverse relationship between K and pK and that between acid and base strength of a conjugate pair, it is seen that pK^*_a actually measures the strength of the base, according to their definition.

By combining Equations 7 and 9 we get

$$H_0 = \log \frac{[B]}{[BH^+]} + pK^*_a \tag{10}$$

From this equation it is obvious that H_0 may be calculated from the known value of pK^*_a for the indicator and the ratio $[B]/[BH^+]$ determined colorimetrically.

The complete significance of H_0 is now evident from Equations 7 and 10. From the latter it is seen that H_0 is the pK^*_a value of a simple basic indicator * which is half converted into its conjugate acid when placed in the solution whose acidity it is wished to measure. Since K^*_a is the thermodynamic equilibrium constant for the reaction $HIn^+ \rightleftarrows H^+ + In$, in which $In = B$, pK^*_a measures the thermodynamic tendency for the reverse reaction to occur and is thus in a way the measure of the base strength of the indicator, although it is not in accord with our previous definitions of acid and base strengths. In the same sense we may say that H_0 is a measure of the strength of any base of the neutral charge type which is half converted to its salt in the solution in question. H_- has a similar significance when the base is negatively charged, like OH^-.

From Equation 7 it is evident that the value of H_0 is not independent of the basic indicator used unless the ratio f_B/f_{BH^+} is the same for all indicators of the same charge type. Hammett assumes that this ratio is constant, and much experimental work indicates the approximate correctness of the assumption. Granting the assumption, it is apparent from Equation 7 that H_0 increases with the pH^* of the solution and becomes equal to it in an ideally dilute solution where $f_B/f_{BH^+} = 1$. Thus $-H_0$ is a measure of the acidity of the solution (defined as the hydrogen ion potential), the accuracy of the measurement being determined by the correctness of the basic assumption.

It should incidentally be emphasized that acidities in different solvents, as measured by (H^+), have already been shown to be strictly comparable if a common standard state is chosen. The same cannot be said of acidities measured by H_0 unless the above ratio, f_B/f_{BH^+}, is independent of the solvent as well as being independent of the base. Hammett claims that this requirement is also met within a very small margin of error.

* They define a simple basic indicator as "a nonionized or neutral substance capable of adding one hydrogen ion per molecule without any complicating further reactions and in such a way that a color change is determined by the extent of the reaction."

Ionic Dissociation and Solvent Basicity

The extent to which salts dissociate when dissolved in a solvent depends primarily on the dielectric constant of the solvent, as is evident from the well-known theory of Debye and Hückel.[20] When, however, we are dealing with acids, another factor becomes of great importance, the basicity of the solvent. In a basic solvent of high dielectric constant, a strong acid like HCl appears to be highly dissociated because of proton transfer to the solvent, in accord with Equation 1. If the dielectric constant is low, as in dioxane, the reaction between solvent and acid will still take place, but a hydrogen bond is now formed and the acid is not dissociated.[21] It will now exist in "ion pairs" or in combinations of greater complexity.

If a solvent has amphiprotic properties it can undergo self-ionization or autoprotolysis, as described in Appendix IV. It is customary to refer to the ion produced by adding a proton to a solvent molecule as the "lyonium ion," while the "lyate ion" is the one produced by removing a proton from a solvent molecule.[22] For solutions of constant ionic strength in any given solvent the product of the concentrations of the lyonium and lyate ions is a constant, the autoprotolysis constant, K_{auto}. Examples of such constants for several solvents are given in Table I. The practical significance of this constant lies in the fact that it gives a measure of the range of lyonium ion concentrations which is possible in a given solvent.[23] To make this point clear, consider 0.1 molar aqueous solutions. The highest possible concentration of H_3O^+ ions (that produced by a very strong acid) is then 0.1 M; the lowest (that produced by a very strong base) is 10^{-13}. If liquid ammonia ($K_{\text{auto}} = 10^{-22}$) were used instead as a solvent, the range would be much larger, viz., from 0.1 to $10^{-21}M$.

Let us now turn to the problem of measuring the basicity of solvents. The base function of a solvent is represented by the equation

$$S + H^+ \rightleftarrows SH^+ \tag{11}$$

and the solvent is considered to be more basic the greater the equilibrium displacement of the reaction toward the right. Hammett [13c] has chosen the thermodynamic equilibrium constant of Equation 11 as a measure of solvent basicity.

$$K^*_b = \frac{(SH^+)}{(S)(H^+)} \tag{12}$$

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[20] For an excellent discussion of this theory see Falkenhagen, *Electrolytes*, translation by R. P. Bell, Oxford Press, 1934.

[21] Rodebush and Ewart, *J. Am. Chem. Soc.*, **54**, 419 (1932).

[22] Bjerrum, *Chem. Rev.*, **16**, 287 (1935).

[23] Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., 1940, p. 255.

TABLE I

SOLVENT PROPERTIES

Solvent	Temp. °C	pK_{auto}	Conventional constants		Lit.
			pK_{acid}	pK_{bas}	
Sulfuric acid		3.0	−9.1 *	12.1 *	19, 25
Formic acid	25	6.3	1.3 *	5.0 *	24
Acetic acid		12.6	7.5	5.1	25
Water	25	14.0	14.0	0.0	
m-Cresol	23	14.66			26
Methanol	25	16.7			19
Ethanol	25	19.0	16.2	2.8	25
Ammonia	−33.4	22			25

* Based on assumption that $H_0 = -\log(H^+)$.

It is apparent that solvent basicity, so defined, includes the effects of all solvent properties, such as the dielectric constant, which would affect the work of accession of protons by the solvent.

This definition unfortunately has one serious deficiency. If we wish to compare the basicities of different solvents, the values of K^*_b are not truly comparable because the standard states of the different lyonium ions cannot be made the same. In view of this difficulty let us seek another measure of solvent basicity.

Our former statement of the factors which contribute to the acidity of a solution may now be expressed by the equation

$$\ln(\mathrm{H}^+) = \ln\left[\frac{k[\mathrm{HB}]A_{\mathrm{HB}}}{B_s}\right] \tag{13}$$

in which $\ln(\mathrm{H}^+)$ is a measure of the acidity of the solution, k is a constant, A_{HB} is the intrinsic acidity of HB, not defined beyond the statement that it is measured at unit concentration of HB and is independent of the environment at a given temperature, and B_s is some adequate measure of solvent basicity, determined either for the pure solvent or for an infinitely dilute solution. It occurs in the denominator because the

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[24] (*a*) Hammett and Dietz, *J. Am. Chem. Soc.*, **52**, 4795 (1930); (*b*) Hammett and Deyrup, *ibid.*, **54**, 4239 (1932).

[25] N. F. Hall, personal communication.

[26] D. C. Griffiths, *J. Chem. Soc.*, 815 (1938).

greater the proton affinity of the solvent, the less would be the proton-escaping tendency.

The simple proportionality expressed in Equation 13 is not strictly justified. For example, if we are dealing with a given solute in a given solvent, the equation reduces to the familiar relationship $(H^+) = k'[HB]$, in which k' is now seen to be the mean activity coefficient, which is well known to vary with the concentration and, unfortunately, with the kind of acid. However, the equation gives us a clear picture of what is meant by solvent basicity and intrinsic acid strength and is apparently capable of yielding a semi-quantitative measure of relative solvent basicities measured at a fixed concentration of a single acid in different solvents. It is, of course, understood that (H^+) is measured in all solvents with reference to a single standard state.

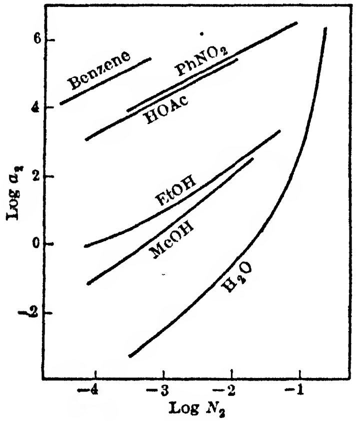

FIG. 1.[27] Activities of HCl in different solvents as a function of the mole fraction.

As a first application of Equation 13 let us examine the work of Heston and Hall[27] on the relative basicities of solvents. They determined the activity of HCl in glacial acetic acid solutions by measuring the e.m.f. of cells without liquid junction and correlated their results with those of other investigators[28] to obtain Figure 1. In this figure N_2 is the mole fraction of HCl. Since the same acid is used in all cases, Equation 13 becomes

$$(H^+) = \frac{k'[HB]}{B_s} \tag{14}$$

where $k' = kA_{HB}$. Thus, if we may identify (H^+) with the mean ionic activity of HCl referred to ideally dilute aqueous solutions, it is apparent that the activities of HCl at the same concentration in different solvents give a relative but inverse measure of the basicities of those solvents. Thus from Figure 1 we see that the increasing order of solvent basicity is $Ph \cdot H < PhNO_2 < HOAc < EtOH < MeOH < H_2O$. The authors warn us that a change of acid solute "would undoubtedly produce small changes in the position and character of the curves due to the difference

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[27] Heston and Hall, *J. Am. Chem. Soc.*, **56**, 1462 (1934).

[28] (*a*) Carmody, *ibid.*, **54**, 188 (1932); (*b*) Woolcock and Hartley, *Phil. Mag.* [7], **5**, 1133 (1928); (*c*) Nonhebel and Hartley, *ibid.* [6], **50**, 729 (1925); (*d*) Wynne-Jones, *J. Chem. Soc.*, 1064 (1930).

in the properties of the solvates formed. These changes should not be great enough to cause the curves for the alcohols to fall below that for water or for the two alcohol curves to exchange places." It is also of interest to note from Figure 1 that the solvents which have little tendency to accept protons give solutions which obey Henry's law. Furthermore, they have high values of log (HCl) showing the proton-escaping tendency to be greater from their solutions than from the more highly ionized solutions in the more basic solvents. This is reminiscent of Hantzsch's early work in which he proved to the astounded world that the degree of ionization of an acid does not necessarily parallel the acidity.[29]

Another method of measuring solvent basicity, which should closely parallel Hall's method, has been developed by Gordy and Stanford.[30] It was found that when CH_3OD is dissolved in benzene the infrared absorption band occurs at very nearly the same frequency as it does in CH_3OD vapor, but that when it is dissolved in basic or amphiprotic solvents there is a shift to lower frequencies accompanied by a broadening and an intensification of the band. This was demonstrated to be due to the formation of deuterium bonds or bridges, and the magnitude of the shift in frequency was quite reasonably assumed to parallel the donor properties of the solvent. Support for this assumption was found in the fact that there is no correlation between the observed shifts in frequency and the dipole moments of the solvents while there is a linear relation between these shifts and the logarithms of the basicity constants of 17 out of 20 bases chosen for the test, viz.,

$$\Delta\mu = 0.0147 \log K_b + 0.194$$

where $\Delta\mu$ is the shift, expressed in microns, which was observed for 1-molar solutions of CH_3OD in the solvent in question while $K_b = K_i/K_w$, K_i being the basic ionization constant of the above "solvent" when it is acting as a solute in water solution and K_w being the ion product of water. The authors point out that one would not expect strongly associated liquids like the glycols or ketoximes to follow this relationship. It might be added that likewise one would expect no parallelism between K_b in water solution and the basicity B_s for the pure liquid base when the latter is associated. Hence we might reasonably hope for a fair degree of parallelism between $\Delta\mu$ and B_s. It is of further interest that there is a correlation between the solubility of CO_2 and $\Delta\mu$. Since the solubility

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[29] See Appendix IV.

[30] (*a*) Gordy, *J. Chem. Phys.*, **7**, 93 (1939); (*b*) Gordy and Stanford, *ibid.*, **8**, 170 (1940); (*c*) *idem*, **9**, 204 (1941); (*d*) Gordy, *ibid.*, **9**, 215 (1941).

of CO_2 is probably influenced by the formation of complexes with the solvents it should depend on the donor properties of the solvent.

Of related interest is the fact that further experiments,[30d] in which D_2O and HCl were substituted for CH_3OD, showed that the shifts produced by different liquids upon the D_2O band and the HCl band bear a linear relation to those produced by the same liquids on the CH_3OD band. There were frequent but small variations from linearity. Thus the evidence from this series of papers, as far as it goes, indicates that the relative order of solvent basicities is the same with respect to at least three acceptors: hydrogen ion, deuterium ion, and carbon dioxide. Furthermore it is definitely shown that this order does not depend on whether the deuterium atom is linked to CH_3O— or to DO—.

A few of the data of Gordy and Stanford are assembled in Table II. They may presumably be used to compare the relative basicities B_s of different solvents.

TABLE II

SHIFTS IN THE OD BAND PRODUCED BY DIFFERENT SOLVENTS [30b]

SOLVENT	$\Delta\mu$	SOLVENT	$\Delta\mu$
Benzene	0.00	Benzaldehyde	0.12
Bromobenzene	0.	Amyl acetate	0.13
Ethylene chloride	0.02	Acetone	0.14
Chlorobenzene	0.02	Dioxane	0.14
Ethyl nitrate	0.03	*n*-Butyl ether	0.16
Nitrobenzene	0.04	Cyclohexanone	0.17
o- or *m*-Nitrotoluene	0.07	Diethyl ether	0.19
Acetonitrile	0.09	*o*-Toluidine	0.26
Anisole	0.10	Aniline	0.27
Methyl ethyl ketone	0.11	Pyridine	0.27
Diethyl ketone	0.11	Quinoline	0.27
n-Butyronitril	0.11	Ethylene glycol	0.31
Ethyl acetate	0.12	Piperidine	0.37

Brönsted[31] suggests the use of his own conventional acidity and basicity constants to measure the acidity and basicity of solvents. We have already seen that these constants are not ideally suited for such comparisons. However, they seem to have roughly quantitative significance in practice.

Brönsted gives the following definitions: If the acid function of a solvent is represented by the equation

$$HB \rightarrow H^+ + B^-$$

and the base function by

$$H^+ + B \rightarrow BH^+$$

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[31] Ref. 12, p. 302.

then the rational acidity constant is

$$K_{\text{acid (rat)}} = \frac{[B^-](H^+)}{[HB]} \tag{15}$$

while the corresponding conventional constant is

$$K_{\text{acid (conv)}} = [B^-](H^+) \tag{16}$$

and similarly

$$K_{\text{bas (conv)}} = \frac{[BH^+]}{(H^+)} \tag{17}$$

The product of the conventional constants for a solvent gives

$$K_{\text{acid}} \times K_{\text{bas}} = (H^+)[B^-] \times \frac{[HB^+]}{(H^+)} = [B^-][HB^+] = K_{\text{auto}} \tag{18}$$

Their ratio gives

$$\frac{K_{\text{acid}}}{K_{\text{bas}}} = \frac{(H^+)^2[B^-]}{[HB^+]} \tag{19}$$

Since $[B^-] = [HB^+]$ in a pure solvent, it follows that

$$(H^+) = \frac{K_{\text{acid}}}{K_{\text{bas}}} \tag{20}$$

Equation 20 is not a thermodynamic equation, of course. However, granting their approximate nature, it is evident that Equations 18 and 20 may be solved simultaneously to give the values of K_{acid} and K_{bas} if experimental values are available for (H^+) and the ion product, K_{auto}. These two values may be determined by any of the usual methods.

The values of the acidity and basicity constants given in Table I were computed by the use of Equations 18 and 20. Inspection of these values makes clear that the acid strength of a solvent is by no means inversely proportional to its base strength. It is also to be noted that, as far as comparison is possible with Figure 1, the two methods give the same order of solvent basicities.

The Role of the Dielectric Constant

It may have been noticed in studying Figure 1 that the acidity of HCl solutions is greatest in solvents of low dielectric constant *—in fact the parallelism is complete. Since the term "solvent basicity" includes the effects of many solvent properties, it is a matter of interest to study the effect of the dielectric constant alone and hence to discover to what extent the above parallelism is fortuitous.

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* See Table III for a list of dielectric constants.

Brönsted[32] has shown that the effect of changing dielectric constant on the activity coefficients of acids may be roughly approximated by a simple calculation. The electrostatic potential, ψ, of a spherical particle of radius r and charge ϵZ (where ϵ is the unit charge of electricity and Z is the number of unit charges on the particle, taking no cognizance of algebraic sign) in a medium of dielectric constant D is given by the familiar equation

TABLE III

The Dielectric Constants of Common Solvents

Solvent	D	Temp., °C	Solvent	D	Temp., °C
Hydrogen cyanide (liq)	95	21	Pyridine	12.5	20
Water	81.07	18	Aniline	7.2	20
Formic acid	47.9	18.5	Acetic acid	7.1	17
Nitromethane	39.4	20	Ethylamine	6.3	21
Acetonitrile	38.8	20	Chlorobenzene	5.9	20
Nitrobenzene	36.1	20	Chloroform	5.0	20
Methanol	33.7	20	Diethyl ether	4.33	20
Ethanol	25.7	20	Triethyl amine	3.1	21
Ammonia (liq)	21	−34	Dioxane	2.28	20
Acetone	21.4	20	Benzene	2.28	20
Acetic anhydride	20.5	20	Carbon tetrachloride	2.24	20
Butanol	17.8	25	Pentane	1.8	20.3

$$\psi = \frac{\epsilon Z}{Dr}$$

The electrical energy, E, of the particle is then

$$E = \frac{1}{2}\,\epsilon Z \psi = \frac{\epsilon^2 Z^2}{2Dr}$$

and the work which can be gained by transference from medium 1 to medium 2 is $E_1 - E_2$. This is electrical work and hence may be equated to $-\Delta F$. Thus

$$E_1 - E_2 = -\Delta F = \frac{\epsilon^2 Z^2}{2r}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \tag{21}$$

But $-\Delta F = RT \ln (a_1/a_2)$. Hence if the two solutions are compared at equal concentrations

$$-\Delta F = RT \ln \frac{f_1}{f_2} \tag{22}$$

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[32] Ref. 12, p. 296.

Finally, combining Equations 21 and 22 we get

$$\ln \frac{f_1}{f_2} = \frac{\epsilon^2 Z^2}{2RrT}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \tag{23}$$

Note that in the above derivation it was assumed that the change in activity was due entirely to electrostatic influences. This means that all chemical influences were ignored. With these limitations in mind we may conclude from Equation 23 that the transfer of protons from a solvent of high to one of low dielectric constant (e.g., from water to benzene) is accompanied by an increase in the hydrogen ion activity coefficient. This is in accord with Figure 1. Thus whatever the chemical effects may be, the electrostatic effects alter the hydrogen ion activity in the direction actually observed.

The electrostatic effect on K_{acid} of changing from a solvent of high to one of low dielectric constant is summarized by Brönsted in Table IV.

TABLE IV[12]

CHANGES ACCOMPANYING THE TRANSFER OF AN ACID FROM A SOLVENT OF HIGH TO ONE OF LOW DIELECTRIC CONSTANT

Charge type					
Acid	Base	Δf_{HB}	Δf_{B}	$\Delta(f_{\text{HB}}/f_{\text{B}})$	ΔK_{acid}
−	=	+	++	−	−
0	−	0	+	−	−
+	0	0	+	+	+
++	+	++	+	+	+

To make clear the meaning of the table, let us consider the first case. The acid is a monovalent negative ion (e.g., HSO_3^-) and its conjugate base doubly negative (e.g., $SO_3^=$). The change in the activity coefficient of the acid (Δf_{HB}) is an increase, by Equation 23; that of its conjugate base, an even greater increase (++) due to its greater charge. Thus the ratio $f_{\text{HB}}/f_{\text{B}}$ decreases as shown by the negative sign in the fifth column. Now by definition

$$K_{\text{acid}} = \frac{(\text{H}^+)[\text{B}]}{[\text{HB}]} = \frac{(\text{H}^+)(\text{B})}{(\text{HB})} \cdot \frac{f_{\text{HB}}}{f_{\text{B}}} = K^*_a \frac{f_{\text{HB}}}{f_{\text{B}}} \tag{24}$$

Since K^*_a is a thermodynamic constant for each acid and is independent of the medium when a common standard state is used, it follows that variations in K_{acid} will depend only on the variations of the activity coefficient ratio. Thus the fifth and sixth columns show parallel variations.

Examination of the sixth column reveals that a given change of medium may either increase or decrease K_{acid}, depending on the charge type of the acid, and that hence we should not expect the order of acid strengths for acids of different charge types to be the same in one solvent as in another.

General experience has shown that the changes produced in K_a by changes of solvent are in the same direction as those predicted for K_{acid} (Table IV). As an example, the data of Deyrup[33] are presented in Table V. From Deyrup's figures it is evident that electrically neutral acids are weaker in alcohol than in water, while the reverse is found for positively charged acids. However, it will be noticed that the change of pK is much greater for the former. This is in rough accord with a simple qualitative theory suggested earlier by Brönsted.[34] He considered different charge types of acids, such as

TABLE V

DISSOCIATION CONSTANTS OF ACIDS[33]

ACID	pK_a (EtOH)	pK_a (H_2O)
Nitric	3.57	...
Picric	4.0	0.8
Trichloroacetic	5.46	0.7
Oxalic	6.58	1.3
Monochloroacetic	7.74	2.9
2,4-Dinitrophenol	7.74	3.9
Anilinium ion	3.73	4.6
o-Toluidinium ion	4.00	4.4
Dimethylanilinium ion	4.13	5.0
Pyridinium ion	4.33	5.3

$$HB \rightleftarrows H^+ + B^-$$

$$HB^+ \rightleftarrows H^+ + B$$

$$HB^{++} \rightleftarrows H^+ + B^+$$

and pointed out that in the first type a high dielectric constant of the solvent should aid the separation of unlike charges, in the second type it should be without effect, whereas in the last type it should hinder the ionization.

Hammett[35] has remarked, in relation to Deyrup's figures, that since K_a for the positively charged acids is greater in alcohol than in water, while Brönsted's dielectric constant rule would predict no change, the

[33] Deyrup, *J. Am. Chem. Soc.*, **56,** 60 (1934).

[34] Brönsted, *J. Phys. Chem.*, **30,** 777 (1926).

[35] Ref. 23, pp. 260–261.

discrepancy must be accounted for by ascribing a greater basicity to alcohol than to water. If this were true it would explain why the reaction

$$\mathrm{HB}^+ + \mathrm{S} \rightleftarrows \mathrm{SH}^+ + \mathrm{B} \qquad (25)$$

proceeds farther to the right in alcohol. But we have already seen that Heston and Hall [27] consider alcohol as less basic than water, as does also Kolthoff.[36] The clash is actually one of definition. We have already pointed out that solvent basicity, as defined by Equation 13, includes the effect of the dielectric constant as well as an effect which, for lack of a better name, we may call the intrinsic basicity of the solvent. Hammett referred to the latter. The chief interest in this clash of terminology lies in the fact that it discloses a weakness in the definition of solvent basicity given by Equation 13. Thus an increase in solvent basicity is considered by Heston and Hall and by Kolthoff to lower the proton activity by forcing reaction 25 farther to the right. This would increase K_a. But according to Table IV, transfer to a more basic solvent of higher dielectric constant would displace reaction 25 to the left. Thus if the basicity of a solvent, as defined by Equation 13, is determined by the use of an acid solute of the neutral charge type and this value of the basicity is then used with the same equation when an acid of the positive charge type is involved, the predicted value of the acidity of the solution will be in error.

These considerations disclose that, when acids of different charge types are involved, the dielectric constant and the "intrinsic solvent basicity" may exert opposing influences in one case and parallel influences in another and hence the practice of lumping the two effects together under one name, viz., "solvent basicity," is not an ideal procedure. Nevertheless, until tables of "intrinsic solvent basicities" are available and a more satisfactory equation than Equation 13 is deduced, we will find it convenient to retain our definition of "solvent basicity" when dealing with acids of the neutral charge type.

Another relationship involving the dielectric constant has been developed by Wynne-Jones.[37] By a procedure similar to that used in deriving Equation 23, he deduced the following relationship for uncharged acids:

$$\Delta \ln K_r = \frac{\epsilon^2}{2kT}\left(\frac{1}{r_0} - \frac{1}{r}\right) \cdot \Delta\left(\frac{1}{D}\right) \qquad (26)$$

K_r is the ratio, K/K_0, of the ionization constants of the given acid and the standard acid (benzoic acid) while r and r_0 are respectively the radii of the given and the standard acid molecules. $\Delta(1/D)$ is the change in

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[36] Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).

[37] Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

the reciprocal of the dielectric constant produced by transferring the acids from one medium to another. That K_r is largely independent of the intrinsic basicity of the solvent is easily demonstrated as follows. Consider that the dissociation of an acid takes place in two steps

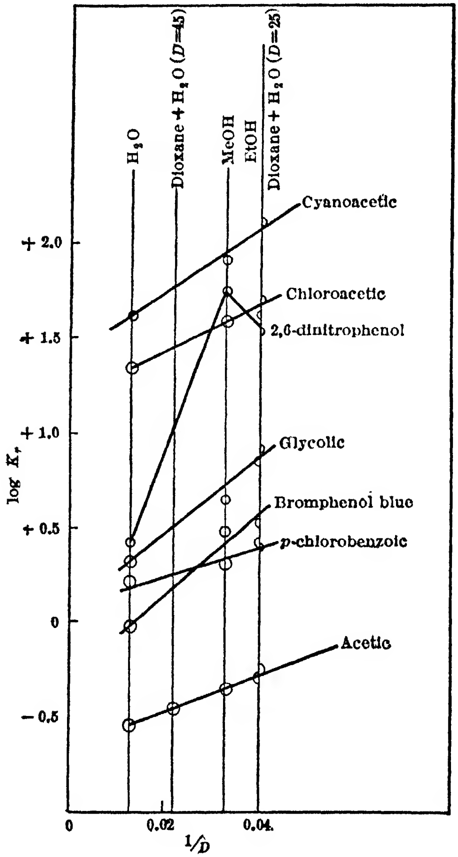

Fig. 2.[38] Relative strengths of acids in solvents having different dielectric constants.

$$HB \rightarrow H^+ + B^-$$

$$H^+ + S \rightarrow SH^+$$

and let K_1 and K_2 be the respective equilibrium constants. Then the over-all dissociation constant K_a is $K_a = K_1K_2$. Since K_2 is independent of the acid,

$$K_r = \frac{K_a}{K^0_a} = \frac{K_1K_2}{K^0_1K_2} = \frac{K_1}{K^0_1}$$

and we now see that K_r is independent of the intrinsic basicity of the solvent in so far as it is involved in the work of solvating the proton. However, its value does depend on the dielectric constant of the solvent, since the work of separating two charged particles is a function of the dielectric constant of the medium; and the acidic or basic properties of the solvent may alter the value of K_r by changing the effective dipole moment of a molecule, as will be described in detail later in this chapter.

Equation 26 lacks quantitative accuracy since it was developed on the assumption that the solvent is a continuous dielectric and that the ions are spherical. But it should have semi-quantitative significance. Thus it predicts a linear relationship between $\ln K_r$ and $1/D$ for each acid. Such a relationship is actually observed between $D = 25$ and $D = 80$, as Figure 2 illustrates.[38]

Minnick and Kilpatrick [38] found that there was good agreement between the values of K_r for carboxylic acids in ethanol and in dioxane-water mixtures of the same dielectric constant, thus showing that the intrinsic basicity of the solvent is rather effectively ruled out by this method.

One important feature of the linear relationships shown in Figure 2 is the possibility of extrapolating the curves to $1/D = 0$, i.e., to infinite dielectric constant. In this state the electrostatic attraction between the solute molecules would be completely destroyed and, since K_r is independent of intrinsic solvent basicity, the above investigators contend that a measure of intrinsic acid strength is thus achieved.

Change of Acid Strength with Solvent

It has already been pointed out that K_a is not a valid measure of the change in acid strength produced by a change in solvent, since the intrinsic basicity of the solvent exerts a disturbing influence. We have also seen that this disturbing influence is eliminated when K_r is used instead. Hence we may take the values of pK_r in Table V as means of comparing the order of strengths of acids in different solvents. In general it is found that this order is the same in all solvents if we compare acids of the same charge type and omit consideration of strong acids which would be "leveled" by the solvent. But exceptions are frequently found;[39] in Table VI they are indicated by square brackets. The most frequent offenders are acids in which a strongly polar group is close to the acidic proton, as in *ortho*-substituted benzoic acids.

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[38] Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939).

[39] See, e.g., References 17 and 37; also Halford, *J. Am. Chem. Soc.*, **53**, 2994 (1931), and Kilpatrick, Mears, and Elliott's paper presented at the 99th meeting of Am. Chem. Soc., Cincinnati (1940).

Wooten and Hammett[40] make the interesting observation that substituents which increase the strength of an acid (K_a) also increase its relative strength (K_r) when the solvent is changed from water to butanol. Likewise those which decrease K_a decrease K_r. This is shown by the last column in Table VI. The comparison is restricted to *m*- and *p*-substituted benzoic acids and, as far as existing data go, is equally true in other solvents having lower dielectric constants than water.*

TABLE VI

Acid	pK_r						$pK_r(\text{BuOH}) - pK_r(\text{H}_2\text{O})$
	H_2O $D = 81$	EtOH $D = 25$	Dioxane-H_2O, $D = 25$	BuOH $D = 18$	PhCl $D = 6$	C_6H_6 $D = 2$	
Dichloroacetic	−2.9		−3.00	−3.1	−2.33	−2.83	......
o-Nitrobenzoic	−2.01			−1.74			+0.27
Cyanacetic	−1.63	−1.92	−2.11				
Chloroacetic	−1.34	−1.58	−1.70	−1.71	−1.35	−1.68	−0.37
Salicylic	−1.23	−1.52	−1.67	−1.50	−1.32	[−2.03]	−0.27
p-Nitrobenzoic	−0.80			−1.12			−0.32
m-Nitrobenzoic	−0.74			−1.09			−0.35
Formic	−0.45			−1.09		−0.94	−0.64
2,6-Dinitrophenol	−0.41	[−1.76]	−1.55		−0.58		
m-Chlorobenzoic	−0.38		−0.54	−0.60			−0.22
Glycollic	−0.33	−0.65	[−0.93]				
p-Chlorobenzoic	−0.22	−0.44	−0.39	−0.42			−0.20
o-Methoxybenzoic	−0.12			−0.31			−0.19
m-Toluic	+0.05			+0.09			+0.04
p-Toluic	+0.17			+0.21			+0.04
Anisic	+0.28			+0.40			+0.12
Acetic	+0.56	+0.31	+0.25	[+0.05]	+0.42	+0.60	−0.51
Literature	38, 40	38	38	40	41	42	

Frequently it is desired to calculate the value of K_r in one solvent from its value in another. Halford[43] has suggested a method which is frequently of practical importance. He develops the equation

$$(pK_r)_1 - (pK_r)_2 = \log\left[\frac{a_2\sigma^2{}_1}{a_1\sigma^2{}_2}\right]_A - \log\left[\frac{a_2\sigma^2{}_1}{a_1\sigma^2{}_2}\right]_B \qquad (27)$$

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[40] Wooten and Hammett, *J. Am. Chem. Soc.*, **57**, 2289 (1935). Their solutions contained 0.05 *M* LiCl.

* The original paper should be consulted for the relationship of this effect to the work required to ionize an acid containing a substituted polar group.

[41] D. C. Griffiths, *J. Chem. Soc.*, 818 (1938).

[42] LaMer and Downs, *J. Am. Chem. Soc.*, **55**, 1840 (1933).

[43] Halford, *J. Am. Chem. Soc.*, **53**, 2939 (1931).

where A and B indicate that the symbols within the two brackets refer respectively to the two acids A and B (charge type: neutral), the subscripts 1 and 2 refer to the two solvents, a is the activity of the acid and σ is the mean activity of the ions of a salt of the acid. Equation 27 may be used for a convenient approximation of K_r by assuming that solubilities, when sufficiently low, may be employed to replace the activities. Thus a becomes the solubility of the acid and σ that of its salt. Using silver salts in water and 50% alcohol, Halford showed that this approximate method gave satisfactory results for acetic, benzoic, salicylic, *o*-nitrobenzoic, and α-naphthoic acids. A similar method was previously proposed by Bjerrum and Larsson.[44]

The change in Brönsted's K_{acid} produced by changing the solvent cannot be calculated quantitatively, as the individual character of the acid and base are of great significance [45] but the direction of the change can be predicted from Table IV.

THE BRÖNSTED THEORY OF ACID AND BASE CATALYSIS

Outline of the Theory

It is common knowledge today that the speed with which reactions take place in solution is influenced by the presence of salts. In fact reaction velocity depends very much on the total ionic strength of the solution, whether this is contributed by the reactants themselves or by other substances. If the effect depends on the total ionic strength of the solution it is referred to as the primary salt effect. The secondary salt effect depends for its influence on common ion effects and can be formulated on a mass action basis.

In addition to the salt effects, acids and bases frequently have profound catalytic influences. Sometimes the effect is specific, i.e., one acid or base will catalyze the reaction while another will not. In other cases "general acid catalysis" or "general base catalysis" is found, i.e., all acids or all bases have catalytic influence. Finally, there is a class of reactions which exhibits general acid *and* base catalysis. Our interest at the moment lies in Brönsted's theory of general acid and/or base catalysis.[12] In fact it was just this field in which the value of his definitions of acids and bases became most evident.

A qualitative understanding of his theory follows naturally from his definitions of acids and bases and from the widely held theory that most reactions proceed by the formation of unstable intermediate complexes.

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[44] Bjerrum and Larsson, *Z. physik. Chem.*, **127**, 358 (1927).

[45] Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).

In general acid catalysis, the substrate (the initial reactants in a catalytic reaction are called the substrate [46]) takes up protons from the catalyzing acid to form an unstable molecule or ion, the "critical complex." Likewise in general basic catalysis the catalyst abstracts protons from the substrate. Brönsted assumes that, in every reaction catalyzed by acids and/or bases, the rate-determining step is the formation of a critical complex. Hence the reaction velocity will depend on the probability of the formation of the critical complex, and this in turn can be shown to be related to the acid or base strength of the catalyst.

Let us now proceed to the quantitative formulation of the theory.[47] The over-all equation for a given reaction may be written

$$X \rightarrow Y \tag{28}$$

If this reaction is subject to acid or base catalysis we may write for the velocity of the catalyzed reaction

$$\text{Vel.} = k_{\text{un}}\,[X] + k_c\,[C]\,[X] \tag{29}$$

where k_{un} is the velocity constant for the "uncatalyzed" reaction in the solvent alone, C is the catalyst and k_c is the so-called catalytic constant. Now if we consider, for example, that this is a case of general acid catalysis, the formation of the unstable intermediate complex (or at any rate, the first such complex) may be represented by the equation

$$X + HB \rightleftarrows XH + B \tag{30}$$

in which we purposely refrain from committing ourselves as to the charge types involved. Reaction 30 is very similar to the ordinary reaction of solvolytic dissociation of an acid:

$$S + HB \rightleftarrows SH + B \tag{31}$$

and Brönsted assumes that the probability of a proton passing from HB to X (Eq. 30) is proportional to the velocity of dissociation of HB according to Equation 31 since they are such closely similar reactions. Hence we may relate the velocity constant k_c of the formation of the critical complex, Equation 30, to the velocity constant k_{diss} of the solvolytic dissociation of the acid, Equation 31, as follows:

$$(k_c)_A = G_1 k_{\text{diss}} \tag{32}$$

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[46] Schwab, Taylor, and Spence, *Catalysis*, D. Van Nostrand Co., 1937, p. 8.

[47] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); Ref. 12, p. 320.

where G_1 is a constant dependent on temperature, pressure, medium, and substrate. If now we let K_A be the equilibrium constant for reaction 31, the kinetic concept of equilibrium leads to the relationship

$$K_A = \frac{k_{\text{diss}}}{k_{\text{ass}}} \tag{33}$$

where k_{ass} is the velocity constant for the reverse of Equation 31. If now it is further assumed that, as we pass from one acid to another, k_{diss} increases at the expense of k_{ass}, which therefore must decrease, then it becomes apparent that K_A must increase faster than k_{diss}. Brönsted considers that this is a reasonable assumption, at least for acids which are closely alike. Hence we may not write $k_{\text{diss}} = G_2K_A$, but must express the fact that K_A is increasing faster than k_{diss}. The following equation expresses this relationship,

$$k_{\text{diss}} = G_2 K^x{}_A \tag{34}$$

if x is a proper fraction. The numerical value of x cannot be estimated *a priori*, but it is reasonable to assume that x is a continuous function of K_A for acids of the same type.

If now Equations 32 and 34 are combined, we arrive at the main equation of the Brönsted theory:

$$(k_c)_A = GK^x{}_A \tag{35}$$

In general basic catalysis a similar equation may be derived:

$$(k_c)_B = G'K^{1-x}{}_B \tag{36}$$

where $K_B = 1/K_A$ and x have the same values for the basic catalyst as for its conjugate acid and are independent of the nature of the substrate.

Tests of the Brönsted Theory

Equation 35 may be written in the form

$$\log (k_c)_A = x \log K_A + G_3 \tag{37}$$

If one keeps in mind the remarks which have already been made concerning G and x, it is apparent that if a given reaction at a given temperature is catalyzed by a series of chemically similar acids in a given solvent and if log $(k_c)_A$ is plotted against log K_A, all the experimental points should fall on a smooth curve, since x is a continuous function of K. If this smooth curve happened to be a straight line (which it usually is) then the slope x should be the same if the same series of acids were allowed to act on a different substrate or if the conjugate bases of this same series were used to catalyze a reaction subject to general basic catalysis. These predictions are amenable to experimental verification, and many such experiments are recorded in the literature.

One of the earliest tests of the theory was made on the decomposition of nitramide in aqueous solution.[48]

$$H_2N \cdot NO_2 \rightarrow H_2O + N_2O \qquad (38)$$

The reaction was already known to be catalyzed by hydroxyl ions. It was now shown to be catalyzed by negatively charged bases such as acetate ion, by neutral bases such as aniline and other amines, and by positively charged bases such as $Co(NH_3)_5OH^{++}$. Furthermore, plots of $(k_c)_B$ against log K_B gave three straight lines: one for the anions of mono- or dibasic carboxylic acids (in the latter case a statistical correction had to be made to eliminate the unfair advantage the dibasic acids had over the monobasic acids), another for nuclear substituted anilines, and a third for other amines. Thus the Brönsted theory was proved satisfactory from two points of view: (1) it was shown that Brönsted's generalized bases all had catalytic effects similar to hydroxyl ions, and (2) that the magnitudes of the catalytic effects bore the correct relations to the values of K_B.

Similar results were obtained by Lowry and Smith,[49] who studied the mutarotation of glucose. This reaction shows general acid and base catalysis. They showed that it was catalyzed by the acids HCl, H_3O^+, HOAc, and NH_4^+ and by the bases OH^- and OAc^- as well as by water itself. The same reaction was studied by Brönsted and Guggenheim,[50] who concluded that they could predict the catalytic effect, correct to one power of ten, of any acid or base whose value of K_A or K_B is known.

Similar results have been obtained in many other investigations. A few of them are listed in Table VII.

Another feature of the Brönsted equations which must be subjected to test is the prediction that the values of x are independent of the substrate and that the catalyzing acid will have the same value of x as its conjugate base. These predictions are not borne out by experiment. Accordingly we must conclude that there is an effect of the substrate for which the Brönsted theory does not account.[51]

Inasmuch as G, G', and x vary with both substrate and solvent, it is apparent that the Brönsted equations cannot be used to make predic-

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[48] (*a*) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); (*b*) Brönsted and Duus, *ibid.*, **117**, 299 (1925); (*c*) Brönsted and Volqvartz, *ibid.*, **155A**, 211 (1931).

[49] Lowry and G. F. Smith, *J. Chem. Soc.*, 2539 (1927).

[50] Brönsted and Guggenheim, *J. Am. Chem. Soc.*, **49**, 2554 (1927).

[51] M. Kilpatrick and M. L. Kilpatrick, *Chem. Rev.*, **10**, 213 (1932).

TABLE VII

ACID AND/OR BASE CATALYZED REACTIONS

Reaction	Solvent	Temp. (° C)	Type of catalyst	Lit.
Nitramide decomposition	H_2O	15	$RCOO^-$ $X \cdot C_6H_4 \cdot NH_2$	48*a* 48*b*
Nitramide decomposition	Cresol	20	$RCOO^-$ $X \cdot C_6H_4 \cdot NH_2$	52
Glucose mutarotation	H_2O	18	$RCOO^-$, RCOOH	50
Acetone + iodine	H_2O	25	RCOOH, $RCOO^-$	53
N-Bromoacetanilide, Rearr.	PhCl	25, 100	RCOOH	54*f*, 55
Depolymerization of dimeric glycol aldehyde	H_2O	25	acids, bases	56

tions of k_c when only K_A or K_B are known for the catalyzing acid or base in a given solvent. But when values of k_c have been determined for a given reaction in a given solvent under the catalytic influences of two different catalyzing acids (or bases) whose values of K_A (or K_B) are known in that particular solvent, then the Brönsted equations enable us to predict k_c for the same reaction in the same solvent when other acids or bases of the same chemical type are used, provided that their values of K_A or K_B are known.

If, however, a given problem calls only for qualitative or very roughly quantitative predictions, there are a number of comparisons that can be made. Thus there is much work which indicates that if a group of chemically similar catalyzing acids or bases are arranged in a sequence according to the values of their dissociation constants in water, then the values of their catalytic constants for different reactions in different solvents will occur in the same order. This fact has been demonstrated by Bell and his coworkers[54] for the following acid-catalyzed reactions in a variety of nondissociating solvents: the rearrangements of *N*-bromo and

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[52] Brönsted, Nicholson, and Delbanco, *Z. physik. Chem.*, **A169**, 379 (1934).

[53] (*a*) Dawson, *Trans. Faraday Soc.*, **24**, 640 (1928); (*b*) Dawson, Hall, and Key, *J. Chem. Soc.*, 2844 (1928); (*c*) Dawson and Lowson, *ibid.*, 1217 (1929); (*d*) Dawson, Hoskins, and Smith, *ibid.*, 1884 (1929); (*e*) Dawson and Smith, *ibid.*, 2530 (1929); 79 (1930); (*f*) Dawson and Spivey, *ibid.*, 2180 (1930).

[54] (*a*) R. P. Bell, *Proc. Roy. Soc.* (London), **A143**, 377 (1934); (*b*) Bell and Levinge, *ibid.*, **A151**, 211 (1935); (*c*) Bell and J. F. Brown, *J. Chem. Soc.*, 1520 (1936); (*d*) Bell, Lidwell, and Vaughan-Jackson, *ibid.*, 1792 (1936); (*e*) Bell and Caldin, *ibid.*, 382 (1938); (*f*) Bell and Lidwell, *ibid.*, 1096 (1939).

[55] Bell and Danckwerts, *J. Chem. Soc.*, 1774 (1939).

[56] Bell and Hirst, *ibid.*, 1777 (1939).

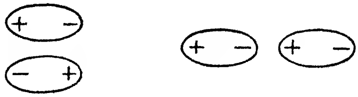
N-chloroacetanilide into the corresponding *p*-halogeno compounds, the rearrangement of *N*-iodoformanilide, the depolymerization of paraldehyde, the inversion of menthone, and the rearrangement of *N*-bromobenzanilide. Rather surprisingly it was found that trichlorophenol fell into line with the carboxylic acids, although picric acid did not.

In making such comparisons, one should naturally be on guard against the leveling effect. Similar considerations apply if we wish to compare the catalyzing power of one acid in different solvents. Thus Hantzsch showed that oxygen-containing solvents cut down the catalyzing power of acids by coordinating with their protons;[57] Weissberger et al.[58] showed that the reactivity of hexane solutions of trichloroacetic acid with indicators and with diazoacetic ester is lowered by adding ethers or carbonyl compounds; and Bell et al.[54d] showed that anisole and amyl acetate markedly cut down the catalytic effect of trichloroacetic acid in the depolymerization of paraldehyde.

THE EFFECT OF THE SOLVENT ON DIPOLE MOMENTS

The problem of calculating quantitatively the change in dipole moment attending the transfer of molecules from the gaseous state to solution is one which has been attacked vigorously by several investigators. It is, however, an exceedingly complex problem, and the best that can be said of the efforts to solve it is that they give results of the correct order of magnitude. But even this is heartening as it gives some substantiation to the physical models which have been constructed to explain the observed effects.

Interaction between dipoles would be expected to result in two different types of orientation, represented as follows:



Such interactions could result in either association or solvation. The latter has been the problem of chief interest to theorists, and they have attacked it by working in solutions so dilute that the association factor is ruled out. The total polarization at infinite dilution is symbolized as P_∞ or ${}_\infty P_2$.

When a molecule is transferred from the gaseous state to solution both ${}_\infty P_2$ and the corresponding moment, μ, usually decrease, even when

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[57] See Appendix IV.

[58] (*a*) Weissberger and Hogen, *Z. physik. Chem.*, **156**, 321 (1931); (*b*) Weissberger and Fasold, *ibid.*, **157**, 65 (1931).

the solvent is a hydrocarbon ("negative solvent effect"). Sometimes, however, a small increase is observed ("positive solvent effect"). Occasionally there is no appreciable change.[59]

Figure 3 [60] shows the variation of ${}_{\infty}P_2$ with the dielectric constant of the solvent for a number of solutes differing among themselves in dielectric constant. It will be observed that substances such as CS_2 and CCl_4, which have no total moment, show no variation. This is even true of p-$C_6H_4Cl_2$ which has zero total moment but large partial moments. From these facts it is concluded that only the total moment is responsible for solvation. It should also be observed that the slopes of the curves become greater as ${}_{\infty}P_2$ increases.

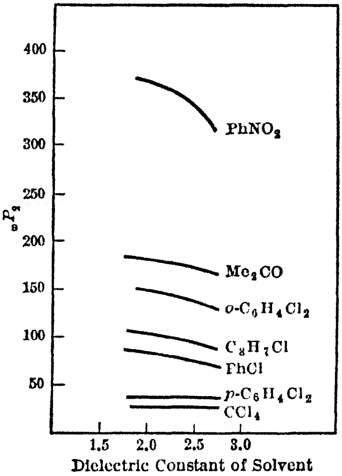

FIG. 3.[60] Effect of dielectric constant of solvent on polarization of solutes.

The theoretical interpretation of these solvent effects is a matter of great interest and complexity. No attempt will be made to review it here[61] beyond a consideration of the physical model described by Frank,[61g] since this model seems to be essentially correct and is adequate for our purposes.

When a polar molecule is placed in a polarizable medium it produces polarization in the medium. The magnitude of this induced polarization (μ') is given by the familiar equation

$$\mu' = \alpha F \tag{39}$$

The value of F will obviously be proportional to the dipole moment of the solute molecule and α is the polarizability of the medium. Figure 4 gives a picture of the polarization produced in the surrounding solvent molecules (indicated by their arrows) by a spherical solute molecule

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[59] See, e.g., Cowley and Partington, *J. Chem. Soc.*, 1598 (1938).

[60] F. H. Müller, *Physik. Z.*, **34**, 689 (1933); *Trans. Faraday Soc.*, **30**, 729 (1934).

[61] The following papers are of interest in relation to the theory: (*a*) Raman and Krishnan, *Proc. Roy. Soc.*, **117A**, 589 (1928); (*b*) Mizushima and Higashi, *Proc. Imp. Acad.* (*Tokyo*), **8**, 482 (1932); (*c*) Weigle, *Helv. Chim. Acta*, **6**, 681 (1933); (*d*) Higashi, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **13**, 1167 (1934); (*e*) Rau, *Proc. Indian Acad. Sci.*, **1A**, 498 (1935); (*f*) Debye, *Physik. Z.*, **36**, 100 (1935); (*g*) F. C. Frank, *Proc. Roy. Soc.*, **A152**, 171 (1935); (*h*) Higashi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **28**, 284 (1936); (*i*) Schwarzenbach and Egli, *Helv. Chim. Acta*, **17**, 1183 (1934).

having a dipole acting in the direction shown by the heavy arrow. There are four induced moments opposed to the primary moment and two augmenting it, but each augmenting moment is twice as large as each opposing moment so that the net effect is zero. Thus the polarization of the solvent has no effect on the moment of the solute molecule when the latter is spherical. Usually it is not spherical, in which case we may picture it by imagining the solvent molecule on the right of Figure 4 replaced by a hydrocarbon radical covalently linked to the spherical primary dipole. Since, as a first approximation, we have neglected the secondary effects of a second layer of solvent molecules, we may now consider that when this elongated molecule is placed in the solvent medium there is no longer any moment of consequence induced to the right of the solute molecule. Thus the induced moments opposed to the primary dipole preponderate. This means a negative solvent effect. Furthermore it is apparent from Equation 39 that this negative solvent effect becomes greater as α becomes greater, i.e., as the dielectric constant of the solvent increases. (If the solvent molecules also contain permanent dipoles, their orientation polarization will contribute to the effect. The dielectric constant, of course, is a function of both effects.) This explains the results shown in Figure 3.

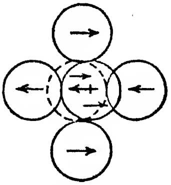

FIG. 4.[61g] Dipole moments induced in surrounding solvent molecules by primary dipole (←+).

Returning to Figure 4, it is apparent that if the radical linked to the primary dipole made an angle of 90° with the axis of the primary dipole, it would be replacing a solvent molecule having an induced moment in opposition to that of the primary dipole. Thus in this case the solvent effect would be positive.[61c] As the angle changed from 90° to 0° the solvent effect would decrease to zero and then would attain progressively larger negative effects until it reached a maximum at angle 0°. The nearest approximation to the case in which bound radicals are fixed at right angles to the dipole axis is found in triethyl amine, which shows a positive solvent effect as the theory would demand. Hobbs [62] warns us, however, that compound formation or high energy associations should be definitely excluded before the positive effects are taken too seriously.

Negative solvent effects are shown by organic monohalides, [60, 63] nitriles,[64] nitro compounds,[60] and ketones.[60] Small positive solvent

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[62] Hobbs, *J. Chem. Phys.*, 7. 849 (1939).

[63] Cowley and Partington, *J. Chem. Soc.*, 130 (1937).

[64] *Idem*, 1184 (1936).

effects are shown by some amines, alcohols, ethers, and chloroform.[65] It is important to remember that these results, for the most part, were obtained for aliphatic compounds. The aromatic amines show almost no solvent effect in aprotic solvents. In aniline at 20°, ${}_{\infty}P_2$ for the vapor is 78.4 cc, in hexane 77.0 cc, and in toluene 79.5 cc.[65] Diphenyl ether and ditolyl ether show no solvent effects while their bromo derivatives show a negative effect,[66] as do chlorobenzene and nitrobenzene.[60] Apparently, then, we may conclude that positive solvent effects rarely if ever occur in benzene derivatives.

It is also a matter of incidental interest to note that it has been shown that polar solvents induce moments in nonpolar solute molecules such as benzene, diphenyl and *p*-dichlorobenzene.[67]

THERMODYNAMIC ASPECTS OF THE SOLUTION PROCESS

General Remarks

The role of the solvent in altering the physical properties of solute molecules may be said to be due to one solvent property, solvation. Except for thermodynamic purposes, however, the term "solvation" is too broad for practical use. It ranges from one extreme, in which the exercise of donor and acceptor properties results in definite and stable compound formation, through the intermediate manifestations of solvation, such as unstable coordination compounds and dipole association (the latter including the dielectric constant effect), and finally to the opposite extreme where only the weak and indefinite van der Waals forces are operative.

The analysis of the problem into these various factors, although highly useful, is difficult, and consequently when the thermodynamic method of treating solvation as a single influence is applicable it is the most practical one to use. It suffers, of course, from the well-known defect that when the necessary thermal data are lacking it gives us no way of supplying the deficiency by calculation. This deficiency is being vigorously attacked, however, and auxiliary methods are being developed. A second defect of thermodynamics is that, although it gives us a means of calculating the equilibrium concentrations for a reaction, it fails to predict how much time will be consumed in reaching equilibrium. Thus from the practical point of view, although a negative free energy change is a necessary condition for reaction, it is not a sufficient condition. On the other hand a positive value of ΔF is not a necessary but is a suf-

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[65] Ref. 59 and references there given.

[66] Coop and Sutton, *J. Chem. Soc.*, 1869 (1938).

[67] C. G. LeFevre and R. J. W. LeFevre, *ibid.*, 487 (1936).

ficient condition for the failure of a reaction. These criteria for spontaneity may, of course, be applied either to an over-all reaction or to any of its steps. The latter application is of kinetic importance when a reversible step precedes the rate-controlling step. The former application is of thermodynamic importance only; we will proceed to see how it can be applied in problems involving solvation.

The Addition of Hydrogen Bromide to Ethylene

Every organic chemist knows that the addition of hydrogen halides to olefins does not occur at all in dilute aqueous solutions, and in concentrated aqueous solutions the reaction takes place with less ease than in aprotic solvents. The thermodynamic reasons for this procedure become obvious from a study of the following equations:

$$HBr(g) + C_2H_4(g) \rightarrow C_2H_5Br(g); \quad \Delta F^\circ_{298} = -\ 5.660 \text{ kcal} \quad (40a)^{68}$$

$$HBr(Aq) \rightarrow HBr(g); \quad \Delta F^\circ_{298} = +12.055 \quad (40b)^{68}$$

$$C_2H_4(Aq) \rightarrow C_2H_4(g); \quad \Delta F^\circ_{298} = -\ 3.931 \quad (40c)^{69}$$

$$C_2H_5Br(g) \rightarrow C_2H_5Br(Aq); \quad \Delta F^\circ_{298} = -\ 0.278 \quad (40d)^{70}$$

Addition of the above equations gives

$$HBr(Aq) + C_2H_4(Aq) \rightarrow C_2H_5Br(Aq); \quad \Delta F^\circ_{298} = +\ 2.186 \text{ kcal} \quad (40e)$$

Comparison of Equations 40*a* and 40*e* shows that, although the reaction is thermodynamically possible in the gaseous state, it is not in dilute aqueous solution. The situation results from the combination of two factors: (1) that the free energies of solution of the organic compounds are small, and (2) that of the hydrogen bromide is large. This is equivalent to saying that before the proton of HBr can be added to ethylene in aqueous solution it must first be removed from the H_3O^+ ion. (The hydration of the Br^- ion is relatively unimportant.) This decreases the ease of reaction. Furthermore the final equilibrium is not much aided by the slight liberation of energy attending the condensation and solution of the volatile and rather insoluble ethyl bromide.

If the same reaction were carried out in an aprotic solvent, it is apparent that the proton of HBr could no longer exercise its acceptor prop-

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[68] Parks and Huffman, *Free Energies of Some Organic Compounds*, Chemical Catalog Co., 1932.

[69] Calculated from data given by J. A. V. Butler, *Trans. Faraday Soc.*, **33**, 229 (1937).

[70] Calculated roughly from vapor pressure data in I.C.T. and solubility data of VanArkel and Vles, *Rec. trav. chim.*, **55**, 407 (1936).

erties, the free energy change corresponding to Equation 40*b* would sink into insignificance, and the over-all free energy change would be but little different from that of the gaseous reaction.

These rather obvious relationships can, for the sake of convenience, be generalized in terms of another qualitative "basic principle":

P 28. A solvent will increase the thermodynamic probability of a reaction if the products are more firmly solvated than the reactants; if the reverse situation obtains, the solvent will decrease the thermodynamic probability of reaction.

It is understood, of course, that the term "solvated" encompasses all the phenomena between the two extremes of weak van der Waals's forces and covalence formation, and that the firmness of solvation is measured by the free energy decrease attending the process of solution.

The Accurate Calculation of the Free Energy of Solution

The free energy change attending the transfer of one mole of a solute from its pure state to a large amount of solution of a definite concentration is accurately given by the equation

$$F_2 - F^\circ_2 = \Delta F = RT \ln \frac{f_2}{f^\circ_2} \tag{41}$$

where f_2 is the fugacity of the solute from the given solution and f°_2 is its fugacity in the pure state. For most purposes sufficient accuracy is achieved if vapor pressures are used in place of fugacities; hence Equation 41 becomes

$$\Delta F = RT \ln \frac{p_2}{p^\circ_2} \tag{42}$$

If the pure solute is taken as the standard state, Equation 41 may be written

$$\Delta F = RT \ln a_2 \tag{43}$$

in which a_2 is the activity of the solute in the given solution.

It is apparent that if the solute is a liquid its free energy of solution may readily be calculated from its partial pressure above the solution, p_2, and its vapor pressure in the pure state, p°_2. If the pure solute is a gas at a pressure of 1 atmosphere, p°_2 becomes unity; if it is a solid it is no longer practicable to determine its partial pressure above the solution, and hence it is necessary to replace Equation 42 by the following:

$$\Delta F = RT \ln \left[\frac{a_2}{(a_2)_s} \right] \tag{44}$$

where $(a_2)_s$ is the activity of the solute in a saturated solution. Both activities may be determined by standard methods.[71] If the solute is a strong electrolyte its activity is defined as [72]

$$a_2 = a_+ a_- \tag{45}$$

or

$$a_2 = a^2_\pm \tag{46}$$

where a_+ and a_- are respectively the activities of the positive and negative ions and $a_\pm$ is the mean ion activity. Equation 44 has the advantage that it is independent of the convention used to fix the standard state; but in using it one must be on guard lest the composition of the solid in equilibrium with the saturated solution has been altered by solvation.

Auxiliary Methods of Estimating the Free Energy of Solution

(*a*) *The Sign of the Entropy Change.* There is a regrettable tendency on the part of many chemists to use $-\Delta H$ as a criterion of spontaneity when values of $-\Delta F$ are not available. The danger of this procedure is evident if we consider the equation

$$\Delta F = \Delta H - T\Delta S \tag{47}$$

from which it is apparent that ΔF and ΔH will not be of the same sign unless either: (1) ΔS is of the opposite sign to ΔH, or (2) $T\Delta S$ is smaller than ΔH. In general, neither one of these requirements may be safely assumed to be met, as will be evident from the following discussion.

The relationship between entropy and molecular "freedom" was briefly discussed in Chapter VII. From that discussion it is evident that if a system is subject to large constraining forces, as in a crystal, its entropy is low, whereas in the gaseous condition it is high. Thus the entropy of sublimation or vaporization is positive. Analogously, ΔS would be expected to be negative for the solution of a gas in a liquid (cf. Table VIII) and positive if the solute were a solid. Both situations should commonly be encountered if one liquid is dissolved in another. Or again, if one molecule decomposes into two, the freedom and hence the entropy is increased.

It is frequently possible from considerations such as those in the last paragraph to predict the sign of an entropy change. If this turns out to be opposite to the sign of ΔH, then one may safely conclude that ΔH and ΔF will be of the same sign and hence ΔH may safely be used as a

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[71] See Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., 1923, Chapters 22 and 23.

[72] See Appendix IV.

TABLE VIII[73]

Free Energies, Entropies, and Heats of Solution of Gases at 25°

Solute (g, 1 atm.) → Solute (soln., $a = 1$)

Standard state convention: $a/N = 1$ when $N = 0$

Solute	Solvent	ΔF kcal/mole	ΔH kcal/mole	$T\Delta S$ kcal/mole	ΔS cal/deg/mole
C_2H_4	H_2O				−44.5
CH_4	H_2O				−45.0
C_2H_6	H_2O	10.05	−4.43	−14.48	−48.6
CH_3Cl	H_2O	7.65	−6.30	−13.95	−46.8
$CHCl_3$	H_2O	7.14	−9.84	−16.98	−57
Me_2CO	H_2O	4.29	−10.09	−14.38	−48
EtOAc	H_2O	5.11	−11.71	−16.82	−56
$EtNH_2$	H_2O	3.58	−12.91	−16.49	−55
MeOH	H_2O	3.09	−11.24	−14.33	−48
EtOH	H_2O	3.19	−12.88	−16.07	−54
n-PrOH	H_2O	3.38	−14.42	−17.80	−60
n-BuOH	H_2O	3.49			−65
n-AmOH	H_2O	3.73			−71
iso-PrOH	H_2O	3.45	−13.45	−16.90	−56
iso-BuOH	H_2O	3.68	−15.24	−18.92	−63
sec.-BuOH	H_2O	3.59			−63
tert.-BuOH	H_2O	3.69	−14.44	−18.13	−61
HOAc	H_2O	1.50			
EtCN	H_2O	4.36			
CS_2	Me_2CO	4.239	−5.84	−10.08	−33.8
C_6H_6	Me_2CO	2.843	−7.74	−10.58	−35.5
$CHCl_3$	Me_2CO	2.551	−8.69	−11.24	−37.7
PhCl	Me_2CO	1.695	−9.66	−11.36	−38.1
SO_2	EtOH	4.543	−6.61	−11.15	−37.4
NH_3	EtOH	4.459	−6.81	−11.27	−37.8
CS_2	EtOH	4.410	−6.71	−11.12	−37.3
CCl_4	EtOH	3.689	−7.94	−11.63	−39.0
C_6H_6	EtOH	3.579	−8.31	−11.89	−39.9
$CHCl_3$	EtOH	3.337	−8.91	−12.25	−41.1
PhCl	EtOH	2.446	−9.98	−12.43	−41.7

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[73] (*a*) J. A. V. Butler, Ramchandani, and D. W. Thomson, *J. Chem. Soc.*, 280 (1935); (*b*) Butler and Reid, *ibid.*, 1171 (1936); see also Ref. 69; (*c*) Barclay and Butler, *Trans. Faraday Soc.*, **34**, 1445 (1938).

TABLE IX

HEATS OF SOLUTION

Solute	State	Solvent	Conc. of solute	Temp. (° C)	ΔH kcal/mole	Lit.
Br_2	g	H_2O	dil.	18	− 8.85	75
Br_2	g	CCl_4	any diln.	18	− 7.15	75
Br_2	g	CS_2	dil.	18	− 6.25	75
Br_2	g	$CHCl_3$	dil.	18	− 7.05	75
Br_2	g	Br (1)			− 7.65	75
Br_2	g	n-C_6H_{14}	0.00615 M	20	(− 8.76)	75, 78
Br_2	g	EtOH	0.00615	20	−20.65	75, 78
Br_2	g	HOAc	0.00615	20	−18.50	75, 78
Cl_2	g	H_2O	satd.	18	− 5.3	75
Cl_2	g	CCl_4	dil.	18	− 4.5	75
I_2	g	CCl_4	dil.	25	− 8.88	76
ICl	g	CCl_4	dil.	25	− 6.99	76
HBr	g	H_2O	0	18	−19.89	75
HCl	g	H_2O	0	18	−17.62	75
HCl	g	EtOH	dil.	18	−10.6	75
HCl	g	CCl_4	dil.	18	− 3.68	75
MeOH	g	H_2O	dil.	25	−11.24	69
MeOH	g	C_6H_6	dil.	25	+ 5.6	74
EtOH	g	H_2O	dil.	18	−12.86	75
EtOH	g	$PhNH_2$	dil.	18	−10.55	ICT
EtOH	g	HOAc	dil.	18	− 9.52	ICT
EtOH	g	C_7H_{16}	dil.	18	− 9.22	ICT
EtOH	g	Me_2CO	dil.	18	− 8.78	ICT
EtOH	g	C_6H_6	dil.	18	− 6.01	ICT
C_2H_2	g	H_2O	dil.	18	− 4.0	75
HCN	g	H_2O	0.01 N	18	− 6.8	75
HOAc	l	H_2O	dil.	18	− 0.3	75
$(CO_2H)_2$	s	H_2O	dil.	18	+ 2.26	75
$(CO_2H)_2$	s	MeOH	dil.	18	+ 0.87	75
$(CO_2H)_2$	s	EtOH	dil.	18	+ 1.27	75
$PhCO_2H$	s	CCl_4	dil.	room	+ 7.140	77
PhOH	s	C_6H_6	dil.	room	+ 4.41	ICT
PhOH	s	$CHCl_3$	dil.	room	+ 4.00	ICT
PhOH	s	HOAc	dil.	room	+ 2.39	ICT
PhOH	s	EtOH	dil.	room	+ 0.60	ICT
PhOH	s	Et_2O	dil.	room	+ 0.08	ICT
PhOH	s	pyridine	dil.	room	− 1.70	ICT

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[74] Butler and Harrower, *ibid.*, **33,** 171 (1937).

[75] Bichowsky and Rossini, *Thermochemistry of the Chemical Substances*, Reinhold Publishing Corp., 1936.

[76] Blair and Yost, *J. Am. Chem. Soc.*, **55,** 4489 (1933).

[77] Evans and Polanyi, *Trans. Faraday Soc.*, **32,** 1333 (1936).

[78] Lauer and Oda, *Ber.*, **69B,** 141 (1936).

TABLE X

FREE ENERGIES OF SOLUTION OF GASES AT 1 ATM. AND 25° C IN DILUTE SOLUTIONS

Solute	Solvent	$\Delta F°$ kcal/mole	Lit.
HBr	H_2O	−12.03	ICT
HCl	H_2O	− 8.67	ICT
Cl_2	H_2O	+ 1.65	ICT
Cl_2	CCl_4	+ 1.03	ICT
Br_2	H_2O	− 0.22	ICT
Br_2	CCl_4	− 0.37	76
I_2	CCl_4	− 1.97	76
ICl	CCl_4	− 0.76	76
HCN	H_2O	− 1.40	ICT
MeOH	H_2O	− 0.84 *	73
MeOH	C_6H_6	+ 0.73 *	73
MeOH	CCl_4	+ 0.84 *	73
n-PrCl	cyclohexane	− 0.24 *	73
n-PrCl	CCl_4	− 0.40 *	73
n-PrCl	C_6H_6	− 0.54 *	73

* Butler's values, given for $p = 1$ mm, corrected to give $p = 1$ atm.

criterion for spontaneous change. But only too often the reverse is found to be true.

A study of Table VIII shows that the values of ΔH and ΔF for the solution of methanol and other attenuated gases are likely to be opposite in sign and that the $T\Delta S$ term is by no means negligible. Such is the situation, e.g., in methanol. If, however, we turn to Tables IX and X we find that ΔH and ΔF have the same sign in methanol vapor at one atmosphere. This results from the fact that for a gas $(\delta F/\delta P)_T$ is large while $(\delta H/\delta P)_T$ is comparatively small. We may conclude that extreme caution should be used in judging the sign of ΔF from that of ΔH.

(*b*) *Ideal Solutions.* In addition to the sign of ΔS much importance attaches to its magnitude. In ideal solutions, this may readily be calculated. An ideal solution is one in which the fugacity of each constituent is proportional to the mole fraction of that constituent.[79] This modernization of Raoult's law may be expressed as

$$f = f°N \qquad (48)$$

where $f°$ is the fugacity of the substance in question when existing in its pure state. An ideal solution of two liquids is further characterized by

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[79] Ref. 71, p. 222.

the fact that ΔH and ΔV for the mixing process are both zero, while for an ideal solution of a gas in a liquid $-\Delta H$ is the same as the heat of condensation of the gas and for a solid solute it is equal to the heat of fusion.

The combination of Equations 48 and 41 gives for a perfect solution

$$\bar{F}_2 - F^\circ_2 = RT \ln N_2 \tag{49}$$

for the free energy of solution.

Since $\Delta H = 0$ when a perfect solution is composed of two liquid components, we may for this case combine Equations 47 and 49 to give

$$\bar{S}_2 - S^\circ_2 = -R \ln N_2 \tag{50}$$

If the solute is a gas or a solid, the heat of condensation or fusion, respectively, may be used in conjunction with Equations 47 and 49 to yield a value for ΔS. Such calculations, however, are of very limited value since nearly ideal solutions occur only when solute and solvent are closely similar. Most examples of perfect solutions involve nonpolar substances.

(*c*) *Regular Solutions.* The remarks made previously about the relation between entropy and volume are in keeping with Equation 50, which shows that the entropy increases as the volume occupied by a mole of solute increases, i.e., as the mole fraction decreases. But this relationship between the entropy and the concentration is only valid when a completely random distribution of molecules obtains. If the molecules associate, their freedom of motion is no longer measured alone by the volume they occupy but becomes a function also of the restraint caused by the association. Nevertheless the thermal motion of the molecules will, if it is sufficiently intense and if the restraining forces are not too great, insure complete mixing of solute and solvent and even though the solution no longer obeys Raoult's law and ΔH is no longer the same as in an ideal solution, its behavior will be in accordance with Equation 50.* Such solutions are called regular solutions.[80] They may be expected in cases "where both components are comparatively nonpolar and the chemical effects of solvation, association and compound formation are absent."[80b]

(*d*) *The Magnitude of the Entropy Change.* In further relation to the general problem of estimating the magnitude of ΔF or ΔS by extrathermodynamic methods, it should be pointed out that many attempts

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* Strictly speaking, Equation 50 must be corrected for the slight volume change attending the formation of most regular solutions.

[80] (*a*) J. H. Hildebrand, *J. Am. Chem. Soc.*, **51**, 66 (1929); *Proc. Nat. Acad. Sci.*, **13**, 267 (1927); *J. Am. Chem. Soc.*, **57**, 866 (1938); (*b*) Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

have been made to devise a procedure whereby ΔH, ΔF, and ΔS could all be evaluated for a reaction when any one of them had been determined experimentally. We have just learned how this can be done for processes of solution when regular solutions are involved. As a preliminary to further study of this subject let us subdivide the general problem into two smaller ones,[81] viz., to establish the desired relation (*a*) for a given solute in a series of different solvents, and (*b*) for a series of different solutes in the same solvent.

Evans and Polanyi [77] enjoyed some success in establishing a relationship of type *a*. They developed the equation

$$\frac{\Delta S}{R} = \frac{\alpha \Delta H}{RT} + \beta \tag{51}$$

in which ΔS and ΔH refer to the solution of the same solute in any given solvent and α and β are constants independent of the solvent but dependent on the solute. This equation may be rewritten as

$$\frac{\Delta S}{R} = \rho \Delta H + \sigma \tag{52}$$

where ρ and σ are constants. In this form it is readily seen to constitute a linear relationship between ΔH and ΔS at a given temperature. It was tested out on the solutes listed in Table X and a large variety of solvents and, with the exception of anthracene and carbazole, it was shown to be valid to about the extent illustrated for one case in Table XII. Since the solutes involve such different chemical types as hydrocarbons, phenols, and fairly strong carboxylic acids and the solvents cover a range from hydrocarbons to organic acids and bases, it would seem that the general validity of Equation 52 was pretty well established. No data for water are to be found on the list but it is significant that even for the solution *o*-nitrophenol in *p*-toluidine and in the naphthylamines the equation was found valid.

Turning now to the question of relationships of type *b*, i.e., for a series of different solutes in the same solvent, Evans and Polanyi found that Equation 52 does not apply very well unless the solutes are of the same chemical type. Bell [81] corroborated their statement in so far as solid and liquid solutes are concerned but concluded that for gaseous solutes Equation 52 applies to type *b* relationships but not to type *a*. Butler and Reid [73b] studied the hydration of different alcohol vapors (see Table VIII) and found that ΔH increases in the same order in which ΔF and ΔS decrease. Here too there is a linear relation between ΔH and ΔS

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[81] R. P. Bell, *Trans. Faraday Soc.*, **33**, 496 (1937).

but it does not coincide with that of the nonpolar solvents.[69] In a later paper Barclay and Butler criticized the accuracy of Evans and Polanyi's data and showed that for the solution of various gases in acetone and ethanol (Table VIII) a linear relationship exists between ΔH and ΔS in each solvent and that ΔF and ΔH change in the same direction. They also made a plot of ΔS against ΔH for various gases in a number of non-associated solvents and found that all the data fell pretty well on a single straight line. They remark, "It cannot be claimed that if complete accuracy were obtained all these points would lie on a single straight line. It is possible that there is in fact a sheaf of straight lines approxi-

TABLE XI [77]

THE CONSTANTS OF EQUATION 53 FOR DIFFERENT SOLUTES

SOLUTE	$\rho \times 10^4$	σ
Benzoic acid	5.43	0.057
Naphthalene	6.16	0.016
Phenanthrene	5.84	0.016
o-Dinitrobenzene	5.34	0.102
Benzene	7.84	0.000
Acenaphthene	5.87	0.040
Carbazole	4.57	−0.221 or −1.000
Nitrobenzene	7.79	0.022
o-Nitrophenol	6.96	−0.042
p-Dinitrobenzene	4.13	0.472
m-Dinitrobenzene	5.94	0.030
α-Chloroacetic acid	6.55	−0.017
Benzoyl chloride	8.06	−0.023
Ethylene dibromide	6.05	0.466
Phenol	6.92	0.008
Fluorene	5.63	0.006

TABLE XII

THE HEATS AND ENTROPIES OF SOLUTION OF NAPHTHALENE IN DIFFERENT SOLVENTS

Solvent	ΔH, cals/mole	$\Delta S/R$ (found)	$\Delta S/R$ (calc.)
Acetone	5660	3.513	3.505
Ethyl ether	5370	3.326	3.326
Ethyl acetate	5310	3.282	3.295
Carbon tetrachloride	5100	3.159	3.159
Ethylene bromide	4420	2.739	2.739
Pyridine	4380	2.717	2.717
Ethylene chloride	4360	2.702	2.703
Chloroform	4200	2.598	2.605

mating to the general relation, but as an approximation it cannot be doubted that up to heats of solution of ca. 12 kcals such a general relation exists." This generalization is of particular interest to organic chemists who do not demand high precision in such data, for it means that if they know either ΔH or ΔS for the solution of a gas in a given nonassociated solvent, they can readily get approximate values for ΔF. The generalization applies equally well to the solution of a gas in its own liquid, i.e., to the process of condensation or vaporization, and in this relation the generalization may be considered as an improvement on Trouton's rule.

Considering their own data together with the data of other workers, Butler and Reid at first concluded that, on the whole, entropies of hydration are strikingly independent of the chemical nature of the solute and seem to depend chiefly on the size of the solute molecule, increasing as it increases. Thus the entropy of hydration ($-\Delta S$) of the inert gases increases from helium to radon and in a homologous series it increases about five units for each additional CH_2 group. This property of the entropy has an important effect on the relative solubilities of homologous compounds. From Equation 47 it follows that a constant value of ΔS would mean that the heat of solution would determine the solubility since the latter depends on $-\Delta F$. Since $-\Delta H$ increases with the molecular weight (Table VIII) so would the solubility. The observed decreases in solubility are thus due to this property of the entropy. They suggest that this entropy effect will probably be found to be characteristic of associated solvents.

Butler [69] later modified his views on the entropy of solution when he found that "the presence in the solute molecule of hydroxyl and similar groups which form 'hydrogen bonds' with water evidently introduces a new factor, which increases the partial entropy in solution as compared with nonpolar compounds having the same heat of solution." He also conceded that, since the entropy is a measure of the number of possible configurations of a system having a given energy, "when the solute molecule is brought into the field of force of the solvent there may be some restriction of its possible configurations, which will lower the entropy, and this effect might well be proportional to the energy of interaction of the solute with the solvent. Conversely the solvent molecules around the solute will be affected in the same way, and any change in entropy which arises therefrom will appear in the partial entropy of the solute."

In relation to our general search for extra-thermodynamic methods of estimating the values of ΔF, ΔH, or ΔS of solution it should be mentioned that Butler [69] has shown for a few cases that the heat of hydration of a molecule is an additive function of the contributions made by its constituent groups. Each different group, such as C—H, C—OH, C—NH_2, C—O—C, etc., makes a different but constant contribution to the total heat effect accompanying the hydration of the gaseous solute molecule.

Finally it should be mentioned that attempts have been made to calculate the internal energy or entropy changes attending solution by considering that the solute is brought into solution by two steps: first a cavity large enough to hold the solute is made in the solvent; then the solute is put into the cavity.[82] Thus one may write

$$\Delta S = \Delta S_C + \Delta S_A \tag{53}$$

where the subscripts C and A refer respectively to the two steps above. A similar equation could be written for the changes in internal energy (ΔE). Methods for evaluating ΔS_C, ΔS_A, ΔE_C, and ΔE_A do not agree very well and we must therefore consider this problem an unsolved one. But these attempts do, at least, serve to focus our attention on the fact that energy and entropy changes attending the process of solution depend not only on the forces between solute and solvent but also on the self-association tendencies of the solvents and on the size of the solute molecules, which are naturally factors in cavity formation. Eley [82d] showed, for a series of solutes having no pronounced donor or acceptor properties, that ΔE_A of any solute is about the same in water as in carbon tetrachloride solution but that ΔE_C is smaller for water. This is obviously related to the fact, also demonstrated by Eley, that the partial molal volume of a solute is smaller in water than in organic solvents.

(*e*) *Intermolecular Attraction and Free Energy of Solution.* Since fugacity is a measure of the escaping tendency it is clear from Equation 41 that the free energy of solution is a measure of the change in escaping tendency attending the transfer of the pure solute to a solution. *A priori* it would seem reasonable to suppose that the escaping tendency of a solute from a solution would increase with its concentration and decrease as the attractive forces of solvation become greater. It should also increase as the self-associating tendency of the solvent results in a greater tendency to squeeze out the solute molecules. Thus as the concentration is increased the escaping tendency of the solute increases until finally $f = f^\circ$ and, according to Equation 41, $\Delta F = 0$. The solution is then saturated. The effect of the intermolecular attractive forces on the saturation point, i.e., on solubility, may be illustrated by ether and water. The attraction of water molecules for each other is very high but is low

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[82] (*a*) Uhlig, *J. Phys. Chem.*, **41**, 1215 (1937); (*b*) Lange and Martin, *Z. physik. Chem.*, **180**, 238 (1937); (c) Eley, *Trans. Faraday Soc.*, **35**, 1281 (1939); (*d*) *Idem*, 1421.

for ether molecules. Hence if the escaping tendency of the water from the two phases is to be equalized the advantage of low attractive forces in the ether solution must be counterbalanced by greater dilution in that phase. We say, then, that water is not very soluble in ether. If the ether is replaced by another liquid which has a greater attraction for water the equilibrium solution will not need to be so dilute; and if this liquid in turn is successively replaced by others whose attraction for water is successively greater, a point will eventually be reached at which it will be impossible to make the solution of water in this liquid sufficiently concentrated to produce equilibrium. We then say that the two liquids are miscible in all proportions.

In further pursuit of justification for these *a priori* suppositions, it may be pointed out that, if the intermolecular attractive forces are the same between solvent and solute molecules as they are between either species for itself, the free energy of solution should depend on the concentration effect alone. This is shown to be the case by Equation 49, which was derived for the special case of the perfect solution.

We may say with some confidence, therefore, that there are two factors contributing to the free energy of solution: (1) the concentration effect, and (2) the association effect. The latter, in turn, may be subdivided further into (2*a*) association of solute molecules with each other, (2*b*) association of solvent molecules with each other, and (2*c*) association of solute with solvent molecules. Much work has been done in disentangling these four influences. If the reader is interested in delving into the intricacies of this field he should read Hildebrand's review of the subject.[83] For our present purposes it will be sufficient to recognize that by working in dilute solutions factor 2*a* can be reduced essentially to zero and factor 2*b* can be held practically constant as long as only one solvent is involved. If it is desired to work with more concentrated solutions, Equation 43 may be used.

It is apparent, then, that in order to study the relation between factor 2*c* and such associating influences as dipole interaction and the exercise of donor-acceptor relationships, we may examine the free energies of solution of gases at one atmosphere in solutions of equal molecular concentration in the same solvent. The choice of the gaseous state for the pure solute presents the most favorable condition for theoretical interpretation since it avoids the complication of the associating forces operative in condensed phases.

The desired material is given in Tables VIII, IX, and X, except that equal activities do not correspond strictly to equal concentrations.

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[83] J. H. Hildebrand, *Solubility of Non-Electrolytes*, Reinhold Publishing Corp., N. Y., 1936.

These data, however, should be capable of showing us the most important trends.

It should be recognized at the outset that Equation 41, coupled with the above argument relating escaping tendency and forces of association, demands that there be a parallelism between these forces and the free energy decrease attending the process of solution. It makes no corresponding demand on the heat of solution, but our experience with bond energies leads us to expect a parallelism here also. Next, in regard to the question as to how we can use theory to predict trends in associating forces, we naturally suspect that the exercise of donor and acceptor properties will be the most important factor, with dipole association as a poor second. If the solute is an acid, then, according to our definitions of acid strength and solvent basicity, as given in Equation 13, it would be demanded that the fugacity of the solute, and hence its free energy, should decrease as the acid becomes stronger and/or the solvent more basic. If the solute is not an acid but is an acceptor we would guess that the same relations would hold, i.e., we would guess that the relative donor properties of solvents should be independent of the particular acceptor used. Lewis [3] has expressed doubt that such a single monotonic order of donor (or acceptor) properties exists. However, the work of Koch [84] indicates that the same order of solvent basicities serves to account for observed variations in the activities of both the silver ion and the hydrogen ion. A few of his results are reproduced in Table XIII, in which the solvents are arranged in order of decreasing basicities, defined with relation to hydrogen ions, and the solvation activity coefficient corresponds to the transfer of silver ions from a vacuum to the solution. Its trend parallels that of the ΔF of solvation. The lack of parallelism between the values of the dielectric constant and γ_s serves to emphasize that, in cases where donor and acceptor properties are exercised, the dielectric constant plays a decidedly minor role.

The existence of a single monotonic order of donors and acceptors of the same charge type arranged according to the strength is also indicated by a vast amount of work in the field of ion catalysis. Only infrequent exceptions have been noted. We might, however, expect exceptions to occur when the acceptor molecules are relatively complex and involve resonance between different valence bond structures.

With these points in mind, let us examine the tables in search of evidence. Table X shows a large difference between the ΔF's of hydration of the halogen hydrides and the weaker acids, such as HCN or CH_3OH. The halogens and ICl do not show large values for ΔF of hydration as would be expected from their weak donor properties.

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[84] Koch, *J. Chem. Soc.*, 269 (1928); 1551 (1930); *Phil. Mag.* [7], **11**, 579 (1931).

In examining Table VIII it is seen that ΔF of hydration increases in the order HOAc < ROH < Me_2CO < MeCl < C_2H_6, which is the order that we might reasonably have predicted in view of the amphiprotic nature of water. The values of ΔH increase in the same direction, if the alcohols are considered as a group, although within this group the variation is in the reverse order owing to the volume entropy effect already discussed, which may apparently become important in associated solvents when the solutes compared have about the same acid strength. It is then to be noted, however, that all ΔH values are negative, whereas those of ΔF are all positive.

TABLE XIII

SOLVATION ACTIVITY COEFFICIENTS (γ_s) FOR SILVER ION IN DIFFERENT SOLVENTS

SOLVENT	DIEL. CONST.	γ_s
Pyridine	12.4	2.1×10^{-6}
Aniline	6.9	4.9×10^{-3}
Acetonitrile	36.4	5.2×10^{-2}
Phenylacetonitrile	15	8.6
Benzonitrile	26.3	10.9
Methanol	35.4	81
Ethanol	25.4	150
Acetone	21	6040

If we consider ethanol as a weak acid we would predict that ΔF would increase in the following order as the solvent is changed: H_2O < $PhNH_2$ < HOAc < Me_2CO < hydrocarbons. Our table of free energy changes does not include these cases, but Table IX shows that ΔH increases in this order, except that heptane seems distinctly anomalous.

In further accord with these trends we find that the ΔF of solution of methanol is negative in water and positive in the aprotic solvents. Thus all available evidence for these alcohols indicates that again there is a parallelism between ΔH and ΔF as the solvent is changed.

Phenol presents similar evidence, for here we find the trend in ΔH to be exactly what we would have predicted for ΔF.

Examination of the remaining data presented by Evans and Polanyi[77] shows the same general trends in the case of all acidic solutes, although exceptions are to be noted, especially where two solvents are about equally basic.

As a result of our not too exhaustive survey we may tentatively conclude, at least as a first approximation to the truth, that (1) for one solute in different solvents the trends in ΔH and ΔF are in the same direction, although in any one individual case ΔH and ΔS may have opposite signs; (2) for different solutes in the same solvent the trends of ΔH and ΔF are in the same direction except when the solutes are closely alike in their acid or base strengths, in which case an entropy change dependent on molecular size may reverse the relationship if the solvent is associated; (3) the values of ΔH and ΔF of solution are preponderantly determined by the exercise of donor and acceptor properties and dipole interaction is a secondary influence; (4) the order of solvent basicities is the same toward all simple acceptors of the same charge type; (5) there is approximately a single linear relationship between ΔH and ΔS of solution for all gaseous solutes in all nonassociated solvents.

In connection with these five tentative conclusions it is highly important to remember a sixth point: (6) In the case of solutions in which the solute and solvent mutually exercise donor and acceptor relationships, it follows from the definition given by Equation 13 that the value of ΔF of solution will become smaller (or more negative) as the intrinsic acid strength of the solute and/or the basicity of the solvent become greater. A similar relation would hold for the intrinsic base strength of the solute and the acidity of the solvent.

INFLUENCE OF THE SOLVENT ON REACTION VELOCITY

Effect of the Solvent on the Activation Energy

In Chapter VII it was found convenient to study the effect of structural changes on reaction velocity by considering separately their influence on the activation energy and the *PZ* factor. The same procedure will be used in discussing the influence of the solvent. In this section attention will be focused chiefly on the activation energy.

A change of solvent can exert a powerful influence on reaction rate, frequently causing a variation of one thousand fold, there being a general tendency for higher rates in polar solvents.[85] In seeking the theoretical interpretation of such effects, let us adopt the picture developed in Chapter VII by the fusion of the Lapworth theory of electrophilic and nucleophilic reactivity with the transition state theory. According to this combined theory the step involving the lowest activation energy will be the one which involves interaction between the two centers of highest electrophilic and nucleophilic reactivity.

The magnitude of the values of $\Delta H^{\ddagger}$ which would obtain for the interaction of any pair of reaction centers may frequently be estimated by the laborious mathematical procedures of the transition state theory or, for purposes of rough comparison, they may presumably be approximated by calculating from the table of "ionic bond energies" which

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[85] R. P. Bell, *Ann. Repts. Prog. Chem.*, **36**, 82 (1939).

pair of centers could react with the minimum absorption of energy. Such calculations give us $\Delta H^{\ddagger}$ or $\Delta H^{\ddagger}{}_{*}$ but, as in all over-all reactions so also with these individual steps, the probability that the reaction will proceed depends not on $\Delta H^{\ddagger}$ but on $\Delta F^{\ddagger}$, and the two are related through $\Delta S^{\ddagger}$. Thus whether or not interaction takes place preferentially through the step involving the lowest activation energy depends on the sign and the magnitude of the entropy term. The relationship between P and $\Delta S^{\ddagger}$ has been discussed in Chapter VII and the above statement concerning $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is, in terms of the collision theory, equivalent to saying that the activation energy alone does not determine which one of all conceivable reaction steps is going to be the rate-controlling step but that the probability factor P is also of importance.

It seems likely that substituents and environment alike influence PZ or $\Delta S^{\ddagger}$ by altering the randomness of distribution and orientation (i.e., the "freedom") of the molecules in the reacting system. Such alterations may be due to intermolecular association of various kinds, to purely geometrical influences,[86] or to an alteration of the number of bonds over which the energy of collision can be distributed.

A further point of importance in the combined theory is that substituents and environment alike are supposed to exert their influences on the activation energy by altering the polarizations and polarizabilities of valence bonds. To this we must add that the activation energy must also depend on the strength of any solvation bonds which have to be broken in forming the critical complex. If the reactants and the critical complex are equally solvated in the sense that they have equal heats of solvation, then the solvent should be without influence on the activation energy.[87] This state of affairs is most likely to obtain when both the reactants and the products are molecules of low polarity. On the basis of the rather scanty experimental material which is available for testing this prediction, Bell [85] has drawn the following conclusion: "Bimolecular reactions in which both the reactants and the products are of low polarity take place at approximately the same rate in the gas phase as in solution, and their rate varies little with the nature of the solvent."

If, on the other hand, the reactants and the "critical complex" are solvated to different extents, we may expect a change of solvent to alter the reaction rate by affecting both the factors $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. In partial support of this contention, approximate calculations show that solvation of a polar critical complex can materially reduce the activation energy.[88]

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[86] Cf. Hildebrand, *J. Chem. Phys.*, **7**, 233 (1939).

[87] Cf. Polanyi, *Z. Elektrochem.*, **35**, 561 (1929).

[88] (*a*) Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 605 (1935); (*b*) A. G. Evans and M. G. Evans, *ibid.*, **31**, 86 (1935).

Since such an effect is almost surely due to the energy made available by the formation of a bond between the critical complex and the solvent, it certainly seems that **P 28** should be applicable in such cases. For kinetic purposes it may be restated as follows:

P 29. A solvent will decrease the activation energy of a reaction if the critical complex is more firmly solvated than the reactants; if the reverse situation obtains, the solvent will increase the activation energy.

This basic principle can readily be put into quantitative form. If we consider a reaction of the form

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X} \rightarrow \mathrm{C} + \mathrm{D} \tag{54}$$

where X is the critical complex, and if we designate the solution state by s and the gaseous state by g, we may formulate the effect of solvation as follows:

$$\begin{aligned} \mathrm{A_g} + \mathrm{B_g} &\rightarrow \mathrm{X_g}; & \Delta F &= +\Delta F^{\ddagger}{}_{\mathrm{g}} \\ \mathrm{A_s} &\rightarrow \mathrm{A_g}; & \Delta F &= -\Delta F_{\mathrm{A}} \\ \mathrm{B_s} &\rightarrow \mathrm{B_g}; & \Delta F &= -\Delta F_{\mathrm{B}} \\ \mathrm{X_g} &\rightarrow \mathrm{X_s}; & \Delta F &= +\Delta F_{\mathrm{X}} \end{aligned} \tag{55}$$

Addition gives:

$$\mathrm{A_s} + \mathrm{B_s} \rightarrow \mathrm{X_s};\ \Delta F^{\ddagger}{}_{\mathrm{s}} = \Delta F^{\ddagger}{}_{\mathrm{g}} - \Delta F_{\mathrm{A}} - \Delta F_{\mathrm{B}} + \Delta F_{\mathrm{X}} \tag{56}$$

Introduction of the thermodynamic equation

$$\Delta F = \Delta H - T\Delta S$$

transforms Equation 56 into the form

$$\Delta F^{\ddagger}{}_{\mathrm{s}} = \Delta F^{\ddagger}{}_{\mathrm{g}} - \Delta H_{\mathrm{A}} - \Delta H_{\mathrm{B}} + \Delta H_{\mathrm{X}} + T\Delta S_{\mathrm{A}} + T\Delta S_{\mathrm{B}} - T\Delta S_{\mathrm{X}} \tag{57}$$

Now let $\Sigma\Delta H_{\mathrm{s}} = \Delta H_{\mathrm{X}} - \Delta H_{\mathrm{A}} - \Delta H_{\mathrm{B}}$ and $\Sigma\Delta S_{\mathrm{s}} = \Delta S_{\mathrm{X}} - \Delta S_{\mathrm{A}} - \Delta S_{\mathrm{B}}$.

The introduction of these two relationships into Equation 57 gives

$$\Delta F^{\ddagger}{}_{\mathrm{s}} = \Delta F^{\ddagger}{}_{\mathrm{g}} + \Sigma\Delta H_{\mathrm{s}} - T\Sigma\Delta S_{\mathrm{s}} \tag{58}$$

Combination of Equation 58 with the fundamental equation of the transition state theory (cf. Chapter VII, Eq. 18):

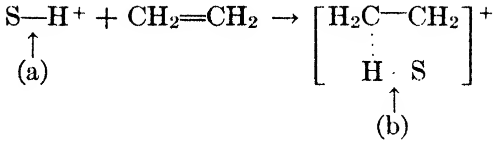
$$k = \kappa \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} \tag{59}$$

gives the following comparison of the rates of a given reaction in the gaseous state and in solution:

$$\frac{k_{\mathrm{s}}}{k_{\mathrm{g}}} = e^{-\Sigma\Delta H_{\mathrm{s}}/RT} \cdot e^{\Sigma\Delta S_{\mathrm{s}}/R} \tag{60}$$

This equation has been derived by Glasstone, Laidler, and Eyring, using a somewhat different method.[89]

It is apparent that the application of **P 29** involves our questionable knowledge of the state of solvation of the critical complex. However, it seems likely that we can estimate it rather reliably from our general knowledge of the electron theory. Thus in the case of the slightly polar reactants considered by Bell (see above) it seems reasonable to expect the critical complex also to have low polarity and hence the degree of solvation should change but little during the rate-determining step. In case polar reactants are involved it would seem to make very little difference whether the rate-controlling step is pictured in terms of a transition complex, e.g.,



$$\underset{\substack{\uparrow \\ (a)}}{\mathrm{S{-}H^+}} + \mathrm{CH_2{=}CH_2} \rightarrow \left[\begin{array}{c} \mathrm{H_2C{-}CH_2} \\ \vdots \\ \underset{\substack{\uparrow \\ (b)}}{\mathrm{H \cdot S}} \end{array}\right]^+$$

where it is readily seen that the solvation bond (a) must be stronger than (b); or whether it is pictured analogously to Conant's formulation of irreversible redox reactions in which the rate-controlling step is preceded by a rapid reversible step:

$$\mathrm{SH^+} \underset{\text{fast}}{\rightleftarrows} \mathrm{S} + \mathrm{H^+}$$

$$\mathrm{H^+} + \mathrm{CH_2{=}CH_2} \xrightarrow[\text{slow}]{} \mathrm{H_3C{-}\overset{+}{C}H_2}$$

In this case the speed of the second step depends on the equilibrium concentration of the hydrogen ions, which in turn depends on the firmness of the $\mathrm{S{-}H^+}$ bond. From the qualitative point of view either picture leads to the same conclusion, that the more basic the solvent the slower the reaction.

When an over-all reaction is of the type

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$$

Glasstone, Laidler, and Eyring [90] state that, in general, the activated complex may be expected to resemble C rather than A + B.

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[89] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., 1941, p. 408.

[90] Ref. 89, p. 414.

The Effect of the Solvent on PZ and $\Delta S^\ddagger$

It was seen in Chapter VII that the PZ factor is ordinarily considered as a unit, but when it is desired to theorize about P alone it is customary to assume that the value of Z in solution is the same as that calculated for the gaseous condition at the same temperature. This procedure is justified by the fact that there are a large number of cases in which PZ in solution is approximately equal to the value of Z calculated for the gas reaction and only relatively few cases in which PZ exceeds Z by more than a factor of ten.[85]

In further relation to this point, Fairclough and Hinshelwood [91] have remarked that "although the solvent impedes diffusion and thus cuts down the number of collisions which a given solute molecule makes in unit time with fresh ones, it hems in pairs of solute molecules and causes them to make repeated collisions with each other, the two effects probably nearly balancing. For the purposes of ordinary slow chemical reactions, the repeated collisions are as effective as fresh encounters. Thus the large changes in PZ over several powers of ten which are often found must be due to changes in P. But the smaller changes within a given order of magnitude may, as far as theory can decide, equally well be due to changes in Z."

There is a limited amount of evidence in support of this last point. Thus experiments made with mechanical models [91, 92] supply evidence that, in so far as steel balls in a box may be likened to molecules in a container, increasing the density of the solvent or making the solute molecules smaller than those of the solvent results in an increase in the numbers of repeated collisions at the expense of fresh encounters of solute molecules with themselves. The total collision rate, however, remains constant. The same thing is observed when the solute molecules are larger than those of the solvent, provided the latter have moderate densities, but at very high densities the total solute collision rate rises sharply. Thus if the incompatibility of packing patterns results in the exclusion of the solute from certain regions of the solvent, we should expect an increase in Z.

In order to find out whether or not the behavior observed in mechanical models carries over into the realm of reacting molecules, Fairclough and Hinshelwood [91] studied the rates of esterification of acids, ranging from acetic to behenic acid, by methanol, ethanol, and cyclohexanol, the alcohol in each case serving as solvent. Since the activation energy remains constant for butyric acid and the higher acids, the change in

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[91] Fairclough and Hinshelwood, *J. Chem. Soc.*, 593 (1939).

[92] Rabinowitch and Wood, *Trans. Faraday Soc.*, **33**, 1225 (1937).

velocity must be due to changes in *PZ*. Over this range of acids *PZ* was found to increase with the size of the acid molecules when no second catalyzing acid was present. This was in accord with expectations, since in such cases autocatalysis would occur and hence the rate-controlling step would depend on the rate of collision of the acid molecules with each other, which would be enhanced if they became segregated by exclusion from certain regions of the solvent. But when hydrogen chloride was used as a catalyst, *PZ* remained essentially constant, as would be expected, because in this case the rate-controlling step involves the collision of hydrogen ions with the organic acid molecules and since the former are not excluded from the pattern of the solvent their distribution is normal and abnormally long sets of repeated collisions with the fatty acid molecules would not be expected. Other possible explanations were rejected by these authors. Thus the increase of *PZ* observed to attend the increase in size of the fatty acid molecules could not be ascribed to the greater collision areas because only collisions with carboxyl groups lead to reaction. Furthermore, if the behavior is at all like that in gases, increasing the molecular weight would decrease *Z*. The authors conclude, therefore, that the observed variations in *PZ* are due, at least preponderantly, to variations in *Z*. The observed variations, however, are rather small, being within one power of ten.

It was seen in Chapter VII that there is a tendency for the *PZ* factor to increase as *E* increases. This suggests that perhaps there is an invariable influence which operates in this direction but that other factors are also involved. In seeking the answer to this problem Raine and Hinshelwood [93] studied the rate of formation of quaternary ammonium salts in a series of benzene-nitrobenzene mixtures and found that log *PZ* could be broken up into two factors, one increasing linearly with *E* while the other increased regularly with the polarity of the solvent.[94] The same two influences were found to be operative in the "Diels-Alder addition" of benzoquinone to cyclopentadiene although it was not so pronounced, due presumably to the less polar character of the product.[95]

This last-named factor (the one related to the polarity of the solvent) may find its explanation in a suggestion made by Norrish.[96] He symbolizes displacement reactions taking place in solution by the equation

$$\textcircled{A} + \textcircled{B} \rightleftarrows AB \rightleftarrows C + D \rightarrow \textcircled{C} + \textcircled{D}$$

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[93] Raine and Hinshelwood, *J. Chem. Soc.*, 1378 (1939).

[94] See Rampino and Svirbely, *J. Am. Chem. Soc.*, **61**, 3534, 3538 (1939).

[95] Fairclough and Hinshelwood, *J. Chem. Soc.*, 236 (1938).

[96] Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937); a similar theory was suggested by Hinshelwood, *ibid.*, **32**, 970 (1936); **34**, 138 (1938).

where the circles represent stable molecules and AB is the critical complex. The nascent products C and D become stabilized by the solvent. Thus if they are ions or dipoles they become solvated and if they are free radicals they react with the solvent in the manner indicated in the last chapter. Norrish remarks that "formally no great distinction need be made between the transition complex AB and the nascent products C + D, and the process AB $\rightleftarrows$ C + D can now be regarded as a vibration of the transition complex which does not lead to final reaction unless either C or D become stabilized by the solvent." If C and D are trapped in a "cage" of solvent molecules they will tend to regenerate AB; if they are ions they will tend to become stabilized by solvation, and this tendency should increase with the polarity of the solvent. This explains why *P* has a tendency to increase with the polarity of the solvent when quaternary ammonium ions are produced. This tendency is illustrated by Table XIV. The values of *P* there given were calculated [97] from the velocity data [98] for the reaction between aniline and bromoacetophenone in various solvents. Although these data make clear that there is a tendency for *P* to increase with D, they make it equally clear that some other influence is also operative, which is in accord with our previous considerations.

TABLE XIV

THE REACTION OF ANILINE WITH BROMOACETOPHENONE

SOLVENT	DIEL. CONST.	*P*
Benzene	2.28	4×10^{-11}
Chloroform	5.0	6×10^{-9}
Acetone	21.4	1.7×10^{-7}
Nitrobenzene	34.0	4.0×10^{-6}
Methyl alcohol	33.7	4.3×10^{-6}
Ethyl alcohol	25.7	3.9×10^{-5}
Butyl alcohol (*n*)	17.8	3.9×10^{-5}
Benzyl alcohol	....	4.9×10^{-5}

The papers reviewed so far in this section were all written from the standpoint of the collision theory. Let us now turn to the transition state theory and see what further light it can throw on the subject.

If the rate-controlling step involves a decrease in solvation it is attended by a decrease in orientation (or an increase in "freedom") and hence by an increase in entropy ($\Delta S^\ddagger$ or PZ).[99] Thus if a reaction involves the combination of A^+ and B^- ions the critical complex will

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[97] Norrish and Smith, *J. Chem. Soc.*, 129 (1928).

[98] Cox, *ibid.*, **119**, 142 (1921).

[99] Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

have no net charge, the extent of solvation by a polar solvent will materially decrease, and $\Delta S^{\ddagger}$ (and PZ) will increase relative to the gas reaction. Similarly a reaction between ions of like charge will result in a decrease of $\Delta S^{\ddagger}$. The same qualitative conclusions have been reached by a purely electrostatic treatment in which the solvent is treated as a uniform dielectric.[85, 100] In keeping with these predictions it has been found that reactions between ions of like charge give P factors as low as 10^{-8}, whereas in reactions involving oppositely charged ions P can become as great as 10^{8}. These calculations were made on the assumption that Z in solution is the theoretical collision number as calculated for gaseous reactions.

When reactions occur between polar but uncharged reactants, the transition state should be more polar and more solvated in so far as dipole association is concerned. This should normally result in small values of $\Delta S^{\ddagger}$ and PZ, and such has been found to be the case for most reactions of this type.[85] However, the possibility may be foreseen that an initially solvated basic atom might act as donor in the formation of the critical complex, thus losing its ability to form a coordinate bond with the solvent. This might overbalance the increase in solvation due to greater dipole association. Such an effect might be expected in the reaction

$$NR_3 + RI \rightarrow [NR_4]^+ I^- \qquad (61)$$

but it is conspicuously absent, the P factor being small.[85] However, in the formally similar reaction

$$Et_2S + EtBr \rightarrow [Et_3S]^+ Br^- \qquad (62)$$

P is close to unity.[101] In comparing these two reactions Bell [85] rightly concludes that "it is clearly dangerous to attempt *a priori* conclusions as to the nature of the critical complex."

Dipole Moments and the Solvent Effects

When all substances concerned in the rate-controlling step of a bimolecular reaction go into solution without appreciably exercising donor and acceptor properties and without any significant dipole interaction, the reaction in solution may be expected to proceed two or three times as fast as in the gas phase. A problem of the next higher degree of complexity arises when coordinating tendencies are still absent but appreciable dipole moments appear. In such a case the free energy of

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[100] (*a*) Moelwyn-Hughes, *Proc. Roy. Soc.*, **A155**, 308 (1936); (*b*) LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

[101] Corran, *Trans. Faraday Soc.*, **23**, 605 (1927).

transfer of a strong dipole from a medium of unit dielectric constant to one of dielectric constant D has been shown by Kirkwood[102] to be

$$\Delta F = kT \ln \alpha = -\frac{\mu^2}{r^3} \cdot \frac{D-1}{2D+1} \tag{63}$$

where r is the molecular radius and α is the activity coefficient referred to the highly attenuated gaseous condition ($D = 1$) as the standard state. For a given polar solute dissolved in various nonpolar solvents it has been shown in a number of cases that the plot of $\ln \alpha$ against $(D - 1)/(2D + 1)$ gives a straight line, as required by Equation 63. Exceptions have been encountered, however.

If Equation 63 is combined with the fundamental equations of the theory of absolute reaction rates, the following equation may be derived for the case $A + B \rightarrow X^{\ddagger} \rightarrow$ products:[103]

$$\ln k = \ln k_0 - \frac{1}{kT} \cdot \frac{D-1}{2D+1}\left(\frac{\mu^2{}_A}{r^3{}_A} + \frac{\mu^2{}_B}{r^3{}_B} - \frac{\mu^2{}_{\ddagger}}{r^3}\right) \tag{64}$$

where k_0 is the rate constant, at very low pressures, for the gas reaction or at low concentrations for the reaction in an ideal solution. It must be remembered that we have already assumed the absence of any nonelectrostatic interactions. This equation demands that, for a given reaction in different solvents, a straight line should result when $\ln k$ is plotted against $(D - 1)/(2D + 1)$. Such relationships have been observed in a number of cases.[103]

The Influence of Ionic Strength on Reaction Velocity

So far emphasis has been given to those changes in thermodynamic environment which can be described as due to a change in solvent. Equally important environmental changes may sometimes result from alterations in the kind or concentration of solutes which, in addition to the reactants, are also present in solution. This is particularly true in cases where one or more of the reactants are ions and the ionic strength of the solution is altered.

Brönsted[104] and Bjerrum[105] have independently developed the following equation:

$$k = k^s{}_0 \frac{f_A f_B}{f_{\ddagger}} \tag{65}$$

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[102] J. G. Kirkwood, *J. Chem. Phys.*, **2,** 351 (1934).

[103] Ref. 89, pp. 419, 420.

[104] Brönsted, *Z. physik. Chem.*, **102,** 109 (1922); **115,** 337 (1925).

[105] Bjerrum, *ibid.*, **108,** 82 (1924).

in which the activity coefficient f is defined in terms of the infinitely dilute solution as the standard state and k^s_0 is the rate constant for the infinitely dilute solution. If this equation is combined with the Debye-Huckel expressions for the activity coefficients, the following approximate equation may be derived,[106]

$$\ln k = \ln k^s_0 + 2AZ_AZ_B\sqrt{\mu} \tag{66}$$

in which μ is the ionic strength and A is a constant for a given temperature. The value of A is given by the equation

$$A = \frac{N^2\epsilon^2(2\pi)^{1/2}}{(DRT)^{3/2}(1000)^{1/2}} \tag{67}$$

where N is Avogadro's number. For aqueous solutions Equation 66 reduces to

$$\log k = \log k^s_0 + 1.02\ Z_AZ_B\sqrt{\mu} \tag{68}$$

Equation 68 has received considerable experimental verification.[107] If either A or B is a neutral molecule the last term in the equation becomes zero and the rate becomes essentially independent of the ionic strength. It should be emphasized that the mathematical development of these equations assumes the absence of chemical coordination.

The Hughes-Ingold Theory of Solvent Action

The apparent fact that alkyl halides, for example, may undergo nucleophilic substitutions by two different mechanisms, S_N1 and S_N2, was discussed in Chapter V and will be discussed further in the following chapter. It will be recalled that the S_N1 mechanism is assumed to involve an ionization reaction as the rate-controlling step. This implies the existence of a critical energy of ionization. Hughes and Ingold [108] consider that "a condition which would lead to such a critical energy is that, beyond a certain degree of extension of the polarized link, the increasing solvation due to the separating electric charges contributes a fall of energy which is more rapid than the rise that would have occurred in the absence of solvation; this condition satisfied, a slow ionization results. With full recognition of the circumstances that the process of separation is continuous, the degree of extension referred to may be said to characterize a 'critical complex.' "

These authors then proceed to make three assumptions which seem highly plausible in terms of the physicochemical studies already covered

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[106] Ref. 89, p. 428.

[107] LaMer, *Chem. Rev.*, **10**, 179 (1932); *J. Franklin Inst.*, **225**, 709 (1938).

[108] Hughes and Ingold, *J. Chem. Soc.*, 252 (1935).

in this chapter. When solvation occurs as the result of electrical charges associated with solute molecules we may expect that (1) solvation will increase with the magnitude of the charge, (2) solvation will decrease with increasing distribution of a given charge, (3) the magnitude of these effects will be greater in strongly solvating (ionizing) than in feebly solvating solvents.

The applications of these three assumptions in conjunction with **P 29** leads directly to the predictions summarized in Table XV. It seems reasonable to suppose that the appearance or disappearance of charges in the critical complex will in general be a more powerful influence than the distribution of a given charge in the critical complex. It is therefore apparent in reactions of the third type, viz., $Y^- + \overset{+}{R}X$, that the use of a more polar solvent would slightly favor the S_N1 mechanism since the attending increase in E is due to charge distribution in the case of S_N1 and disappearance of charge in the case of S_N2. However, in reactions of the type $Y^- + RX$ the opposing effects of the polar solvent on the two mechanisms favors S_N1 very strongly. The possibility that change of solvent might change the mechanism in such a case may readily be foreseen. Indeed such a trend has been detected experimentally by Olivier,[109] who found that the hydrolysis of benzyl chloride, which is approximately bimolecular in 50% aqueous acetone, becomes much more nearly unimolecular in water.

TABLE XV

SOLVENT EFFECTS

Type	Mechanism	Charges concerned in rate-determining stage			Effect on charges of forming complex		Effect of ionizing media on E
		Reactants	Complex	Products	Magnitude	Distribution	
a	S_N1	$Y^- + RX$	$R^{\delta+}\ldots X^{\delta-}$	$R^+ + X^-$	Increase	....	Decrease
	S_N2		$Y^{\delta-}\ldots R\ldots X^{\delta-}$	$YR + X^-$	None	Dispersed	Increase
b	S_N1	$Y + RX$	$R^{\delta+}\ldots X^{\delta-}$	$R^+ + X^-$	Increase	....	Decrease
	S_N2		$Y^{\delta+}\ldots R\ldots X^{\delta-}$	$\overset{+}{Y}R + X^-$	Increase	....	Decrease
c	S_N1	$Y^- + \overset{+}{R}X$	$R^{\delta+}\ldots X^{\delta+}$	$R^+ + X$	None	Dispersed	Increase
	S_N2		$Y^{\delta-}\ldots R\ldots X^{\delta+}$	$YR + X$	Decrease	....	Increase

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[109] Olivier, *Rec. trav. chim.*, **53**, 891 (1934).

The predictions of Table XV are in good accord with experiment. Tertiary butyl chloride, which was shown in Chapter V to hydrolyze by a unimolecular mechanism (type *a* 1) hydrolyzes more rapidly as the proportion of water is increased in an aqueous-alcoholic solvent.[110] Methyl and ethyl iodides (type *a* 2) hydrolyze more slowly as the proportion of water in aqueous alcohol is increased.[111] Likewise the rate of racemization of secondary iodides in acetone (*a* 2) was found to be decreased on addition of a small proportion of water.[112] Menschutkin [113] found the combination of ethyl iodide with triethylamine (*b* 2) to proceed more rapidly in alcohols than in hydrocarbons, and subsequently the same general sequence has been observed for other primary alkyl halides and various amines and sulfides by other investigators.[114] The decomposition of triethylsulfonium iodide (*c* 1) is slower in alcohols than in acetone [115] and the hydrolysis of the dimethyl-*tert.*-butyl sulfonium cation (*c* 1) is decreased by the addition of water to an aqueous alcoholic solvent.[116] Finally, the speed of hydrolysis of the trimethylsulfonium cation, which was shown to be bimolecular (*c* 2), is also decreased by the same change of solvent.[117]

THE INFLUENCE OF SOLVENTS ON ELECTRON DISPLACEMENT

The way in which solvents alter the dipole moments of solute molecules has already been studied. In view of the close connection between the dipole moment of C—X and the I_s effect of X postulated by the English theory, it would seem that the positive or negative solvent effects on dipole moments would be more or less paralleled by corresponding changes in the associated I_s effects. Similar considerations might be expected to apply to the dipole moment of C═C—X and the *M* effect of X, although this case is more complicated.

That such expectations are reasonable is indicated by the rather satisfactory linear relationship that exists between the dipole moments of the

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[110] E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

[111] deBruyn and Steger, *Rec. trav. chim.*, **18**, 41, 311 (1899).

[112] Bergmann, Polanyi, and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[113] Menschutkin, *ibid.*, **5**, 589 (1890).

[114] (*a*) Carrera, *Gazz. chim. ital.*, **24**, i, 180 (1894); (*b*) Hemptinne and Bekaert, *Z. physik. Chem.*, **28**, 225 (1899); (*c*) von Halban, *ibid.*, **84**, 128 (1913); (*d*) Cox, *J. Chem. Soc.*, **119**, 142 (1921); (*e*) Hawkins, *ibid.*, **121**, 1170 (1922); (*f*) Muchin, Ginsberg, and Moissejera, *Ukrain Chem. J.*, **2**, 136 (1926); (*g*) McCombie, Scarborough, and Smith, *J. Chem. Soc.*, 802 (1927); (*h*) Essex and Gelormini, *J. Am. Chem. Soc.*, **48**, 882 (1926).

[115] von Halban, *Z. physik. Chem.*, **67**, 29 (1909).

[116] Hughes and Ingold, *J. Chem. Soc.*, 1571 (1933).

[117] Gleave, Hughes, and Ingold, *ibid.*, 236 (1935).

PhX series and the values of K^*_a for the $X \cdot C_6H_4 \cdot CO_2H$ and $X \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ series determined in water solutions.[118] If, therefore, this parallelism exists when μ is altered by changing from one substituent group to another, it seems likely that the parallelism will persist when μ is varied, not by changing X, but by changing the solvent. If, furthermore, it is recognized that the parallelism between μ and K^*_a means that there is a parallelism between μ and the electron displacement effects which relay the influence of X to the carboxyl group, then it is apparent that the theoretical method previously developed for predicting the effect of the solvent on dipole moments may be used equally well in predicting the effect of the solvent on the I_s and M effects.

The next logical step in our inquiry is to see how well this theory predicts the effect of solvent change on any of the phenomena which are customarily interpreted in terms of the I_s and M effects. Since these effects, unlike the "polarizability effects," are not time-variable and since rate problems involve time-variable effects, only equilibrium phenomena may properly be chosen for our test. Among these the acid-base equilibria are most convenient.

A solvent may influence the strength of a substituted acid both by its effect on the dipole moment of the C—X bond and by its direct action on the carboxyl group. Since our theory, as developed so far, only permits us to make predictions in relation to the former of these two variables, it would be desirable to devise a means of eliminating the latter. If we assume, as a first approximation, that any solvent effects on the carboxyl group cancel out when we compare the strengths of two carboxylic acids,[119] then the changes in the value of K_r for any one substituted acid produced by alteration of the solvent should be due solely to changes in the I_s and M electron displacements associated with the substituted group.

Values of K_r for different acids dissolved in different solvents have been given in Table V. From the point of view of the present inquiry, there are two comparisons of interest which can be made with these data: (1) the effect of changing dielectric constant of the solvent on the strength of any one acid, and (2) the relative magnitudes of this effect as related to the magnitudes of the bond moments of C—X. Let us examine them in order.

(1) The customary negative solvent effect would cut down the effective bond moment of C—X, and hence weaken an acid if it were stronger than the unsubstituted acid and strengthen it if it were weaker. If now it is remembered that $pK_r = pK_a - pK°_a$ (benzoic acid being the ref-

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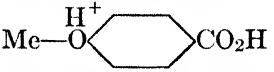
[118] Dippy and Lewis, *J. Chem. Soc.*, 1008 (1937).

[119] Cf. Smallwood, *J. Am. Chem. Soc.*, **54**, 3048 (1932).

erence acid) it becomes evident that, as the dielectric constant of the solvent increases, all values of pK_r should change in the direction of the pK_r values for the respective unsubstituted acids. The data in Table V for monosubstituted acids are in rather good accord with this prediction. If we consider transfers of an acid from benzene to chlorobenzene to water, or from *n*-butanol to water, the agreement is perfect except for *o*-nitrobenzoic acid. It should be remarked, however, that although there is some justification for assuming the absence of a positive solvent effect in benzene derivatives, there is no such justification for acetic acid derivatives, and we should thus expect glycolic acid to change in a direction opposite from the others. It does not.

(2) The application of the theory to the second point of comparison leads at once to the prediction that the solvent effect should be greater, the greater the value of the substituted bond moment in the solute. The desired comparison is given by the values of $(pK_r)_{\mathrm{BuOH}} - (pK_r)_{\mathrm{H_2O}}$ in the last column of Table V, from which it is evident that the *meta*- and *para*-substituted benzoic acids are in complete accord with predictions.

The agreement between facts and theory achieved in these two comparisons is perhaps better than one would dare to have hoped, in view of the simplifying assumptions involved, and it is a strong indication that dipole association does influence the I_s and M effects (including the D effect) in the manner described.

The Frank theory takes no cognizance of the possible formation of coordinate covalences between solvent and solute and hence applies accurately only to aprotic solvents. The above comparisons involving amphiprotic solvents owe their success to the following circumstances. K_r is independent of intrinsic solvent basicity in so far as work of proton solvation is concerned.[120] But if the state of coordinative saturation of the acid is changed at a point other than that whose ionizing tendency is being measured, the I and M effects will be altered. For example,  would have a greater $-I$ and a smaller $+M$ effect than anisic acid itself and hence should be stronger. Furthermore the charge type would thereby be somewhat changed and the dielectric constant would have a different effect. These circumstances were not encountered, however, in the work summarized in Table V since it is hardly likely that water is sufficiently acidic to form oxonium compounds with the OCH_3 or CN groups, or basic enough to cause appreciable ionization of the alcoholic hydroxyl group in glycolic acid. Salicylic acid is the sole exception. It does give an anomalous value of $(pK_r)_{\mathrm{BuOH}}$

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[120] See p. 334.

$- (pK_r)_{H_2O}$, but unfortunately there are other reasons to regard it with suspicion.

The addition or removal of protons would also alter the I_s effect of a group. Recognition has already been given to this fact in Chapter V by assigning different places to $-NH_2$ and $-NH_3^+$, and to OH and $-O^-$ in tables of I_s effects. It must be realized, however, that, for example, the transition from $-NH_2$ to $-NH_3^+$, as the solvent is changed gradually from the aprotic to the acidic type, is not abrupt but continuous (in the statistical sense) and the extent to which it takes place is conditioned by the acidity of the solvent. Furthermore we should be prepared to encounter such combinations as $RClH^+$ in very strongly acidic solvents, and RNH^- in very strongly basic solvents. All of these effects can be foreseen and approximately corrected by the theory of solvent influence.

In studying solvent influences it is natural to ask what light such a study throws on the validity of using values of K_a or K_r, determined in aqueous solution, as a means of establishing scales of relative I_s effects (including, of course, D effects). The answer is that the solvent effect is a minor difficulty. We have already shown that the relative strengths of acids are not frequently altered by a change from aprotic to amphiprotic solvents or from one amphiprotic solvent to another. The real difficulty lies in the fact that substituted acetic acids are subject to disconcerting proximity effects, such as chelation; that *o*- and *p*-substituted benzoic acids are complicated by mesomeric effects, and that even *m*-substituted benzoic acids seem to suffer from inductive relays of mesomeric displacements.[121] Thus, since the effects of *beta* substituents in propionic acid are too weak to afford an adequate measure of the I_s effect, we are left without a suitable series of acids (or bases) on which to make the desired measurements. Probably *m*-substituted benzoic acids are the most satisfactory for the purpose.

MISCELLANEOUS EXAMPLES OF ORGANIC REACTIONS IN SOLUTION

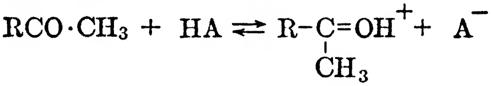
Our physicochemical study of the influences which affect chemical reactions in solution, although by no means exhaustive, is now adequate to elucidate many important and interesting reactions, and the remainder of this chapter will be dedicated to that purpose. The examples have been chosen so that they illustrate the application of as many of the foregoing principles as possible. Not even a feeble attempt has been made to include all the examples of solvent influence and acid-base catalysis with which the literature abounds.

[121] Dippy and Lewis, *J. Chem. Soc.*, 644 (1936).

The Halogenation of Carbonyl Compounds

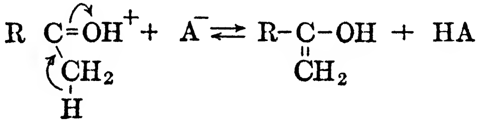
Lapworth's kinetic investigation of the bromination of acetone[122] already has become a classical example of reaction mechanism study. He found that the rate of the reaction in dilute aqueous solution is proportional to the concentration of acetone but independent of the bromine concentration. The generality of the phenomenon was later established by others, who showed that the halogenation of acetaldehyde, various ketones[123] including acetophenone,[124] and pyruvic and levulinic acids[125] showed the same peculiarity. It was also established that the rates of chlorination, bromination, and iodination are the same and that these reactions show general acid catalysis.[122, 126]

The following mechanism is in accord with all known facts concerning the acid catalyzed reaction.



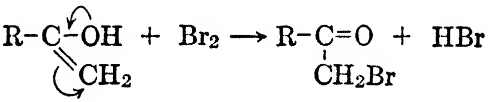
$$\mathrm{RCO\cdot CH_3 + HA \rightleftharpoons R-\underset{CH_3}{\underset{|}{C}}=OH^{+} + \overset{-}{A}}$$

(69*a*)



$$\mathrm{R\;\underset{\underset{H}{\underset{|}{CH_2}}}{\underset{\backslash}{C}}=OH^{+} + \overset{-}{A} \rightleftharpoons R-\underset{CH_2}{\underset{\|}{C}}-OH + HA}$$

(69*b*)



$$\mathrm{R-\underset{CH_2}{\underset{\backslash\backslash}{C}}-OH + Br_2 \longrightarrow R-\underset{CH_2Br}{\underset{|}{C}}=O + HBr}$$

(69*c*)

The first step (69*a*) should be instantaneous because it involves the reaction of a primary acid with a primary base. The second step (69*b*) will be slow because the formation of a C═C bond furnishes insufficient driving force to break both the C—H and C═O bonds. The third step (69*c*) will presumably be more rapid since the rupture of the double bond is facilitated by the $+T$ effect of the hydroxyl group, and the "ionic bond energy" of $\mathrm{C^-Br^+}$ (the bond being formed) is 294, whereas that of $\mathrm{Br^-Br^+}$ (the bond being broken) is only 236 kcal. The proton is probably eliminated subsequently to form HBr, another exothermic step. Thus the second step is rate-controlling. The tautomeric displacements there indicated are aided by the free positive pole on the catalyzing proton, and the coordination of $\mathrm{A^-}$ with the hydrogen atom of the methyl group gives the necessary added increment of driving

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[122] Lapworth, *J. Chem. Soc.*, **85,** 30 (1904).

[123] Dawson et al., *ibid.*, **95,** 1860 (1909); **97,** 2048 (1910); **99,** 1740 (1911); **101,** 1503 (1912); **105,** 1275 (1914); see also Ref. 53.

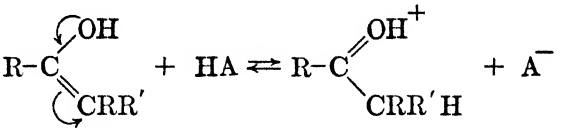
[124] Zucker and Hammett, *J. Am. Chem. Soc.*, **61,** 2791 (1939).

[125] Hughes and Watson, *J. Chem. Soc.*, 1945 (1929).

[126] Dawson and Carter, *ibid.*, 2282 (1926); and Ref. 53.

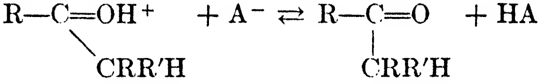
force to make the step successful. These considerations make the catalytic effect of HA quite plain.

This mechanism is also supported by the fact that the rates of halogenation and racemization are practically the same.[127] The rate-controlling step should be the same in either case. In racemization this step would be followed by the reaction



(70*a*)

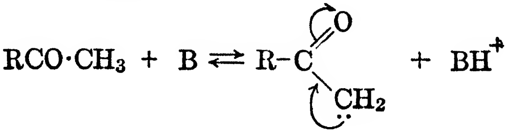
in which the chances are equal that the dextro or levo form will be produced. Reaction 70*a* would be relatively rapid because the HA bond is weak and the rupture of the double bond is aided by resonance. The final step would follow rapidly:



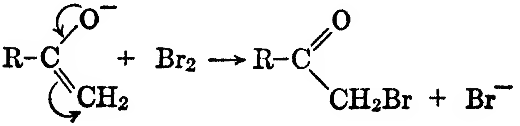
(70*b*)

No completely satisfactory explanation of the effect of substituents on the rates of halogenation of carbonyl compounds has yet been found. This is no doubt due in part to the fact that when unsymmetrical ketones are used, the yields of the two products may well be affected, not only by the relative rates of formation of the two possible intermediate enols but also by the possibility of establishing an equilibrium between the products, altering the original ratio in which they were formed.[127b]

The halogenation of ketones is also accelerated by bases of all kinds. In this case the mechanism is:



(71*a*)



(71*b*)

Effect of the Solvent on Keto-Enol Equilibria

In Table XVI are given typical data for the effect of solvents on keto-enol equilibria. The equilibrium constants are defined as K = [enol]/

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[127] (*a*) Ingold and Wilson, *J. Chem. Soc.*, 773 (1934); (*b*) Bartlett and Stauffer, *J. Am. Chem. Soc.*, **57**, 2580 (1935); (*c*) Bartlett, *ibid.*, **56**, 967 (1934).

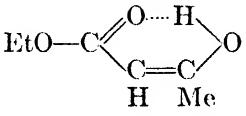
[keto]. The order of solvents has been found to be essentially constant for the β-diketone or β-ketonic ester types.[128] A glance at the table shows that the order of solvent influence on the keto-enol equilibrium cannot be correlated with either the dielectric constants or relative basicities of the solvents.

TABLE XVI

EFFECT OF SOLVENTS ON KETO-ENOL EQUILIBRIA

Solvents			Values of K^{128}		
Names	Diel. const.	Order of basicities	Et aceto-acetate	Me benzoyl acetate	Acetyl acetone
Water	81	1	0.004	0.008	0.24
Formic acid	47.9	4	0.011	0.028	0.9
Acetic acid	7.1	5	0.061	0.16	2.8
Methanol	33.7	2	0.074	0.16	2.6
Chloroform	5.0	6	0.089	0.19	3.8
Ethanol	25.7	3	0.15	0.35	5.3
Benzene	2.28	7	0.22	0.45	5.7
Hexane	1.8	7	0.9	2.2	12.0
Vapor			0.9		11.5

It is highly probable that the enolic forms of the above compounds are chelated.[129] Thus acetoacetic ester would have the formula



Since the resonance associated with the hydrogen bond [130] is a stabilizing influence, it stabilizes the enol relative to the keto form. Thus any solvent which would hinder chelation would favor the keto form. A solvent could do this in two different ways: (1) acting as donor to the hydroxylic hydrogen atom of the enol, or (2) acting as an acceptor toward the ketonic oxygen atom of the enol. Thus either the basic or acidic properties of a solvent might be called into play and would in either case favor the ketonic form. Such considerations as these seem sufficient to explain the observed order of solvent influence. Thus

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[128] (*a*) K. H. Meyer, *Ber.*, **45**, 2843 (1912); **47**, 826 (1914); (*b*) K. H. Meyer and F. G. Wilson, *ibid.*, **47**, 832, 837 (1914).

[129] Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925).

[130] Cf. Chap. VI, p. 163.

water, being highly basic, is most effective. Going down the list in Table XVI the remaining solvents down to the aprotic pair fall in an order which might well be the order of their acidities, since chloroform would be expected to have appreciably acidic properties.

Another influence is probably also at work.[129] The ketonic form is almost surely more polar than the enolic form since ketones have significantly larger dipole moments than alcohols and the difference would be augmented by chelation. This being so, the more polar solvents would associate preferentially with the keto form (dipole association) and this would be tantamount to preferential solvation of the keto form in the absence of other associating influences. Thus by **P 28** the equilibrium would be shifted toward the keto form as the dielectric constant of the solvent increased. Indeed Table XVI shows a trend in this direction broken only by chloroform and acetic acid.

The Effect of Acids on Furan Derivatives

Furan and many of its derivatives are extremely sensitive to acids.[131] Since the common property of acids is an ability to give up protons, this sensitivity may logically be ascribed to the instability or reactivity of the ion formed by the coordination of the furan oxygen atom with a proton. It is known that furan derivatives containing electronegative groups such as NO_2, CO_2H, SO_3H, CHO, and RC=O are relatively stable toward acids, and it has been shown that furfuryl chloride is less stable than its 5-nitro derivative.[132] All these observations find a ready explanation in the fact that electronegative groups weaken the donor properties of furan, whereas electron-releasing groups like methyl have the opposite effect.

The Addition of Hydrogen Halides to Unsaturated Compounds

It has already been shown that the addition of hydrogen chloride to olefins is thermodynamically impossible in dilute aqueous solutions; but the reaction can be carried out in concentrated aqueous solutions. Hence it should be possible in dilute solutions in moderately basic solvents. In such cases our interest reverts once more to kinetics. Since the attack on the olefin is made by the hydrogen ion, **P 29** would predict that the speed should become less as the solvent becomes more basic, i.e., as the proton becomes more firmly solvated.

Recent evidence showing this prediction to be correct has been furnished by Hennion and his collaborators.[133] They studied the addition

[131] Gilman and Wright, *Chem. Rev.*. **11**, 323 (1932).

[132] Gilman and Young, *Rec. trav. chim.*, **51**, 761 (1932).

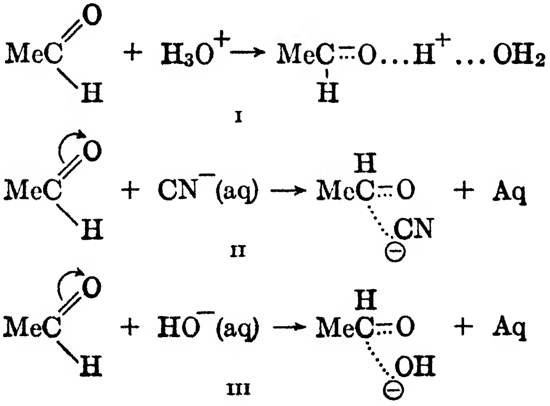
[133] (*a*) O'Connor, Baldinger, Vogt, and Hennion, *J. Am. Chem. Soc.*, **61**, 1454 (1939); (*b*) Hennion and C. F. Irwin, *ibid.*, **63**, 860 (1941).

of HCl and HBr to cyclohexene and 3-hexene in various solvents and found that the solvents arranged themselves in the following increasing order with respect to their facilitation of the reactions: Et_2O < dioxane < $CHCl_3 \leqq PhNO_2$ < BuBr < xylene < C_7H_{14}. This order corresponds exactly to the decreasing order of solvent basicity as given in Table II, as far as comparison is possible. They also investigated the addition of HBr and HCl to pinene in various solvents. The order of increasing reaction rates were found to be (1) for HBr: Et_2O < EtOBu < dioxane < $PhNO_2$ < C_7H_{14} < xylene < $CHCl_3$; and (2) for HCl: Et_2O < EtOBu < dioxane < MeOH < $PhNO_2$ < xylene < $CHCl_3$. The general order is what might be expected except that methanol is out of place.

Cyanhydrin Formation

The addition of hydrogen cyanide to acetaldehyde is a convenient example to illustrate the application of the method developed at the end of Chapter VII to reactions in solution. We shall attempt to make calculations which will show (1) whether the reaction is favored by basic or acidic solutions and (2) whether the aldehyde is electrophilic or nucleophilic.

In an acid solution either HCN or H_3O^+ could be the attacking reagent. Of these two, H_3O^+ is favored because it would call the electromeric effect of the carbonyl group into play more strongly than would the uncharged HCN; moreover, H_3O^+ is the stronger acid and hence would lose its proton more easily. In a basic solution the attack would be more apt to be made by CN^- or OH^- ions, because of their high concentrations, and to other factors which the calculations below will make clear. Accordingly there are three possible rate-controlling steps to be considered:



I

II

III

In calculating the corresponding values of $\Delta H^{\ddagger}_{\text{com}}$, $\Delta H_{C=O}$ may be omitted since it is common to all three. Thus, if the solvation process is symbolized by (s), we may write

$$\text{(I)} \quad \Delta H^{\ddagger}_{\text{com}} = \Delta H_{O\text{-}H^+} - \Delta H_{H^+(s)} = -334.4 + 365.6 = 31.2\ \text{kcal}$$

$$\text{(II)} \quad \Delta H^{\ddagger}_{\text{com}} = \Delta H_{C^+—^-CN} - \Delta H_{CN^-(s)} = -285.5 - 86.9 = -372.4$$

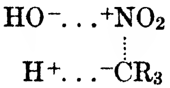
$$\text{(III)} \quad \Delta H^{\ddagger}_{\text{com}} = \Delta H_{C^+—^-OH} - \Delta H_{OH^-(s)} = -240.9 - \text{(unknown)}$$

The values for the heats of hydration of the ions are taken from the table of Bichowsky and Rossini[134] and are computed relative to the heat of formation of aqueous hydrogen ion, which is taken as zero. This convention does not complicate the use of these values in connection with other thermodynamic data for the above comparison, since one such value occurs in each equation. The substitution of $\Delta H_{C^+—^-C}$ for the unavailable $\Delta H_{C^+—^-CN}$ no doubt introduces some error, and no value is available for the heat of hydration of the hydroxyl ion, which is probably of the same order of magnitude as $\Delta H_{CN^-(s)}$; but the overpowering influence of the large value of $\Delta H_{H^+(s)}$ renders these inadequacies negligible in comparison. Thus, although the calculations do not make clear whether the hydroxyl or cyanide ion will lead the attack, they clearly establish the electrophilic character of the aldehyde in basic solutions (i.e., either II or III is more probable than I) and indicate that more facile addition is to be expected in basic than in acidic solutions, all of which is in accord with Lapworth's conclusions.[135]

It is interesting to note that whereas the English theory deduces the electrophilic character of aldehyde on the basis of the tendency of the positively charged carbonyl carbon atom to form a covalence, the present analysis points to the hydration of the hydrogen ion as being the determinative factor.

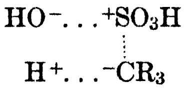
Nitration and Sulfonation

Since the nitration and sulfonation of hydrocarbon links involve the union of carbon with nitrogen or sulfur, respectively, and since the hydrogen ion is eliminated from the hydrocarbon and the hydroxyl ion from the acid, it seems inevitable that the critical complex be represented by some such pictures as



$$\begin{array}{c} HO^- \ldots {}^+NO_2 \\ \vdots \\ H^+ \ldots {}^-CR_3 \end{array}$$

and



$$\begin{array}{c} HO^- \ldots {}^+SO_3H \\ \vdots \\ H^+ \ldots {}^-CR_3 \end{array}$$

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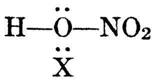
[134] Bichowsky and Rossini, *Thermochemistry of the Chemical Substances*, Reinhold Publishing Corp., 1936.

[135] See p. 54.

when nitric or sulfuric acids, respectively, are the active agents. If this is to be the case, it is obvious that any reagent which could weaken the O^-—N^+ or O^-—S^+ links would aid the reaction. This could be accomplished by any sufficiently strong acceptor, X, which could coordinate as follows:



$$\mathrm{H}{-}\underset{\underset{\mathrm{X}}{\cdot\cdot}}{\overset{\cdot\cdot}{\mathrm{O}}}{-}\mathrm{NO_2}$$

thus shifting the electrons of the O—N (or O—S) bond toward the oxygen atom. However, a very powerful acceptor would be required to do this, since HNO_3 and H_2SO_4 are not very basic. This suggests a strongly acidic solvent, like concentrated H_2SO_4. In cases where this is unsufficient the still stronger acceptor sulfur trioxide can be dissolved in the solvent medium. Thus the well-known practice of using "mixed acid" for nitrations and fuming sulfuric acid for sulfonations is readily explained. In this relation it is of interest to note that it has been shown by kinetic studies that when anthraquinone is sulfonated in fuming sulfuric acid only the sulfur trioxide acts as a sulfonating agent, the sulfuric acid merely serving as a solvent.[136]

It is also obvious that the water formed during the reaction will exercise its basic properties in competing with the nitric or sulfuric acids for the possession of X, thus impeding the main reaction. The nitration and sulfonation of anthracene in glacial acetic acid or ethyl alcohol solution have been found to be unmeasurably slow,[137] as one would expect in view of their weak acceptor properties and in the appreciable basicity of the ethyl alcohol.

Benford and Ingold [138] have studied the rates of nitration of aromatic hydrocarbons in various solvents and have classified the solvents studied as follows. Slow solvents: dioxane, glacial acetic acid, acetonitrile. Intermediate solvents: nitromethane, acetic anhydride. Fast solvent: concentrated sulfuric acid.

The "slow solvents" are either basic or weakly acidic and hence lack the strong acceptor properties which the reaction demands and which the fast solvent, sulfuric acid, possesses. But it seems surprising, at first thought, that nitromethane and acetic anhydride are "faster" solvents than the more acidic glacial acetic acid. Benford and Ingold believe that this is due to the ability of acetic anhydride and the aci-form of nitromethane to react with nitric acid to produce mixed anhydrides, $AcONO_2$ and $CH_2{=}NO{\cdot}ONO_2$, both of which are stronger

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[136] Lauer and Oda, *J. prakt. Chem.* [2], **144**, 32 (1935).

[137] Lauer and Oda, *Ber.*, **69B**, 141 (1936).

[138] Benford and Ingold, *J. Chem. Soc.*, 929 (1938).

nitrating agents than nitric acid itself, a fact which could have been predicted from the knowledge that nitric acid is an electrophilic reagent and hence $X^{-}—^{+}NO_2$ should be a stronger nitrating agent than $HO^{-}—^{+}NO_2$ if X is more electronegative than OH (**P 2**). This condition is met by the electronegative groups AcO^{-} and $CH_2{=}NO{\cdot}O^{-}$ in the above compounds.

Interesting sulfonation experiments have recently been carried out by Suter, Evans, and Kiefer.[139] They demonstrated that the addition of the acceptor sulfur trioxide to the donor dioxane produces addition products containing one or two moles of sulfur trioxide per mole of dioxane. When dioxane was added to the ternary complex in CCl_4 suspension it regenerated the binary complex with the evolution of heat, showing that a mobile neutralization, in the Lewis sense, was involved in all of these reactions. They refer to these two addition products, either separately or in mixtures, as the "D.S. reagent." This reagent was shown to sulfonate benzene slowly and *m*-xylene and anisole rapidly at room temperature. Naphthalene sulfonates somewhat more rapidly than benzene.

These reactions are readily understood. Since the SO_3 molecule is easily detached from the D.S. reagent it could readily undergo a partition between two bases. Although benzene is not a base, it is subject to attack by a strongly electrophilic reagent like SO_3, and since there was a large excess of benzene a sort of partition took place, resulting in the irreversible sulfonation of benzene. Similar reactions have been observed with the corresponding compound of SO_3 and pyridine,[140] but this addition compound is much less reactive than the D.S. reagent, as would be expected from the fact that pyridine is a stronger base than dioxane.

Among the reactions of the D.S. reagent is its ability to cause the addition of SO_3 to double bonds. In many such cases it has an advantage over the direct addition of SO_3 because the latter is too vigorous.

Bromination of Aromatic Hydrocarbons

Lauer and Oda [141] investigated the effect of different solvents on the velocity of bromination of anthracene. Their results are summarized in the following table where *k* is the bimolecular velocity constant and $-\Delta H_s$ is the heat of solution of bromine in kcal/mole in 0.00615 molar solutions at 20°. The fact that an essentially constant value (about 5.6

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[139] Suter, Evans, and Kiefer, *J. Am. Chem. Soc.*, **60**, 538 (1938).

[140] (*a*) Wagner, *Ber.*, **19**, 1158 (1886); (*b*) Baumgarten, *ibid.*, **59**, 1976 (1926); (*c*) Burkhardt and Lapworth, *J. Chem. Soc.*, 686 (1926).

[141] Lauer and Oda, *Ber.*, **69B**, 141, 146 (1936).

TABLE XVII[141]

KINETICS OF THE BROMINATION OF ANTHRACENE

Solvent	k (15°)	PZ	E	$-\Delta H_s$	$E + \Delta H_s$
Cyclohexane	13.0	2.7×10^6	6.890		
n-Hexane	18.3	2.3×10^6	6.750	1.110	5.640
Benzene	89.8	5.8×10^6	6.750		
Ethanol	144.0	5.7×10^{16}	18.600	13.000	5.600
Acetic acid	355	2.8×10^{10}	10.850	5.180	5.670

kcal) is obtained on subtracting the heat of solution of bromine from the activation energy is interesting. Lauer and Oda interpret this value as the activation energy for the gas reaction, assuming that the heat of solution of anthracene in these solvents is negligibly small. However, in the similar case of naphthalene (Table XII) the heat of solution is neither negligible nor is it constant as the solvent is varied, so that the interpretation of this quantitatively constant difference becomes difficult. If, however, we content ourselves with a less exacting explanation it is obvious that the parallelism between E and the heat of solution of bromine is just what we would have predicted from **P 29** since the bromine would largely have to break its coordination with the solvent in order to coordinate with the anthracene. In regard to the significant changes in PZ observed on passing from the nonpolar solvents to acetic acid and ethanol, it is seen that PZ increases with E, as so frequently is found to be the case. But if the increase in E is due exclusively to the solvation of bromine (as Lauer and Oda inferred from the constancy of $E + \Delta H_s$) it means that the bonds in the critical complex are more rigid (as they would be if the increase in E were due to electron-attracting substituents) and hence the theory of Fairclough and Hinshelwood, which explained the parallelism between E and PZ as due to a greater frequency of vibration in the more rigid intermediate complex, could not apply here.

Turning next to Norrish's theory we find a possible explanation in that HBr is a reaction product and would be more stabilized the more basic the solvents, thus leading to higher values of P in the order: hydrocarbons < acetic acid < ethanol. If, alternatively, one applies the point of view of the transition state theory, he must first decide whether or not solvation increases with the formation of the critical complex. Solvation effects due to greater dipole association with the more polar critical complex would presumably be second order effects as compared to solvation associated with the donor or acceptor properties of the bromine. The latter type of solvation would decrease on entering the transition state, the decrease being proportional to the acidity of the solvent if the bromine acted as donor, or to the basicity of the solvent if the coordinatively unsaturated bromine acted as acceptor. Owing to the high electronegativity of the halogens, their donor properties must be slight and hence we should not be surprised to find, as we did in Table XVII, that the bromine is most firmly solvated in the most basic solvent. The argument may now be quickly concluded. The formation of the critical complex involves the greatest desolvation when the solvent is most basic. Since desolvation means less orientation and more "freedom," $\Delta S^{\ddagger}$ (or PZ) must increase with the basicity of the solvent. This result was actually observed.

It is easy to see why the "general tendency" of PZ to increase with E is to be found in cases like this one where variations in PZ and E are the result of changing the solvent. It is merely that the breaking of solvation bonds requires energy (thus increasing E) and results in greater "freedom" (thus increasing PZ).

Our theory, then, predicts that increasing solvent basicity will be accompanied by higher values of both E and PZ. Since, however, E and PZ have opposite effects on the velocity constant it is necessary to know which one is larger if we are to know whether the velocity constant is increasing or decreasing, and our qualitative theory is incapable of doing this. Actually the variation of k is complex (Table XVII) and cannot be simply correlated with either E or PZ. Furthermore, the observed differences between the three hydrocarbon solvents would not have been predicted.

Lauer and Oda [142] also studied the bromination of benzene in various solvents and found definite evidence of the association of benzene. Their results in glacial acetic acid solution are given in Table XVIII, from which it is seen that both E and PZ rise rapidly after a certain concentration is exceeded. Since association would have much the same effects on E and PZ as solvation, the arguments used in connection with the bromination of anthracene may be applied here, with the result that the observed trends are in accord with the hypothesis that association occurs. Spectroscopic measurements corroborated the association hypothesis.

More of their data are reproduced in Table XIX. The figures chosen were obtained at essentially the same concentration, thus minimizing the effect of the associative influence. The trends in E and PZ on

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[142] Lauer and Oda, *Ber.*, **69B**, 851 (1936).

TABLE XVIII [142]

KINETICS OF THE BROMINATION OF BENZENE IN GLACIAL ACETIC ACID

Conc. (moles/l)	E (kcal/mole)	$PZ \times 10^{-10}$
0.00898	20.15	6.3
0.04440	20.15	5.5
0.04520	20.10	5.3
0.09100	21.60	50.0
0.11600	22.00	63.0

TABLE XIX [142]

KINETICS OF THE BROMINATION OF BENZENE

Solvent	Conc. (moles/l)	$k_{30°} \times 10^5$	E (kcal)	PZ
CCl_4	0.0680	2.19	6.90	1.96
HOAc	0.0560	4.45	29.15	3.70×10^{16}
C_6H_{14}	0.0444	21.0	20.15	5.50×10^{10}

passing from hexane to acetic acid are the same as those found in anthracene (Table XVII) and hence need not be discussed again; but the decided difference betweeen hexane and carbon tetrachloride calls for an explanation. In view of the facts that the dielectric constants and basicities of these two solvents cannot be essentially different, it is difficult to offer an explanation of this unexpected difference. The only significant difference between the two solvents is in their molecular geometry and hence the effect may be of a steric nature, as suggested by Lauer and Oda.

CHAPTER XI

ELECTRON-SHARING DISPLACEMENT REACTIONS

The two preceding chapters have been devoted to a consideration of the fundamental characteristics of electron-pairing reactions and the electron-sharing reactions of a certain group of substances which exhibit those properties commonly attributed to acids and bases. There remain for consideration those electron-sharing reactions which involve greater chemical inertia than the acid-base reactions and which, therefore, are in general slower. Typical of this class are the hydrolytic reactions of organic compounds.

In Chapter V brief consideration was given to the application of the English theory to hydrolytic reactions. It was pointed out that all substances fitted pretty well into either of two classes from the viewpoint of the effect of substituents on their speed of hydrolysis. If electron-releasing substituents facilitate hydrolysis, the substance is classified as "type A" and if the reverse is true, as "type B." The outstanding difficulty was the *a priori* classification of a given substance.

A continuation of the above discussion will be attempted in this chapter, attention being given in particular to questions of mechanism.

THE HYDROLYSIS OF ALKYL HALIDES

The Hughes-Ingold theory of the mechanism of the hydrolysis of alkyl halides was introduced in Chapter V, where their older work on the "molecularity" (unimolecular or bimolecular) of the reactions was correlated with the electron-releasing properties of the alkyl groups in the alkyl halide molecules and with the electron-attractive properties of negative ions which might compete with the hydroxyl ions of water for the possession of the alkyl ions. The announcement of the above theory resulted in a flood of polemics,[1, 2] which culminated in a group

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[1] (*a*) Wm. Taylor, *J. Chem. Soc.*, 1853 (1937); *J. Am. Chem. Soc.*, **60**, 2094 (1938); (*b*) Olson and Halford, *ibid.*, **59**, 2644 (1937); (*c*) Steigman and Hammett, *ibid.*, **59**, 2536 (1937); (*d*) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937); (*e*) P. D. Bartlett, *ibid.*, **61**, 1630 (1939); (*f*) Winstein, *ibid.*, **61**, 1635 (1939); (*g*) Ogg, Jr., *ibid.*, **61**, 1946 (1939).

[2] (*a*) Hughes et al., *J. Chem. Soc.*, 1252 (1937); 881 (1938); (*b*) Bateman, Hughes, and Ingold, *J. Am. Chem. Soc.*, **60**, 3080 (1938).

of papers published simultaneously by the Hughes-Ingold school.[3] The controversy centered on the question of the validity of the kinetic methods used to establish the molecularity of the hydrolyses.

The evidence presented by the Hughes-Ingold group is very extensive and very involved, but the high points are conveniently summarized in the following five sections.

The Kinetic Form of Substitution Reactions

It is well known that the order of a solvolytic reaction is not diagnostic of its mechanism. Thus the hydrolysis of sugar, although bimolecular, involves a first order rate equation. If, however, the hydrolysis of an alkyl halide is correctly represented by the equation

$$\mathrm{RCl} \underset{2}{\overset{1}{\rightleftarrows}} \mathrm{R^+ + Cl^-} \xrightarrow[+\mathrm{H_2O}]{3} \mathrm{ROH + H^+ + Cl^-} \qquad (1)$$

it is possible to devise tests which yield decisive information on the molecularity of the rate-controlling step. The argument is as follows:

Let v_1, v_2, and v_3 be the instantaneous rates of the three reactions represented in Equation 1. If v_1 is much smaller than v_3 the over-all rate may be shown to be $v_1v_3/(v_2 + v_3)$. If step 1 is to be considered as the sole rate-determining step it is obvious that a further restriction must be introduced, viz., $v_2 \ll v_3$. It appears that ordinarily this second restriction is not very well satisfied, and it may be shown that when it is not the calculated first order rate constants should diminish with the progress of the reaction at a rate which is greater the higher the initial concentration of the alkyl chloride. In case the hydrolysis involves a bimolecular mechanism and if, as above, it is irreversible from the standpoint of practical kinetics, it should proceed at a first order rate which is uniform and independent of the initial concentration of the alkyl halide. Experiments made on those alkyl halides which previously had been considered to involve unimolecular hydrolysis showed that most of them deviated from a first order rate law in accord with the above predictions and, furthermore, showed just that particular form of kinetics which the unimolecular mechanism predicts.

In the particular case of *tert.*-butyl chloride, recent additional evidence indicates the unimolecularity of its hydrolysis. Koskoski, Thomas, and Fowler[4] measured the rate of the exchange reaction between radioactive chloride ion and *tert.*-butyl chloride in formic acid solution and found the rate of ionization to be the same as the rate of hydrolysis of

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[3] Hughes et al., *J. Chem. Soc.*, 913, 920, 925, 935, 940, 945, 949, 956, 960, 966, 971, 974, 979 (1940).

[4] Koskoski, Thomas, and Fowler, *J. Am. Chem. Soc.*, **63**, 2451 (1941).

tert.-butyl chloride in formic acid as determined by Bateman and Hughes.[5]

The Criterion of Product Composition

The effect of the solvent on product composition furnishes good evidence as to mechanism. If, for example, *tert.*-butyl chloride is subjected to the solvolytic action of an alcohol-water mixture, one would expect the formation of both Me_3COH and Me_3COR regardless of whether the mechanism were S_N1 or S_N2. But the proportion of these two products in the latter case should be predictable from the values of the bimolecular rate constants for the competing hydrolysis and alcoholysis. Such bimolecular constants were calculated by Olson and Halford[1b] and shown by Bateman, Hughes, and Ingold[2b] not to predict the correct ratio of the two products. The S_N1 mechanism would demand that the ratio of the products should be proportional to the mole ratio of water and alcohol, and such is found to be approximately the case.[1e]

The Effect of Salt Additions on the Reaction Rates and the Products

Regardless of whether the mechanism is uni- or bimolecular, it is known that, if the ionic strength of the reacting solution is increased by the addition of salts, the reaction rate will increase and the calculated first order constants will rise with the progress of the reaction.

The theory of this effect is perhaps most easily understood in terms of the Hughes-Ingold theory of solvent action discussed in the preceding chapter, according to which the activation energy of reaction 1 in Equation 1 may be decreased by the exothermic solvation of the ions, which begins to take effect long before ionization is complete and which accordingly results in a transition complex. This view leads to the conclusion that solvents should increase the speed of this reaction in proportion to their ability to solvate ions. Furthermore the solvent effect is much greater in the unimolecular than in bimolecular substitutions because of the greater diffusion of charges in the transition state of the latter. Similarly the transition state charges can stabilize themselves if they can collect suitable ionic atmospheres, and this stabilization results in a decrease in activation energy.

In the unimolecular mechanism there will be superimposed on this ionic strength effect a mass action effect operating in the reverse direction if the negative ion of the salt is identical with that of the alkyl halide. Thus in Equation 1 the addition of chloride ions would accelerate reaction 2 and thus decrease the rate of hydrolysis. This effect would not be expected if the hydrolysis were bimolecular.

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[5] Bateman and Hughes, *J. Chem. Soc.*, 1187 (1937).

These "ionic strength" and "mass action effects" were given quantitative expression and the experimentally determined rates of hydrolysis for the S_N1 group of alkyl halides were shown to be in accord with the predictions made on the basis of the S_N1 mechanism.

The mass action effect of the common ions seems to constitute especially good evidence for the S_N1 mechanism since it shows clearly that more than one stage is involved, "that some earlier stage than the product-forming one is rate determining, that some earlier stage than the product-forming one is reversible, and that one product of the reversible stage is the halide ion deriving from the alkyl halide."

Further evidence derived from experiments on added salts is obtainable from the addition of sodium azide. The azide ion competes with the hydroxyl ion for union with the alkyl ion, and since the alkyl azides are not hydrolyzed, the amount in which they are formed can be conveniently determined. Experiment showed that the amounts of alkyl azides formed were not those which would be predicted on the basis of a bimolecular mechanism.

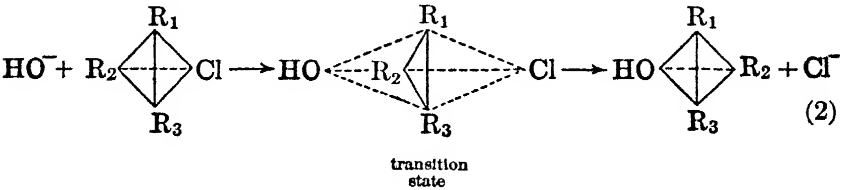
Similar experiments were performed in which two different halides of the same alkyl were hydrolyzed in aqueous acetone in the presence of sodium azide. If parallel reactions are carried out with RCl and RBr and if the reaction is bimolecular, "no particular relation should exist between the composition of the products obtained in the two experiments, because the added anion is attacking different entities, the alkyl chloride and the alkyl bromide molecules. On the other hand, the unimolecular mechanism involves the definite requirement that the composition of the two products should be identical, because in this mechanism the added anion attacks the alkyl cation, which is the same for both alkyl halides. This, then, is essentially a test for the unimolecular mechanism. The necessary comparison of product compositions is available in the reactions of benzhydryl chloride and benzhydryl bromide in aqueous acetone containing sodium azide. The rates of these reactions are very different, but . . . the product compositions are identical to within the limits of precision of the measurements; that is to say, the requirement of the unimolecular mechanism is satisfied."

Stereochemical Evidence

The Hughes-Ingold theory of substitution in general and hydrolysis in particular receives support from studies made on reactions which proceed with stereochemical inversion. Since reactions of this type, usually classified as "Walden inversions," have not yet been discussed in this book, it will be well to digress momentarily from the subject of hydrolysis in order to make clear the present theoretical status of these phenomena.

The initial discovery of the Walden inversion was made by Walden in 1893 and developed by him in the succeeding years.[6] As an example may be mentioned the conversion of l-chloro and l-bromosuccinic acids by means of the various basic reagents. He found that the hydroxides of potassium, rubidium, and ammonium gave practically pure *d*-malic acid, moist silver oxide gave pure *l*-malic acid, and the hydroxides of sodium, barium, lead, and lithium gave mixtures in which the *l*-acid was in excess. These pioneer investigations have been followed by a multitude of others which have established the generality of the phenomenon. It may now be said with some assurance that when an atom or group attached to an asymmetric carbon atom is replaced by another atom or group, optical inversion results [7] although the phenomenon is frequently obscured by successive reactions.

The theory of the Walden inversion has also undergone considerable development.[8] Most of the theories advanced have one idea in common, viz., the formation of an intermediate complex in which the entering group becomes attached to the asymmetric carbon atom in such a position as to force inversion. The most satisfactory picture of this intermediate complex is the one given by the modern transition state theory, which would consider that the new bond is being formed simultaneously with the rupture of the original bonds. On this basis optical inversion would result if conditions were such that the entering group were forced to make its attack on that face of the carbon tetrahedron opposite the group about to be expelled. The process is illustrated in Equation 2, which shows how optical inversion could result from the



(2)

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[6] Walden, *Ber.*, **26**, 210 (1893); **28**, 2769 (1895); **29**, 133 (1896); **32**, 1833 (1899).

[7] (*a*) Olson, *J. Chem. Phys.*, **1**, 418 (1933); also Ref. 8*o*; (*b*) Olson and Long, *J. Am. Chem. Soc.*, **58**, 393 (1936); (*c*) Young and Olson, *ibid.*, **58**, 1157 (1936).

[8] (*a*) E. Fischer, *Ann.*, **381**, 126 (1911); (*b*) Werner, *Ber.*, **44**, 873 (1911); *Ann.*, **386**, 70 (1912); (*c*) Pfeiffer, *ibid.*, **383**, 123 (1911); (*d*) Le Bel, *J. chim. phys.*, **9**, 323 (1911); (*e*) Gadamer, *J. prakt. Chem.*, **87**, 372 (1913); (*f*) G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, 1923, p. 113; (*g*) Lowry, *Conseil de Chim. Solvay*, 130 (1925); (*h*) Meisenheimer, *Ann.*, **456**, 126 (1927); (*i*) Holmberg, *Ber.*, **60**, 2194 (1927); (*j*) Kenyon and Phillips, *Trans. Faraday Soc.*, **26**, 451 (1930); (*k*) Lipscomb, *J. Chem. Soc.*, 415 (1930); (*l*) Rördam, *ibid.*, 2017 (1930); (*m*) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); (*n*) Olson, Ref. 7*a*; (*o*) Cowdry, Hughes, Ingold, Masterman, and Scott, *J. Chem. Soc.*, 1252 (1937).

displacement of a chloride by a hydroxyl ion. On the other hand, if the hydroxyl ion could launch its attack on the carbon atom from the side of the chlorine atom, retention of configuration would surely result. It is thus seen to be important to include in the theory a consideration of the forces determining the direction of attack.

Meer and Polanyi [8m] pointed out that in reactions like that of Equation 2 the dipole field in the C—Cl bond would force the hydroxyl ion to approach from the side opposite the chlorine atom. Hughes and Ingold,[8o] however, advanced quantum mechanical reasons for believing that, independently of the above electrostatic repulsions, the minimum activation energy would obtain when the attacking ion approached from that direction which would lead to inversion; moreover, they expressed the belief that the quantum mechanical forces are more powerful than the electrostatic ones. As a critical test of their contention they chose the hydrolysis of 'onium cations. In this case it would be expected, if the electrostatic forces are determinative, that the attack of the hydroxyl ion on $\mathrm{C—\overset{+}{N}R_3}$ would lead to a transition state in which the negative and positive poles would be as close to each other as possible and substitution would ensue with retention of configuration. Actually inversion has been shown to take place in such a reaction,[9] thus supporting Hughes and Ingold.

It is apparent, therefore, that reactions occurring by the S_N2 mechanism should result in optical inversion, since the space relationships in their transition states would be as pictured in Equation 2. The picture for the unimolecular mechanism is quite different, however, for in this case the carbonium ion might exist free for a length of time comparable with the period of vibration associated with its stereochemical inversion.[8l] In this case racemization would occur. If, however, there is a sufficiently high concentration of the ions which are to react with the carbonium ion, or if the solvent is reactive enough to fulfill the same function, or if the carbonium ions in question are highly reactive, the result will be that the second stage of the reaction will occur before the stereochemical configuration of the ion has had time to change.[8o] Retention of configuration would then result. It is also possible, when the carbonium ion is short lived, that at the moment of the onset of the secondary reaction the ejected ion will still be close enough to its former partner to produce a dissymmetric shielding of the latter, and substitution with inversion will be preponderant.[8o] Obviously cases involving the unimolecular mechanism are subject to so many influences that an accurate analysis of such problems is difficult. However, one simple

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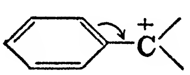
[9] Read and Walker, *J. Chem. Soc.*, 308 (1934).

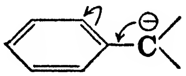
conclusion emerges from these considerations, that the chances are very great that in reactions of the S_N1 or S_E1 types, producing respectively carbon cations or anions, either retention of form or appreciable racemization will result. Furthermore, since neither of these occurrences would be expected with bimolecular attacks on the asymmetric carbon atom, it is evident that they may be taken as diagnostic of the unimolecular mechanism.

The highly satisfactory concordance achieved by the kinetic method and the optical method of establishing mechanism is shown in Table I, which summarizes certain experiments made by the Hughes-Ingold group.[10] The first four columns need no explanation; the fifth and sixth present the results of kinetic studies. A second order reaction always means a bimolecular mechanism, whereas, as explained above, a first order reaction may mean either a uni- or bimolecular mechanism. The next column lists the qualitative effect of substitution on configuration (Rac means racemization, Ret retention, and I inversion) and the last column the proportionate retention of optical purity associated with the inversion or retention of configuration.

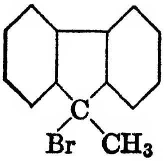
The ability of substituents to promote the unimolecular mechanism has already been discussed in Chapter V. It might be added, however, that the presence of an unsaturated group such as phenyl, at the seat of substitution, would stabilize the ion by resonance:



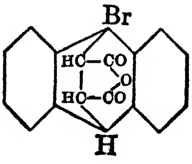
or



It would also flatten the ion. The net result will be greater racemization. Conversely, any influence which prevents coplanarity of the atoms or rings attached to the carbon atom which is striving to become an ion will raise the energy hump which is associated with the formation of the ion. As an example of this phenomenon Bartlett and Cohen [11] showed that whereas 9-bromo-9-methyl fluorene (I) in ethyl alcoholic solution at 25° formed bromide ion at a unimolecular rate with a half period of about 5 minutes,



I



II

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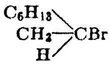
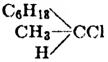
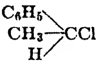
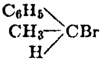
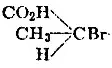
[10] Cowdrey, Hughes, and Ingold, *J. Chem. Soc.*, 1224 (1937).

[11] Bartlett and Cohen, *J. Am. Chem. Soc.*, **62**, 1183 (1940).

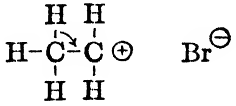
TABLE I[10]

RELATION OF OPTICAL EFFECT TO KINETICS AND MECHANISM OF SUBSTITUTION

Halide substituted	Substitution process	Solvent	Attacking reagent	Reaction		Effect on configuration	Retention of optical purity
				Order	Mech.		
 $(C_6H_{13})(CH_3)(H)CBr$	Hydroxylation	60% EtOH	OH^-	2	S_N2	I	96%
	Hydroxylation	60% EtOH	H_2O	1	S_N1	Rac + I	66
	Ethoxylation	60% EtOH	OEt^-	2	S_N2	I	96
	Ethoxylation	60% EtOH	EtOH	1	S_N1	Rac + I	74
	Ethoxylation	Anhyd. EtOH	OEt^-	2	S_N2	I	~ 100
 $(C_6H_{13})(CH_3)(H)CCl$	Ethoxylation	Anhyd. EtOH	OEt^-	2	S_N2	I	~ 100
 $(C_6H_5)(CH_3)(H)CCl$	Hydroxylation	H_2O	H_2O	..	S_N1	Rac + I	17
	Hydroxylation	60% aq. acetone	H_2O	1	S_N1	Rac + I	5
	Hydroxylation	80% aq. acetone	H_2O	1	S_N1	Rac + I	2
	Methoxylation	Anhyd. MeOH	MeO^-	2	S_N2	I	High
	Methoxylation	Anhyd. MeOH	MeOH	1	S_N1	Rac + I	Low
	Ethoxylation	Anhyd. EtOH	OEt^-	2	S_N2	I	High
	Ethoxylation	Anhyd. EtOH	EtOH	1	S_N1	Rac + I	Low
 $(C_6H_5)(CH_3)(H)CBr$	Hydroxylation	H_2O	H_2O	..	S_N1	Rac + I	Low
 $(CO_2H)(CH_3)(H)CBr$	Hydroxylation	Dil. aq. H_2SO_4	H_2O	1	S_N2	I	~ 100
	Methoxylation	Anhyd. MeOH	MeO^-	2	S_N2	I	~ 100
	Methoxylation	Anhyd. MeOH	MeOH	1	S_N2	I	~ 100
 $(CO_2^-)(CH_3)(H)CBr$	Hydroxylation	H_2O	OH^-	2	S_N2	I	80–100
	Hydroxylation	H_2O	H_2O	1	S_N1	Ret	90–100
	Methoxylation	Anhyd. MeOH	OMe^-	2	S_N2	I	85–100
	Methoxylation	Anhyd. MeOH	MeOH	1	S_N1	Ret	90–100

forming 9-methyl-9-ethoxyfluorene in 52% yield, the compound II, which presents a similar structural environment for the bromine atom, suffers no bromine replacement when boiled for 15 to 18 hours with 15% to 30% potassium hydroxide. These results are most satisfactorily accounted for on the basis of steric hindrance. It is unlikely that compound II would suffer bromine replacement by mechanism S_N2, not only because it is a tertiary halide but also because the attacking negative ion could not approach the carbon atom in question from the preferred direction, viz., the direction which would produce stereochemical inversion. The alternative mechanism, S_N1, demands the production of a carbonium ion, and such an ion could not be stabilized by resonance unless the carbonium carbon atom, the attached bridge atom, and both benzene rings are all in one plane.[11] This is obviously impossible in compound II for steric reasons but readily possible in compound I.

On the basis of these arguments one might wonder how a secondary or tertiary alkyl halide can yield a carbonium ion which is sufficiently stable to permit of a S_N1 reaction. The explanation is readily found in the concept of hyperconjugation. Thus no stabilization by resonance is possible in the carbonium ion produced from methyl bromide, whereas in ethyl bromide it becomes conceivable



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}\oplus \qquad Br^{\ominus}}$$

and in secondary and tertiary halides it becomes still more probable owing to the increasing number of contributing structures (**P 13**).

The Effect of Structural Changes

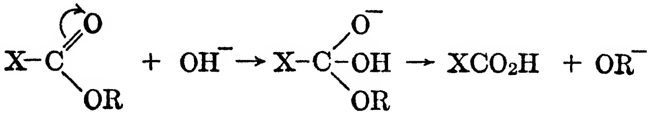
In the preceding sections we have found excellent concordance between the mechanism of homogeneous nucleophilic substitution reactions as deduced from their kinetic form, the accompanying phenomena of optical inversion found when substitution takes place on asymmetric carbon atoms, and the effects produced by variation in ionic strength and solvent. In order to round out the mass of dovetailing evidence which has been accumulated we need only mention the effects of substitution of the alkyl halide and of alteration of the attacking reagent, which were discussed in Chapter V. Much evidence of this sort has accumulated, but its detailed discussion would profit us little. Suffice it to say that these last two sources of evidence fit well into the general picture.

THE HYDROLYSIS OF CARBOXYLIC ESTERS

Probably no reaction has been more extensively studied than carboxylic ester hydrolysis, and certain conclusions drawn from this multitude of studies have become such common knowledge that there is no need to do more than list them here. These reactions are slow reversible reactions whose equilibrium conversions are readily measured. They are catalyzed both by hydrogen and hydroxyl ions. The alkaline hydrolysis of an ester is a second order reaction between the ester molecules and the hydroxyl ions, whereas the acid hydrolysis may probably best be represented as a ternary reaction between ester, water, and the catalyzing acid.

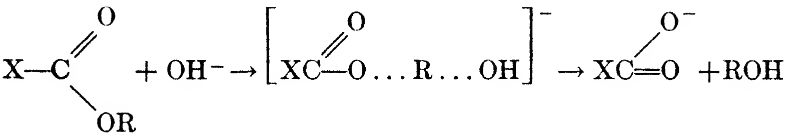
Mechanism

A priori there seem to be two equally possible mechanisms for the alkaline hydrolysis of esters: first, a nucleophilic attack on the carbonyl carbon atom by the hydroxyl ion followed by the elimination of the OR^- ion which reacts simultaneously or subsequently with water:


(3a)

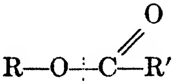
$$OR^- + H_2O \rightarrow ROH + OH^- \qquad (3b)$$

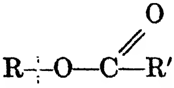
or, second, a nucleophilic attack on R by OH^- ion resulting in a typical three-center displacement reaction:


(4)

The latter mechanism would surely result in stereochemical inversion if ROH were an optically active alcohol. The fact that such inversion has never been observed[12] indicates strongly that Equation 4 does not correctly represent the mechanism. The close analogy between Equation 3 and the thoroughly investigated addition of cyanide ions to carbonyl compounds makes the first mechanism much more probable.

It will be noticed that according to mechanism 3 the bond attaching the oxygen atom to the carbonyl group in the ester is broken, whereas mechanism 4 demands that the O—R link be broken. Definite proof that the former occurs has been furnished by Polanyi and Szabo,[13] who employed the principle of "labeling" the oxygen of the hydrolyzing water by shifting the ratio of the isotopes O^{16} and O^{18} contained in it and determining, after the alkaline hydrolysis of amyl acetate, whether or not the labeled oxygen atoms were present in the alcohol. This was accomplished by dehydrating the alcohol and determining the isotopic ratio of the oxygen in the water thus produced. The ratio was found to be normal, thus showing that the cleavage occurred in accordance with *A* and not *B:*


(*A*)


(*B*)

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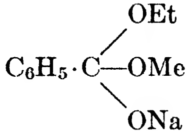
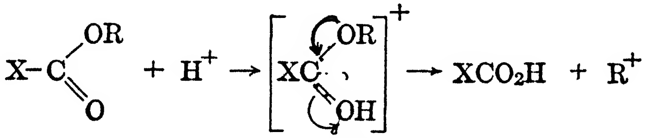
[12] (*a*) Holmberg, *Ber.*, **45**, 2997 (1912); (*b*) Fischer, *Ann.*, **394**, 360 (1912); (*c*) Hückel and Frank, *ibid.*, **477**, 137 (1930); (*d*) Verkade, *ibid.*, **477**, 287, 297 (1930).

[13] Polanyi and Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

since, if *B* had occurred, hydroxyl ions from the water would have combined with R to produce $RO^{16}H$ and $RO^{18}H$. This is in accord with mechanism 3 and not mechanism 4. That intermediate compounds or ions such as the one postulated in Equation 3 may have at least a transitory existence is indicated by the fact that an addition compound of ethyl benzoate with sodium methoxide was actually isolated by von Pechmann,[14] who assigned it the following structure:



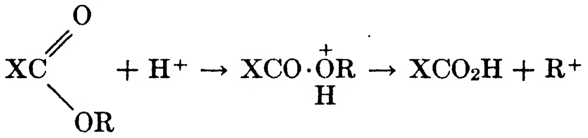
The acid catalyzed hydrolysis, which is almost surely an example of general acid catalysis,[15] likewise could be assigned several reasonable mechanisms on an *a priori* basis. Thus it is known that the carbonyl oxygen atom has definite basic tendencies[16] which would be enhanced by its electromeric properties, $>C\overset{\curvearrowright}{=}O$, and the following mechanism is conceivable:[17]



(5a)

$$R^+ + HOH \rightarrow ROH + H^+ \qquad (5b)$$

However, since the singly linked bicovalent oxygen atom would be expected to be more strongly basic than the carbonyl oxygen it would seem more likely that this oxygen atom would be the one to coordinate with the proton. In this case the reaction could proceed by alternative paths, depending upon which of the two oxygen bonds is broken:



(6a)

$$R^+ + H_2O \rightarrow ROH + H^+ \qquad (6b)$$

$$XCO_2R + H^+ \rightarrow XCO\cdot\underset{H}{\overset{+}{O}}R \rightarrow X\overset{+}{C}{=}O + ROH \qquad (7a)$$

$$X\overset{+}{C}{=}O + H_2O \rightarrow XCO_2H + H^+ \qquad (7b)$$

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[14] von Pechmann, *Ber.*, **31**, 503 (1898).

[15] I. Roberts and Urey, *J. Am. Chem. Soc.*, **61**, 2584 (1939).

[16] Baker, *J. Chem. Soc.*, 307 (1931).

[17] C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 756 (1932).

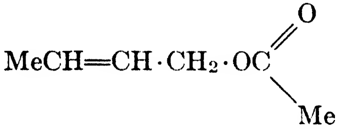
It will be noticed that both mechanisms 5 and 6 postulate the transitory existence of R^+ ion. That such an ion is probably not produced in acid hydrolysis and hence that mechanism 7 is the only one of the three which is possible was demonstrated by the Ingolds,[17] who based their work on the previous demonstration of Burton [18] that the anionotropic isomerization

$$\mathrm{ACHX{\cdot}CH{=}CHB} \rightarrow \mathrm{ACH{=}CH{\cdot}CHBX} \qquad (8)$$

involves the liberation of the free alkyl ion which we would expect to have the mesomeric structure

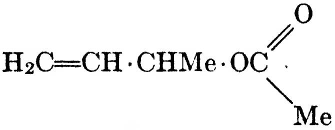
$$\mathrm{ACH{-}CH{=}CHB^+}$$

This mesomerism readily accounts for the isomerization. With this knowledge in mind the Ingolds hydrolyzed crotyl acetate (I) and α-methylallylacetate (II)



$$\mathrm{MeCH{=}CH{\cdot}CH_2{\cdot}OC({=}O)Me}$$

(I)



$$\mathrm{H_2C{=}CH{\cdot}CHMe{\cdot}OC({=}O)Me}$$

(II)

in acid solution until upward of 90% of hydrolysis had occurred; the reactions were then forced to completion by alkaline saponification and the alcohols isolated. It was found that no isomerization had occurred in either case, thus strongly indicating that the crotyl and α-methylallyl ions had never been liberated.

More recently the same conclusion has been reached by a heavy oxygen study of acid catalyzed ester hydrolysis.[19]

The probable existence of the intermediate compound postulated in mechanism 7 is indicated by the fact that Maas and McIntosh,[20] working at −36°, isolated a saltlike addition compound of ethyl acetate and hydrogen bromide. Further evidence of such compound formation was furnished by Kendall et al.[21] from the analysis of freezing point data.

We are thus finally led to the conclusion that mechanisms 3 and 7, applying respectively to basic and acidic hydrolysis, are in accord with the experimental facts thus far discussed. A further understanding of these reactions emerges from an application of our basic electronic principles. Thus in Equation 3*a* the addition of the hydroxyl ion

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[18] Burton, *ibid.*, 1650 (1928).

[19] Datta, Day, and Ingold, *J. Chem. Soc.*, 838 (1939).

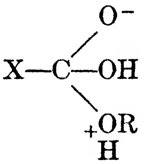
[20] Maas and McIntosh, *J. Am. Chem. Soc.*, **34**, 1272 (1912).

[21] (*a*) Kendall and Booge, *J. Chem. Soc.*, **127**, 1768 (1925); (*b*) Kendall and C. V. King, *ibid.*, **127**, 1778 (1925).

destroys the resonance which was initially present in the ester molecule, thus weakening the C—OR linkage. This same bond is further weakened by the $+I$ effect of the free negative pole which makes the oxygen atom still more electron-rich so that when the bond breaks the binding electrons will go with the oxygen atom. Similarly, in Equation 7, the positive pole in the intermediate ion exerts a strong $-I$ influence on the $\mathrm{C{-}\overset{+}{\underset{H}{O}}R}$ link, weakening it and making the oxygen atom more electron-rich (in relation to this one bond).

There is some uncertainty, however, about Equations 3*b* and 7*b* since it may well be, according to the transition state theory, that neither of the bond-weakening agencies described above are alone sufficient to break the bond but are required to act together, the negative pole pushing the electrons of the C—OR bond from one side and the positive pole pulling them from the other side. This viewpoint is the modern equivalent of the older Lowry theory[22] in which the flow of electrons through the molecule from one pole to the other is considered as analogous to electrolysis, the theory being called, therefore, the "electrolytic theory of catalysis."

On the basis of this theory we might be tempted to consider that either the H^+ or OH^- of the catalyst would first add to the ester and that the other ion (OH^- or H^+, respectively) would be furnished by the water to give in each case the same intermediate complex:



Lowry points out, however, that since hydrogen and hydroxyl ions cannot coexist in the same solution in very large concentrations, it follows that a molecule of water, and not merely one of its ions, must add to the ester molecule along with the hydrogen or hydroxyl ion donated by the catalyst. Whether these additions take place simultaneously or in two successive steps cannot be predicted, but Moelwyn-Hughes[23] points out that "it may be assumed that reaction takes place whenever a water molecule collides with sufficient violence against a substrate molecule, a

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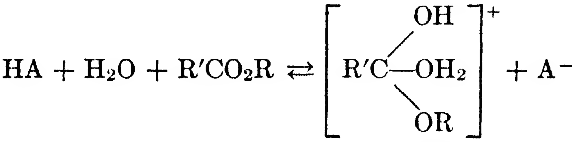
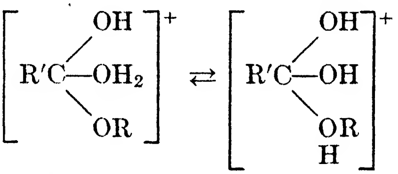
[22] (*a*) Lowry, *J. Chem. Soc.*, 1381 (1925); 2554 (1927); *Trans. Faraday Soc.*, **24**, 545 (1928); (*b*) Waters and Lowry, *Physical Aspects of Organic Chemistry*, Van Nostrand Co., 1936, pp. 267–272.

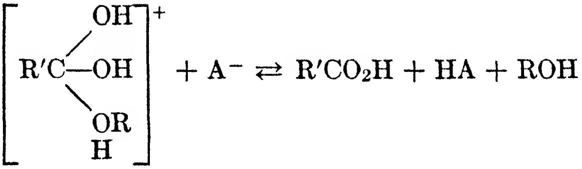
[23] Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Press, 1933, p. 250.

hydrogen ion being in the collision zone. This is equivalent to making the rate of change dependent upon ternary collisions with unit probability that the activated ternary complex will undergo transformation." Calculations made on this basis for the hydrolysis of several esters gave velocity constants in fair accord with experiment.

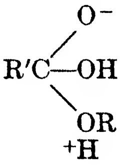
Roberts and Urey [15] have also presented evidence which indicates that the reactive complex in acid hydrolysis (or its reverse, esterification) must involve both water molecules and the acid catalyst. These authors point out that the mechanism proposed by Ingold, involving the intermediate ion $X\overset{+}{C}O$ (Eq. 7) is eliminated since none of its steps contains the correct reactive complex. By the same argument they rule out a recent theory by Watson.[24] Several possible mechanisms survive their attack, among them the one proposed by Lowry. Roberts and Urey formulate it as follows:


(9a)


(9b)


(9c)

The complex produced in step 9*b* is readily seen to have the required structure for Lowry's "internal electrolysis" if we consider one of the hydroxyl groups to be somewhat ionized:



There seems to be no need to press this point, however.

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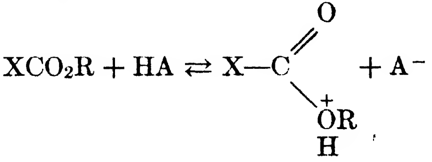
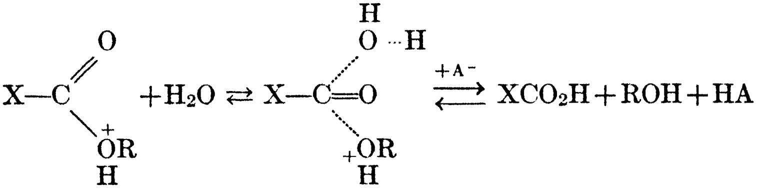
[24] (*a*) Evans, Morgan, and Watson, *J. Chem. Soc.*, 1168 (1935); (*b*) Watson, *Modern Theories of Organic Chemistry*, Oxford Press, 1937, pp. 130, 211.

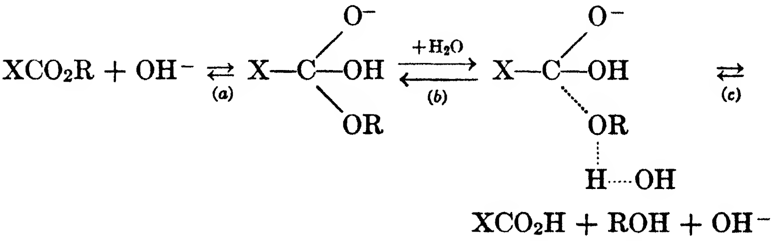
All the requirements discussed above are met equally well by the following formulation:


(10a)


(10b)

which attempts to represent the reaction in terms of the transition state theory. The hydrogen ion from the acid coordinates with the oxygen atom of the OR group (this step will involve little if any activation energy[24c]) while the oxygen atom of the water molecule leads a nucleophilic attack on the central carbon atom, causing the stretching and the eventual rupture of the $\mathrm{C}\text{—}\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{R}$ bond which has already been weakened by the positive charge conferred by the proton. Since the second step (10*b*) involves bond rupture it must be the rate-controlling step. It will incidentally be noticed that the critical complex pictured in Equation 10*b* contains both water and hydrogen ion, as demanded by the considerations set forth by Roberts and Urey. This picture is simply a modernization of the Lowry mechanism.

The basic hydrolysis can be similarly formulated, taking into consideration that it is a second order reaction between ester and hydroxyl ion and involves the rupture of the C—OR link.


(11)

In this case the main idea of the Lowry theory is kept by interposing the electrophilic attack of the water molecule which, by a displacement

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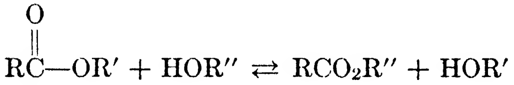
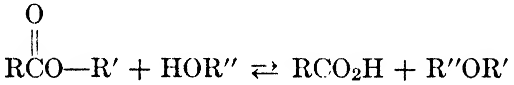
[24c] Newling and Hinshelwood, *J. Chem. Soc.*, 1357 (1936).

mechanism, breaks the C—OR linkage which has already been weakened by the repulsive effect of the free negative pole. Steps *a* and *b* may, of course, be simultaneous.

It may have been noted in the above discussion that the experimental evidence cited in support of the approved mechanisms involved only the esters of primary and secondary alcohols. It has recently been shown [25a] that a different mechanism operates in the alcoholysis and hydrolysis of carboxylic esters of *tert.*-butyl alcohol. Alcoholysis studies have a certain advantage over experiments on hydrolysis in that the latter would yield the same products regardless of whether the O-Alkyl or O-Acyl link is ruptured, whereas this is not the case in alcoholysis, as is shown by the following equations:



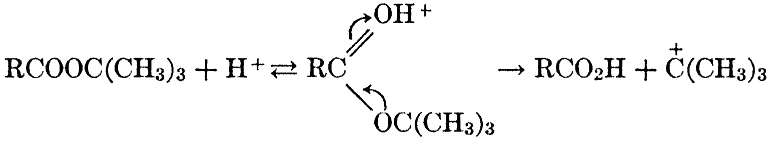
$$\mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}{—}OR' + HOR'' \rightleftarrows RCO_2R'' + HOR'}$$



$$\mathrm{R\overset{\overset{\displaystyle O}{\|}}{C}O{—}R' + HOR'' \rightleftarrows RCO_2H + R''OR'}$$

The work in question showed that the acid-catalyzed and uncatalyzed alcoholysis of the *tert.*-butyl esters proceed by the latter mechanism and hence differ from the corresponding cases involving esters of primary and secondary alcohols. The base-catalyzed alcoholysis, however, proceeds by the former mechanism.

The mechanism suggested by Cohen and Schneider [25a] for the acid-catalyzed reaction is as follows:



$$\mathrm{RCOOC(CH_3)_3 + H^+ \rightleftarrows RC\begin{matrix}{/\!\!/}OH^+\\ \diagdown OC(CH_3)_3\end{matrix} \rightarrow RCO_2H + \overset{+}{C}(CH_3)_3} \qquad (12a)$$

$$\mathrm{\overset{+}{C}(CH_3)_3 + CH_3OH \rightarrow CH_3OC(CH_3)_3 + H^+} \qquad (12b)$$

$$\mathrm{RCO_2H + CH_3OH \rightleftarrows RCO_2CH_3 + H_2O} \qquad (12c)$$

In place of the catalyzing acid the weaker acid methanol might start the reaction, thus resulting in a solvolytic reaction of the S_N1 type.

In order to show that the conclusions reached in their studies on alcoholysis applied equally well to hydrolysis, Cohen and Schneider con-

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[25] (*a*) Cohen and Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941); (*b*) Skrabal and Hugetz, *Monatsh.*, **47**, 17 (1926); (*c*) Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, p. 213; (*d*) Treffers and Hammett, *J. Am. Chem. Soc.*, **59**, 1708 (1937); (*e*) Newman, *ibid.*, **63**, 2431 (1941); **64**, 2324 (1942); (*f*) Newman and McCleary, *ibid.*, **63**, 1539 (1941).

ducted experiments on *tert.*-butyl -2,4,6-trimethylbenzoate (I). The construction of a mechanical model of this molecule showed that the oxygen atoms are not strongly hindered but the carbonyl carbon atom is. This means that steric hindrance should prevent or discourage both alcoholysis and hydrolysis by a mechanism involving an attack on the carbonyl carbon atom (cf., Eqs. 3, 9, 10) but should have little effect if one of the oxygens is attacked. They conducted experiments which showed that the basic alcoholysis and hydrolysis of I (involving a nucleophilic attack by OR^- or OH^- on the carbonyl carbon atom) refused to take place, while the acid catalyzed alcoholysis and hydrolysis resulted in good yields of the acid (Eq. 12*a*), showing incidentally that steric inhibition prevented the reaction of Equation 12*c* from occurring as it did in the case of *tert.*-butylbenzoate where steric hindrance is absent. Furthermore the basic hydrolysis of the methyl ester of 2,4,6-trimethylbenzoic acid would not yield to the acid catalyzed alcoholysis, presumably because the electron-releasing powers of the methyl group are insufficient to permit of reaction 12*a*, and the alternative mechanism of Equation 9 or 10 is rendered impossible by steric hindrance. Taken all together these experiments constitute strong evidence that in the acid-catalyzed alcoholysis or hydrolysis of *tert.*-butyl esters a different mechanism is involved than in the corresponding reactions of the esters of primary and secondary alcohols, thus reminding us of the corresponding situation in the hydrolysis of alkyl halides. The final touch was put on the argument by pointing out that, in the hydrolysis of acetic esters, the rate of the base-catalyzed reaction falls off in the order $Me > Et > Pr^\beta > Bu^\gamma$, whereas in the acid-catalyzed hydrolysis the rate goes through a slight minimum and rises again, that of the *tert.*-butyl ester being about 15% faster than that of the methyl ester.[25b, c]

Of related interest is the fact that measurement of the freezing point depression, produced by dissolving various organic acids in sulfuric acid, yields van't Hoff *i* factors * of nearly two, corresponding to the equation

$$B + H_2SO_4 \rightleftarrows BH^+ + HSO_4^- \qquad (12d)$$

whereas in 2,4,6-trimethylbenzoic acid the value of *i* is nearly four,[25d] which is interpreted by Hammett as follows:

$$(CH_3)_3C_6H_2CO_2H + 2H_2SO_4 \rightleftarrows$$
$$(CH_3)_3C_6H_2\overset{+}{C}{=}O + H_3O^+ + 2HSO_4^- \qquad (12e)$$

Furthermore, methyl-2,4,6-trimethylbenzoate was hydrolyzed completely by dissolving in concentrated sulfuric acid and pouring into water,

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* The van't Hoff *i* factor gives the ratio of the freezing point depression observed to that which would have resulted if no dissociation had occurred.

whereas methylbenzoate was recovered unchanged after similar treatment.[25d] The latter reaction may be represented by the equation

$$C_6H_5CO_2CH_3 + H_2SO_4 \rightleftarrows C_6H_5CO_2CH_3 \cdot H^+ + HSO_4^-$$

$$C_6H_5CO_2CH_3 \cdot H^+ + H_2O \rightleftarrows C_6H_5CO_2CH_3 + H_3O^+$$

and the former by

$$(CH_3)_3C_6H_2CO_2CH_3 + 2H_2SO_4 \rightleftarrows$$

$$(CH_3)_3C_6H_2\overset{+}{C}{=}O + CH_3OH \cdot H^+ + 2HSO_4^-$$

$$(CH_3)_3C_6H_2\overset{+}{C}{=}O + H_2O \rightleftarrows (CH_3)_3C_6H_2CO_2H + H^+$$

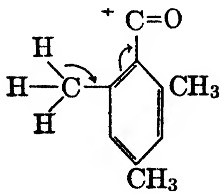
Here, then, we find evidence that a *methyl* ester may be hydrolyzed by a carbonium ion mechanism provided that it is first dissolved in a very strong acid and subsequently poured into water. This differs from the *tert.*-butyl esters studied by Cohen and Schneider in that the latter hydrolyze by a carbonium ion mechanism in dilute aqueous solutions of acids.

These same considerations have been employed in solving the erstwhile difficult problem of esterifying the sterically hindered acid, 2,4,6-trimethylbenzoic acid, by first dissolving it in 100% sulfuric acid and then pouring the solution into alcohol:[25e]

$$(CH_3)_3C_6H_2CO^+ + ROH \rightleftarrows (CH_3)_3C_6H_2CO_2R + H^+$$

It is significant, however, that 2,4,6-tribromobenzoic acid, which is also sterically hindered, is not esterified by this method.

An explanation of the exceptional ease with which 2,4,6-trimethylbenzoic acid and its ester yield carbonium ions emerges from the recognition that the carbonium ion would be stabilized by resonance, thus:



(III)

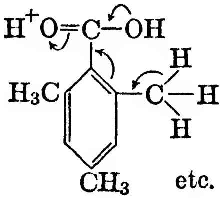
Each methyl group would give rise to a similar resonating structure. However, as pointed out by Newman,[25e] a steric effect also seems operative as evidenced by the fact that freezing point experiments[25d] show that 2,4-dimethylbenzoic dissolved in sulfuric acid has a van't Hoff *i* factor of two, whereas the 2,6-acid has an *i* factor of more than three. Newman suggests the following explanation: If, similarly to Equation

12*a*, we assume that formation of the carbonium ion (II) is preceded by coordination with a proton, we may write

$$RCO_2H + H_2SO_4 \rightleftarrows RCO_2H \cdot H^+ + HSO_4^-$$

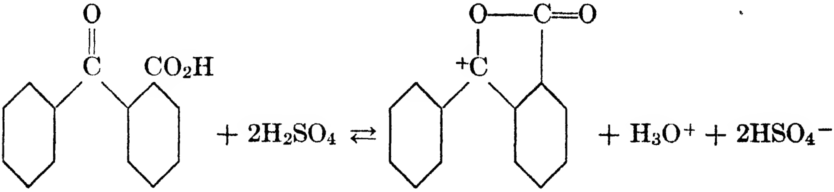
$$RCO_2H \cdot H^+ \rightleftarrows RCO^+ + H_2O$$

The second step will be driven to the right not only by stabilizing the carbonium ion, as explained above, but also by steric influences which render the $RCO_2H \cdot H^+$ less stable. This second influence may be explained by first recognizing that the ion in question must be a mesomeric ion,



and secondly by remembering that such a structure requires the coplanarity of all the carbon and oxygen atoms (**P 21**). This coplanarity would be sterically hindered, as shown by the construction of a mechanical model.

Of closely related interest is the fact that *o*-benzoylbenzoic acid also is quickly esterified by first dissolving in sulfuric acid and then pouring into methanol.[25e] This seems remarkable in that the benzoyl group, unlike the methyl group, would be expected to exhibit a $-T$ effect. A possible explanation emerges from the work of Newman [25f] who showed that the esterification led to the formation of the pseudo-ester and that hence the normally small tendency to form carbonium ions was probably augmented by the tendency of these ions to isomerize into a cylic form:



It was also shown [25f] that the pseudo-ester is and the normal ester is not hydrolyzed by dissolving in sulfuric acid and pouring onto ice. The behavior of the pseudo-ester is probably due to the equilibrium displacement resulting from the isomerization of the cyclic carbonium ion into the normal form.

The Effect of Substituents

Since the important details of the mechanism of ester hydrolysis are known with considerable certainty it should be possible to predict the effects of substituents on the speeds of these reactions by application of the basic principles of the electron theory. This has been done with moderate success.

In base catalyzed ester hydrolysis, Equation 11, step *a* is a nucleophilic attack by hydroxyl ions while step *b* is an electrophilic attack by water; hence changes in the electronegativity of X and R would have opposite effects on the speeds of these two steps. However, step *b* would not be expected to involve much activation energy since it appears to be essentially the formation of a hydrogen bond and is aided by the $+I$ effect of the free negative pole. Furthermore, step *c* need not be considered since it represents a downhill process from the transition state hump. Thus the conclusion is reached by *a priori* reasoning, that step *a* should be the rate-determining step and hence that increasing electronegativity of X or R (especially X, since it is closer to the carbon atom being attacked) should favor the hydrolysis since the attacking reagent in step *a* is nucleophilic.

In seeking experimental data with which to test the theory, we must, of course, avoid using velocity constants of those reactions in which the entropy of activation (the PZ factor) is not essentially constant. Table II presents a set of data meeting this requirement. The reaction is base-catalyzed and hence proceeds as in Equation 11. X is the variable and as it becomes more electronegative the activation energy decreases in accord with the above theoretical predictions. The sequence of the group is just what it should be on the assumption that $-I > +T$ for

TABLE II[26]

RATES OF SAPONIFICATION OF PARA SUBSTITUTED BENZOIC ETHYL ESTERS

Substituent	10^5k_2	E (cals)	$10^{-9}PZ$
NH_2	1.27	20,000	5.42
OMe	11.5	18,650	5.38
Me	25.1	18,200	5.73
H	55.0	17,700	5.32
Cl	237.	16,800	4.93
I	278	16,700	4.93
Br	289	16,800	5.82
NO_2	5670	14,500	2.30

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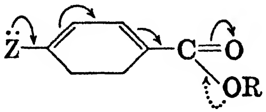
[26] Ingold and Nathan, *J. Chem. Soc.*, 222 (1936).

the halogens (which was the situation in the case of aromatic substitution) except that $E_{Cl} = E_{Br}$ instead of $E_{Cl} > E_{Br}$, as theory predicts. The observed trend is also in accord with the resonance viewpoint since the carbonyl group is conjugated with the benzene ring and hence any group which aids the $+T$ effect of the latter increases the stability of the molecule:



The attack by the hydroxyl ion breaks this conjugation and hence is opposed by the resonance stabilization effect.

Further insight into the electronic interpretation of saponification is given by the data in Table III. Although the substitution of one phenyl group into the *alpha* position of ethyl acetate lowers the activation energy as would have been predicted on the basis of the $-I$ effect of the phenyl group (which it usually exhibits when not conjugated with the side chain), the other phenyl substituted esters show quite the opposite effect. Levenson and Smith[27] interpret these results as being due to a combination of the $-I$ effect and a steric effect of the phenyl group. Thus, assuming that the phenyl and cyclohexyl groups have the same steric effect, they interpret the difference in the energy of activation for the saponification of the two esters (1500 cal/mole) as an approximate

TABLE III[27-29]

KINETICS OF THE SAPONIFICATION OF ETHYL ESTERS AT 25°

Ester	10^3k	E
Diphenylacetate	0.560	16,000
Phenylethylacetate	0.264	15,900
Cyclohexylacetate	0.509	15,600
Hydratropate	0.802	15,400
Butyrate and higher homologs	1.83	14,900
γ-Phenylbutyrate	2.69	14,900
δ-Phenylvalerate	2.28	14,700
Acetate	6.92	14,700
Propionate	3.55	14,700
Hydrocinnamate	5.04	14,500
Phenylacetate	10.1	14,100

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[27] Levenson and H. A. Smith, *J. Am. Chem. Soc.*, **62**, 2324 (1940).
[28] H. A. Smith and Levenson, *ibid.*, **61**, 1172 (1939).
[29] Evans, Gordon, and Watson, *J. Chem. Soc.*, 1439 (1938).

value of the $-I$ effect of the α-phenyl group and the corresponding difference between ethyl acetate and ethyl cyclohexylacetate (900 cal/mole) as a measure of the steric effect. This interpretation, of course, neglects the effect of substitution on hyperconjugation which may, however, be very small, judging from the essentially constant activation energy found in ethyl acetate and its higher homologs. The strong influence of steric factors on ester hydrolysis has also been emphasized by others,[30] and it may well be that the electronic interpretation of the data in Table II owed its success to the essentially constant steric effect there involved.

Let us now turn to the acid-catalyzed hydrolysis of esters. We have already decided by the *a priori* application of our basic principles that Equation 10*b* represents the rate-controlling step. Since this step involves the nucleophilic attack by water on carbon it should be favored by high electronegativity of either R or X, X being the more important because of its proximity to the reaction center.

Newling and Hinshelwood [24c] concluded, on the basis of experimental results, that practically all of the activation energy is required for the step involving the addition of water. In this relation they point out that "the rate must thus be determined as in alkaline hydrolysis by the addition of hydroxyl to the carbonyl carbon atom, but, whereas in alkaline hydrolysis free hydroxyl ions are available in high concentration, in acid hydrolysis they must be torn from water molecules. The latter fact probably explains why the activation energy is several thousand calories greater for the acid hydrolysis."

The data in Table IV may be used as a test of our theoretical predictions. The equal activation energies of methyl and ethyl formates show that this small variation of R (Eq. 10) has no effect, as we would have predicted in view of the separation of R from the carbonyl carbon by the oxygen atom, the polarizability of whose bonds are slight (**P 3** and **P 4**). A similar observation may be made in methyl and phenyl acetates. If, on this basis, we may assume E is the same for ethyl as for methyl acetate, we see that one α-chlorine atom raises E, contrary to expectations, although two chlorines lower it, in accord with theory. The lowering of E observed in the isobutyrate cannot be ascribed to steric hindrance, since this would raise E.[24c] It might, however, be ascribed to the decrease in hyperconjugation attending the replacement of a C—H by a C—C link, which would decrease the resonance with the carbonyl group and hence lower the stability and the activation energy. The same explanation could be called upon when methyl formate and methyl acetate are compared. The very high value of E found for the benzoate

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[30] See, e.g., Ingold, *J. Chem. Soc.*, 1375 (1930).

TABLE IV [25]

Kinetics of the Acid-Catalyzed Hydrolysis of Esters in Aqueous Acetone

(40 cc of water in each 100 cc)

Ester	10^7k at 25°	E (cals)
Ethyl dichloroacetate	136	14,750
Ethyl isobutyrate	210	15,300
Ethyl formate	10,700	15,600
Ethyl chloroacetate	382	17,000
Ethyl benzoate	1.29	18,900
Ethyl *m*-nitrobenzoate	1.10	19,600
Methyl formate	10,100	15,600
Methyl acetate	549	16,250
Phenyl acetate	267	16,700

is no doubt due to the resonance stabilization resulting from the conjugation of the benzene ring with the carbonyl group. The still higher value of E found for the *m*-nitrobenzoate is unexpected.

The above examples clearly indicate that the theory is not completely adequate to deal with the effect of substituents.

ELIMINATION REACTIONS

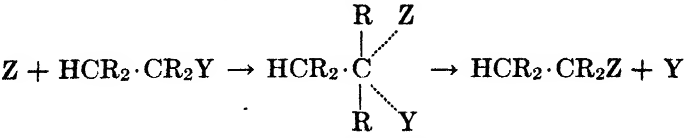
"Substitution" reactions, in the Ingold sense (symbol: S) are frequently accompanied by the formation of olefins, in which case they are called elimination reactions (symbol: E) and have the general form [31]

$$Z + H\vdots\!-\!CR_2\cdot CR_2\vdots\!-\!Y \rightarrow ZH + R_2C{=}CR_2 + Y \tag{13}$$

in which the dotted lines show the disposition of the electrons when the bonds are ruptured. Z is basic and may be either negatively charged or neutral, while Y is electron-attracting and may be either positive or neutral.

From the standpoint of the transition state theory the interaction of Z with $HCR_2\cdot CR_2Y$ may conceivably take place by the following mechanisms:

I. A nucleophilic attack by Z on C_α.



$$Z + HCR_2\cdot CR_2Y \rightarrow HCR_2\cdot\underset{R\ \ \ Y}{\overset{R\ \ \ Z}{C}} \rightarrow HCR_2\cdot CR_2Z + Y \tag{14}$$

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[31] Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927).

This would be a bimolecular substitution (S_N2) showing a second order dependency on the two reactants indicated.

II. A nucleophilic attack by Z on a β-hydrogen atom. In the light of our present knowledge alternative formulations seem to be equally likely:

$$\mathrm{Z+HCR_2\cdot CR_2Y \rightleftarrows Z\ldots H\ldots CR_2\cdot CR_2Y \rightarrow ZH+{}^-CR_2CR_2Y} \quad (15a)$$

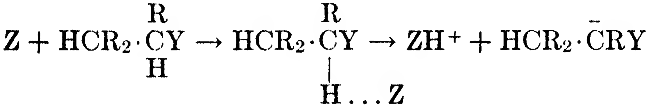
$$\mathrm{{}^-CR_2\cdot CR_2Y \rightleftarrows [R_2C\underset{\cdots}{-}CR_2\ldots Y]^- \rightarrow R_2C{=}CR_2+Y} \quad (15b)$$

or a single transition state may be involved:

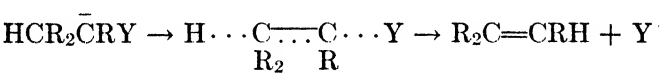
$$\mathrm{Z + HCR_2\cdot CR_2Y \rightleftarrows Z\ldots H\ldots CR_2\underset{\cdots}{-}CR_2\ldots Y \rightarrow}$$
$$\mathrm{ZH^+ + CR_2{=}CR_2 + Y} \quad (16)$$

If the first alternative obtains, either 15*a* might be the rate-controlling step, in which case the reaction would be a second order elimination reaction (*E* 2), or 15*b* might be the slower step, in which case, like Conant's formulation of irreversible redox reactions, the over-all reaction speed would again depend on the concentrations of both Z and $\mathrm{CHR_2\cdot CR_2Y}$ and hence would be catalogued as *E* 2. Equation 16 also is obviously of the *E* 2 type.

III. A nucleophilic attack by Z on an α-hydrogen atom, if there is one.



$$\mathrm{Z + HCR_2\cdot \underset{H}{\overset{R}{C}}Y \rightarrow HCR_2\cdot \underset{H\ldots Z}{\overset{R}{C}}Y \rightarrow ZH^+ + HCR_2\cdot \overset{-}{C}RY} \quad (17a)$$



$$\mathrm{HCR_2\overset{-}{C}RY \rightarrow H\cdots \underset{R_2}{C}\underset{\cdots}{-}\underset{R}{C}\cdots Y \rightarrow R_2C{=}CRH + Y} \quad (17b)$$

Here again we might adopt an alternative one-step mechanism similar to Equation 16. In either event the reaction is of the *E* 2 type.

IV. A nucleophilic attack by the solvent on a β-hydrogen atom. The equation would be the same as Equation 14 except that S would replace Z and there would be an eventual partition of the proton between S and Z. This would be a pseudo-unimolecular elimination reaction. The corresponding case involving an α-hydrogen atom may be disregarded, for reasons to be given later.

V. An electrophilic attack by the solvent on Y.

$$\mathrm{HCR_2\cdot CR_2Y + S \rightarrow HCR_2\cdot CR_2\ldots Y\ldots S \rightarrow}$$
$$\mathrm{HCR_2\cdot \overset{+}{C}R_2 + YS} \quad (18)$$

This is a solvolytic ionization and is the rate-controlling step. It may be followed either by substitution (S_N1) as discussed previously:

$$\mathrm{HCR_2\cdot \overset{+}{C}R_2 + Z \rightarrow HCR_2\cdot \overset{+}{C}R_2Z} \quad (19)$$

or by an elimination (*E* 1):

$$Z + HCR_2\cdot\overset{+}{C}R_2 \rightarrow ZH^+ + R_2C{=}CR_2 \qquad (20)$$

Let us now discuss these various possibilities in more detail. We may conveniently start by eliminating III as a possibility. On the experimental side there is evidence that the α-hydrogen atom is incapable of elimination in reactions such as these since ethylene has never been detected among the decomposition products of tetramethylammonium hydroxide nor has stilbene been obtained from benzyltrimethylammonium hydroxide.[31] Furthermore, alkyltrimethylammonium hydroxides having no α-hydrogen atoms decompose in the normal manner:[32]

$$RCH_2\cdot CMe_2\cdot\overset{+}{N}Me_3 + OH^- \rightarrow RCH{=}CMe_2 + NMe_3 + H_2O \qquad (21)$$

in which a β-hydrogen atom is eliminated. On the theoretical side the factors which operate to favor the elimination of a β-hydrogen atom can be made evident by calculating the values of $\Delta H^{\ddagger}_{\text{com}}$ for the two cases. Comparing Equations 15*b* and 17*b* we see that in each case a $C\cdots Y$ bond must be broken and a $C{=}C$ bond formed, but in addition Equation 17*b* involves the rupture of a $C\cdots H$ bond. Thus III involves an extra source of "chemical inertia" and will be a slower reaction. The same conclusion is reached by adopting the alternative one-step mechanism.

The remainder of our general discussion may be conveniently subdivided under the headings (*a*) Factors influencing reaction mechanism, (*b*) Factors influencing the *S*/*E* ratio, and (*c*) Factors influencing orientation in elimination reactions.

Factors Influencing Reaction Mechanism

Mechanism *E* 1 will be favored relative to *E* 2 by any change which facilitates the ionization of Y in its electron-rich state. Since alkyl groups are electron-releasing, their *alpha* substitution into compounds of the type $CHR_2\cdot CH_2Y$ should increase the probability of reaction by the *E* 1 mechanism.

On the experimental side it has been shown that most of the elimination reactions of primary alkyl 'onium salts and halides are second order (*E* 2). For example, this was shown by kinetic measurements to be the case for the following reaction:[33]

$$OH^- + PhCH_2\cdot CH_2\cdot\overset{+}{N}Me_3 \rightarrow H_2O + Ph\overset{-}{C}H\cdot CH_2\rightarrow\overset{+}{N}Me_3 \rightarrow H_2O + PhCH{=}CH_2 + Me_3N \qquad (22)$$

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[32] Kohn, Schlegl, and Morgenstern, *Monatsh.*, **28**, 491, 525 (1907).

[33] Hughes and Ingold, *J. Chem. Soc.*, 523 (1933).

The possibility that water might replace hydroxyl ion as the nucleophilic reactant in similar cases is readily foreseen. Water is a weaker base than hydroxyl ion but this deficiency may be counterbalanced by introducing a strongly electronegative group into the quaternary salt molecule; e.g., if β(*p*-nitrophenyl)-ethyltrimethylammonium iodide is dissolved in water the reaction becomes first order (type IV). No doubt this is a pseudo-unimolecular reaction as indicated, for instance, by the large increases in speed which are observed when small amounts of some stronger base than water, e.g., trimethylamine, are added initially.

Turning now to halides and 'onium compounds containing secondary or tertiary alkyl groups, we find an experimental record showing that they follow the E 1 mechanism in whole or in part. Thus Hughes, Ingold, and Scott[34] showed that α-phenylethyl chloride and *tert.*-butyl chloride dissolved in formic acid undergo reversible olefin elimination by a mechanism which is very probably unimolecular. In the former case the rate of the forward reaction is nearly the same as the rate of racemization in the same solvent,[35] strongly indicating that the same rate-controlling step, viz., ionization, is operative in each case. Furthermore, the rate in *tert.*-butyl chloride in dry formic acid is the same as its rate of unimolecular hydrolysis in wet formic acid, again suggesting an identity of the rate-controlling steps.

β-*n*-octyl halides in acidic aqueous ethanol solution undergo simultaneous substitution and elimination reactions. Both are unimolecular.[36] The same thing was shown to be true of *tert.*-butyl halides[37] and *tert.*-amyl halides.[38]

Changes in thermodynamic environment also have an influence on mechanism. Thus when we remember that the E 1 mechanism may only operate when the solvent makes an electrophilic attack on Y (type V) and that usually this means an attack by incipient hydrogen ions, it becomes clear that the E 2 mechanism should be favored by increasing *p*H or greater solvent basicity. It has been shown experimentally that increasing alkalinity of solution favors the E 2 mechanism.[39]

Another variable is Z. As its nucleophilic properties increase, reaction by the E 2 mechanism becomes more probable since this involves capturing a proton (Eq. 15–17).

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[34] Hughes, Ingold, and Scott, *J. Chem. Soc.*, 1271 (1937).

[35] Bodendorf and Bohme, *Ann.*, **516,** 1 (1935).

[36] (*a*) Hughes and Shapiro, *J. Chem. Soc.*, 1192 (1937); (*b*) Hughes, Ingold, and Shapiro, *ibid.*, 1278 (1937).

[37] Cooper, Hughes, and Ingold, *ibid.*, 1280 (1937).

[38] Hughes and McNulty, *ibid.*, 1283 (1937).

[39] (*a*) Hughes and Ingold, *ibid.*, 244 (1935); (*b*) Hughes, Ingold, Masterman, and McNulty, *ibid.*, 899 (1940).

Factors Influencing the *S/E* Ratio

Another important phase of the general problem is the study of the relative amounts in which substitution and elimination occur. Mechanism S_N2 involves a nucleophilic attack of Z on C_α while $E\,2$ involves an attack on H_β; hence the influence of different variables on the $S_N2/E\,2$ ratio may be deduced from their relative influences on the electrophilic properties of C_α and H_β (**P 2**). On the other hand, the rate-controlling step in the S_N1 and $E\,1$ cases is the same, viz., the solvolytic ionization of the C—Y bond, and hence the $S_N1/E\,1$ ratio depends on the relative tendencies of the ion to unite with Z and to undergo an elimination reaction.

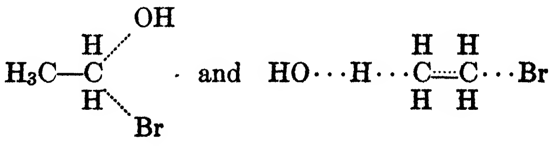
In Table V are given velocity data for the hydrolysis of alkyl bromides in ethyl alcohol solution. The values in parentheses relate to concentrated alkaline solutions (normal or greater) and the first and second order velocity constants are designated by k_1 and k_2 respectively.

TABLE V[89b]

RATES OF THE FOUR REACTIONS CONSTITUTING THE HYDROLYSIS OF ALKYL BROMIDES IN DRY ETHANOL AT 55°

Bromide	S_N1 10^5k_1	S_N2 10^5k_2	$E\,1$ 10^5k_1	$E\,2$ 10^5k_2
Ethyl	....	200 (120)	....	2.0 (1.2)
Isopropyl	$\not> 0.017$	5.0 (2.1)	$\not> 0.001$	15 (7.5)
tert.-Butyl	14	.... ($\not> 2.0$)	5.5	... (~50)
α-Phenylethyl	19	.... (~100)	$\not> 0.5$	... (~50)
β-Phenylethyl	....	~30	....	600

In examining Table V we are first struck by the fact that very little ethylene is produced by the action of alcoholic potassium hydroxide on ethyl bromide (only about 1%) in contradiction to the statements commonly made in text books of organic chemistry. In seeking an explanation of the preponderance of the substitution reaction we might formulate the two transition states as



$$H_3C\text{—}\overset{\overset{OH}{\vdots}}{\underset{\underset{Br}{\vdots}}{C}}H_2 \quad \text{and} \quad HO\cdots H\cdots \underset{H}{\overset{H}{C}}\text{=}\underset{H}{\overset{H}{C}}\cdots Br$$

and then proceed to calculate values for $\Delta H^{\ddagger}{}_{\text{com}}$ in each case, as follows.

S_N2 MECHANISM (TYPE I)

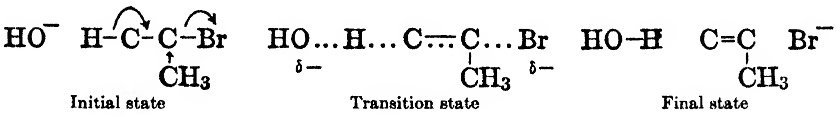
$$\begin{array}{lr}
CH_3\cdot CH_2Br \rightarrow CH_3\cdot\overset{+}{C}H_2 + Br^-; & \Delta H = 231 \text{ kcal} \\
CH_3\overset{+}{C}H_2 + OH^- \rightarrow CH_3\cdot CH_2\cdot OH; & \Delta H = -241 \phantom{\text{ kcal}} \\
\hline
 & \Delta H^{\ddagger}{}_{\text{com}} = -10 \text{ kcal}
\end{array}$$

$E\,2$ MECHANISM (TYPE II)

$$\begin{array}{lr}
H^+ + OH^- \rightarrow H_2O; & \Delta H = -334 \text{ kcal} \\
CH_3\cdot CH_2Br \rightarrow {}^-CH_2\cdot CH_2Br + H^+; & \Delta H = 367 \phantom{\text{ kcal}} \\
{}^-CH_2\cdot CH_2Br \rightarrow {}^-CH_2\cdot\overset{+}{C}H_2 + Br^-; & \Delta H = 231 \phantom{\text{ kcal}} \\
{}^-CH_2\cdot\overset{+}{C}H_2 \rightarrow CH_2{=}CH_2; & \Delta H = -268 \phantom{\text{ kcal}} \\
\hline
 & \Delta H^{\ddagger}{}_{\text{com}} = -4 \text{ kcal}
\end{array}$$

Although the calculations indicate an advantage for the substitution reaction we must not take them too seriously because the transition states are very different and hence may involve entirely different degrees of thermodynamic coupling.

Continuing the comparison of S_N2 with $E\,2$ we note that with the *alpha* substitution of alkyl groups S_N2 decreases rapidly and $E\,2$ increases moderately (Table V). The decrease in S_N2 occurs because the electron-releasing alkyl groups make C_α less electrophilic (**P 2**). In the opinion of Ingold et al.,[39b] $E\,2$ increases because the alkyls exert a quasi-conjugative stabilizing influence on the transition state. Their explanation is as follows. "Anything analogous to conjugation always stabilizes a system. Considering, first, the initial and the final states of reaction $E\,2$, one can see that the energy level of the latter will be depressed more than that of the former by the 'conjugated' α-alphyl substituent:



But if this is true, the energy level of the transition state must also be lowered more than that of the initial state, because in the transition state some unsaturation has already developed between the α- and β-carbon atoms. Therefore facilitation of the reaction is to be expected. Obviously a properly conjugated α-phenyl substituent should exhibit the effects considerably more powerfully than an α-methyl substituent."

In regard to $E\,1$ the favorable influence of electron-releasing groups in the *alpha* position is due to their facilitation of the rate-controlling ionization, as explained before.

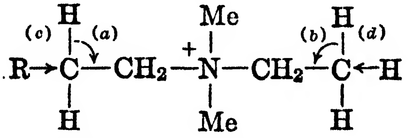
The above discussion makes it evident that the S/E ratio depends on the very complicated inter-relationships of four different mechanisms and hence, in general, is difficult to predict. However, the situation can be simplified in certain cases by working in acid solutions which favor the unimolecular reactions to such an extent that, in the most favorable cases, we are only left with two variables of practical importance, viz., the velocity constants corresponding to S_N1 or $E\,1$. The simplifying influence of strongly alkaline solutions can also be foreseen, as can that obtaining when the constitution of the compound being used strongly predisposes it to either uni- or bimolecular mechanisms.

As an example of such simplifying influences, it was found [36b] that in acidic aqueous alcoholic solutions of *s*-octyl bromide the bimolecular reactions became negligible while S_N1 took place to the extent of 90.3% and $E\,1$ only 9.7%.

Factors Influencing Orientation in Elimination Reactions

It frequently happens that there is the possibility of more than one olefin being formed by elimination from a given compound. Long ago two empirical rules were devised to serve as guides in such cases. The first of these, Hoffmann's rule, applies to primary alkyl groups in ammonium or sulfonium hydroxides and states that the least alkylated of the possible alkyl ethylenes will be primarily formed. The second, Saytzeff's rule, relates to secondary and tertiary groups in alkyl halides and states that the most alkylated of the possible ethylenes will be formed most rapidly. The Hughes-Ingold group have shown that these rules, as well as exceptions to them, are encompassed in the electronic theory of these reactions.[2, 39b, 40]

Dimethylethyl-*n*-propylammonium hydroxide yields mainly ethylene, thus following Hoffmann's rule. Remembering that olefin production demands the elimination of a β-hydrogen atom, we need consider only two possible cases, indicated by *a* and *b* in the following formula.



$$\mathrm{R}\rightarrow\overset{(c)\;\mathrm{H}\;(a)}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{+\;\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{N}}}-\mathrm{CH_2}-\overset{(b)\;\mathrm{H}\;(d)}{\underset{\mathrm{H}}{\mathrm{C}}}\leftarrow\mathrm{H} \tag{23}$$

In this case R is a methyl group. Since greater electron release is experienced at *c* than at *d*, the carbon atom at *d* will be most electrophilic,

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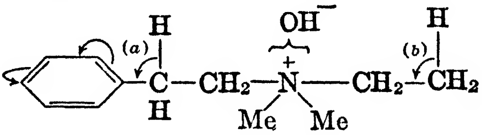
[40] Dhar, Hughes, Ingold, Mandour, Webb, and Wolf, *Nature*, **147**, 812 (1941).

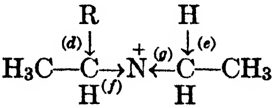
and *b* will take place more easily than *a*. Thus the least alkylated olefin is produced.

In compounds of this type it is found that when R successively becomes H, Me, Et, etc., there is first a sharp decrease in the bimolecular rate of elimination followed by successively smaller decreases. Since the attacking hydroxyl ion does not call for electron release at *c*, this $+I$ effect cannot be inductomeric (**P 5**), but must be, at least partly, a $+I_s$ effect induced in the C—R bond of the normal molecule by the positive pole on the nitrogen atom. This $+I_s$ effect may be aided somewhat by second order hyperconjugation, but, if hyperconjugation alone were operative, CH_3 would be more effective than either H or C_2H_5. If R = Ph, the ionization of the β-hydrogen atom would be facilitated by first order hyperconjugation:



with the result that $a > b$ and styrene would be eliminated instead of ethylene. This has been experimentally observed.[2] A *p*-nitro group substituted into the above molecule further facilitates the elimination of the aryl ethylene, as it should. These two results would not have been predicted by Hoffmann's rule, nor would the following: when R (Eq. 23) is methyl, the main product corresponds to $b \gg a$; when R is amino, $b > a$; when R is hydroxyl, $a = b$ (approximately); when R is chlorine, $a \gg b$.[2] These results accord with the relative $-I_s$ effects of the groups, viz., $CH_3 < NH_2 < OH < Cl$.

It has been found that 'onium salt reactions proceeding by mechanism *E* 2 display "Hoffmann influences" (at least when no unsaturated groups are present) whereas those proceeding by *E* 1 show "Saytzeff influences." [40] In the latter case (type V) the olefin will be formed from that radical which, of the four attached to the nitrogen atom, is most easily split off as a positive ion. Thus in a molecule of the type



$$H_3C-\underset{H^{(f)}}{\overset{R}{\overset{(d)\downarrow}{C}}}\rightarrow\overset{+}{N}\overset{(g)}{\leftarrow}\underset{H}{\overset{H}{\overset{\downarrow(e)}{C}}}-CH_3$$

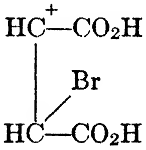
the electron release at *d* is greater than that at *e* and hence the bond *f* will be broken more easily than *g*, with the eventual result that $CH_2{=}CHR$ will be formed in preference to ethylene, in accord with Saytzeff's rule.

STEREOCHEMICAL ASPECTS OF OLEFIN ADDITION REACTIONS

At the end of Chapter IV it was promised that the stereochemical evidence in favor of the Lapworth theory of stepwise addition of reagents to olefins would later be reviewed. We are now ready for that discussion.

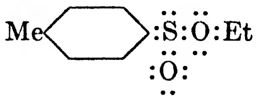
There is considerable evidence which indicates that the addition of halogens to olefinic double bonds almost always takes place by a process of *trans*-addition.[41] If we consider, for example, the addition of bromine to maleic acid, and assume that the bromine molecule adds simultaneously to the two olefin carbon atoms, *cis*-addition would surely result, and this would produce a dibromosuccinic acid whose two halves are mirror images of each other (i.e., it would be the *meso* form) whereas a one-step *cis*-addition to fumaric acid would result in a racemic mixture. These predictions are contrary to fact.

If, on the other hand, a two-step addition of bromine occurs, it could presumably do so either *cis* or *trans*. Taking Lapworth's theory as a working hypothesis, the electron-poor bromine atom would appropriate one electron pair of the double bond, giving, in the case of maleic acid, the following structure:



(24)

Since the indicated positive pole (unlike a negative pole, which consists of a lone pair of electrons) is located on the nucleus of the carbon atom and hence does not occupy one of the tetrahedral positions, or orbitals, of the valence shell of the carbon atom, there would be no reason to suppose that the asymmetry of the carbon atom in question should be maintained as it is in the case of the sulfur atom in the molecule



(25)

which has been shown to exist in two stereoisomeric modifications.[42] Consequently the remaining electron-rich bromine atom could add in a position either *cis* or *trans* to the first bromine atom. If this were the

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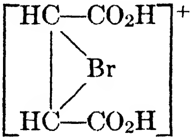
[41] (*a*) McKenzie, *Proc. Chem. Soc.*, **27**, 150 (1911); *J. Chem. Soc.*, **101**, 1196 (1912); (*b*) Holmberg, *Svensk. Kemisk Tidskrift* (1911) through *Chem. Abst.*, **6**, 2072 (1912); (*c*) Frankland, *J. Chem. Soc.*, **101**, 673 (1912); (*d*) cf. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., 1940, pp. 147–149.

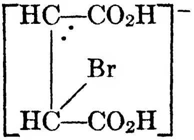
[42] Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

case, both maleic and fumaric acids should yield the same intermediate ion (Eq. 24) and hence the same final product. They do not: maleic acid yields almost exclusively racemic dibromosuccinic acid, whereas fumaric acid yields chiefly the *meso*-compound, showing clearly that in both cases *trans*-addition occurs.

A possible explanation is as follows.[43] Since the bromine atom pictured in formula 24 has unshared electrons which could be used to complete the octet of the electron-poor carbon atom, it might be expected to do so, forming a ring similar to the ethylene oxide ring:



Now, if an electron-rich bromine atom should attack either of the ring carbon atoms, it should (*a*) attack from a direction to cause stereochemical inversion and (*b*) easily succeed in breaking one of the existing C—Br bonds and forming a new C—Br bond, since the ionic bond energy of the former is weakened by ring strain and hence $\Delta H^{\ddagger}_{*}$ would be a negative quantity. Owing to the stereochemical inversion accompanying the displacement step, the net result would be a *trans*-addition. The same would be true for fumaric acid. This theory, if experimentally supported, would result in both an extension and a verification of the Lapworth theory, since it clearly necessitates the addition of two bromine atoms and also seems to indicate that the initial attack is made by the electron-poor bromine atom (which may, of course, still be part of a polarized bromine molecule), because if the electron-rich bromine atom led the attack, formula 24 would be replaced by the following:



and not only would there be almost no tendency for ring formation but, similarly to compound 25, the electron pair would probably maintain its position in the valence shell of carbon[44] and hence force the second bromine atom to add in a position which would result in a net *cis*-addition, contrary to experimental evidence.

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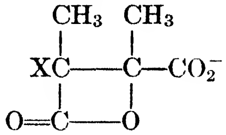
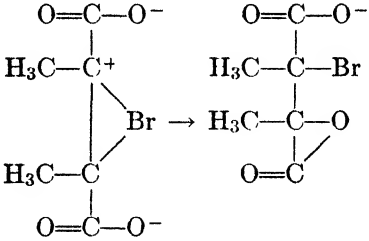
[43] Roberts and Kimball, *J. Am. Chem. Soc.*, 59, 947 (1937).

[44] None of the authors of Ref. 43 is responsible for this particular argument. If it should turn out to be ill founded, the responsibility is distinctly my own.

The desired support for this theory has, indeed, been furnished.[45] The addition of bromine or chlorine to aqueous solutions of sodium dimethylmaleate yields a halogenated β-lactone having the structure



where X is either Br or Cl. If sodium dimethylfumarate is used the lactones produced are stereoisomeric with those obtained from the maleate. It was demonstrated that, under the conditions of the experiment, neither the dibromodimethylsuccinate nor the corresponding bromohydrine can form the lactone. Hence neither of these products may be considered as intermediates, and the presumption is strong that the reaction proceeds as follows,[43]



the negative carboxylate ion making an internal nucleophilic attack on the neighboring carbon atom, thus displacing the bromine and breaking the three-membered ring. The last step would, of course, result in stereochemical inversion in each of the two cases and explains the production of stereoisomeric lactones.

In view of these facts it is difficult to understand [46] why the addition of bromine to maleate and fumarate ions results in the same end product, viz., *meso*-dibromosuccinate ion.[47]

THE ORIENTATION PROBLEM IN ELECTRON-SHARING REACTIONS

The foregoing discussion of hydrolysis and elimination reactions was given in great detail because together they illustrate most of the points which are important in applying the electron theory to the electron-sharing type of reactions and, since the main goal we are seeking is to learn to use the electron theory as an aid in solving general problems in

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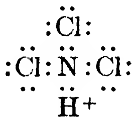
[45] Tarbell and Bartlett, *J. Am. Chem. Soc.*, **59**, 407 (1937).

[46] See Ref. 43 for a suggested explanation.

[47] Kuhn and Wagner-Jauregg, *Ber.*, **61**, 519 (1928).

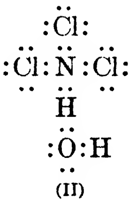
organic chemistry, a clear understanding and mastery of these details was deemed necessary. It is obvious, however, that if the remaining examples of electron-sharing reactions were discussed in equal detail, this book would grow to an unreasonable size. As an alternative it seems well to close this chapter with a general discussion of a question which is, after all, the one of greatest qualitative importance to the organic chemist. The question can be posed as follows: When two or more substances are mixed together, how can we predict which linkages will be broken and which will be formed? This is a problem of orientation in the broadest sense of that word.

In Chapter IV it was pointed out that Abegg's rule relating hydrolytic orientation to the polar character of a bond was subject to suspicion on the grounds that substances such as nitrogen trichloride and chlorimidoketones give hypochlorous acid on hydrolysis. Mention was also made of Sidgwick's suggestion that in the hydrolysis of nitrogen trichloride, for example, there might be formed an intermediate compound in which the hydrogen ion from water had become attached to the nitrogen atom, thus predisposing the molecule to the formation of ammonia, in which also the hydrogen and nitrogen atoms are linked. Viewed from the standpoint of our present knowledge, this appears to have been a very important suggestion. In the first place, our calculations of $\Delta H^{\ddagger}_{\mathrm{com}}$ made in Chapter VII indicate that the most likely method of attack is an electrophilic attack of hydrogen on nitrogen. If this is so there should be initially formed, without any activation energy, one of the following intermediates:



$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \\ \mathrm{H}^{+} \end{array}$$

or

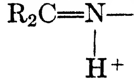


$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \\ \mathrm{H} \\ :\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H} \end{array}$$

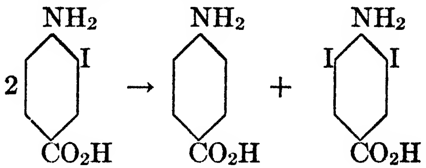
(I) (II)

In I the free positive pole associated with the proton should cause an electron displacement in its direction, thus tending to eject the chlorine in an electron-poor condition. Similarly in II the same influence would operate as a result of the strong electron pull associated with the coordinate covalence. From the standpoint of orientation it follows that the chlorine acts as an electron-poor atom, not because it is electron-poor in nitrogen trichloride but because this is its condition in the intermediate complex.

Another argument against the Abegg hydrolysis rule is this: If the polar character of a bond determined the direction of its cleavage on undergoing an electron-sharing type of double decomposition, then the reagent used should be without influence on the orientation. This is not so, as shown, for example, by the fact[48] that the hydrolyzable S—N bond in $—SO_2N=$ structures is split to $—SO_2 \cdot OH + HN=$ in acidic but not in basic media, whereas basic hydrolysis appears to split the bond to $—SO_2H + HON=$. Similarly, in aryl sulfonic acids, alkaline hydrolysis yields phenols, whereas the hydrocarbon is formed in acidic solutions.

It appears, then, that Sidgwick's point of view, when properly modernized, should form a reliable basis upon which to build a qualitative theory of electron-sharing orientation phenomena. If, in order to sketch in a rough outline of the theory, we neglect for the moment details which are usually of secondary importance, we may say that high concentrations of any ion, such as hydrogen ion or hydroxyl ion, give that ion a mass action advantage as an attacking reagent and this will be a powerful influence in determining whether the attack will be electrophilic or nucleophilic. If the attack is made by hydrogen ion it is reasonable to suppose that it will attach itself to the most basic atom in the molecule being attacked. Thus with a chlorimidoketone the proton will attach itself to the nitrogen rather than to the chlorine atom, giving  $R_2C{=}\underset{\underset{H^+}{|}}{N}{—}Cl$, and thus, through the strong $-I_s$ effect of the positive pole, predispose the N—Cl link to break in such a way as to yield a positive chlorine ion.

Electrophilic attacks by hydrogen ion also occur where no lone pair exists to serve as the point of attack. This is frequently true in cases involving "positive halogens." Thus the following reaction takes place in a few minutes in boiling hydrochloric acid:[49]



As Nicolet[50] has pointed out, the fact that the replaced iodine attacks a second aromatic ring is good evidence that it is replaced in the "positive" condition. Nicolet also points out that "alkali is incomparably less effective than acid in removing such 'positive' halogens."

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[48] Hurd in Gilman's *Treatise on Organic Chemistry*, John Wiley & Sons, 1938, p. 631.

[49] Wheeler and Liddle, *Am. Chem. J.*, **42**, 453 (1909).

[50] Nicolet, *J. Am. Chem. Soc.*, **43**, 2081 (1921).

The interpretation is reasonably clear. The reaction is an electrophilic attack by hydrogen ion on carbon, the iodine being replaced as a positive ion. Being an electrophilic attack, it is aided by the strong $+T$ effect of the amino group which can build up a high electron density on the carbon atoms *ortho* or *para* to it. Other iodine and bromine derivatives of phenols or aromatic amines in which the halogen is *ortho* or *para* to the hydroxy or amino group also show the properties of "positive" halogens.[51]

When nucleophilic attacks are involved the orientation problem is not usually simple. The point of preferential attack and the linkage preferentially broken depend on a balancing of chemical driving forces and chemical inertia associated with the dual process of making one link and breaking another. This subject was discussed in Chapter VII. As a first rough estimate, one may use the method of calculating $\Delta H^{\ddagger}_{\text{com}}$ for the alternative processes. Unfortunately, however, such estimates are subject to dismaying uncertainties: the degrees of thermodynamic coupling may vary from case to case, the ionic bond energies may be altered by electron displacements (I or T) due to substituents or to solvation, chelation, association, etc. Of course the disturbing uncertainties of the effects of substituents and association frequently harass electrophilic attacks as well, and both types of reactions are subject to the more or less unpredictable entropy factors. These subjects have all been discussed in previous chapters and at this point we need do no more than call on them to pass in review.

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[51] Nicolet et al., *ibid.*, **49**, 1796, 1801, 1806, 1810 (1927).

APPENDIX I

AN ELEMENTARY EXPOSITION OF THE THEORY OF ATOMIC AND MOLECULAR STRUCTURE

In the year 1916 G. N. Lewis published a paper[1] in which he set forth the main details of the theory which now bears his name. A few years later he expanded his ideas in a monograph[2] which may still be read today without finding it necessary to delete any essential portion of the subject matter as incorrect. Of course the theory has grown in the intervening years, but for the most part the later ramifications will not be discussed in this introductory chapter, which aims only to give the reader an understanding of the basic principles of the theory.

The Lewis theory, as it is accepted today, may be said to be built about the Rutherford theory of atomic structure which pictures any atom as being a submicroscopic solar system in which negatively charged electrons are revolving about a positively charged nucleus. Essentially all of the mass of the atom is associated with the nucleus. The electrons in all elements are the same kind of particles, but the nuclei of the atoms of one element differ from those of another in charge and mass. Their average masses are proportional to their "atomic weights," whereas their charges, expressed as multiples of the electronic charge, are equal to their atomic numbers as deduced from Mendeleeff's table or from the X-ray spectra of the elements (Mosely). Since atoms are neutral, the number of planetary electrons in each atom must also be numerically equal to the atomic number.

The extranuclear electrons were initially envisioned as being arranged in concentric shells. Starting with the hydrogen atom, which has but one electron, the extranuclear electronic structures of each of the succeeding elements may be built up by adding one more electron to the extranuclear structure of the preceding element. The first two electrons go in the first shell (*K* shell), the next eight go in the second shell (*L* shell), etc., as shown in Table I, which has been modernized in a way

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[1] G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

[2] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Co., 1923.

TABLE I

The Extranuclear Electronic Structure of Atoms in Their Normal States

	At.	*K*	*L*		*M*			*N*				*O*			*P*			*Q*
	No.	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
H	1	1																
He	2	2																
Li	3	2	1															
Be	4	2	2															
B	5	2	2	1														
C	6	2	2	2														
N	7	2	2	3														
O	8	2	2	4														
F	9	2	2	5														
Ne	10	2	2	6														
Na	11	10 Neon core			1													
Mg	12				2													
Al	13				2	1												
Si	14				2	2												
P	15				2	3												
S	16				2	4												
Cl	17				2	5												
Ar	18				2	6												
K	19	18 Argon core						1										
Ca	20							2										
Sc	21						1	2										
Ti	22						2	2										
V	23						3	2										
Cr	24						5	1										
Mn	25						5	2										
Fe	26						6	2										
Co	27						7	2										
Ni	28						8	2										
Cu	29	2	2	6	2	6	10	1										
Zn	30	28 Copper core						2										
Ga	31							2	1									
Ge	32							2	2									
As	33							2	3									
Se	34							2	4									
Br	35							2	5									
Kr	36							2	6									
Rb	37	36 Krypton core										1						
Sr	38											2						
Y	39									1		2						
Zr	40									2		2						
Cb	41									4		1						
Mo	42									5		1						
Ma	43									6		1						
Ru	44									7		1						
Rh	45									8		1						
Pd	46									10								
Ag	47	2	2	6	2	6	10	2	6	10		1						
Cd	48	46 Silver core										2						
In	49											2	1					
Sn	50											2	2					
Sb	51											2	3					
Te	52											2	4					
I	53											2	5					
Xe	54											2	6					

TABLE I—*Continued*

THE EXTRANUCLEAR ELECTRONIC STRUCTURE OF ATOMS IN THEIR NORMAL STATES

	At.	*K*	*L*		*M*			*N*				*O*			*P*			*Q*
	No.	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
Cs	55	2	2	6	2	6	10	2	6	10		2	6		1			
Ba	56						54								2			
La	57						Xenon core							1	2			
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1	2			
Pr	59										2			1	2			
Nd	60										3			1	2			
Il	61										4			1	2			
Sa	62										5			1	2			
Eu	63										6			1	2			
Gd	64					46					7	8 electrons		1	2			
Tb	65					1*s* to 4*d*					8	in 5*s*		1	2			
Ds	66										9	and 5*p*		1	2			
Ho	67										10			1	2			
Er	68										11			1	2			
Tu	69										12			1	2			
Yb	70										13			1	2			
Lu	71										14			1	2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2	2			
Ta	73													3	2			
W	74													4	2			
Re	75						68							5	2			
Os	76						Hafnium core							6	2			
Ir	77													9				
Pt	78													9	1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10	1			
Hg	80														2			
Tl	81														2	1		
Pb	82						78								2	2		
Bi	83						Gold core								2	3		
Po	84														2	4		
..	85														2	5		
Rn	86														2	6		
..	87	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		1
Ra	88																	2
Ac	89							86									1	2
Th	90							Radon core									2	2
Pa	91																3	2
U	92																4	2

which will be explained later. Thus the ninth element, fluorine, has nine electrons, of which two are in the *K* shell and seven in the *L* shell.

As the shells get larger in radius and surface area they can accommodate more electrons. Thus the maximum number of electrons which may be contained in each of the shells is as follows: $K = 2$, $L = 8$, $M = 18$, $N = 32$. The still larger shells apparently never attain their maxima (see table). Since the intricacies of the electronic structures of the heavier elements are of practically no importance to organic chemistry, they need not be discussed here.

The remaining features of the Lewis theory are built upon a concept which is essentially thermodynamic. All changes which take place in the universe do so in such a way that greater stability is attained as a result. If chemical changes involve the alteration of valence bonds, and if these bonds involve electrons, then chemical changes may reasonably be postulated to take place in such a way that electronic stability is increased in the process. If an element has no tendency to react, then it must have attained electronic stability to an unusual degree. This is, of course, the case with the inert gases, as was previously pointed out by Thomson in the formulation of his electronic theory, and accordingly we may use them as a guide in determining what electronic arrangements are highly stable. Since helium is stable, we may conclude that two electrons in the *K* shell give a highly stable configuration. Likewise, from the structures of the other inert gases, we may deduce that an octet of electrons in any of the larger shells gives electronic stability, at least when that shell is the outermost shell in the atom in question.

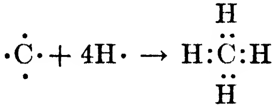
From these considerations it is but a step to the main postulate of the Lewis theory: every atom strives to attain the electronic structure of the nearest inert gas.

This postulate at once leads to an understanding of valence. Thus if a neutral lithium atom is to become electronically like the nearest inert gas, helium, it must lose its one *L* electron. This will leave it with two electrons in the *K* shell, like helium, but unlike helium it will bear a single positive charge as the result of losing one electron. Thus it forms a univalent positive ion. Similarly magnesium, in its attempt to attain the electronic structure of neon, would lose its two *M* electrons and become thereby a divalent positive ion. The nonmetallic elements will have to gain electrons to become like the *nearest* inert gas. Thus fluorine has seven electrons in its *L* shell and needs one more "to complete its octet." After gaining this one electron it will have attained the electronic structure of neon, which is the nearest inert gas, but will bear a single negative charge corresponding to unit valence.

Lewis devised a symbolism for representing the electronic structure of atoms. He used the ordinary atomic symbol to represent the atomic kernel (the kernel of an atom is that portion which remains after stripping off the outermost, or valence, shell of electrons) and then surrounded it with as many dots as it has valence electrons. Thus we have $\mathrm{Ca}\!:$, $\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$, $:\overset{\cdot\cdot}{\mathrm{O}}:$, $:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{F}}}:$, etc.

If an alkali metal atom and a halogen atom collide, the electronic requirements of each may be met by the transfer of an electron from the metal to the halogen. The transfer will be complete and two ions will be formed which are held together only by electrostatic (or "coulombic") forces. Such a valence union is customarily spoken of as an "electrovalence," or it is said to be a "heteropolar" union. It is readily broken by the solution of the compound in a solvent of high dielectric constant, the process being the familiar one we call ionization. The following equation represents the reaction: $\mathrm{Na}\cdot + :\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{Cl}}}: \longrightarrow [\mathrm{Na}]^{+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^{-}$. Square brackets are usually used, as above, to indicate electrovalence, although the following alternative symbolism is also frequently found: $\mathrm{Na}^{+}\}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^{-}$.

In addition to the above process, in which electrons are completely transferred, there is another way in which the electronic requirements of atoms may be met, viz., by the "sharing" of electron pairs. This process is well illustrated by the case of methane. The carbon atom requires four electrons to complete its octet. While four hydrogen atoms could furnish four electrons for this purpose, the complete transfer of these electrons would not give hydrogen a structure like that of the nearest inert gas, helium, which has two K electrons. But if these four electrons could remain in the K shells of the hydrogen atoms at the same time they were occupying positions in the L shell of the carbon atom, and if at the same time each of the four electrons initially belonging to the carbon atom could enter the K shell of one of the hydrogen atoms without leaving the L shell of the carbon, then the carbon atom would have the octet and each of the hydrogen atoms would have the pair of electrons required respectively by the two kinds of atoms for electronic stability. This process is called "sharing" and is symbolized by writing the shared electrons between the two atomic kernels in question. Thus we have:

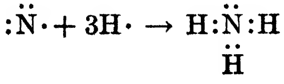


$$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot + 4\mathrm{H}\cdot \rightarrow \mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}}}:\mathrm{H}$$

$$2:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{Cl}}}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

$$\mathrm{H}\cdot + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot \rightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:$$

$$2\mathrm{H}\cdot + :\overset{\cdot\cdot}{\mathrm{O}}: \rightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

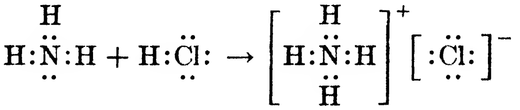


$$:\overset{\cdot\cdot}{\mathrm{N}}\cdot + 3\mathrm{H}\cdot \rightarrow \mathrm{H}:\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{H}$$

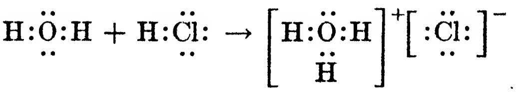
In none of these examples are electrons completely transferred; in all of them every atom combines the functions of electron donor and electron acceptor. Thus ions are not formed, and the atoms are held together, not by electrostatic attraction, but by that force, whatever be its nature, which is responsible for electron sharing. The linkages thus formed are called "covalences" or "homopolar" unions. When the compounds in question are put into solution, they either do not ionize at all or they do so by an essentially different process of ionization than that exhibited by sodium chloride.

In the case of the formation of the chlorine molecule, each atom gives and each one accepts a share in an electron. Furthermore, since the two atoms are identical, each one gives and each one accepts equally. The result is that there is no concentration of electric charge around either atom. The covalence may then be said to be strictly nonpolar. But this same situation does not obtain in hydrogen chloride. Here the chlorine is more electronegative (i.e., more highly electron attracting) than the hydrogen and hence it accepts a larger share and gives a smaller share of electrons than the hydrogen does. The result is a concentration of negative charge around the chlorine atom and of positive charge around the hydrogen atom, and the covalence is now said to be polar. The resulting combination gives rise to an electric dipole. The polarity of any linkage is obviously a function of the difference in the electronegativities of the two atoms bound together. The polarity is smaller in the N—H linkages and practically zero in the C—H linkages.

Let us now return to the question of the ionization of covalent linkages. Liquid hydrogen chloride is practically a nonconductor of electricity, yet its solutions in water and liquid ammonia are highly conducting. The behavior contrasts strongly with that of sodium chloride, which is a good conductor when in the liquid state. The explanation of the ionization of hydrogen chloride is indicated in the following equations.



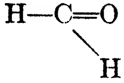
$$\mathrm{H:\overset{\displaystyle H}{\underset{\cdot\cdot}{\ddot{N}}}:H + H:\underset{\cdot\cdot}{\ddot{Cl}}: \rightarrow \left[H:\overset{\displaystyle H}{\underset{\underset{\displaystyle H}{\cdot\cdot}}{\ddot{N}}}:H\right]^{+}\left[:\underset{\cdot\cdot}{\ddot{Cl}}:\right]^{-}} \qquad (1)$$

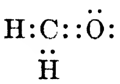


$$\mathrm{H:\underset{\cdot\cdot}{\ddot{O}}:H + H:\underset{\cdot\cdot}{\ddot{Cl}}: \rightarrow \left[H:\underset{\underset{\displaystyle H}{\cdot\cdot}}{\ddot{O}}:H\right]^{+}\left[:\underset{\cdot\cdot}{\ddot{Cl}}:\right]^{-}} \qquad (2)$$

In each equation it will be noticed that unshared electrons are present in the solvent molecule. Whether the hydrogen atom satisfies its electronic demands by sharing an electron pair with the chlorine or with the nitrogen (or oxygen) atom should presumably depend on which could be done more easily. We have already seen under our study of polarity that a hydrogen atom gets a larger share of the binding electron pair, the less electronegative the other atom is. Accordingly it should be better satisfied sharing electrons with nitrogen (or oxygen) than with chlorine. This explains Equations 1 and 2, from which it is apparent that hydrogen ions do not exist in solution as bare hydrogen nuclei (protons) since they would not then be electronically like helium. Rather, they exist as ammonium or hydronium ions. Since now electrovalences have been created, ordinary ionization ensues.

Multiple linkages are represented by Lewis by the sharing of four or six electrons, as in ethylene and acetylene: $H:\underset{\overset{\cdot\cdot}{H}}{C}::\underset{\overset{\cdot\cdot}{H}}{C}:H$ and $H:C:::C:H$. A consideration of the formulas thus far given make it clear that the classical valence bond is now to be represented by a shared pair of electrons. Thus there is a similarity in the classical and the Lewis structural formulas:





$$H:\underset{\overset{\cdot\cdot}{H}}{C}::\overset{\cdot\cdot}{O}:$$

The only essential difference between these two examples is seen to be the indication of the unshared electrons in the second. This is a very important difference.

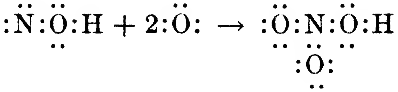
In certain other cases, however, more striking differences appear. The history of this phase of the subject starts with Lewis's attempt to explain why two compounds as closely related as CO_2 and SiO_2 have such very different properties, especially in relation to their states of aggregation. He finally decided that the difference must lie in the presence of double bonds in CO_2 and their absence in SiO_2. Thus the silicon atom, being electronically unsatisfied, would try to complete its octet by combining with the unshared electrons of an oxygen atom in another "molecule" of SiO_2. This process would partially satisfy the first silicon atom, but the second one would be completely unsatisfied unless it in turn could share electrons with a third "molecule" of SiO_2. In this way huge structures might be built up which would exhibit low volatility because the "intermolecular" forces within them would have to be broken down before vaporization could take place.

Generalizing on this idea, Lewis postulated that only elements of the first short period could form double bonds. Although modern chemists do not entirely agree with him on this score, his applications of the idea are, for the most part, still in good standing. A consideration of the structure of oxygen acids will serve to illustrate these applications.

The structure of nitric acid may be built up as follows:

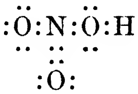
$$:\overset{\cdot\cdot}{O}: + H\cdot \rightarrow \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

$$:\overset{\cdot\cdot}{N}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \rightarrow :\overset{\cdot\cdot}{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$



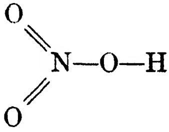
$$:\overset{\cdot\cdot}{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H + 2:\overset{\cdot\cdot}{O}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\underset{\underset{:\underset{\cdot\cdot}{O}:}{\cdot\cdot}}{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

The nitrogen atom does not now have a complete octet. Since it is in the first Mendeleeff period it may complete its octet by sharing an additional electron pair with one of the oxygen atoms, i.e., by forming one double bond. The molecule then takes the final form



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\underset{\underset{\underset{:O:}{\cdot\cdot}}{\cdot\cdot}}{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

which is very different from the classical formula

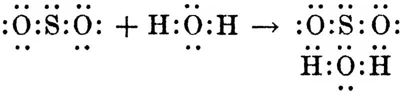


in which we find two double bonds instead of one.

As a second example let us choose the oxygen acids of sulfur.

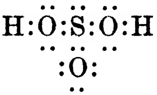
$$:\overset{\cdot\cdot}{S}: + 2:\overset{\cdot\cdot}{O}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{S}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$$

The sulfur cannot form a double bond and hence cannot complete its octet at this stage. The addition of water, however, makes this possible.



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{S}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: + H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\underset{H:\underset{\cdot\cdot}{O}:H}{\cdot\cdot}}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$$

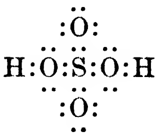
The hydrogen atoms are very mobile, however, and hence we could just as well write



$$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\underset{:\underset{\cdot\cdot}{O}:}{\cdot\cdot}}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

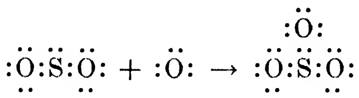
This formula for sulfurous acid contrasts strikingly with the classical structural formula which involves two double bonds and gives sulfur a valence of six.

Sulfurous acid is readily oxidized to sulfuric in virtue of the unshared electron pair on the sulfur. This pair can be appropriated by another oxygen atom to complete its octet, giving



$$\begin{array}{c} :\ddot{O}: \\ H:\underset{..}{\ddot{O}}:\underset{..}{\ddot{S}}:\underset{..}{\ddot{O}}:H \\ :\underset{..}{O}: \end{array}$$

Similarly



$$:\underset{..}{\ddot{O}}:\ddot{S}:\underset{..}{\ddot{O}}: + :\ddot{O}: \rightarrow \begin{array}{c} :\ddot{O}: \\ :\underset{..}{\ddot{O}}:\ddot{S}:\underset{..}{\ddot{O}}: \end{array}$$

The modern quantum mechanical theory gives somewhat different pictures for formulas such as this one and the one for nitric acid.

All that remains to complete this elementary exposition is a brief consideration of the unexplained details of Table I. The Lewis theory ignored the question of the state of motion of the electrons; indeed, for rough qualitative purposes this knowledge is not needed. However, where phenomena related to electronic structure are to be investigated quantitatively the energies of motion of the electrons become a matter of prime importance. The theory of the origin of spectra is an example of this sort. The first satisfactory step in the solution of this problem was made by Bohr in 1913, who applied Planck's quantum theory to Rutherford's dynamic model of the hydrogen atom.

According to the quantum theory, light of a given frequency, ν, is made up of units of energy, E, called quanta, which are proportional to the frequency:

$$E = h\nu$$

The proportionality constant h is called "Planck's constant." In interactions between matter and energy, only integral numbers of quanta can be emitted or absorbed. In applying this theory to the hydrogen atom, Bohr found it necessary to assume, contrary to the classical electromagnetic theory, that an electron may revolve around a nucleus in a fixed orbit without emitting energy. If, however, it absorbs or emits energy it does so in such a way that a definite integral number, n, of quanta are involved and the frequency of the radiation absorbed or emitted is given by the equation

$$\nu = \frac{E_2 - E_1}{h}$$

where E_2 and E_1 respectively represent the energy of the electron in its final and initial state. These two states were envisioned as two different orbits. In circular orbits the restrictions imposed by the quantum theory reduce to the statement that only those orbits are possible in which the angular momentum of the electron is $\frac{nh}{2\pi}$. The integer n is called the total quantum number. It has the values 1, 2, 3 . . . in the K, L, M . . . shells, respectively.

In addition to circular orbits the Bohr theory also postulates elliptical orbits. Thus in the nth quantum state of the hydrogen atom, n orbits are allowed, one of them circular and the remainder elliptical. These elliptical orbits may differ from one another in their major axes and in their eccentricities, and two more quantum numbers, called respectively the radial and azimuthal quantum numbers, become necessary to distinguish between the possible paths electrons may take. Bohr's calculations led to values of the frequencies of the lines in the hydrogen spectrum which agreed with experimental values within the limits of experimental error.

The old quantum theory underwent considerable development in the hands of Heisenberg (1925) and Schroedinger (1926). The new theory is frequently referred to as wave mechanics. Although Bohr's geometrical pictures still have significance in terms of the new theory, it is preferable to look upon the different shells and orbits as representing different energy states of the electrons and upon the quantum numbers as being parameters which determine just which of these energy states a given electron is occupying. Four quantum numbers in all are required to determine completely the state of an electron, and no two electrons in the same atom may exist in the same quantum state (Pauli restriction principle).

In describing the state of an electron it has become conventional to indicate its state with respect to the total quantum number as 1, 2, 3 . . . etc., depending upon whether it is in the K, L, M . . . etc., shell, and to symbolize the azimuthal quantum numbers 0, 1, 2, 3 as *s, p, d, f*. Thus if $n = 2$ and the azimuthal quantum number has a value of zero, the state of the electron with respect to these two limiting conditions would be indicated as the 2*s* state. For reasons which need not be discussed here, only these two quantum numbers are indicated in Table I.

The relative stability of electrons in various energy states depends upon how close to the nucleus the electrons are. Electrons in the K shell of a given atom are more stable (i.e., held under greater constraint) than those in the L shell, etc. Furthermore, if we compare the different electrons in a given shell of one atom, the *s* electrons penetrate most deeply into the atom and hence are most stable. The order of stability is $s > p > d > f$.

Table I is self-explanatory. It describes different atoms in terms of the number of electrons present in each which have the same total and azimuthal quantum numbers.

APPENDIX II

REFRACTIVITY AND CHEMICAL CONSTITUTION

The Electromagnetic Theory of Light

This theory was developed mathematically by Maxwell (1831–1879) and forms the basis of any real understanding of the modern theory of refraction. In the development of the theory,[1] Maxwell introduced the concept of "displacement currents." To understand this concept, imagine each plate of an electrical condenser connected through a separate galvanometer to a battery. If by means of a variable resistance the condenser is gradually charged, each galvanometer will register the same current and the result will be the same as if a current were passing between the plates. Maxwell envisioned such a "displacement current" as actually existing. Its magnitude would be proportional to the rate at which the electrical field strength was increasing.

Now it is well known that whereas a stationary electric charge produces no magnetic field, a moving charge does produce one; also a moving magnetic pole will produce an electric field. It follows, therefore, that if we produce a momentary displacement current this in turn will produce a momentary magnetic field, which will produce an electric field, and so on, the net result being an electromagnetic impulse with "electric and magnetic vectors" at right angles to each other. The impulse will be propagated through space. With this picture in mind Maxwell deduced mathematically that the velocity with which such an electromagnetic disturbance travels through space is

$$v = \frac{c}{\sqrt{\mu\epsilon}} \qquad (1)$$

where c is the number of electrostatic units of current in one electromagnetic unit of current; μ is the magnetic permeability, and ϵ the dielectric constant of the medium through which the disturbance is being propagated. In free space where μ and ϵ are unity, $v = c$, and it so

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[1] See Richtmyer, *Introduction to Modern Physics*, McGraw-Hill Book Co., 1928, Chap. IV, and J. K. Robertson, *Introduction to Physical Optics*, D. Van Nostrand Co., 1935, Chap. XVI.

happens that c is the measured velocity of light in free space. Hence light travels with the same velocity as an electromagnetic wave and may thus be presumed to be electromagnetic in character. Further support for this contention is derived from the fact that polarization studies show light waves to be of a transverse type, as was indicated also for electromagnetic waves by the Maxwell equations.

It also follows from Maxwell's theory that light must have its origin in accelerated electric charges. Furthermore, since mere acceleration of a charge would give out a single electromagnetic pulse, a train of light waves must be produced by the charge vibrating back and forth in a linear path or moving with uniform velocity around a circle. Since light is commonly produced by the vibration of material particles in a body heated to a high temperature, it follows that these material particles must be electrical in nature. This particular conclusion, of course, is in entire agreement with present day concepts of the nature of matter.

The Refraction of Light

In many substances the centers of the positive and negative charges (from nuclei and electrons) coincide. When an electromagnetic wave passes through such substances, the electric field of the wave would be expected to displace the nuclei and electrons in different directions, thus producing electrical dissymmetry and giving to the molecule the properties of an electric dipole. If instead the substance were composed of molecules in which electrical dissymmetry existed initially, molecular dipoles would be present even in the absence of the wave and would, of course, be altered by the influence of the wave. Thus all molecules act as electrical dipoles in the presence of electromagnetic waves.

If an electron in any molecule is acted upon by a constant electrical field it will be displaced such a distance that the displacing force equals the restoring force, thus producing equilibrium. If now the exciting field is removed the electron will be forced into vibration by the restoring force and will vibrate with a characteristic "natural frequency" which depends upon the restraints under which the electron exists in that particular molecule. Next, if we consider light waves to traverse the molecule, it is evident that we will encounter the phenomenon of resonance if there are among the waves some whose frequency of vibration is the same or nearly the same as the natural frequency of the electron. If there is no such frequency in the light beam other frequencies may impose forced vibration on the electron. In either case it is evident that there is operative a phenomenon analogous to friction which would impede the progress of the light wave and hence decrease its velocity. The extreme decrease will be encountered in the case of resonance where the wave may be stopped completely. This phenomenon is responsible for the production of absorption bands.

The index of refraction is defined as

$$n = \frac{v_0}{v} \tag{2}$$

where v_0 is the velocity of light in free space and v is the velocity in any particular medium. It happens that for most transparent substances $\mu = 1$ as a close approximation. Hence for such substances Equation 1 becomes

$$v = \frac{c}{\sqrt{\epsilon}} \tag{3}$$

Since $\epsilon = 1$ for a vacuum, we may substitute the values of v and v_0 given by Equation 3 back into Equation 2 and get

$$n = \sqrt{\epsilon} \tag{4}$$

as a good approximation for such substances. This prediction of the electromagnetic theory has been tested experimentally and found to give excellent agreement for a wide variety of substances. However, there are a number of glaring exceptions, such as liquid water, where the refractive index for yellow light is 1.33 and $\sqrt{\epsilon} = 8.9$ at room temperature, using direct or low frequency alternating current. Richtmyer points out[2] "The fact that, in most gases, the predicted equality of n and $\sqrt{\epsilon}$ is observed indicates that the theory leading to this law is, at least in certain particulars, substantially correct; while the disagreement found in the case of most liquids and solids indicates that the theory is incomplete—that certain factors have not been taken into account."

One such factor which was not included in Maxwell's development is the contribution of the molecular dipoles in the dielectric to the effective current density. If this effect is introduced into the mathematical development, the following equation is obtained:[3]

$$n^2 = 1 + \frac{e^2}{\pi m} \sum \frac{N}{(\nu_0{}^2 - \nu^2)} \tag{5}$$

where e is the charge on the electron, N is the number of electrons per unit volume, m is the mass of the electron, ν is the frequency of light, and ν_0 is the natural frequency of vibration of the electrons. It is at once apparent that the refractive index depends upon the frequency of the

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[2] Ref. 1, p. 113.

[3] Ref. 1, p. 118.

light. It is also well known that the dielectric constant depends on the frequency of the alternating current used in its measurement and on the temperature. This suggests that if the refractive index and the dielectric constant are to be compared, as in Equation 4, they should ideally be measured at the same temperature and by use of electromagnetic waves of the same frequency. When this is done, using low frequency waves, the agreement of n and $\sqrt{\epsilon}$ becomes much more satisfactory: e.g., 8.89 and 8.94, respectively, for water.

For our immediate purpose the most important conclusion to be drawn from Equation 5 is that, for a given frequency of light, the refractive index depends on the natural frequency of vibration of the electrons in the substance involved; this in turn depends on the constraints under which the electrons exist. Thus in refraction studies we have a tool for investigating the firmness with which electrons are held in molecules.

Specific and Molar Refraction

The refractive index does not lend itself to the study of chemical generalizations, but when instead we use the specific refraction, which was defined by Lorentz and Lorenz as

$$\Sigma = \frac{n^2 - 1}{(n^2 + 2)d}$$

where d represents the density of the substance, we find that such generalizations appear. The Lorentz-Lorenz formula, which was developed from the electromagnetic theory, has the advantage that the value appears to be independent of the physical state of the compound and is also practically independent of temperature and pressure. For chemical purposes it is customary to use the "molecular refraction," which is the product of the specific refraction and the molecular weight. Since the molecular refraction depends on the wave length of the light used it is customary to indicate the wave length by means of subscripts. Thus if the hydrogen *alpha* line were used in making the determination, the molecular refraction would be designated by M_α, while the symbol M_D would indicate that the sodium D line had been used. Sometimes the alternative symbol $[R_M]_D$ is used.

Atomic and Ionic Refractions

From what has already been said it should be obvious that the molecular refraction is the sum of the individual contributions made by all the electrons in a molecule. The contribution of each electron will, of course, in turn depend on the constraints under which it exists, and in general these will depend primarily upon what kind of atom or atoms it is a part, although they will also be influenced to some extent by the structure of the rest of the molecule. It has accordingly been found possible to analyze the molecular refractions into the contributions of the constituent atoms (atomic refractions) which are found to be reasonably constant when certain constitutive influences are taken into account. For example, the atomic refraction of nitrogen is different in primary, secondary, and tertiary amines. However, when such variations are taken into account molecular refractions may usually be calculated with a surprising degree of accuracy from the atomic refractions.

The following table presents some of the values of atomic refractions given by Auers and Eisenlohr,[4] who undertook a critical recalculation of these constants.

TABLE I

ATOMIC REFRACTIONS AND DISPERSIONS

Atom or group	Na_D line	Dispersion $H_\gamma - H_\alpha$
$—CH_2—$	4.618	0.113
C	2.418	0.056
H	1.100	0.029
O (carbonyl)	2.211	0.078
O (ether)	1.643	0.019
O (hydroxyl)	1.525	0.015
Cl	5.967	0.168
Br	8.865	0.340
I	13.900	0.775
N (*prim.* amine)	2.322	0.086
N (*sec.* amine)	2.499	0.119
N (*tert.* amine)	2.840	0.186
S (mercaptan)	7.69	0.35
C═C (double bond)	1.733	0.200
C≡C (triple bond)	2.398	0.171

The application of such data to problems of molecular structure should be obvious. Thus Henrich [5] cites acetoacetic ester, for which the molecular refraction calculated for the keto form using the *D* line is 31.573, whereas it is 32.620 for the enol form. The measured value of the molecu-

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[4] Auers and Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911); *Refractometrisches Hilfbuch*, p. 128.

[5] Henrich, Johnson, and Hahn, *Theories of Organic Chemistry*, John Wiley & Sons, 1920, p. 298.

lar refraction was found to be 32.00, indicating that the ester is a mixture of the two tautomers.

The refractions of individual ions is also a subject that has been much studied. For a detailed discussion of the subject the student is referred to the excellent discussions by Sidgwick[6] and by Smyth.[7] We shall attempt nothing here except a summary of the conclusions drawn from these studies, much of the credit for which we must assign to Fajans and his collaborators. The main conclusions may be summarized as follows:

(1) Ions are not rigid structures but are deformed by electric fields, such as electromagnetic waves or the electric fields of neighboring ions. The cause of this deformation was discussed under the heading: "The refraction of light."

(2) The polarizability (deformability) of ions of the same "effective atomic number" (i.e., having the same actual number of planetary electrons in the ion) is greater the smaller the positive charge of the nucleus. This is to be expected, since a greater nuclear charge would subject the constant number of electrons to the influence of a more intense positive field, and this would result in holding them more firmly. The refractivity of the following ions will serve to illustrate the case.

$$O^{=} = 7.0, \quad F^{-} = 2.4, \quad Ne = 1.0, \quad Na^{+} = 0.5, \quad Mg^{++} = 0.3$$

(3) In any series with a constant ionic charge the polarizability increases with the atomic number.

(4) The refraction of any ion is due almost wholly to its outer shells of electrons.

(5) Cations suffer relatively little deformation but act essentially as deforming agents. Their deforming power increases with their ionic charge and with a diminution in their diameters.

When a cation comes into close proximity with an anion the latter is naturally deformed by the former. Furthermore, the refractivity of the anion is lessened owing to the restraining influence of the positive field of the cation. If this deformation goes far enough it is not surprising to find that the electronic orbits of the two atoms, which in a salt are separate, interpenetrate, thus forming a covalent linkage. It follows that if a covalent linkage is formed the refractivity of the pair of electrons involved becomes much less than it would be if electrovalence obtained. This is borne out by the fact that the molecular refractions of the hydro-

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[6] Sidgwick, *The Covalent Link in Chemistry*, Cornell Univ. Press, pp. 30–39.

[7] Smyth, *Dielectric Constant and Molecular Structure*, The Chemical Catalog Co., 1931, pp. 142–150.

gen halides are less than the ionic refractions of the halogens.[8] Since the addition of the hydrogen ion adds no electrons, the diminution in refractivity must be due to the increased restraint imposed upon one or all four pairs of valence electrons in the halogen ion. If we assume that only the pair which became covalently bound was affected, then the contribution of the other six electrons to the molar refraction must be three-quarters of the refraction of the halogen ion. Subtracting this value from the molar refraction should give the contribution of the shared electron pair. This difference turns out to be practically zero. One might be tempted to interpret this as meaning that the shared electrons are under such large constraint that their contribution becomes negligible. But in some cases, where the bonds must be more rigid, their contribution, calculated as above, appears to be a negative number. This can only be interpreted by granting that the six unshared electrons must also be put under larger constraint by the addition of the hydrogen ion, a conclusion which is in entire accord with the Lewis-Lucas electron displacement theory, since the decreased screening effect attending the addition of the hydrogen ion would increase the effective kernel charge and hence decrease the polarizability of the unshared electrons.

Definition of Polarizability

So far we have not offered an exact definition of polarizability. To find such a definition we may turn to the work of Lorenz [9] who made his deductions on the basis of the electromagnetic theory of light. The polarization consists in a separation of the centers of positive and negative electricity and is measured by the moment of the electrical dipole thus produced. If q represents the magnitude of the charge on either end of the dipole, l the distance between the two charges, and P the polarization, then

$$P = ql$$

The polarizability, α_0, is defined as

$$\alpha_0 = \frac{P}{I}$$

where I is the strength of the electric field producing the polarization. Combining these equations, we get

$$\alpha_0 = \frac{ql}{I} \qquad (6)$$

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[8] Smyth, *Phil. Mag.*, 50, 361 (1925).

[9] See Ref. 6, pp. 31–32.

Lorenz showed that, if n is the refractive index of the medium for infinite wave length and N the number of molecules in a gram-molecule (Avogadro's number), the polarizability may be expressed as

$$\alpha_0 = \frac{3}{4\pi N}\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{m}{d} \tag{7}$$

where m is the molecular weight and d the density of the medium. It was previously pointed out that the molecular refraction (Lorentz-Lorenz) is given by the equation

$$M = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{m}{d} \tag{8}$$

Hence, combining Equations 7 and 8 we get

$$\alpha_0 = \frac{3}{4\pi N} M_\infty \tag{9}$$

For most purposes the substitution of M_∞ by the molecular refraction for visible light gives sufficiently accurate results.[10] Thus we find that the molar refractivity, as ordinarily determined, gives us directly a measurement of the total polarizability of all the electrons in a given molecule.

Polarizability phenomena may also be considered from the point of view of the restoring forces acting on the displaced electrons. It is customary to consider that the restoring force is proportional to the displacement. Thus if the force eI is exerted by the electric field, the restoring force will produce equilibrium when

$$eI = fx \tag{10}$$

where x is the displacement of the electron from its normal position and f is the restoring force constant. The moment produced by this displacement is

$$ex = \frac{e^2 I}{f} \tag{11}$$

From the definition of α_0 it follows that for a given bond

$$\alpha_0 = \frac{ex}{I} = \frac{e^2}{f} \tag{12}$$

or for the whole molecule

$$\alpha_0 = \sum \frac{e^2}{f} \tag{13}$$

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[10] Ref. 6, p. 32.

When visible light is used, $M = P_E$, where P_E is the polarization due to the displacement of electrons. Then it follows from Equations 7, 11, and 13 that

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d} = \frac{4\pi N}{3} \alpha_0 = \frac{4\pi N}{3} \sum \frac{e^2}{f} \tag{14}$$

Dispersion

Dispersion of light is due to the fact that the refractivity of any substance is different for different frequencies of light. The difference between the molecular refractions of a given substance for two different frequencies (e.g., the α and γ lines of hydrogen) is called the molecular dispersion and is symbolized as $M_\gamma - M_\alpha$ or $M_{\gamma-\alpha}$. If the dispersion is measured in terms of specific refractions it is called the specific refractive dispersion and is symbolized [11] as $\Sigma_\gamma - \Sigma_\alpha$ or $\Sigma_{\gamma-\alpha}$. Auers and Eisenlohr [12] usually express it as 100 times the actual value in order to use a number of more convenient size.

Exaltation

When molecular refractivities are calculated from the atomic constants, adding in such constitutive factors as may be necessary (e.g., double bonds), we frequently find an appreciable difference between this value and the measured value calculated in terms of the Lorentz-Lorenz formula. This difference is called the "molecular exaltation" (symbol: EM) and has been traced to certain constitutive peculiarities such as conjugation. Cornubert,[13] in his review of the subject, speaks of such constitutive peculiarities as "elements perturbateurs." These "elements perturbateurs" act on the index of refraction and the density in such a way that the exaltation becomes multiplied by the molecular weight if EM is used. Thus comparisons between compounds of different molecular weights are obscured. To avoid this difficulty it is customary to use "specific exaltation" which is defined as

$$E\Sigma = 100 \frac{EM}{m} \tag{15}$$

where m is the molecular weight.

Exaltations of the molecular dispersion are also observed. They are designated as $EM_{\beta-\alpha}$ or $E(M_\beta - M_\alpha)$ and exaltation of the specific dispersion as $E\Sigma_{\beta-\alpha}$ or $E(\Sigma_\beta - \Sigma_\alpha)$. There is a parallelism between exaltations of the refractions and the dispersions although dispersions

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[11] Auers and Eisenlohr, *Ber.*, 806 (1910) and subsequent papers.

[12] Eisenlohr, *Spectrochemie organischer Verbindungen*, Enke, Stuttgart, 1912.

[13] Cornubert, *Rev. gén. sci.*, **33**, 433, 471 (1922).

are usually more influenced than refractions by changes in chemical constitution.

Conjugation is the chief "element perturbateur." Two or more double bonds in a molecule produce no exaltation unless they are conjugated. Successive conjugation increases the exaltation, as illustrated by the following values [14] for $E\Sigma_{\gamma-\alpha}$.

$-C{=}CH-$	0.33
$-CH{=}CH-CH{=}CH-$	1.90
$-CH{=}CH-CH{=}CH-CH{=}CH-$	4.20

The amount of exaltation produced is also a function of the substituents. If, in the system $-\underset{(a)}{CH}{=}\underset{(b)}{CH}-\underset{(b)}{CH}{=}\underset{(a)}{CH}-$ we designate the carbon atoms (*a*) as "lateral" and (*b*) as "median" carbon atoms, the substitution of OH, OAlk, OAc groups on one of the lateral carbon atoms increases the exaltation, but if substituted on one of the median carbon atoms its influence is less marked and is variable. In general the effect of these groups in increasing the exaltation is in the order [13] OH > OAlk > OAc.

The double bonds of the benzene ring apparently conjugate with double bonds in side chains as shown by the examples in Table II. The fourth example shows that crossed conjugations produce a smaller change.

TABLE II

EXALTATIONS OF THE REFRACTION AND DISPERSION [13]

Compound	$E\Sigma_D$	$E\Sigma_{\gamma-\alpha}$ (%)
 $-CH{=}CH_2$	1.13	45
 $-CH{=}CH-CH{=}CH_2$	3.69	130
 $-CH{=}CH\cdot CH_3$	1.19	48
$Ph_2C{=}CH\cdot CH_3$	1.01	38

Some isocyclic aromatic compounds, although they involve what appears to be a system of conjugated double bonds, show almost no exaltation. Such is the case with benzene, furan, thiophene, and pyrrole. It has been suggested [14] that "the identity of the calculated and observed molecular dispersion values for these compounds is explained as being

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[14] Brode and Leermakers in Gilman's *Organic Chemistry*, John Wiley & Sons, 1938, p. 1741.

due to the existence of two opposing factors which nearly balance, that of conjugation producing a positive exaltation and that of ring strain or ring closure producing a negative exaltation."

Polycyclic compounds derived from these isocyclic compounds by ring fusion show positive exaltations. Thus $E\Sigma_{\gamma-\alpha}$ for naphthalene is 60%. Brode and Leermakers[14] interpret this fact as indicating "that only one ring in such compounds is truly aromatic, the other rings producing the exaltation characteristic of normal unsaturated conjugation."

It is of course to be expected that such groups as C═O, C═N, etc., will conjugate with the ethylene linkage and produce exaltations. However, it is surprising to find that the same effect is exhibited by atoms or groups having unshared electrons, provided that such electrons appear on the atom which is in the *alpha* position relative to the doubly bound carbon atoms. Examples of such groups are OH, OR, NH_2, etc. An explanation of this phenomenon is to be found in the electronic theory of the English school (Chapter V).

APPENDIX III

DIPOLE MOMENTS

This brief appendix on an important and rapidly growing field of chemical physics is presented merely as a convenient aid to the student whose training has not included this subject. It is in no sense an exhaustive review. The subject has been frequently and extensively reviewed by others and the student is referred to their works on the subject.[1]

If two unit charges (e) are separated from each other by the distance d, the intervening space being filled by any given dielectric substance, the force of attraction between the two charges is given by Coulomb's law:

$$f = \frac{e^2}{\epsilon d^2}$$

where ϵ is a constant for a given dielectric and is referred to as the dielectric constant. When substances having high dielectric constants are placed between the plates of a condenser the latter may be given a higher charge with a given potential difference.

The classical explanation of this phenomenon was based on the principles of Maxwell's electromagnetic theory, discussed in the last chapter. If we consider a condenser to be charged by an alternating current, the alternating field between the plates will polarize the dielectric much as a beam of light would do. The dipoles thus produced would present at each plate of the condenser a sheet of electrical charges of the opposite sign to that on the plate. This would naturally result in pulling more electricity onto the plate.

Quantitative disagreement was frequently encountered, however, and ultimately the theory was modified by taking into account the possibility that in addition to the induced dipoles there might also be permanent dipoles present as the result of unequal attractions of two bound atoms for the binding electrons. This point of view was developed by

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[1] (*a*) Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929; (*b*) Smyth, *Dielectric Constant and Molecular Structure*, Chemical Catalog Co., 1931; (*c*) LeFevre, *Dipole Moments*, Chemical Publishing Co., New York, 1938; (*d*) Waters and Lowry, *Physical Aspects of Organic Chemistry*, D. Van Nostrand Co., 1937; (*e*) Sidgwick, *The Covalent Link in Chemistry*, Cornell Univ. Press, 1933, Chap. 5.

Debye and others and has given satisfactory quantitative agreement between facts and theory.

The following equation was developed by Debye.

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{m}{d} = \frac{4\pi N}{3} \alpha_0 + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \tag{1}$$

where P is the total molar polarization, m the molecular weight, d the density, α_0 the polarizability, μ the permanent moment, k the molecular gas constant, and N Avogadro's number.

The equation shows that the total polarization, measured by the dielectric constant, is the sum of two terms, the first of which is the induced polarization and the other the polarization due to the presence of permanent dipoles (called the "orientation polarization," symbol P_0).

The polarizability α_0 is the sum of two effects: (1) γ_E, the moment induced as the result of the displacement of electrons, and (2) γ_A, that resulting from the displacement of atomic nuclei. Thus Equation 1 may be rewritten as

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{m}{d} = P = \frac{4\pi N}{3} \left(\gamma_E + \gamma_A + \frac{\mu^2}{3kT} \right) \tag{2}$$

or

$$P = P_E + P_A + P_0 \tag{3}$$

Several methods are available for evaluating μ when ϵ, d, and m are known. One depends on the variation of ϵ with the frequency. When low frequency currents are used in making a measurement of the dielectric constant, it is found that the latter is independent of the frequency. When somewhat higher frequencies are used, however, it becomes a function of the frequency because the time taken for a dipole to change its direction of orientation by 180° is slightly greater than the time required for the completion of one cycle by the alternating current and hence the arc of oscillation will be less than 180°. With further increase of frequency the orientation polarization P_0 disappears altogether because the sluggish dipolar molecules are unable to follow the rapid reversals of the field, and at this point $P = P_E + P_A$. If this progressive increase of frequencies is continued, a point is ultimately reached where the heavy atomic nuclei can no longer accommodate themselves to the rapid alternations and at this point $P = P_E$. Now, if we are working at such high frequencies that $P = P_E + P_A$ and if we introduce Maxwell's approximate relation, $n^2 = \epsilon$, then from Equations 2 and 3 we get

$$P = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d} = P_E + P_A$$

Comparing this with Equation 8 of Appendix II we see that $P_E + P_A$ is equal to the molar refraction. Thus, approximately, $P_0 = P - M_D$, where P is now the value measured at low frequencies.

Another method of evaluating μ makes use of the fact that in solids $P_0 = 0$ owing to the inability of the molecules to change their orientation. Still another method depends on the fact that only P_0 is a function of the temperature.

It is also of interest that P_A has been shown to be generally very small.

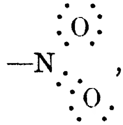
Bond Moments

If only one polar bond is present in the molecule, μ measures its polarity. If several such bonds are present, the problem becomes more complicated. In such cases it is customary to assume that the total dipole moment of the molecule is the vector sum of the constituent "bond moments." Obviously if the molecule has a symmetrical structure with relation to the constituent bond moments its total dipole moment will be zero. Thus CCl_4 has no dipole moment, although $CHCl_3$ has one of fair magnitude. Similarly no permanent moments are observed in CO_2 and CS_2. However, H_2O and H_2S are found to have permanent moments. This must mean that the three atoms do not lie in the same straight line and hence that the effects of the two dipoles do not cancel.

Cis and *trans* isomers also show the effect of symmetry. Thus *cis*-dichloroethylene has a moment of 2.5 × 10^{-18} e.s.u. (or 2.5 D, where D stands for one Debye unit which is 10^{-18} e.s.u.) while the *trans*-isomer, in which there is a point of symmetry, has no moment.

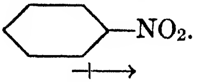
The analysis of molecular dipole moments into bond moments is complicated by the unfortunate fact that the values of the latter are not constant but are altered by the presence of other dipoles. Thus the dipole moment of CH_3Cl is larger than that of CH_2Cl_2, showing clearly that the C—Cl bond moment is much smaller in CH_2Cl_2.

The Sign of Bond Moments

If the nitro group has the structure  $—N\begin{matrix} :\ddot{O}: \\ \cdot\cdot \\ :\ddot{O}\cdot \end{matrix}$, which is clearly unsymmetrical, *p*-dinitrobenzene should have a moment. As a matter of experimental fact, it does not. This has been interpreted as meaning that one pair of electrons oscillates between the two oxygen atoms alternately conferring a double bond on each of them at the respective extremes of the oscillation. In between the two extremes we would have a condition difficult to picture on the basis of the customary concepts of bonds. At any rate, the radical would be symmetrical on the statistical average.

Nitrobenzene has a large moment, which we would expect from the dipolar nature of the group (it contains one coordinate covalence). Dipolar radicals, such as $-\overset{+}{C}\overset{-}{N}$, $=\overset{+}{S}\overset{-}{O}$, and $=\overset{+}{S}\overset{-}{O}_2$, always have large values of μ. Since this is in entire accord with our theory, it gives us the courage to use this same theory as an opening wedge to the solution of an important problem: viz., How may we determine which end of a dipole is negative?

Let us start, then, by assigning the following polar formula to the nitro group: $-\overset{+}{N}\overset{-}{O}_2$. Thus in nitrobenzene the algebraic sign of the moment would be negative and would be indicated by writing



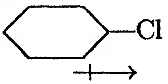
If a substituent is now introduced into the *para* position of nitrobenzene the total moment will be decreased if the individual moment of the new linkage opposes that of the nitro group, and vice versa. Illustrative material may be found in the following table.

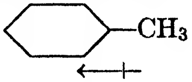
TABLE I

Values of μ in Debye Units

Nitrobenzene	3.9	Nitrobenzene	3.9
Chlorobenzene	1.55	Toluene	0.4
p-Nitrochlorobenzene	2.6	*p*-Nitrotoluene	4.5

From it we may deduce the following signs of the dipole moments:





Note also that the moments are roughly additive. Thus 3.9 − 1.55 = 2.35 which compares favorably with 2.6 for *p*-nitrochlorobenzene.

APPENDIX IV

BACKGROUND FOR THE STUDY OF NONAQUEOUS SOLUTIONS

In Chapter IV of this book we discussed the desirability of making the definitions of oxidation and reduction truly fundamental. The same question arises in respect to the definitions of acids and bases. From the point of view of the Arrhenius theory, which concerned itself only with aqueous solutions, an acid is defined as a substance which dissociates in solution, giving hydrogen ions as a primary dissociation product. A base is a substance which similarly gives hydroxyl ions. Of course numerous other ions are produced by ionogens, but the hydrogen and hydroxyl ions were considered unique in that they combined to form molecules of the weakly ionized solvent.

E. C. Franklin[1] was apparently the first to recognize that water is not fundamentally different from solvents in general and therefore that the classical definitions of acids and bases were not broad enough to be truly fundamental.[2] He showed that in liquid ammonia we have a solvent remarkably similar to water. Like water, it is slightly ionized according to the classical equation $NH_3 \rightarrow NH_2^- + H^+$. It reacts slowly with alkali metals according to the equation $2K + 2NH_3 \rightarrow 2KNH_2 + H_2$ and the resultant solution is basic to phenolphthalein and is capable of neutralizing acids. It is apparent, then, that potassium amide dissolved in liquid ammonia acts like a base. It is called an ammono-base. It is also analogous to potassium hydroxide (an aquo-base) in that it can be produced by replacing a hydrogen atom of the solvent by a metal. Like strong bases in the water system it is highly ionized, resulting in a high concentration of the negative ions of the solvent (NH_2^-). It thus becomes apparent that any substance which yields the same negative ions as the solvent will act like a base in that solvent. Thus sodium acetate is a base when dissolved in glacial acetic acid and we may even consider sodium methyl as a base in liquid methane.

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[1] E. C. Franklin, *J. Am. Chem. Soc.*, **27**, 820 (1905); *Am. Chem. J.*, **47**, 285 (1912); *J. Am. Chem. Soc.*, **46**, 2137 (1924).

[2] For a good review of the chemistry of liquid ammonia solutions see Fernelius and Johnson, *J. Chem. Education*, **5**, 664, 828 (1928); **6**, 20, 441 (1929); **7**, 981, 1291, 1602, 1850, 2600 (1930). Also see E. C. Franklin, *The Nitrogen System of Compounds*, Reinhold Publishing Corp., 1935.

When a hydrogen ion of water is replaced by a nonmetallic atom or group it results in the formation of an aquo-acid, e.g., $HOCl$, $HO\cdot NO_2$, $(HO)_3PO$. Similarly we have the following ammono-acids: $H_2N\cdot CN$, $(NH)_2PNH_2$, $HNPN$, $CH_3\cdot C(NH_2){=}NH$, etc. They all ionize in liquid ammonia solution to give hydrogen ions. Thus, as far as liquid ammonia solutions are concerned, there is no necessity for redefining acids.

If an ammono-acid and an ammono-base are brought together in liquid ammonia solution a neutralization ensues. The following equations bring out the analogy of this case with neutralization in aqueous solutions.

$$KOH + HOCl \rightarrow KOCl + H_2O$$

$$KNH_2 + HNPN \rightarrow KNPN + NH_3$$

This very superficial survey of the chemistry of liquid ammonia solutions makes clear the inadequacy of the classical definition of bases. One may well pause to ask, however, if Franklin's definition is completely satisfactory. What characteristic of the solvent makes its negative ion unique among negative ions? Its most characteristic property, the power to neutralize acids, is only the result of its power to form a weakly ionized molecule when combined with hydrogen ion, and all negative ions have this property to some degree. Furthermore, as G. N. Lewis pointed out,[3] this ability is merely a consequence of the fact that a hydrogen ion is electron-seeking and the basic ion has unshared electrons. He suggested a more general and more fundamental definition of acids and bases, viz., "a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and . . . an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms." According to this definition BCl_3 would be an acid, whereas ethyl ether would be a base. The fact that ether can combine with acids to form oxonium compounds is in complete accord with the concept.

Let us now return to the Arrhenius theory and give critical consideration to another of its concepts. The parallelism between acid strength and degree of ionization enjoyed practically universal recognition. The experimental basis for this concept was found in part in facts such as the following:[4]

(1) Dry hydrogen chloride does not react with dry ammonia gas, dry litmus, or dry calcium carbonate, nor does it destroy the luster of sodium for several weeks.

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[3] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Co., 1923, pp. 141–142.

[4] Stieglitz, *Qualitative Analysis*, vol. I, The Century Co., 1924, p. 72.

(2) Liquid hydrogen chloride is a very poor conductor of electricity and does not react with CaO, $CaCO_3$, Zn, or Mg.

(3) Dry HCl dissolved in benzene shows an extremely feeble conductivity. It has almost no effect on steel or $CaCO_3$.

The above concept is still taught in most freshman chemistry courses despite the fact that early in this century Hantzsch[5] performed a series of beautifully coordinated experiments which definitely disproved it. We will quickly survey the high points of these experiments.

One of the most characteristic properties of "hydrogen ions" is their ability to catalyze certain hydrolyses. According to the classical theory the amount of the catalysis is proportional to the concentration of hydrogen ions. Therefore, if the experiments are conducted in solutions of increasing acid concentration the catalytic effectiveness of an acid (i.e., the ratio of the speed to the concentration) should fall off owing to the decreasing degree of ionization. Actually Hantzsch observed just the opposite effect in studying the rate of inversion of sugar in aqueous solutions. Furthermore, he observed that the rise in "catalytic effectiveness" of different "strong" acids with increasing concentration varied from acid to acid. For example, this rise was much less marked with trichloroacetic acid than with sulfonic acids, and these less than with perchloric acid. In other words, in concentrated solutions the decreasing order of acid strength seemed to be: $HClO_4 > RSO_3H > Cl_3CCO_2H$, whereas they are all equally strong in dilute solutions.

These observations were completely verified when experiments were made on another acid-catalyzed reaction, viz., the decomposition of diazoacetic ester. These experiments were carried into the realm of nonaqueous solvents. Some of his results are summarized in Table I, where the ratios of decomposition velocities to normalities are given.

TABLE I

THE DECOMPOSITION OF DIAZOACETIC ESTER

(Catalyzing Acid: Trichloroacetic Acid)

SOLVENT	k/N	SOLVENT	k/N
Pentane	1.25	Water	1.0
Cyclohexane	0.59	Amyl alcohol	0.001
$CHCl_3$	0.45	Ethyl acetate	0.0007
C_6H_6	0.40	Acetal	0.0002
CCl_4	0.37	Ether	0.00003
Toluene	0.33		

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[5] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923). This paper gives a review of his work in this field.

From these results it is apparent that in the hydrocarbon solvents, where almost no ionization occurs, the catalytic effect is either greater or only slightly smaller than in water, whereas the strength in most oxygen-containing solvents is cut down enormously.

In similar experiments stronger acids were used. When tetralin sulfonic acid was used in chloroform solution it had an activity more than 200 times that of trichloroacetic acid in the same solvent. In this case the "strong" acid was markedly stronger in chloroform than in water.

Another acid property investigated by Hantzsch was the color change induced in indicators. His method was crude but rapid and it enabled him to survey a large field very quickly. It consisted in using a basic azo dye with various acids in various solvents and diluting until a change in color resulted. He considered this color change to be due to solvolysis * of the dye salt and hence to measure the relative strengths of the acids. The results accorded well with the diazo method.

Hantzsch's main conclusions can be summarized as follows:[6]

(1) Acids which are both highly ionized and strongly acidic in aqueous solutions are even more strongly acidic yet practically un-ionized in hydrocarbons and similar solvents, and differ among themselves greatly in their acidity; whereas dilute aqueous solutions of different acids have the same acidity at the same concentration.

(2) Acids, such as acetic, which are weak in water are much weaker in the hydrocarbon type of solvent.

(3) Many solvents containing oxygen, notably ether, give solutions of extremely low acidity. Some acids which are strong in water (nitric, trichloroacetic) are quite weak in ether, and only those acids (HBr, $HClO_4$) which are the most acid in chloroform and similar solvents have an acidity in ether which approaches the value in water.

These conclusions can most easily be explained by the Brönsted-Lowry theory of acidity, which is a direct outgrowth of the ideas of Hantzsch.

THE BRÖNSTED-LOWRY THEORY

Ammonium chloride dissolved in liquid ammonia acts like an acid in all respects. It was early recognized that it could be regarded as a solvated molecule of hydrochloric acid:

$$HCl + NH_3 \rightarrow NH_3 \cdot H^+ + Cl^-$$

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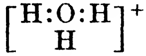
* Solvolysis is a general term applied to that phenomenon, exerted by solvents in general, which is analogous to hydrolysis.

[6] Hammett, *J. Am. Chem. Soc.*, **50**, 2666 (1928).

Hantzsch considered that an analogous reaction occurs whenever an acid is dissolved in water:

$$HCl + H_2O \rightarrow H_2O \cdot H^+ + Cl^-$$

It is readily seen that the solvated proton could be produced in virtue of the unshared electrons of the oxygen atom. The structure of this hydronium (or oxonium or hydroxonium) ion would then be



$$\left[\mathrm{H}:\underset{\mathrm{H}}{\overset{..}{\mathrm{O}}}:\mathrm{H}\right]^+$$

analogous to the ammonium ion, and recalls to mind Lewis's definition of acids and bases.

Much other evidence has been accumulated to prove the existence of the hydronium ion.[7] The most illuminating of these studies are the measurements of the heat of hydration of hydrogen ion. From such data Kolthoff [8] calculated that the equilibrium constant for the reaction

$$H^+ + H_2O \rightleftarrows H_3O^+$$

is 10^{130}. This is convincing evidence that no appreciable concentration of free protons can exist in aqueous solution.

With this in mind we may turn to a consideration of the theory of acidity proposed independently by Brönsted [9] and Lowry [10] in 1923. It will be recalled that this was the same year in which Lewis's monograph appeared. Brönsted and Lowry did not take as broad a view as Lewis, however. They defined a base as a substance whose molecules are capable of forming covalent links with protons. This definition is in no essential way different from that of Lewis; but they defined an acid as a substance capable of giving up protons, thus giving the word a more restricted definition than Lewis did. All three men agreed in attributing acidic and basic properties to the molecules themselves rather than to their solutions. Now the proton is by no means the only substance which can act as an electron acceptor and one might doubt the wisdom of thus restricting the definition of an acid. Brönsted [11] defends his point of view, however, by asserting that a proton is unique because, of all the atoms, it is the only one which consists solely of an atomic

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[7] (*a*) Hantzsch, *Z. physik. Chem.*, **65**, 41 (1908); (*b*) Fajans, *Ber. physik. Ges.*, **21**, 709 (1919); (*c*) M. Born, *Z. Physik*, **1**, 45 (1920); (*d*) Bagster and Cooling, *J. Chem. Soc.*, **117**, 693 (1920); (*e*) Fajans and Joos, *Z. Physik*, **23**, 1 (1924); (*f*) Volmer, *Ann.*, **440**, 200 (1924); (*g*) Klinkenberg and Ketelaar, *Rec. trav. chim.*, **54**, 959 (1935).

[8] Kolthoff, *Rec. trav. chim.*, **49**, 409 (1930).

[9] Brönsted: (*a*) *Rec. P. B.*, **42**, 718 (1923); (*b*) *Chem. Rev.*, **5**, 284 (1928).

[10] Lowry, *J. Soc. Chem. Ind.*, **42**, 43 (1923).

[11] Ref. 9*b*, p. 286.

nucleus. The only competitor for this unique position is the electron. Indeed in the concept of oxidation-reduction we find an exact parallel to the Brönsted-Lowry concept of acids and bases.[11, 12] The following argument will make this clear.

The "half-cell equation" for an oxidation-reduction reaction may be written as follows:

$$\text{Red} \rightleftarrows \text{Ox} + \ominus \qquad (1)$$

If now we follow Brönsted and Lowry in defining an acid as a substance which can give up protons while a base is a substance which can accept them, we may write the following in analogy with Equation 1:

$$\text{Acid} \rightleftarrows \text{Base} + \oplus \qquad (2)$$

An acid and a base which are related to each other in this way are spoken of as being "conjugate."

Returning now to Equation 1, we realize that in actual practice oxidation-reduction reactions are always more complex than this and involve at least two oxidants and two reductants.

$$\text{Red}_1 \rightleftarrows \text{Ox}_1 + \ominus \qquad (3)$$

$$\text{Red}_2 \rightleftarrows \text{Ox}_2 + \ominus \qquad (4)$$

$$\text{Red}_1 + \text{Ox}_2 \rightleftarrows \text{Red}_2 + \text{Ox}_1 \qquad (5)$$

Equations 3 and 4 are the half-cell reactions and Equation 5 represents the net result of the interaction of the two redox systems. If the second system has the higher electron affinity the equilibrium will be displaced toward the right. The actual equilibrium attained in this electron partition process will of course depend on the relative affinities and concentrations of the two systems.

The acid-base reaction may be represented as a proton partition reaction, using strictly analogous equations.

$$\text{Acid}_1 \rightleftarrows \text{Base}_1 + \oplus \qquad (6)$$

$$\text{Acid}_2 \rightleftarrows \text{Base}_2 + \oplus \qquad (7)$$

$$\text{Acid}_1 + \text{Base}_2 \rightleftarrows \text{Acid}_2 + \text{Base}_1 \qquad (8)$$

Equation 8 might be called the fundamental equation of the Brönsted-Lowry theory. It contains implicitly the notion that free protons do not exist in solution.

Let us now turn to an example of the application of the theory. According to the classical point of view, if HCl and NH_3 are dissolved together in water, the NH_3 first becomes hydrated to NH_4OH. The

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[12] Hall, *J. Chem. Education,* **7**, 782 (1930).

acid and base then interact through ionization to produce a salt and eliminate again the molecule of water previously used in the hydration process. According to the Brönsted-Lowry theory this hydration of the ammonia is a side reaction rather than an intermediate reaction. This point of view is rendered plausible by the fact that HCl and NH_3 in benzene solution (all anhydrous) will react rapidly to produce ammonium chloride. Obviously in this case no NH_4OH could have been produced. Formulating this reaction according to Equation 8 we get

$$HCl + NH_3 \rightleftarrows NH_4^+ + Cl^-$$
$$\text{Acid}_1 + \text{Base}_2 \rightleftarrows \text{Acid}_2 + \text{Base}_1$$

If the reaction had been carried out in water solution, the proton partition would also have involved the solvent

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$
$$\text{Acid}_1 + \text{Base}_3 \rightleftarrows \text{Acid}_3 + \text{Base}_1$$

It will be observed that in the above example ammonium ion is listed as an acid, whereas chloride ion is listed as a base. To the student schooled exclusively in the classical theory this usage will seem confusing. However, the theory holds that the state of electrical charge (the "charge type") has no bearing on the fundamental classification of substances as acids and bases although it will certainly affect their acid or base strength. Thus acids or bases may be charged or neutral. The following list gives examples of different charge types of acids and their conjugate bases.

$$HCl \rightleftarrows H^+ + Cl^-$$
$$NH_4^+ \rightleftarrows H^+ + NH_3$$
$$HSO_4^- \rightleftarrows H^+ + SO_4^-$$
$$Co(NH_3)_5OH_2^{+++} \rightleftarrows Co(NH_3)_5OH^{++} + H^+$$

One obvious advantage of the theory is that ionizations, neutralizations, hydrolyses, and acid-base partition reactions are all classified equally well by Equation 8 as proton partition reactions. This is illustrated by the following equations:

Ionization: $HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$

Neutralization: $HCl + OH^- \rightleftarrows H_3O^+ + H_2O$

Hydrolysis: $CN^- + H_2O \rightleftarrows HCN + OH^-$

Partition: $HC_2H_3O_2 + PhNH_2 \rightleftarrows C_2H_3O_2^- + PhNH_3^+$

$HCO_2H + PhNH_2 \rightleftarrows HCO_2^- + PhNH_3^+$

The last reaction represents the partition of a base between two acids. It is particularly to be noted that all these reactions are merely examples of Equation 8.

THE CLASSIFICATION OF SOLVENTS[13]

Solvents may be classified in four different groups from the standpoint of the Brönsted-Lowry theory.

(1) *Acidic.* These give up protons predominantly.

(2) *Basic.* These take up protons predominantly.

(3) *Aprotic.* These neither give up nor take up protons to an appreciable degree.

(4) *Amphiprotic.* These both give up and take up protons with ease.

Amphiprotic Solvents

Water falls in this class. If it takes up protons it is said to exercise its base function; if it gives them up it exercises its acid function. The equation for the base function of water,

$$HX + H_2O \rightleftarrows H_3O^+ + X^- \qquad (9)$$

illustrates that the tendency for water to act as a base is responsible for the ionization of an acid. If the strength of the added acid exceeds a certain critical value, the reaction of Equation 9 will go essentially to completion to the right. Thus even though the intrinsic strengths of two very strong acids are different, when equivalent amounts are dissolved in equal volumes of water, equal concentrations of hydronium ions are produced and the acids appear to be equally strong. This behavior is spoken of as the "leveling effect." It is to be observed that it explains Hantzsch's results, viz., that strong acids which appear to be of different strengths in an aprotic solvent like chloroform seem to be equally strong in water solution and weaker than in the aprotic solvent in which their high intrinsic tendencies to give up protons have not been "leveled" by the water.

In very weak acids, like ethyl alcohol, the acidic qualities are largely masked by the overwhelming prominence of the same property of water.

(*a*) *The Acid Function of Water.* If a strong base, like the ethylate ion, comes in contact with water, the water exercises its acid function:

$$EtO^- + H_2O \rightleftarrows EtOH + OH^- \qquad (10)$$

It is apparent that water would also have a "leveling effect" on strong bases.

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[13] Hall, *Chem. Rev.*, **8**, 191 (1931).

(*b*) *Autoprotolysis.* Since water is both an acid and a base it is capable of self-ionization or "autoprotolysis."

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

This is characteristic of amphiprotic solvents.

Aprotic Solvents

These are typified by hydrocarbons and their halogen substitution products. It is an interesting fact that as long ago as 1912 it was reported that the titration of acids could be successfully carried out in these solvents[14] and more recently it has been demonstrated that even electrometric titrations are possible in benzene.[15] Since aprotic solvents neither give up nor take up protons, autoprotolysis and leveling effects are impossible. Thus very strong acids like $HClO_4$ and very strong bases like $^-CH_3$ (from $NaCH_3$) are much stronger in aprotic solvents than in water. It is probable that here they come very close to exhibiting their intrinsic strengths.

Acidic Solvents

Acidic solvents are themselves, by definition, strong acids. Hence they must be weak bases and autoprotolysis is usually slight. The autoprotolysis of acetic acid is represented by the equation

$$CH_3CO_2H + CH_3CO_2H \rightleftarrows CH_3CO_2^- + CH_3CO_2H_2^+$$

This illustrates the fact that even acidic solvents exhibit weak base functions in addition to their major acid functions.

Their leveling effect is strong on bases but weak on acids. These relationships are brought out well by the pioneer researches of Hall and his collaborators on glacial acetic acid solutions.[16] Their studies were made by the method of potentiometric titration, using a chloranil electrode. They found that acids which are strong in water are still stronger in glacial acetic acid solution and that, whereas they are leveled to equal acidities in water, their strengths in acetic acid are spread over a considerable range. Thus $HClO_4$ is much stronger than H_2SO_4 in these solutions. This is a natural consequence of the very small acid leveling effect of the solvent. In regard to bases, they found that even such weak bases as guanidine could be satisfactorily titrated in acetic acid solution by $HClO_4$, their curves giving sharp breaks at the end points.

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[14] Folin and Flanders, *J. Am. Chem. Soc.*, **34**, 774 (1912).

[15] LaMer and Downes, *J. Am. Chem. Soc.*, **53**, 888 (1931).

[16] (*a*) Hall and Conant, *J. Am. Chem. Soc.*, **49**, 3047, 3062 (1927); (*b*) Hall and Werner, *ibid.*, **50**, 2367 (1928); (*c*) Hall, *ibid.*, **52**, 5115 (1930). See also Ref. 13.

Acetamide, however, is not a strong enough base to show a sharp end point. If an attempt were made to titrate guanidine in water solution, there would be a partition of protons between guanidine and water, whose basic properties are not inconsiderable in comparison with those of guanidine. In glacial acetic acid, however, the basic properties of the solvent are too weak to compete effectively with the much stronger base, guanidine, and the sharpness of the end point is not impaired.

Basic Solvents

This group contains such solvents as liquid ammonia, aniline, pyridine, ether, dioxane, esters, and acetal. Whereas the primary and secondary amines and ammonia show appreciable acid functions in addition to their major base functions, this is not the case with the tertiary amines and ethers, since they could liberate protons only by breaking C—H bonds. Basic solvents show strong leveling effects for acids but not for bases.

Very weak acids can show their intrinsic acidities in ether solution as well as they can in an aprotic solvent. Thus reactions of the type $RH + R'K \rightleftarrows RK + R'H$ (where R and R′ are hydrocarbon radicals) have been studied in ether solution.[17] If the above reaction went to the right, RH could be considered as a stronger acid than R′H. The relative strengths of a few of the acids studied are as follows: acetophenone > $PhC{\equiv}CH$ > indene > fluorene > xanthene > Ph_3CH > Ph_2CH_2.

Reactions of the type

$$Ph_3CH + KNH_2 \rightleftarrows NH_3 + Ph_3CK$$

can take place in liquid ammonia solution.[18] These reactions are possible because liquid ammonia is too weak an acid to cause serious solvolysis of the hydrocarbon salts produced. Solvolysis does occur, however, when sufficiently strong bases, like $PhCH_2^-$, are involved.

THE THERMODYNAMICS OF ELECTROLYTIC SOLUTIONS

This all-too-brief section is added for the student whose knowledge of thermodynamics does not extend beyond the study of single-component systems and gaseous mixtures.

The equilibrium law of Guldberg and Waage does not apply accurately to concentrated solutions of nonelectrolytes or weak electrolytes, nor to any solutions of strong electrolytes. If, however, the molality (m)

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[17] Conant and Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

[18] (*a*) Kraus and Rosen, *J. Am. Chem. Soc.*, **47**, 2741 (1925); (*b*) Wooster and Mitchell, *ibid.*, **52**, 688 (1930).

of each molecular or ionic species is multiplied by an empirical correction factor, f, called the activity coefficient, then experimental facts are brought into accord with the equilibrium law. Unfortunately the value of f varies with the concentration. The product fm is called the activity (a). Thus $a = fm$. The thermodynamic activity is thus seen to be the corrected concentration. The two are measured in the same units.

The activity is most satisfactorily defined by the following equation:[19]

$$F - F^o = \mathrm{RT} \ln \frac{a}{a^o} = \mathrm{RT} \ln a$$

where F is the molal free energy. The superscript o refers to the standard state in which the activity is unity. Because of certain thermodynamic relationships this definition is equivalent to the one given above in terms of the equilibrium law. $F - F^o$ represents the maximum amount of useful work obtainable from any system when it passes from the standard state to any other given state.

The use of a standard state is necessary since F and F^o cannot be measured individually (only their difference can be measured). Any state may be chosen as a standard state but as a matter of practical convenience it is customary to choose the standard state so that the activity of the solute is equal to its mole fraction or its molality in an infinitely dilute solution. If the mole fraction is chosen, then the activity coefficient is known as the rational activity coefficient; if the molality is chosen, then it is called the practical activity coefficient.

With strong electrolytes like NaCl, a somewhat different procedure is used. The standard state is chosen in such a way that at infinite dilution the activity of each ion is equal to its molality, which in turn is equal to the stoichiometric concentration of the salt, if we assume complete ionization. If a_+ is the activity of the Na^+ ion, a_- that of the Cl^-, and a_2 that of the undissociated NaCl, then from the equilibrium law we have

$$\frac{a_+a_-}{a_2} = K$$

In order to avoid the use of meaningless approximations for the value of a_2, it is defined as follows:

$$a_2 = a_+a_-$$

thus making K unity by definition. At infinite dilution, where dissociation is complete,

$$a_+ = a_- = \sqrt{a_2}$$

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[19] Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., 1923.

In the realm of finite concentrations the lack of reliable knowledge of the degree of dissociation forces us to use the "mean ion activity,"

$$a_{\pm} = \sqrt{a_+a_-} = \sqrt{a_2}$$

The mean activity of the ions divided by the stoichiometric molality gives the "mean activity coefficient." This has been called the "thermodynamic degree of dissociation." Brönsted calls it the "stoichiometric activity coefficient" to differentiate it from the ion activity divided by the assumed ion molality.

Another concept of much practical importance in the study of electrolytic solutions is the "ionic strength." It is defined by the equation

$$\mu = \tfrac{1}{2}\Sigma[(m_+{z^2}_+) + (m_-{z^2}_-)]$$

where z is the valence or charge carried by each ion and m is the stoichiometric molality. By way of illustration let us calculate the ionic strength of a 0.01 molal solution of $MgCl_2$.

$$\mu = \frac{(0.01 \times 4) + (0.02 \times 1)}{2} = 0.03$$

There is an important principle applying to solutions of strong electrolytes, which may be stated as follows: [19] *In dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.*

For a description of the methods used in measuring activities, the student must refer to the textbook of Lewis and Randall.[19]

APPENDIX V

TABLE OF BASIC PRINCIPLES

The main objective of the present volume has been the presentation and correlation of those developments in the field of physical and theoretical chemistry which seem to offer chemists new and useful methods of attacking the problems of preparative organic chemistry. Occasionally these developments have culminated in quantitative relationships. In such cases the equations have been given. It is characteristic of equations, however, that they demand for their application extensive tables of experimentally determined constants, and it is characteristic of preparative organic chemistry that such data are usually nonexistent for the compounds of greatest interest. For this reason the author has been deeply interested in recording qualitative generalizations of wide applicability in organic chemistry. Those which, in the opinion of the author, are most reliable and most useful have been called "basic principles" (symbolized by **P**) and they are collectively recorded in this section of the appendix. No attempt will be made to present a similar review of the many equations which also may be of very great general use either because of their quantitative or qualitative implications.

BASIC PRINCIPLES

P 1. Substances react as a result of their affinities for electrons (electrophilic) or atomic nuclei (nucleophilic). Bimolecular reactions are initiated by and at those parts of molecules which are most strongly electrophilic and nucleophilic in such a way that nucleophilic and electrophilic centers are brought together.

P 2. If, by substitution or by change in the thermodynamic environment, the electron density is increased at a given atom in a molecule, there will result an increase in the nucleophilic and a decrease in the electrophilic properties of that atom. Electrons are more easily removed from an atom the higher the electron density around it, and more easily attracted the lower the electron density.

P 3. The directions and relative magnitudes of the inductive, inductomeric, electromeric, and mesomeric effects of different atoms and groups may be deduced by well-established methods from considerations of the atomic diameter, nuclear charge, and the screening effect, except that the $+T$ effects decrease with increasing atomic number in any periodic group.

P 4. The magnitude of an inductive displacement becomes progressively and rapidly less as it proceeds away from the atom producing it. The extent to which the effect is transmitted is greater, the greater the polarizability of the intervening bonds.

P 5. Polarizability effects are brought into operation only under the influence of an external field. In chemical reactions this means only at the moment of reaction and only if they meet the electronic demands of the attacking reagent.

P 6. The extent (P) to which a polarizability effect is brought into play is given by the equation $P = \alpha F$, in which P is the induced polarization, α is the polarizability of the bond in question, and F is the strength of the distorting electrical field.

P 7. The change in electron density produced at a given atom by the operation of polarizability effects is proportional to the sum of the polarizations induced in the valence electrons of that atom.

P 8. Other things being equal, the electromeric effect will operate more readily the more extended the conjugation becomes.

P 9. The electromeric effect, except when unusally weak, is a much more powerful electron displacement agency than the inductive and inductomeric effects.

P 10. If it is possible to write two or more electronic structures for a given molecule without changing the arrangement of the atoms, then none of these structures represents the true state of the molecule, which is correctly represented by an intermediate mesomeric state. Thus these contributing structures will always undergo a mesomeric displacement in the direction of this intermediate state.

P 11. If resonance occurs in any molecular structure, that structure is more stable than any other closely related structure in which resonance is either less or absent.

P 12. Appreciable resonance only occurs between contributing structures having nearly the same energy. This resonance reaches a maximum when the contributing forms are identical.

P 13. Other things being equal, the amount of resonance increases with the number of contributing forms.

P 14. Each contributing form must be represented by the same geometrical arrangement of the atomic nuclei and the same number of unpaired electrons.

P 15. With atoms arranged in a ring, only those valence bond structures for which the bonds do not cross need be considered as contributing to resonance; all others can be represented as resonance combinations of these.

P 16. Contributing forms in which adjacent atoms have electrical charges of the same sign contribute much less to resonance than other structures.

P 17. Other things being equal, the most stable resonance form will have the greatest number of covalent bonds.

P 18. Other things being equal, the most stable resonance form will have a formal negative charge on the atom of highest electronegativity.

P 19. Other things being equal, molecules having the least "Baeyer strain" will be most stable.

P 20. An increase in the ionic character of bonds increases the heat of formation of the molecule.

P 21. Coplanarity is demanded of valence bonds entering into conjugative resonance (mesomerism) with each other.

P 22. Carbon to hydrogen bonds may enter into hyperconjugative resonance with suitably situated double or triple bonds (first-order hyperconjugation) or with other suitably placed carbon-to-hydrogen single bonds (second-order hyperconjugation). Both orders of hyperconjugation show the customary effects of resonance but these effects are stronger in first-order hyperconjugation.

P 23. The normal tendency for a substituent to alter the activation energy in accord with its effect on the attraction between the attacking reagent and the active center of a molecule, will be weakened with the weakening or removal of any well-defined positive or negative center in the attacking reagent. When such a center has become weak enough there will be a reversal of the effect, and the influence of the substituent will now be determined by its effect on the bond energy.

P 24. If the same molecule is attacked by two different reagents whose charges do not differ greatly, then as the total activation energy increases it is influenced by substituents in the attacked molecule less and less in the sense predicted from the change in the repulsion of the reagent and may, for very large activation energies, become subject to influences parallel with those of the substituent on the bond strength.

P 25. If the value of the *PZ* term (or $\Delta S^{\ddagger}$) for a given reaction is not altered by substitution or by a change of solvent, then the activation energy and the velocity constant become functions of potential energy changes alone and, at constant temperature, the velocity constant is a function of the activation energy alone.

P 26. Displacement reactions of the electron-pairing type may only occur (1) in a nonpolar environment as the result of primary photochemical or thermal dissociation or (2) in any environment in the presence of a sufficiently powerful monoelectronator or monodelectronator.

P 27. If a reaction is considered to occur in a logical succession of unit steps, then the minimum activation energy for the reaction may be calculated by adding together the ΔH values of the first endothermic step and those of any succeeding steps which, on the basis of the transition state theory, could be coupled with it.

P 28. A solvent will increase the thermodynamic probability of a reaction if the products are more firmly solvated than the reactants; if the reverse situation obtains, the solvent will decrease the thermodynamic probability of reaction.

P 29. A solvent will decrease the activation energy of a reaction if the critical complex is more firmly solvated than the reactants. If the reverse situation obtains, the solvent will increase the activation energy.

APPENDIX VI

TABLE OF SYMBOLS

C_p	Heat capacity at constant pressure.
D	Direct or field effect.
E	Elimination reaction (always followed by 1 or 2 to indicate mono- or bimolecular).
E	Electromeric effect.
E	Energy of activation.
E_h	Reversible e.m.f. referred to the normal hydrogen electrode as zero.
E'_0	Normal potential at constant pH.
E_c	Critical potential.
F	Field or direct effect.
$\bar{F}$	Partial molal free energy.
f	Activity coefficient.
f	Restoring force constant.
I	Inductive mechanism.
I_d	Inductomeric effect.
I_s	Inductive effect.
K	Equilibrium constant.
K^*	Thermodynamic equilibrium constant.
K^*_a	Thermodynamic acid ionization constant.
K_r	Relative ionization constant.
k	Velocity constant.
$\boldsymbol{k}$	Boltzmann constant.
M	Mesomeric effect.
N	Mole fraction.
P	Polarization.
P	Probability factor in rate equation.
P_∞ or ${}_\infty P_2$	Total polarization at infinite dilution.
pH	$-\log\ [H^+]$.
pH*	$-\log\ (H^+)$.
pK	$-\log$ K.
R	Ideal gas constant.
S	Absolute entropy.
S	Solvent molecule.
S_E	Electrophilic substitution reaction.
S_N	Nucleophilic substitution reaction.
T	Tautomeric mechanism.
Z	Collision number.
α_0	Polarizability.
ΔF	Free energy increase.
ΔF°	Standard free energy increase (all substances in their standard states).

$\Delta F^{\ddagger}$	Free energy of activation.
ΔH	Increase in heat content.
$\Delta H^{\ddagger}$	Heat of activation.
ΔS	Entropy increase.
$\Delta S^{\ddagger}$	Entropy of activation.
$\delta+$ or $\delta-$	Small fraction of a unit positive (or negative) charge.
ϵ	Dielectric constant.
κ	Transmission coefficient.
μ	Dipole moment.
μ	Ionic strength.
$[\ ]$	Concentration of.
$(\ )$	Activity of.
$\}$	Electrovalence.

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