ELECTRO-ORGANIC CHEMISTRY

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BY

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TO

M. P. B.

WHOSE TENDER SYMPATHY AND INTEREST
BRIGHTENED THE PERIOD DURING WHICH
THESE PAGES WERE WRITTEN

FOREWORD

THE mutual convertibility of "electrical" and "chemical" energies is, of course, a fact long ago established. The quantitative relations of the energies have been the subject of much study and investigation. In many chemical industries electrolytic methods have supplanted those employing heat or differential chemical energy—in the winning of metals and the transformation of chemical compounds. The recent development of the theory of "ions," and increased knowledge of the part played by electricity in the structure and behavior of atoms and molecules, have directed increased attention to the intimate relations of the two energies, and electrolytic methods have found increased application in laboratory procedure in chemical investigations.

The study of the electrolysis of the carbon ("organic") compounds is a comparatively new (as it is a peculiarly difficult) field of investigation.

Professor Brockman has rendered a distinct service to Chemistry in his recapitulation and critical review of the work done in this field, and his bibliography of the principal papers which have been contributed on the subject.

I can testify, personally, to the great zeal, unflagging industry and true scientific spirit of accuracy with which he has prosecuted the immense labor necessary to the production of this volume. It is an important contribution to chemical literature and should be a valuable addition to the library of the Chemist.

H. C. WHITE.

UNIVERSITY OF GEORGIA,
September, 1925.

AUTHOR'S PREFACE

The fact that the American Electrochemical Society held a symposium in 1915 in New York City and another in Philadelphia in 1924 indicates that there is a definite interest in Electro-organic Chemistry. There has been a rejuvenation of enthusiasm and interest in this particular field during the past several years.

Several compilations of the work in Electro-organic Chemistry have appeared from time to time. Some of these have been of more value than others, but each of them has been more or less specialized in one particular group of reactions. There has, however, been no publication in English since 1905. For these reasons, therefore, no apologies need be offered for another compilation of the data of Electro-organic Chemistry. In organizing the data and reviewing the literature, an effort has been made to make this book a complete picture of the progress which has been made. If the writer has failed to uncover all the extant information, or if he has misquoted anyone or anything, he begs of the authors their lenience. He sincerely hopes that the readers will be kind enough to make him cognizant of any errors of commission or omission which have unfortunately been included.

In searching the literature the author has made frequent use of all texts dealing wholly, or in part, with Electro-organic Chemistry, among which the most important are the following: Haber and Moser, "Elektrolytische Prozesse der organische Chemie," Halle, 1910; Foerster, "Elektrochemie der wässerige Lösungen," Leipzig, 1922; Blount, "Practical Electrochemistry," New York, 1903; Müller, "Elektrochemisches Praktikum," Dresden, 1924; Löb-Lorenz, "Organic Electrochemistry," New York, 1905; Perkin, "Practical Methods of Electrochemistry," New York, 1905; Tommasi, "Traité d'Électrochemie," 1889; National Research Council, Washington, D. C., "Bibliography of Electro-organic Chemistry" (*in press*); Marie, "Manuel de Manipulations d'Électrochemie," Paris, 1906; Le Blanc, "Lehrbuch der Elektrochemie," Leipzig, 1922; Hale, "Manufacture of Chemicals by Electrolysis," New York, 1919; Hale, "The Applications of Electrolysis in Chemical Industry," London, 1918; Thompson, "Applied Electrochemistry," New York, 1925; Lüpke–Muir, "Elements of Electrochemistry," London, 1903; Elbs, Übungsbeispiele für die elektrolytische Darstellung chemische Präparate," Halle, 1911; Brand, "Die elektrochemische Reduktion organischer Nitrokörper und verwandter Verbindungen," Stuttgart, 1908; Nernst, "Theoretical Chemistry," New York, 1923; Creighton, "The Principles of Electrochemistry," New York, 1924; Oettel, "Exercises in Electrochemistry"; Löb, "Leitfaden der praktischen Elektrochemie," Leipzig, 1899; Löb, "Die Elektrochemie der organischen Verbindungen," Halle, 1905; Möller, "Die elektrolytischen Reduktion der Nitroderivative organischer Verbindungen in experimenteller und theoretischer Beziehung," Halle, 1904; Peters, "Angewandte Elektrochemie, Band 3," Leipzig, 1898; Lorenz, "Elektrochemisches Praktikum," Göttingen, 1901; Ahrens, "Handbuch der Elektrochemie," Stuttgart, 1903.

The author is indebted to Drs. H. C. White of the University of Georgia, Alexander Lowy of the University of Pittsburgh, Fr. Fichter of the University of Basel, Switzerland, Erich Müller, of Dresden, Germany, and Duncan Burnet, the Librarian of the University of Georgia, who rendered excellent and most valuable assistance in getting the literature in hand. The Librarian of the University of North Carolina was very generous in permitting the author to borrow journals from his files.

Dr. V. S. Babasinian, Professor of Chemistry at Lehigh University, and Dr. H. Jermain Creighton of Swarthmore College read and criticized the manuscript and made many suggestions which greatly improved it. The author's colleagues in the Faculty of the University of Georgia willingly gave him their assistance whenever it was needed.

If, in writing this book, the author has made a contribution that will create an interest in this phase of Electrochemistry, he is satisfied.

C. J. Brockman.

University of Georgia,
September, 1925.

TABLE OF CONTENTS

PART I

REACTIONS AT THE ANODE

PART II

REACTIONS AT THE CATHODE

ELECTRO-ORGANIC CHEMISTRY

CHAPTER I

INTRODUCTION

A. HISTORY

ELECTRO-ORGANIC Chemistry attracted the attention of scientists as early as the beginning of the nineteenth century. It was known at that time that many organic compounds were able to conduct the electric current but no evidences of a decomposition had been reported. Dilute aqueous solutions of alcohol[1] and indigo white[2] were electrolyzed and the fact determined that there was an oxidation taking place. In 1830,[3] a more detailed study was made of the oxidation of alcohol at different electrodes, and a partial determination of the gaseous products was reported. Michael Faraday,[4] in studying secondary reactions at various electrodes, investigated the action of an electric current upon aqueous solutions of acetic acid and acetates, tartaric acid and tartrates.

Schönbein became interested in Döbereiner's study of the catalytic effect of platinum on the combination of gases, and studied, as did Becquerel,[5] the effect of spongy platinum on the evolution of gases during the electrolysis of alcohol. Becquerel found that in the electrolysis of acidulated water, if spongy platinum and gold were employed for one of the electrodes, the other being a plate of platinum, decomposition was facilitated, but a great proportion of the gas was absorbed by that electrode which was made with the sponge. This effect is always produced by finely divided platinum. Schönbein employed spongy platinum

[1] Reinhold, Gilb. Ann., **7**, 97 (1801); Erman, ibid., **8**, 206 (1801).

[2] Grotthus, Ann. Chim. et Phys., (1), **63**, 18 (1804).

[3] Ludersdorf, Pogg. Ann., **19**, 77 (1830); Connell, J. prakt. Chem., (1), **5**, 167 (1835).

[4] Experimental researches, vol. I, sections 749 and 750, 773–777; London (1839).

[5] Becquerel, Ann. chim. et phys., **11**, 162 and 257 (1844); Compt. rend., **18**, 862 (1844); Arch. d'Elect., **1**, 281 (1841); Schönbein, Arch. d'Elect., **2**, 241 (1842); Pogg. Ann., **47**, 570 (1839).

as the positive electrode, for the purpose of combining the oxygen arising from the water contained in the alcohol with this latter substance, and thus forming a more oxygenated product.

In 1845, Kolbe[6] completely decomposed trichloromethylsulphonic acid in an aqueous solution at a platinum electrode, to form CO_2, HCl, and H_2SO_4, at the anode, and H_2 at the cathode, concerning which he said, "This acid, being most stable to the strongest oxidizing media, breaks down completely under the action of anodic oxygen." At a zinc anode, the action is different,[7] the result being trimethylsulphonic acid with no evolution of H_2 at the cathode; but zinc oxide is formed when an alkaline electrolyte is used. The difference in the behavior of the platinum and zinc electrodes will be taken up later in the study of the relations of the electrodes, current density, potential, etc., to the course of electrolytic reactions.

This brief historical introduction brings us to the time when Kolbe laid the foundations of Electro-organic Chemistry, in 1849. In this year he made the first statement of what he considered to be the mechanism of electrolytic oxidation of the aliphatic acids.

Up to this time, most investigations had been directed merely toward the observation of the evolution or non-evolution of gases at the electrodes, without regard to the composition of the gases, the factors relating to oxidations and reductions at the end of the passage of the current, or the presence of new materials in the solution. The modern study of electrolysis has dealt more completely with the general survey of the composition of the gases and electrolytes.

In the beginning, studies in the field of Electro-organic Chemistry were necessarily qualitative, but at the very end of the nineteenth century the quantitative relations were brought into prominence by Elbs, Haber, and others. To-day we are likely to become confused in the midst of the complications presented by over-voltage relations, "heredity" and "environment" of electrodes, current density, catalytic action, choice of solvent and electrode materials, etc. In fact, the problem, though it started simply enough, has become a complicated study of Electrochemistry which will be untangled only by a judicious combination of Physical and Organic Chemistries.

To trace more minutely the historical development of Electro-organic Chemistry from the time of Kolbe to the present would not only be of slight value at this point but would be a duplication of the material presented later in the text. The leading investigators in the various phases of this work can readily be noted throughout the book;

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[6] Kolbe, J. prakt. Chem., (1), **41**, 138 (1847).

[7] Kolbe, Ann., **34**, 174 (1845).

their names will stand out prominently. In several Chapters the "historical method" of treatment is used.

The applications of alternating current to the electrolysis of organic compounds have scarcely been of sufficient importance to warrant segregation into a single chapter, and therefore are included in the proper chapters as the predominating reactions are oxidations or reductions.

B. METHODS AND APPARATUS

For all this work, a suitable source of direct current is, of course, required. A storage battery gives the best results for small-scale work. A potential of about 10 to 14 volts is required for most work. A battery containing a small number of cells requires recharging at short intervals, and therefore is not very satisfactory. A battery with a capacity of, say, 25–30 kilowatt-hours is the most efficient. In order to vary the current density at the electrode, a suitable variable resistance must be included in the circuit. Descriptions of good resistances may be obtained from any of the larger texts on Physics and Electricity.

The current consumption in small-scale apparatus is not over several amperes and can be measured by a low-reading ammeter. The measurement of potential drop between electrodes will require a voltmeter. The current and voltage need not be read continuously, but only at regular intervals so as to check the values and keep them constant. The cell voltage, of course, is a function of the temperature, current strength, the conductivity of the electrolyte, and the polarization of the electrodes. The electrode potentials are measured, as usual, by means of a millivoltmeter and a probing electrode. An excellent set-up is given by Hibbert and Read.[8]

The determination of the total current consumption, i.e., ampere-hours, is another problem. From this value the current yields are calculated. The various methods that are available have been critically studied many times, but the criticisms need not be reviewed here, since all of the methods are suitable for control work. The following are in common use:

1. Silver coulometer.
2. Copper coulometer.
3. Gas coulometer.
4. Ampere-hour recorder (mechanical).

The silver and copper coulometers are seldom used; they are suitable for the most accurate work, requiring a refinement which is not needed

[8] Hibbert and Read, J. Am. Chem. Soc., 46, 992 (1924).

in ordinary control work. The gas coulometer is the easiest and most desirable to use, because it gives information that can be utilized directly.[9]

The gas coulometer evolves a quantity of gas directly proportional to the current which passes through the electrolytic cell during the time of the electrolysis. Gas coulometers are of two kinds: One measures the total quantity of both gases, oxygen and hydrogen, as evolved from both electrodes. This is known as the hydrogen-oxygen or "knall-gas" coulometer and is the simplest type. The other type is the one in which the electrode gases are measured separately. A convenient form of "knall-gas" apparatus is shown in Fig. 1. The electrolyte should be 15 per cent NaOH, free from chlorides, and should fill the cell so as to cover the electrodes completely and go part way up the glass tube leads. Since the passage of the current decomposes the solvent water, it is essential that the level of the electrolyte be kept nearly constant by frequent additions of water; unless the electrolyte is so leveled, the gas measurements will not be correct. There is also danger of the mixed gases being exploded by the catalytic action of the nickel electrodes if the surface of the electrolyte gets too low.

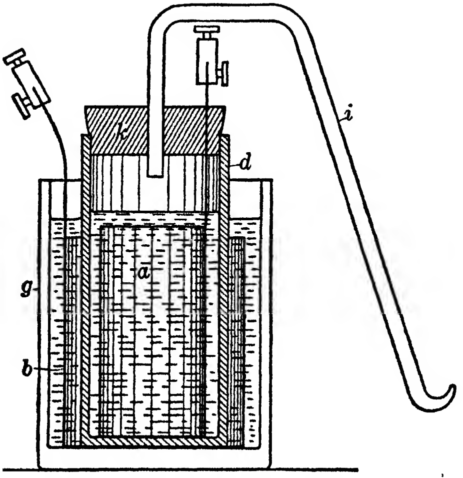

Fig. 1.—"Knall-Gas" Coulometer.
From Müller's "Elektrochemisches Praktikum."

Before connecting in the circuit for a gas measurement, the freshly filled cell should be used alone for a time, because fresh alkali has a tendency to foam. The foam, of course, passes into the gas-measuring apparatus and vitiates the reading.

The cell for measuring the gas from only one electrode is shown in Fig. 2. A clay cell or diaphragm separates the anolyte from the catholyte. The clay cell is sealed with a two-hole rubber stopper, one hole being for the gas tube and the other for the electrode lead. The electrodes should be concentric cylinders of Ni in an electrolyte of 15 per cent NaOH. For oxidation reactions, in which the oxygen evolution in the coulometer is measured, the inner electrode is made the anode;

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[9] See Creighton's "Principles of Electrochemistry," Chapter 2.

but for reductions, in which the hydrogen is measured, the outer electrode is the anode. The gas evolved from the inner electrode is the one measured in all cases. For long electrolyses at high current densities, the ordinary chemical coulometers are too cumbersome and a mechanical, self-recording instrument is preferable. 96,494 coulombs = 1 faraday (F) = 26.8 ampere-hours = 107.88 g.Ag = 31.785 g.Cu = 11.2 liters H_2 = 5.6 liters O_2 = 16.8 liters mixed gases, O_2 and H_2, measured at 0° C. and 760 mm.

If A is the amount of gas evolved by the coulometer and B the amount of gas evolved by the electrolytic cell, then $A - B$ is the amount of gas absorbed by the electrolytic reaction, and the current efficiency is $100(A-B)/A$ per cent.

Battery jars or beakers are excellent retaining vessels, because they may, if desired, be sealed with rubber stoppers. The shape of the vessel is not so important as the shape of the electrodes. The vessel should be of glass that will stand a large range of temperature without failure. Some electrolyses require a cold, and others a boiling, electrolyte. Thin beaker glass is very good. When one electrode must be very large compared with the other, the retaining vessel may be made of the desired metal and used as the one electrode; this is particularly the case with lead electrodes.

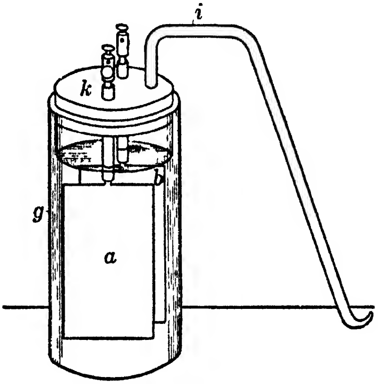

Fig. 2.—Hydrogen or Oxygen Coulometer. From Muller's "Elektrochemisches Praktikum."

The use of a diaphragm is necessary in some cases, while in others it may not be necessary. A divided cell, of course, increases the voltage requirements and so increases the energy consumption during the course of the electrolysis. However, it has been shown that an oxidation in the anolyte and a reduction in the catholyte may be conducted simultaneously. While very little has been reported on such combinations, there are cases in which they are possible.

Such a combination of oxidation and reduction reactions lowers the costs by increasing the yields of salable products. The choice of a diaphragm is, of course, optional with the operator, but depends to some extent on the shapes required. "Electrofiltros" diaphragms seem to give satisfaction in most cases. Burned, unglazed clay diaphragms are available in a variety of shapes.

When a diaphragm is used, the solution and the products obtained in the course of the reaction must not form an impervious layer of tar or resin on the surface, nor clog the pores of the diaphragm. If the pores are clogged, it is absolutely necessary to clean the diaphragm, if the energy consumption is to be kept down to a low value; and this is sometimes very difficult to do well.

Opinion is divided as to the advisability of using the diaphragm. Some electrochemists go so far as to say that its use prevents the industrial application of a process, because of the trouble involved in keeping the cell in good working order. On the other hand, the use of the diaphragm is considered essential by another group of men. Undoubtedly there are modifying circumstances which make both viewpoints correct in different cases.[10]

Stirring may be accomplished by several methods. A mechanical stirrer of glass or metal may be used, with an electric motor or water turbine or a hot-air engine as the prime mover. The paddle may be of any desired shape. In many cases it is desirable to make use of one of the electrodes as the stirrer. When the reaction is such that air will not affect its course, the simplest method of getting a good circulation in the electrolyte is to pass a rapid stream of air bubbles through the liquid. If the reaction at the electrode is accompanied by the evolution of gas, the bubbles, if in large enough quantity, will cause sufficient agitation to make external methods unnecessary. Circulation by means of a syphon and pump is used in many cases. It is also possible to use two liquids of different specific gravities, letting them into the cell at different points so that the lighter liquid rises through the heavier electrolyte, thus causing sufficient agitation.[11] An excellent method of stirring is the modification of the Mylius–Fromm procedure, as described by Müller.[12]

Stirring is absolutely necessary for the successful prosecution of an electrolysis. The rate of diffusion is seldom equal to the rate of electrolytic reaction; therefore, unless some mechanical means is used for bringing the depolarizer to the electrode surface, there will, as a rule, be an undesired evolution of gas, which means a loss in current efficiency. The depolarizer is the material which reacts with the electrode gases; it may be dissolved or suspended in the liquid of the cell or it may be the solvent itself.

Electrodes are made from sheets, wire, wire gauze, or sticks of any conducting material. In order to keep the area of the electrode in

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[10] See Discussion, Trans. Am. Electrochem. Soc., **45**, 105 (1924).

[11] See Swedish P. 41675 (1916), Ges. f. Chem. Ind.

[12] E. Müller, Elektrochemisches Praktikum, 37–38.

contact with the electrolyte constant, the connection to the electrode from the source of the current should be sealed into glass tubing. The leads should be welded on to the electrodes, instead of being soldered. As platinum is expensive and mercury is difficult to purify, they must be used with care. The ordinary heavy metals can be used as cathodes in dilute acid, neutral, or dilute alkali solutions because they are not attacked during the passage of the current. In a strongly acid solution, copper, nickel, or lead may be used; and in a strongly alkaline solution, copper, nickel, or iron. In all cases the metal should be the purest obtainable, especially when the metal is not noble; otherwise, the reactions will not always be typical of the metals that are used. When the electrolyte fumes, even the contacts above the bath must be protected from corrosion, because the particles of corroded material fall into the electrolyte and contaminate it.

As anodes, platinum, platinized-platinum, carbon (graphite), lead, nickel, and iron are most useful. Platinum, being very expensive, should not be used in halide anolytes because of the danger of attack by the halogens set free at the anode; otherwise platinum is the best for most purposes. Carbon in the form of graphite or retort carbon is excellent, except that it is brittle and readily disintegrated by electrolytically evolved oxygen. Graphite is the most desirable form of carbon, because of its high conductivity, chemical inertness, and pliability. Graphite is good in all solutions.

Magnetic oxide of iron, Fe_3O_4, is very valuable but little known as an anode material. Lead dioxide, PbO_2, is used as a coating for most Pb anodes in H_2SO_4 solution up to a sp. gr. of 1.6, all concentrations of H_3PO_4, and aqueous acid or neutral solutions of sulphates, phosphates, carbonates, and chromates.

Nickel anodes are not attackable in alkaline or alkaline carbonate solutions in the absence of ammonium salts. The absence of ammonium salts is not necessary in the case of the iron anodes, because they usually contain ferrites or ferrates.[13]

The meaning of "electrode potential" is discussed in the chapters on oxidation and reduction.

For ordinary work with a moderate current density, the largest electrode possible should be used in order to lower the resistivity of the bath. When a large current density is required, the size of the electrode may be reduced. The electrodes should have the form of concentric cylinders, in order to get an equal distribution of the current and the lines of force over the surface of the metal. If the distribution is not

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[13] Other discussions of the uses of the various electrodes are given throughout the text.

uniform throughout, there will be spots on the surface where the current density will vary greatly from the desired value and cause side reactions.

In many cases, where cooling is required, the use of a metallic tube as the electrode facilitates matters; a current of water at any temperature may be circulated through the tubing. This eliminates the cooling apparatus, which is usually cumbersome, and prevents local overheating on the electrode. Ordinarily, however, it may suffice to put the electrolytic bath in a vessel of ice-salt mixture.

The current density (hereinafter indicated by c. d.) is the number of amperes per square decimeter of electrode surface, and is, of course, the determining factor in the speed of reaction, though very little is known about the variation of reactions with the c. d. The rate at which oxygen or hydrogen is evolved at the electrodes depends on the c. d. If a reduction reaction is desired, a complete absorption of the hydrogen is required for high current yields. Therefore, there is a maximum c. d. at which the depolarizer is just able to absorb all the electrolytically evolved gas, even with continuous and violent stirring. Not only is the c. d. important, but the current concentration [14]

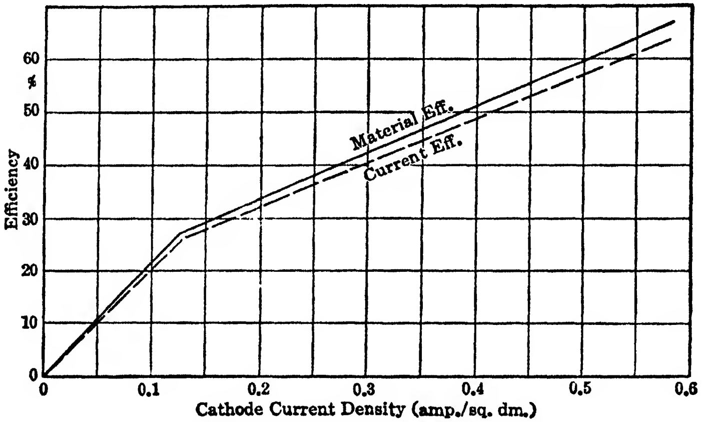

FIG. 3.—Effect of Current Density. Constant Conditions: Temperature = 70°; acidity = 10% H_2SO_4; *m*-Nitrobenzenesulphuric acid = 10 g. per liter Cathode = bright lead. Taken from Doolittle, Trans. Am. Electrochem. Soc., **45**, 57 (1924).

$$= \left(\frac{\text{current strength in amperes}}{\text{one liter of solution}}\right)$$

also plays an important role.

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[14] Tafel, Z. phys. Chem., **34**, 201 (1900)

With the exception of some preliminary investigations, no report has been made on the variation of the electrode potential produced by superimposing an alternating current on the direct current passing through the electrode.[15] A lowering of the cathodic potential was studied by Knobel for electrodes of platinum, lead, and copper. The magnitude of the depolarization is determined by the ratio of the alternating to the direct current, and appears to be independent of the electrodes and c. d. The effect varies slightly with the frequency, the tendency being to increase as the frequency is diminished. For a variation in frequency from 2 to 200 cycles, the depolarization increases only about 50 millivolts. The conclusion is that the depolarization is probably due to the action of the liberated oxygen on the hydrogen.

The foregoing discussion of Methods and Apparatus is necessarily brief. The place for a complete discussion of *modus operandi* is in a laboratory manual of Electrochemistry.

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[15] Foerster, "Wässerige Lösungen," 807; Knobel, Trans. Am. Electrochem. Soc., **37**, 617 (1920); Reitlinger, Z. Elektrochem., **20**, 261 (1914); Ghosh, J. Am. Chem. Soc., **36**, 2333 (1914).

PART I

REACTIONS AT THE ANODE

CHAPTER II

INTRODUCTION TO ELECTROLYTIC OXIDATION

WHEN an aqueous solution of an acid or a base is subjected to the action of an electric current at a potential of 1.7 volts between unattackable electrodes, there is a regular evolution of oxygen at the anode and of hydrogen at the cathode. Any voltage smaller than 1.7 will not cause the steady evolution of these gases at their respective electrodes. The voltage 1.7 is known as the decomposition voltage of the electrolyte provided the gases produced at the electrodes are allowed to escape at 760 mm. pressure. If a substance that readily absorbs oxygen is put into the anolyte some oxygen will be absorbed and will be freed, not at atmospheric pressure, but below it; the anodic potential and also the decomposition voltage will be correspondingly decreased. This process is known as depolarization and the compound that absorbs the oxygen is known as the depolarizer. To produce a steady flow of oxygen and hydrogen by the electrolysis of a solution of KOH with polished platinum electrodes requires 1.7 volts. If acetylene is passed through the anolyte over the face of the anode the voltage required to produce a passage of the current through the solution decreases to 1.2 volts. The acetylene reacts with the anodic oxygen to produce formic acid. There is no reaction when the voltage is below 1.2 because then there is a polarizing action. Between

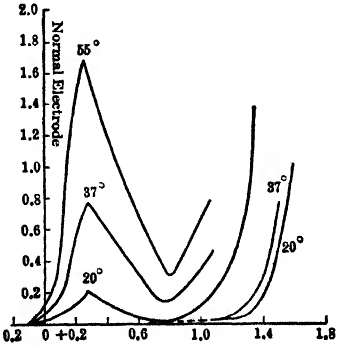

FIG. 4.—Current-potential Curves for Formic Acid on a Smooth Platinum Anode.

1.2 and 1.7 volts there can be no oxygen evolution at the anode (the voltage required to evolve oxygen at atmospheric pressure is 1.7); but there is a reaction between the acetylene and the anodic oxygen. Above a potential of 1.7 volts there is the evolution of oxygen together with an interaction of the acetylene with the oxygen.[1]

In the electrolytic oxidation of organic compounds the material to be oxidized is usually the depolarizer. As a rule, organic compounds are too poor conductors of electricity to be used without an added electrolyte. Since it is very difficult to regulate the electrode potential for any one reaction it is not often that all the oxygen is absorbed by the depolarizer; that which is not absorbed will therefore be evolved at the anode as a gas. The amount of oxygen absorbed by the depolarizer depends on several conditions, which include first the nature of the depolarizer, because some compounds are more easily oxidized than others. The c. d. also directs the reaction because it influences the rate of evolution of oxygen at the electrode, one faraday liberating one equivalent of oxygen. Other influences which will be considered are diffusion of the depolarizer and its concentration, the size of the anode surface, the effect of stirring the electrolyte, the catalytic influence of added compounds, temperature, the nature of the anode material, and the solvent.

The concentration of the depolarizer is, at times, probably of greater importance than the c. d. The oxygen is evolved at the electrode surface and therefore the reaction between the depolarizer and the oxygen must necessarily take place in the immediate neighborhood of the electrode surface. This causes a gradual increase in the concentration toward the middle of the solution where the concentration is the same as it was when the reaction was started. This concentration gradient, as it may be called, will start a diffusion of the depolarizer toward that portion of the system where the concentration is lowest; that is, toward the anode area. This diffusion is not instantaneous; hence the smaller the concentration at the start, and the smaller the surface of the electrode or the larger the current, which means a more local discharge of oxygen, the less opportunity there will be for the depolarizer to function, and more of the current will be used for the evolution of gaseous oxygen instead of an oxidation reaction. Therefore the optimum conditions are a high concentration of the depolarizer together with a large anode surface.[2]

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[1] Coehn and Billiter, Z. Elektrochem., **7**, 681 (1901).

[2] The velocity constant for the oxidation of oxalic acid has been determined by Ageno and Donini, Gazz. chim. ital., **40**, i, 21 (1910). The deduction is that the non-dissociated acid and the ion of $HC_2O_4^-$ are oxidized first. The oxidation

As stated above, the surface of the anode regulates the amount of oxygen discharged per unit of area of anode for a given current. The larger the anode for a given current, the larger the surface over which the oxygen is distributed, with a corresponding decrease in the rate of evolution per unit of area. Oettel[3] investigated the oxidation of oxalic acid solution at different size of anodes of smooth platinum. Three cells were used in series with a copper coulometer inserted into the circuit with each cell. Each of the first two cells contained 100 cc. of oxalic acid solution which was made by dissolving 6.237 g. of oxalic acid in 100 cc. of water containing 5 g. of H_2SO_4, but the solution in the third cell was diluted to one-tenth of this strength. The electrodes were platinum, the first being a perforated platinum cylinder anode with an area of 150 sq. cm., and concentric with this was a platinum spiral wire cathode, with a total surface of 6 sq. cm. In the second and third cells the current was reversed. The current used was 0.2 ampere for a duration of two hours, and at the end of this time 0.4451 g. of copper had been deposited in the coulometer which according to Faraday's law meant the oxidation in each cell of about 0.8856 g. of oxalic acid.

By titration with permanganate solution of samples before and after the passage of the current the following data were obtained:

TABLE I

Cell	Anode	Solution	Amount of Oxalic Acid Oxidized	Theoretical Yield of Oxidation Product in Per Cent
1	Cylindrical	Concentrated	0.840 g.	94.9
2	Spiral	Concentrated	0.324 g.	36.6
3	Spiral	Dilute	0.0263 g.	2.97

These facts explain very clearly the influence of concentration and area of the anode surface with respect to the amounts of oxygen absorbed by the depolarizer. The above factors may be considered as primary conditions, in that during the ordinary electrolysis without any external changes brought about by the hand of the operator, they regulate the course of the electrolysis. The conditions of the operation may be so changed as to modify the results very considerably. A smaller current

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does not proceed at nickel and cobalt peroxides as well as it does at PbO_2 and MnO_2 anodes.

[3] Oettel, Z. Elektrochem., 1, 90 (1895).

or a larger anode surface may be used, both of these amounting to the same thing, i.e., the lowering of the c. d.

The speed with which the depolarizer absorbs oxygen is also of importance. There may be added to the electrolyte certain salts which speed up the absorption of oxygen, so that the rate of oxidation as well as the electrical efficiency of the process is increased. For example, when a suspension of anthracene in 30 per cent sulphuric acid is electrolytically oxidized, the highest yields of 90 per cent are obtained only when a catalyst is added[4] (2 per cent of a cerium salt), the product being anthraquinone.

Cerium sulphate[5] is much more active than chromic acid, and may be employed in a cell without a diaphragm. With chromic acid, on the other hand, a diaphragm must be used to prevent the cathodic reduction of the chromic acid. Since the electrolytic regeneration of the chromic acid does not usually keep pace with its reduction to chromium sulphate by means of anthracene, the electrolyte containing the catalyst must be submitted to electrolytic oxidation from time to time. At the anode the cerium salt is oxidized to the ceric condition which carries the positive charge to the organic depolarizer, the result of which is the reduction of the ceric salt together with the oxidation of the organic compound; the former is then immediately reoxidized at the anode to the ceric salt. This transfer of charges between the carrier and the depolarizer does not necessarily take place at the anode, because of the diffusion of the carrier from the anode. Besides cerium salts,[6] it has been found that manganese,[7] chromium,[8] and vanadium[9] salts are excellent catalysts.

The carriers used will also change the product of the reaction in certain cases. It will be shown later that when a slightly acid solution of hydroquinone is electrolyzed between platinum electrodes the yield is nearly the theoretical quantity of quinhydrone, but when a carrier, as a manganese salt,[10] is added, the product is quinone.

The material from which the anode is prepared has in many instances, a very great influence on the course of the reaction. The use of a platinum anode causes the oxidation of *p*-nitrotoluene to

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[4] A. Fontana and F. M. Perkin, Z. Elektrochem., **11**, 99 (1904).

[5] See Le Blanc, Z. Elektrochem., **71**, 2903 (1900).

[6] D.R.P. 153063, Meister (1902).

[7] D.R.P. 117129, Boehringer (1900).

[8] D.R.P. 109012, Darmstädter (1897), and Fontana and Perkin, Elektrochem. Zeit., **11**, 99 (1904).

[9] D.R.P. 172654, Meister (1903).

[10] Liebmann, Z. Elektrochem., **2**, 497 (1896), and D.R.P. 117129, Boehringer (1900).

p-nitrobenzyl alcohol and *p*-nitrocresol while with a lead dioxide anode the oxidation goes on to *p*-nitrobenzoic acid.[11]

At a smooth platinum anode methanol is oxidized to formaldehyde with 80 per cent yields; at a platinized-platinum anode the yield is very much lower, being about 40 per cent; while at lead dioxide anodes the product is entirely carbon dioxide (see page 81). The same depolarizer leads to the formation of different products when different anode materials are employed. The influence of oxygen overvoltage on the course of these oxidations has not been studied.

The exact function of the anode material and carriers has never been clearly defined. In some cases the difference seems to be due to the difference in anodic potential which the different anodes are capable of producing; on the other hand there are some who consider the catalytic influence of the metal to be of more importance than the potential differences.

The choice of the solvent also has a great influence on the final product of the electrolytic oxidation. The isolation of intermediate products is dependent on whether the intermediate product is soluble or insoluble in the electrolyte. Aniline is oxidized to aniline black in a sulphuric acid solution when a platinum anode is used, and, owing to its insolubility, the latter separates from the electrolyte, thus preventing any further action of electrolytic oxygen which would oxidize it to quinone (see page 116); while in a concentrated sulphuric acid solution with the same anodes the product is *p*-aminophenol (see page 116).

The solvents most frequently used are sulphuric acid, acetic acid, acetone, and pyridine. All strengths of acid, from the most dilute to very concentrated acid, have been used. Of course there is always the chance that the products will vary with different solvents. It is advisable, for obvious reasons, to use in all cases a solvent that is completely miscible in all proportions with water. Electrolytic oxidations proceed as a rule very nicely in acetone, acetic acid, and sulphuric acid solutions; pyridine has a tendency to form tarry substances which are, however, readily soluble in water and so very easily removed; but it also forms complex soluble tars with compounds of the aromatic series, which results in a serious loss of material.[12] With respect to the electrolyte there are several conditions which may be mentioned at this point; namely, that if the depolarizer is soluble, the oxidation goes fairly easily without the use of a catalyst, but if the depolarizer is not soluble, a soluble catalyst is sufficient to produce the oxidation without the need

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[11] Elbs, Z. Elektrochem., **2**, 522 (1896); Coehn, ibid., **9**, 643 (1903). See also later.

[12] H. D. Law, J. Chem. Soc., **89**, 1437 (1906).

of a solvent. On this basis it is found that a good suspension is all that is needed to insure good results. A suspension of aniline, anthracene, or naphthalene in dilute H_2SO_4, well stirred, is very easily oxidized. (See pages 116 et seq.) Practically nothing has been reported on the use of non-aqueous solutions for electrolytic oxidations.

On the nature of the starting material depends the necessity for using a diaphragm. If the product of the anodic oxidation may be reduced by the cathodic hydrogen a diaphragm is required, as when quinone is reduced cathodically to quinol. (See page 104.) However, the use of a diaphragm may be avoided if the area of the cathode is very small compared with the surface of the anode, because then the evolution of hydrogen will be at a minimum as to area of distribution. (See page 22.) Reduction is more difficult in an alkaline solution than in an acid solution.[13]

The cathodic reduction of the organic depolarizer may be prevented by the addition of small amounts of some materials which are very good depolarizers for the cathodic hydrogen, and which react before the organic material can function as the depolarizer. One of these materials is a soluble chromate which under the influence of the cathodic hydrogen forms a thin skin of chromic oxide over the surface of the cathode. This skin acts like a diaphragm and does not permit the organic compound, formed at the anode, to be reduced at the cathode. This chromate is applicable only in neutral or slightly acid solutions because the chromic oxide formed is soluble in strongly acid solutions.[14] A similar protecting action may be obtained by the use of calcium chloride, or of the calcium salts of resin acids,[15] but these have not been applied in the electrochemical oxidation of organic compounds.

Only under certain conditions can an electrolytic oxidation reaction be carefully controlled so as to yield only one oxidation product. Very often the large number of oxidation products formed makes their separation and identification so great a burden that in many cases the field is necessarily uninteresting because of the labor involved. In the oxidation of toluene it will be found that a large variety of oxidation products result when one set of conditions prevails, while under other conditions the reaction may be entirely different. In one case the side chain is attacked and in other cases the ring carbon atoms are attacked.

The fatty compounds are as a rule more easily oxidized than the

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[13] Kolbe, Ann., 54, 174 (1854); Meister, D.R.P. 149983 (1904); Konsortium, D.R.P. 195811 (1908).

[14] E. Müller, Z. Elektrochem., 5, 469 (1899); 7, 398 (1901); 8, 909 (1902).

[15] Schuckert, D.R.P. 141372 (1910); Foerster and E. Müller, Z. Elektrochem., 9, 583 (1903).

ring compounds, and in a great many cases the molecule is entirely disrupted. Cane sugar [16] is almost quantitatively oxidized to carbon dioxide and water. In some cases, as will be discussed later, certain definite stopping points in the oxidation of aliphatic compounds may be found. The oxidation of alcohol by a rigorous regulation of the c. d. and the anodic potential may be stopped at the aldehyde, but with less control acetic acid results.

The oxidation of aliphatic compounds often goes to completion, that is, to water and carbon dioxide. On the other hand, the aromatic compounds have a great tendency to form phenolic compounds which form condensation products of a resinous nature. In a great many cases the formation of resins is a serious handicap to the purification of the final products. When pyridine is used as the solvent this trouble is usually encountered.

The Mechanism of Electrolytic Oxidation

The exact nature of the process of electrolytic oxidation has not been definitely cleared up so as to be acceptable and applicable in all cases which must be considered. Certainly there is an oxidation reaction, but just how this oxidation takes place is more difficult to explain. The anodic potential, the nature of the anode, and other factors change the nature and quantity of the products. The theory of catalysis enters into a great many of the reactions; and at best the theory of catalysis is a large field of discussion.

It may, of course, be assumed that the oxidation is produced by the gas occluded by the electrode, and therefore that the reaction must take place at the very surface of the electrode, while with unattackable electrodes this cannot be the case. The increase in activity of a cathode is dependent on the increase in potential to a certain extent, as is the case with an anode during oxidation reactions. Haber and Sack [17] have shown that in electrolytic reduction with an alkaline solution the reduction is, in certain instances, due to the formation of an alloy of sodium with the electrode material, and that the amount of alloy increases with the potential used, with a corresponding increase in reducing power. This is a suitable explanation for electrochemical reduction reactions, but cannot be applied to electrolytic oxidations. The increase in potential may, of course, be due to the formation of a skin of oxygen on the metallic surface, but the increase in activity is not

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[16] Ulsch, Z. Elektrochem., 5, 539 (1899).

[17] Haber and Sack, Z. Elektrochem., 8, 245 (1902).

in proportion with the increase in potential because of the absorbed oxygen in the electrode.

The alternative theories which may be applied to explain this or that catalytic process in general are (*a*) the formation of intermediate compounds, (*b*) the effects of surface absorption, (*c*) the electrochemical theory, (*d*) the effects of an alteration in the density of the absorbable radiant energy. All of these cannot be applied with success to any one oxidation reaction, though all but the first are possible. There seems to be no reference in the literature to the isolation of any intermediate compounds between the electrode material and the depolarizer. In electrolytic reductions there are evidences that intermediate compounds have been obtained when the electrodes were of lead or mercury.

In only a few instances has the electrochemical oxidation yielded different results from those obtained by the use of ordinary chemical methods. The products are, as a rule, the same as those obtained when hydrogen peroxide is used, so that electrochemical oxidation and oxidation by means of peroxides seem to be somewhat similar mechanisms.

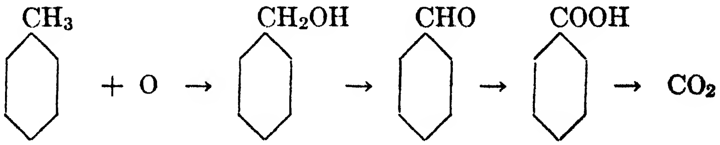
The reactions which take place may be expressed by the following equations in the case of the aliphatic compounds:

$$RCH_2OH + O \rightarrow RCHO + H_2O$$

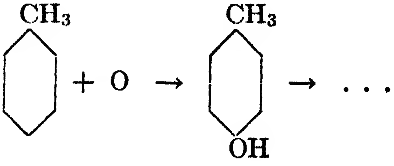
$$RCHO + O \rightarrow RCOOH$$

$$RCOOH + O \rightarrow CO_2 + H_2O$$

In the case of ring compounds either the ring or the side chain is attacked, depending on the conditions under which the oxidation takes place, so that the equations for cyclic compounds may be indicated as follows, toluene being used as the example:



or



Fichter and Stocker[18] have come to the conclusion that anodic oxygen attacks the nuclear hydrogen before the side chain. This is

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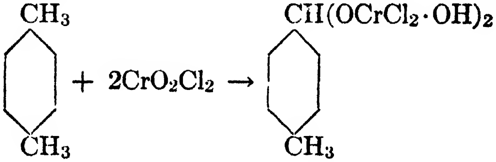
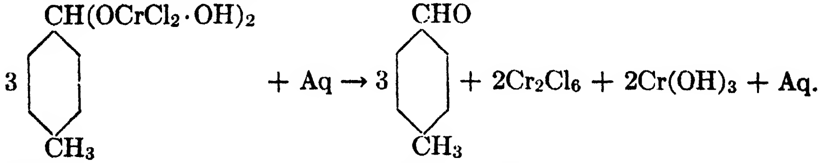
[18] Fichter and Stocker, Ber., 47, 2003 (1914).

entirely comparable to the fact that electrochemical halogenation attacks the nucleus only (see later); and Bruner and Dluska[19] have shown that atomic halogen attacks the nucleus while molecular halogen attacks the side chain. This leads to the conclusion that the hydroxylation of the nucleus of cyclic compounds is accomplished at an anode by the action of atomic oxygen, or by the use of silver, or hydrogen peroxides. The application of other chemical oxidation media, such as chromic acid, nitric acid, permanganic acid, etc., leads to products which are not formed by atomic oxygen and therefore must be due to oxidation by molecular oxygen.

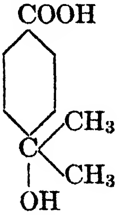
Other theories claim that the oxidation is due to the action of the discharged hydroxyl groups and not the discharged oxygen at the anode.[20] The basis for this assumption is the fact that the oxidation of hydrocarbons by chemical methods does not as a rule yield alcohols, and that the aldehyde is only formed when chromyl chloride is employed as the oxidizing agent. In this latter case the first action is the formation of an unstable combination between the chromyl chloride and one of the methyl groups of the xylene:



This is then decomposed by the water with the formation of the aldehyde so that this may be considered a case of hydrolytic oxidation:



When cymene is oxidized by potassium permanganate,[21] the product is:



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[19] Bruner and Dluska, Bull. Acad. Science, Cracovie, 691 (1907).

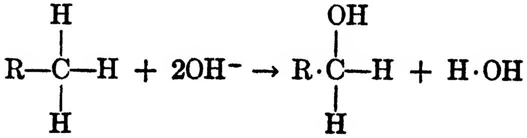
[20] F. M. Perkin, Chem. News, **91**, 55 (1905); H. D. Law and F. M. Perkin, ibid., **92**, 66 (1905).

[21] Ber., **14**, 484 (1881).

In this case the alcohol is produced because the hydrogen atom in the tertiary position is attacked, a tertiary alcohol being the only possible product.

Le Blanc has shown that all the ions in the solution take part in the conduction of the electric current, but only those ions, the separation of which require the least expenditure of work or energy, are deposited or separated at the electrode.[22] In the electrolyte in which the anodic oxidation is being carried on, there are acid ions and hydroxyl ions which travel toward the anode. Since the transport number of hydroxyl ions is larger than that of the other anions, there is a greater concentration of the hydroxyl than of acid ions, around the anode. This increase in the number of hydroxyl ions rather than the discharge of these ions to form oxygen and a molecule of water, is the cause of the oxidation. In order to have this condition prevail it is necessary to work with low current densities of the order of about 1.0 ampere. If a reaction other than this is desired, the current and the concentration of the depolarizer may be increased so that the other ions discharge, as is the practice in the electrolytic formation of persulphuric acid and persulphates, chlorates and hypochlorites.

This hydroxylation may be expressed in the equation as:



$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H + 2OH^- \rightarrow R\cdot\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-H + H\cdot OH$$

In several instances electrolytic oxidations have been used as a means of determining the constitution of compounds.[23]

A variety of compounds of the general form $X\cdot CO\cdot CH(OH)Y$ were studied. It was expected that by changing the X and Y some idea of the course of the reaction at the anode would be obtained. Two reactions may take place, which may be expressed as:

$$X\cdot CO\cdot CH(OH)\cdot Y + O \rightarrow X\cdot CO\cdot CO\cdot Y + H_2O$$

$$X\cdot CO\cdot CO\cdot Y + O + H_2O \rightarrow X\cdot CO\cdot OH + Y\cdot CO\cdot OH$$

$$X\cdot CO\cdot CH(OH)\cdot Y + O \rightarrow X\cdot CO\cdot OH + Y\cdot CHO$$

$$Y\cdot CHO + O \rightarrow Y\cdot CO\cdot OH$$

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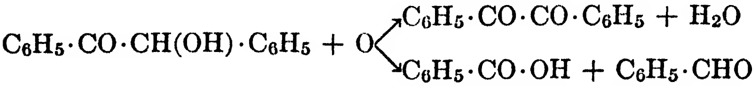
[22] Le Blanc, Text-book of Electrochemistry, page 303, Macmillan (1907).

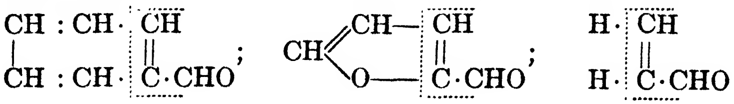
[23] Law, J. Chem. Soc., 89, 1437 (1906).

On this basis benzoin yielded benzil, benzoic acid, and benzaldehyde:



$$C_6H_5\cdot CO\cdot CH(OH)\cdot C_6H_5 + O \begin{array}{l} \nearrow C_6H_5\cdot CO\cdot CO\cdot C_6H_5 + H_2O \\ \searrow C_6H_5\cdot CO\cdot OH + C_6H_5\cdot CHO \end{array}$$

The course of the reaction can not be determined here because the X and Y are the same radical. When X and Y contain unsaturated groups there is another reaction in which resins of unknown constitution are formed. On comparing the structure of the three aldehydes: benzaldehyde, furfural, and acrolein a striking similarity will be seen:



each contains the group CH : C·CHO and each forms complex substances at the anode, the latter two most especially. The potential at the anode has a very marked effect on the formation of these complexes, the amounts produced being greatest when the E.M.F. is highest. This is readily seen in the cases where the acids, H_2SO_4, HCl and HBr are used as electrolytes. The potential of the discharge of the anions of these acids is as follows:

$$SO_4^{=} = 0.7; \qquad Cl^- = 0.31; \qquad Br^- = 0.06$$

In sulphuric acid there is always the formation of some tar, but never in the case of hydrobromic acid. With unsaturated compounds in general there is little action with a low potential. With a higher potential there is an oxidation at the double bond which results in the formation of the tar.

Benzofuroin has two formulae:

$$C_6H_5\cdot CO\cdot CH(OH)\cdot C_4H_3O$$

and

$$C_6H_5\cdot CH(OH)\cdot CO\cdot C_4H_3O$$

The half of the molecule containing the furfurol group most readily decomposes with the formation of tars but the remaining part will yield benzaldehyde or benzoic acid according to which formula is correct:

$$C_6H_5\cdot CO \ldots + O + H_2O \rightarrow C_6H_5\cdot CO\cdot OH + \ldots$$

$$C_6H_5\cdot CH(OH) \ldots + O \rightarrow C_6H_5\cdot CHO + \ldots$$

Benzaldehyde was not detected in the products, therefore the correct formula is:

$$C_6H_5CH(OH)\cdot CO\cdot C_4H_3O \quad .$$

The following compounds were studied in the light of this example, with the production of the corresponding substances:

anisoin → tars only
piperonyloin → only tars
benzoin → benzoic acid, benzaldehyde, benzil, tar
benzil → benzoic acid and tar
benzaldehyde → benzoic acid, tar, and a little CO and CO_2
cuminoin → an acid, an aldehyde, and tar
furoin → furol and tar
benzofuroin → an acid, and tar
ethylbenzoin → benzoic acid, benzaldehyde, and tar
benzoin acetate → benzoic acid, benzaldehyde, and tar
allyl alcohol → acrolein, acrylic acid (?), CO and CO_2
acrolein → acrylic acid (?), CO and CO_2
crotonaldehyde → crotonic acid, CO and CO_2
furfurol → a little CO but no CO_2
menthol and camphor yield no tars

CHAPTER III

THE ELECTROLYTIC OXIDATION OF IONIZED SUBSTANCES—PART I

THE reactions which take place at the anode may be divided into several classes, namely: (1) evolution of oxygen, (2) electrolytic oxidation with an increase in the valence of the cation, (3) electrolytic oxidation with an increase in the oxygen or a decrease in the hydrogen content of the compound, (4) electrolytic oxidation of the anion, (5) electrolytic oxidation of a cation to an anion.

The electrolysis of the alkali salts of the organic compounds, which are ionized and therefore are more or less good conductors of electricity in an aqueous solution, belongs in class (4); sometimes class (3) applies, though not so often.

In most cases, the question of products has been very thoroughly studied. The real problem is the mechanism by which these products are formed under the experimental conditions. This has been the great stumbling-block in the path of chemists for a long time. Failure to describe exactly or reproduce the experimental conditions has led to some confusion in this field. The author will endeavor to show how slight variations in experimental conditions, such as current density, temperature, choice of metal for the electrodes, and acidity of the solution, will lead to different results in many cases.

THE ELECTROLYSIS OF THE ALKALI SALTS OF THE ALIPHATIC ACIDS

GENERAL

Salts of organic acids of the type RCOOM in aqueous solution are almost completely ionized into the ions $RCOO^-$ and M^+. These ions therefore carry the electric current, the action of which is to discharge them at their proper electrodes. Since ions are not isolated as such they either react with each other, or with the non-ionized molecules in solution, or with the solvent about the electrode.

When the alkali salts are electrolyzed, the alkali ion is discharged at the cathode; and, if there is no substance in the solution that is capable of reduction, the products at this electrode will be an alkali hydroxide and hydrogen gas. If there is a cathodic depolarizer present in the electrolyte, the greater part of the hydrogen will be used for reduction, and therefore will not appear as a gas at the cathode.

Kolbe[1] attempted the electrolysis of potassium acetate in the hope of isolating the radical methyl. He obtained at the anode CO_2, H_2, a combustible inodorous gas, and a compound possessing a peculiar ethereal odor and absorbable in sulphuric acid. He showed methyl acetate to be one product of the electrolysis. By varying the c. d. he was able to obtain a gas containing or not containing CO_2. He determined the formation of an ether, showing that its composition corresponded to the theoretical value. He also considered that the solvent water was subjected to the decomposing action of the current.

Kolbe's explanation was that the passage of the current decomposed the solvent water, forming oxygen at the anode and hydrogen at the cathode. The anodic oxygen attacked the organic acid according to the following equations:

$$2CH_3COOH + O \rightarrow C_2H_6 + 2CO_2 + H_2O \tag{1}$$

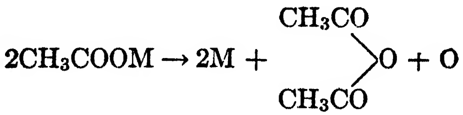
$$2CH_3COOH + 2O \rightarrow C_2H_4 + 2H_2O + 2CO_2 \tag{2}$$

$$2CH_3COOH + O \rightarrow CH_3COOCH_3 + CO_2 + H_2O \tag{3}$$

The yields obtained by Kolbe indicate that the course of the reaction expressed by equation (1) predominates over that of (2) and (3). Very little current was used in the preparation of ethylene. These so-called Kolbe syntheses are not the only " explanations " that have been suggested.[2]

Bourgoin's[3] investigations on this matter led him to assume that the salt itself was broken during the electrolysis into the metal and the acid residue, and that subsequently two acid residues condensed to form a molecule of the anhydride of the acid with the liberation of an atom of oxygen.

(4)



$$2CH_3COOM \rightarrow 2M + \begin{matrix} CH_3CO \\ \\ CH_3CO \end{matrix}\!\!>\!O + O \tag{4}$$

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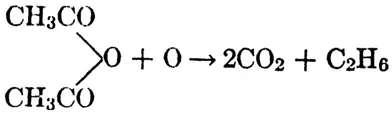
[1] H. Kolbe, Ann., **69**, 279 (1849); H. Kolbe and J. Kempf, Jour. prakt. Chem., **4**, 46 (1871).

[2] See also work by Gibson, J. Chem. Soc., **127**, 475 (1925).

[3] Bourgoin, Ann. chim. et phys., [4], **14**, 151 (1868); Compt. rend., **65**, 892 and 998 (1867).

If this anhydride were unstable in the presence of oxygen, there would occur another reaction with the evolution of carbon dioxide and the formation of a saturated hydrocarbon:

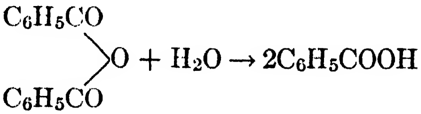
(5)



$$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\rangle O + O \rightarrow 2CO_2 + C_2H_6$$

On the other hand, if the anhydride were stable in the presence of oxygen, as in the case of the benzoate, there would only be a reaction with water to form the free acid:

(6)



$$\left.\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\right\rangle O + H_2O \rightarrow 2C_6H_5COOH$$

There is some purely chemical evidence to support this theory of the oxidation of anhydrides.

Soon after the theory of electrolytic dissociation was formulated, Brown and Walker[4] attempted to prove that, as the cations discharged on the cathode, they assumed the "nascent state," and, according to their nature or the exigencies of the case, they reacted with the solvent water, regenerating the free acid with the liberation of oxygen in the case of aromatic acids.

(7) $$2RCOO^- + H_2O \rightarrow 2RCOOH + O$$

For the aliphatic acids, a different reaction took place, because with potassium acetate the anodic products were not oxygen, but ethane, ethylene, and CO_2, together with some methyl acetate. The assumption was that the discharged anions of acetic acid lost CO_2 with the formation of ethane:

(8) $$2CH_3COO^- + 2 \oplus \rightarrow C_2H_6 + 2CO_2$$

In the case of the other products, i.e., the ester and ethylene, Kolbe assumed a different mechanism, namely:

(9) $$2CH_3COO^- + 2 \oplus \rightarrow CH_3COOCH_3 + CO_2$$

and

(10) $$2CH_3COO^- + 2 \oplus \rightarrow CH_3COOH + CO_2 + CH_2:$$

(10*a*) $$2CH_2 : \rightarrow CH_2 : CH_2$$

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[4] Brown and Walker, Ann., **261**, 107 (1891).

A fourth mechanism was postulated by C. Schall,[5] according to which the discharge of the anions of acetic acid led to the formation of a peracetic acid:

$$(11) \qquad 2CH_3COO^- + 2 \oplus \rightarrow CH_3COO{-}OOCCH_3$$

which was unstable, breaking down to CO_2 and ethane

$$(11a) \qquad CH_3COO \cdot OOCCH_3 \rightarrow C_2H_6 + 2CO_2$$

Which of these four conceptions is the correct one is an open question. However, a brief discussion of them may clear the field to some extent.

It is hardly conceivable that Kolbe's idea of the mechanism is correct, for several reasons. He assumed that the free acid is oxidized by the anodic oxygen; yet the electrolysis of a solution of free acetic acid under the best conditions yields mostly O_2, CO_2 and CO with only traces of ethane.[6] Potassium acetate, under exactly similar conditions, yields just the opposite results, i.e., mostly ethane with very little oxygen. Even though the conductivity of acetic acid is so very much smaller than that of potassium acetate, the number of ions discharged should have very little influence on the result, because the anodic oxygen is supposed to attack the molecule, not the ion. But there is a chance that in the case of the electrolysis of potassium acetate, the concentration of acetate ions at the anode is so large that they react with the water to form free acetic acid and oxygen, the latter gas attacking the newly formed molecule of acetic acid. The Kolbe mechanism is rather difficult to understand. Some of the other theories are very much more plausible.

The second theory in which the formation of an acid anhydride is postulated, is not considered valid by Kaufler and Herzog,[7] who support the Brown-Walker theory.

The peroxide theory of Schall has been supported by some new evidence. Not only may peroxides be intermediates in the formation of the hydrocarbons in question, but even peracids may be present for a short time. If the formation of ethane takes place through the formation of a peroxide when acetic acid is electrolyzed,

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[5] C. Schall, Z. Elektrochem., **3**, 86 (1896).

[6] Lapchin and Tichanowitzch, Neue Peters. Acad. Bull., **4**, 81 (1861); Brester, Zeit. f. Chem., **2**, 60 (1866); Anh. neerland. des sc. ex., **1**, 296, (1866); Bourgoin, Ann. chim. et phys., [4], **14**, 157 (1868); Foerster and Piguet, Z. Elektrochem., **10**, 729 and 924 (1904); Hofer and Moest, ibid., **10**, 833 (1904); Preuner and Ludlam, Z. physik. Chem., **59**, 682 (1907).

[7] F. Kaufler and C. Herzog, Ber., **42**, 3858 (1909); **43**, 266 (1910).

the action of acetyl peroxide as a starting material must lead to the same products, which was proven.[8]

In this case the decomposition of the peroxide has the violence of an explosion and may possibly cause a " cracking process," leading to the formation of the methane. Propionyl peroxide yielded the expected butane and carbon dioxide together with some methane. However, the ratio of CO_2 to C_4H_{10} was 3.46 : 1 instead of the expected 2 : 1. Besides these compounds, some ethyl propionate was also detected.

The formation of alcohols, olefins and esters may also be due to intermediate per-compounds. Peracids which are unstable as well as rich in oxygen have been prepared and somewhat studied in the recent years. The formation of a peracid may be indicated as:

$$\text{RCOOH} + \text{O} + 2\text{F} \rightarrow \text{RCOOOH} \tag{12}$$

The peracid formed, RCOOOH, has in turn, a strong tendency to decompose.[9]

$$CH_3CH_2COOOH = CH_3CH_2OH + CO_2 \tag{13}$$

$$CH_3CH_2OH = CH_2 : CH_2 + H_2O \tag{13a}$$

Butyric peracid decomposes readily to give all the products which are obtained when it is electrolyzed. Even the formation of the ester may be explained on the basis of the peracid theory:

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2COOOH \rightarrow$$

$$CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O + CO_2$$

Fichter has also postulated the possibility of the formation of peroxides or unstable oxides at the anode when organic compounds that do not contain carbonyl groups are electrolyzed. The reaction in question is the oxidation of dimethylaniline, etc.[10] Then, too, the formation of peroxides in the oxidation of benzene derivatives such as benzaldehyde and quinone has been postulated.[11]

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[8] F. Fichter, Z. Elektrochem., **20**, 473 (1914); F. Fichter and E. Krummenacher, Helv. Chim. Acta, **1**, 152 (1918). See Fichter, Z. Elektrochem., **27**, 487 (1921); E. Müller, ibid,, **28**, 101 (1922); A. Nathansohn, ibid., **28**, 129 (1922).

[9] Fichter and Krummenacher, loc. cit.

[10] F. Fichter and E. T. Rothenberg, Helv. Chim. Acta, **5**, 166 (1922); F. Fichter, Trans. Am. Electrochem. Soc., **45**, 131 (1924).

[11] An excellent discussion of the present status of the theory of peracids and peroxides as related to the action of organic compounds at the anode is given by F. Fichter, Am. Electrochem. Soc., **45**, 131 (1924).

Other work on the chemical decomposition of these acid peroxides has been reported in the cases of succinic, fumaric, and benzoic peroxides.[12]

In any electrolysis the analysis of the electrode gases gives some interesting data. The volume of CO_2 is always more than expected from equation (1) on page 24 and is also more than double the volume of ethane formed. The difference is more than can be accounted for on the basis of the solubility of the gases. There is evidently another reaction taking place which produces CO_2 but not ethane. This reaction was discovered by Hofer and Moest,[13] who determined that this oxidation reaction leads to the formation of methanol, especially when the OH^- ion concentration at the anode is high:

$$(15)\quad CH_3COO^- + OH^- + 2\oplus \rightarrow CH_3OH + CO_2$$

Then, too, another reaction may take place, namely:

$$2OH^- + 2\oplus \rightarrow H_2O + \tfrac{1}{2}O_2$$

The free oxygen may be evolved as a gas or may attack the organic molecules with the formation of formaldehyde, or even CO:

$$CH_3OH + O \rightarrow CH_2O + H_2O$$

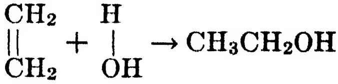
$$CH_2O + O \rightarrow CO + H_2O$$

The alcohol may be formed by the hydrolysis of the ester:

$$(16)\quad CH_3COOCH_3 + H_2O \rightarrow CH_3OH + CH_3COOH$$

or the olefin may add the elements of water:

(17)



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} H \\ | \\ OH \end{matrix} \rightarrow CH_3CH_2OH$$

This hydrolysis theory is rendered less plausible[14] by the fact that the potassium salt of trimethylacetic acid on electrolysis yields isobutylene and some tertiary butyl alcohol but no ester. The ester, on the other hand, is only partially hydrolyzed by boiling for an hour with very concentrated KOH.

The nature of the acid radical, rather than the experimental conditions, directs the course of the reaction. An alkali acetate yields,

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[12] Fichter and Fritsch, Helv. Chim. Acta, **6**, 329 (1923). See also the formation of H_2O_2 during the electrolysis of succinates and malonates by Scholl, Z. Elektrochem., **22**, 422 (1916).

[13] H. Hofer and M. Moest, Ann., **323**, 284 (1902).

[14] J. Petersen, Z. physik, Chem., **33**, 309 (1900).

according to equation (18*b*), page 30, as high as 90 per cent of the theoretical amount of ethane, while the propionate and both butyrates under the same conditions yield the corresponding unsaturated products ethylene and propylene according to equation (18*c*); and trichloroacetic acid salts follow equation (18*d*) almost completely, yielding the trichloromethyl ester of trichloroacetic acid with traces of hexachloroethane.

As a rule, both radicals of the ester formed are identical, but there are several cases known in which there is a rearrangement. One of these cases occurs in the electrolysis of potassium butyrate in which the ester expected is the propyl butyrate, but there are also formed considerable quantities of the rearranged product which is isopropyl butyrate:[15]

$$CH_3CH_2CH_2COO^- \rightarrow CH_3CH_2CH_2COOCH_2CH_2CH_3$$

and

$$CH_3CH_2CH_2COOCH(CH_3)_2$$

In general, the electrolysis of a salt of a normal aliphatic acid yields a secondary alcohol when a weakly acid or neutral electrolyte is used. If a slightly alkaline solution containing small amounts of inorganic salts, such as potassium perchlorate, sulphate, or bicarbonate, is electrolyzed, the product is a primary alcohol in which the carboxyl group of the acid is replaced by a hydroxyl group, thus forming an alcohol containing one less than the number of carbon atoms in the starting acid.[16]

Foerster [17] explains the action of these inorganic salts as due to the fact that the congestion of their anions at the anode decreases the concentration of the organic anions there, thus diminishing the number of the organic anions discharging at the anode while the number of OH^- ions discharging remains nearly constant. Then these anions unite to form an ester which is immediately hydrolyzed in the aqueous solution to the alcohol and the inorganic acid. This has been criticized by Moser [18] on the ground that the formation of these esters with inorganic acids by electrolysis cannot be detected, and therefore it is not certain that the esters so formed would under the prevailing conditions be so easily hydrolyzed as Foerster's theory supposes.

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[15] Engelbach, Krit. Zeitsch. f. Chem., 653 (1864); Hamonet, Compt. rend., **123**, 254 (1896); Petersen, Z. physik. Chem., **33**, 116 (1900).

[16] H. Hofer and M. Moest, Ann., **323**, 248 (1902); M. Moest, D.R.P. 138442 (1902); Zorn, Dissertation, Munich (1904).

[17] F. Foerster, "Wässeriger Lösungen," page 859.

[18] Haber and Moser, "Elektrolytische Prozesse," page 17.

The OH^- ions may be derived from the solvent water, or they may be formed in the regeneration of the inorganic acid at the electrode:

$$ClO_4^- + HOH \rightarrow HClO_4 + OH^-$$

$$\therefore CH_3COO^- + ClO_4^- + H_2O \rightarrow CH_3OH + HClO_4 + CO_2$$

If the reaction is continued for only a short time, very little of the alcohol is oxidized to the corresponding aldehyde. The gradation in the activity of the members of homologous series is in evidence here. In the presence of these inorganic salts, the lower aliphatic acids yield as the main product the primary alcohol, but as the molecular weight increases the per cent of alcohol formed decreases till the reaction practically stops at valeric acid.

The course of electrolysis may be expressed by four equations:

$$2RCOO^- + H_2O \rightarrow 2RCOOH + \tfrac{1}{2}O_2 \tag{18a}$$

$$2C_nH_{2n+1}COO^- + 2\oplus \rightarrow C_{2n}H_{4n+2} + 2CO_2 \tag{18b}$$

$$2C_nH_{2n+1}COO^- + 2\oplus \rightarrow C_nH_{2n} + C_nH_{2n+1}COOH + CO_2 \tag{18c}$$

$$2C_nH_{2n+1}COO^- + 2\oplus \rightarrow C_nH_{2n+1}COOC_nH_{2n+1} + CO_2 \tag{18d}$$

SATURATED ACIDS

Alkali Formates.—Formic acid (in reactions other than those in electrochemistry) does not always behave according to the rules which govern the action of the other members of the series. We must therefore expect some variation here. As seen from an examination of the formula, HCOOH, when the anion is discharged and CO_2 is split off, there remains not a hydrocarbon residue but a hydrogen atom, which indicates that the evolution of hydrogen should occur at the anode instead of the formation of a hydrocarbon by the union of two residues; the evolution of hydrogen, however, has never actually been realized. What really happens when an acidified concentrated solution of alkali formate is electrolyzed,[19] is the evolution of CO_2 and O_2 at the anode.

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[19] Brester, Z. f. Chem., **2**, 60 (1866); Jahresb. f. Chem., 87 (1866); Renard, Ann. Chim. et phys. [5], **17**, 289 (1879); Bourgoin, Ann. Chim. et phys., (4), 14, 157 (1868); Bunge, Ber., **9**, 78 (1876); Jour. Russ. Phys. Chem. Soc., **12**, 415 (1880); Bartoli and Papasogli, Gazz. chim. ital., **13**, 22 (1883); Boungné, Tommasi; "Traite," page 746; H. Jahn, Wied. Ann., **37**, 408 (1889); Hopfgartner, Monatsch., **32**, 523 (1911); J. Petersen, Z. physik. Chem., **33**, 106 (1900); F. Salzer, Z. Elektrochem., **8**, 893 (1902); Bültemann, Dissert., Dresden (1905).

The equations set up by Moser are: [20]

$$2HCOO^- + 2F = 2H + CO_2$$

$$2H + O = H_2O$$

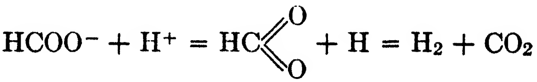
$$2HCOO^- + 2F = HCOOH + CO_2$$

$$HCOO^- + OH^- + 2F = H_2O + CO_2$$

$$HCOOH + O = H_2O + CO_2$$

All the H_2 liberated in the course of the oxidation must be oxidized to water because it never appears in the anode gases. Under certain conditions [21] there is an evolution of oxygen at the anode accompanying the formation and evolution of CO_2, though the quantities of the gases vary with the concentration of the solution and the c. d.

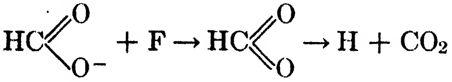
The action of various electrodes on formic acid has been studied [22] in some detail; the results show that in all cases H_2 and CO_2 are evolved. The reaction is assumed to be catalytic in nature:



$$HCOO^- + H^+ = HC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown O}\end{matrix} + H = H_2 + CO_2$$

It is entirely probable that after this catalytic decomposition of formic acid into H_2 and CO_2 the further action of the electric current at the anode causes the oxidation of the H_2 to form water. On the basis of this assumption, Müller [23] studied the potential relations during the oxidation of formic acid at various anodes.

Müller explains these facts as follows: At the lower potential the reaction differs from that at the higher value. The first reaction goes:



$$HC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown O^-}\end{matrix} + F \rightarrow HC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown O}\end{matrix} \rightarrow H + CO_2$$

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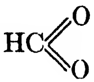
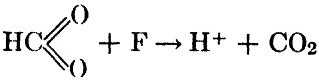
[20] Haber and Moser, "Elektrolytische Prozesse," page 24; Foerster, "Wässerige Lösungen," page 858.

[21] See also Petersen, Z. physik. Chem., **33**, 106 (1900); Salzer, Z. Elektrochem., **8**, 893 (1902).

[22] Rh by Deville and Debray, Compt. rend., **78**, 1782 (1874); Schade, Z. physik. Chem., **57**, 14 (1907); Blackadder, ibid., **81**, 385 (1913); Pd by Zelinsky, Ber., **44**, 2309 (1911); Weinland, ibid., **46**, 2327 (1913); Os by E. Müller, Z. Elektrochem., **28**, 307 (1922).

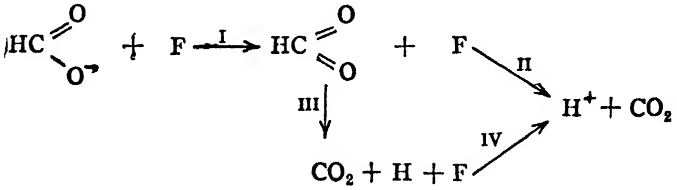
[23] E. Müller, Z. Elektrochem., **29**, 264 (1923). See Fig. 4, page 11.

i.e., the oxy-compound  $\mathrm{HC}\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix}$ is decomposed by the anode metal into H_2 and CO_2. Now, as the anodic potential increases, the metal of the anode is plated over with oxide which inhibits the catalytic action and stops this decomposition of the oxy-compound, but a further passage of the current starts the reaction:

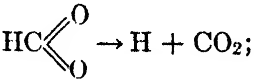


$$\mathrm{HC}\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix} + F \rightarrow H^+ + CO_2$$

He therefore sets up the scheme as follows:



That is, the oxidation may take two courses, I–III–IV, or I–II. The former can take place only in the presence of a metal which catalyzes the decomposition III:



$$\mathrm{HC}\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix} \rightarrow H + CO_2;$$

but as the potential increases, reaction II predominates over III. In no case is the potential low enough to prevent the complete oxidation of the hydrogen to water.

Formic acid behaves differently from acetic acid in yet another manner; it is a well-known reducing agent and is readily oxidized when free, but not so easily in the form of its salts, except in a strongly alkaline solution. Such an oxidation takes place at a smooth platinum, rather than at an iron, anode.

The evolution of hydrogen at the cathode is easily understood, but the formation of an equal volume of carbon dioxide at the cathode demands further explanation. The CO_2 may be formed by a primary reaction corresponding to equation (3) above in which the ester is formed, but in the formate the H atom corresponds to the ester group. The equation would be:

$$2HCOO^- + 2F = HCOOH + CO_2$$

Equation (7) above, in which an alcohol is formed by a primary reaction, is applicable here if water is considered as an alcohol. The equation would be:

$$HCOO^- + OH^- + 2F = CO_2 + HOH$$

The CO_2 may be formed by a secondary reaction in which two hydroxyl ions unite to form water and an atom of oxygen; the oxygen then acting on the formic acid of the first equation in this group to form water and CO_2:

$$2OH^- + 2F = H_2O + O; \quad HCOOH + O = CO_2 + H_2O$$

These equations are in accord with the fact that 2F yield one molecule of hydrogen and one of carbon dioxide when no oxygen is evolved during the electrolysis of acid, alkaline, or neutral solutions of potassium formate.[24]

Alkali Acetates.[25]—The electrolysis of the alkali acetates has received more attention than that of most other salts of the aliphatic acids. The first products isolated were ethane and ethylene.[26] A few years later [27] there were added to these methyl acetate, methyl carbonate, methyl formate, CO, CO_2, and formic acid.

In a study of the effects of concentration, c. d., and temperature upon the course of the electrolysis, using a 20 per cent potassium acetate solution with a current of 2 amperes, Murray detected CO, H_2, O_2, ethane, and methyl acetate,[28] but no ethylene. The following table [28] shows the variation in quantity of ethane and oxygen evolved at the anode as the c. d. changes. A 20 per cent potassium acetate solution was used with a current of 2 amperes. In 1 and 3 a platinum crucible served as the anode and the retaining vessel, while the cathode was a platinum spiral. In 1 the spiral was the anode, and in 3 the current direction was reversed.

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[24] H. Jahn, Ann. Physik, [2], **37**, 408 (1899); J. Petersen, Z. physik. Chem., **33**, 106 (1900); F. Salzer, Z. Elektrochem., **8**, 893 (1902); K. Hopfgartner, Monatsch., **32**, 523 (1911).

[25] See Hopfgartner, Monatsch., **32**, 523 (1911), for the electrolysis of anhydrous glacial acetic acid.

[26] Bourgoin, Ann. chim. et phys., [4], **14**, 157 (1868); Schützenberger, Tommasi, "Traite," page 683; Darling, J. Chem. Soc., **21**, 502 (1868).

[27] Kolbe and Kempf, J. prakt. Chem., [2], **4**, 46 (1871); Renard, Ann. chim. et phys. [5], **17**, 289 (1879); Dumas, Compt. rend., **78**, 313 (1874); Kempf, Chem. News, **24**, 157 (1872).

[28] Murray, J. Chem. Soc. **61**, 10 (1892).

TABLE II

20 per cent potassium acetate solution. Current = 2 amperes.

	Surface of Anode in Sq. Cm.	Current Density = Amperes/dm^2	Constitution of CO_2 Free Gases from Both Electrodes		
			C_2H_6	H_2	O_2
1	0.5	400.	46.6	53.2	0.14
2	6.0	33.	44.5	55.2	0.30
3	55.0	3.6	20.0	72.2	7.80

The influence of concentration and temperature is shown in the following tables:

TABLE III—INFLUENCE OF CONCENTRATION

Temp. = 12°. Current = 1.5 amperes

Per Cent of CH_3COOK	C_2H_6/H_2	Per Cent of O_2 in Gas (CO_2 Free)
60.	0.796	0.16
27.47	0.759	0.68
11.77	0.735	0.66
3.58	0.1605	1.36
0.97	0.2635	10.5
0.5	0.0028	32.47

TABLE IV—INFLUENCE OF TEMPERATURE

20 per cent CH_3COOK. Current = 1.5 amperes

Temperature	C_2H_6/H_2	Per Cent of O_2 in Gas (CO_2 Free)
0°	0.83	0.27
17°	0.8055	0.31
50°	0.6945	0.4
65°	0.575	0.61
80°	0.403	4.17
95°	0.124	25.64

The ratio of ethane to hydrogen is a measure of the per cent of current used in the formation of ethane, because according to Faraday's law 2F evolve one molecule of hydrogen; therefore when the ratio is 1 there will be a 100 per cent formation of ethane.

In repeating some of this work, Petersen [29a] made a very careful and comprehensive study of the reaction, including an accurate analysis of the gases evolved, in order to get the quantitative relations of Kolbe and Kempf, which led to the detection of the ethylene, but which Murray had missed. He set up the equations as follows:

$$2CH_3COOH \rightarrow 2CH_3COO^- + H_2 \qquad (19a)$$

$$2CH_3COO^- + H_2O \rightarrow 2CH_3COOH + \tfrac{1}{2}O_2 \qquad (19b)$$

$$2CH_3COO^- + 2F \rightarrow C_2H_6 + 2CO_2 \qquad (19c)$$

$$2CH_3COO^- + 2F \rightarrow CH_3COOCH_3 + CO_2 \qquad (19d)$$

$$2CH_3COO^- + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O + 2CO_2 \qquad (19e)$$

Of the above equations (19*a*) and (19*c*) predominate, but (19*e*) takes place to but a very slight extent. When a dilute solution is used, reaction (2) predominates, with the evolution of oxygen and the formation of acetic acid, as in the electrolysis of the alkali salts of inorganic acids. When a concentrated solution is used at room temperature with smooth Pt electrodes and a large c. d., the anode gases are mostly ethane and carbon dioxide, containing only a trace of oxygen; therefore, the reaction is according to (3) above. The formation of methyl acetate and ethylene takes place only as a side reaction.[30] In slightly acid or even neutral solutions, some oxygen never appears as a gas because it is used to oxidize completely some acetic acid to water and carbon dioxide according to the equation:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (20)$$

Jahn [31] investigated this reaction quantitatively, even determining the heat of combustion of acetic acid. He found that the anode gas contained more CO_2 than would be expected from equation (19*c*) and the volume was also more than double the volume of the ethane formed. Kolbe [32] obtained $2\frac{1}{3}$ volumes of CO_2 for each volume of ethane.

When potassium formate is electrolyzed in the presence of an inorganic salt, such as an alkali sulphate, bicarbonate, or perchlorate, the

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[29a] Petersen, Z. physik. Chem. **33**, 90 & 295, & 698, (1900)

[30] J. Petersen, Z. phys. Chem., **33**, 108 (1900).

[31] H. Jahn, Ann. phys., [3], **37**, 408 (1899).

[32] H. Kolbe, Ann., **69**, 279 (1849).

alcohol formed will be, of course, water. With potassium acetate the methanol can very easily be separated from the electrolyte. The electrolysis of a weakly alkaline or a neutral solution containing one of the above inorganic salts produces methanol as the main product. According to the theory of Hofer and Moest,[33] the equation for this would be:

$$CH_3COO^- + OH^- + 2 \oplus \rightarrow CH_3OH + CO_2$$

The best yields of alcohol are obtained when potassium bicarbonate is added to the electrolyte.

TABLE V

147 g. potassium acetate per liter. c. d. = 25 amperes. Temp. = 25°

Addition of g. of $KHCO_3$ per Liter	Per Cent Composition of Gas					Per Cent Current Used in Oxidation Reactions
	CO_2	O_2	C_2H_6	H_2	C_2H_6/H_2	
6	21.4	0.1	28.32	49.2	0.576	42.2
15	17.9	0.1	23.8	55.1	0.432	56.6
45	24.9	0.1	11.26	61.18	0.184	81.4
75	32.0	0.4	4.69	63.11	0.077	91.8
90	33.2	0.7	2.96	60.2	0.049	93.7
120	32.9	1.1	1.97	60.2	0.032	94.53

An examination of the table shows, as very little of the oxygen appears as a gas, that, under the conditions of the electrolysis, the portion of the current used in an oxidation reaction is directed almost completely to the formation of methanol, and only a very small portion to the further oxidation of the alcohol to formaldehyde and formic acid, or to the complete and direct oxidation of the acetic acid to CO_2 and H_2O as in equation (20) above. If the percentage of free alkali or of bicarbonate rises to very large values the reaction at the anode is mainly an oxidation.[34]

An aqueous solution of acetic acid yields, under all conditions, only oxygen at the anode,[35] probably because of the slightly ionized condition of the acid, by reason of which the solution contains too few acetate

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[33] H. Hofer & M. Moest, Ann., **323**, 284, (1902).

[34] Bourgoin, Ann. chim. et phys., [4], **14**, 174 (1868).

[35] Brester, Zeit. f. Chem., **2**, 60 (1866); Arch Neerland. des. sc. ex., **1**, 296 (1866); Bourgoin, Ann. chim. et phys., [4], **14**, 157 (1868).

ions to form an appreciable amount of ethane; then, too, acetic acid is very similar in many ways to the non-volatile inorganic acids which on electrolysis yield only H_2 and O_2.

The Influence of the Anode Material on the Course of the Reaction [36]

The material from which the anode is made seems to influence the course of the reaction to as great an extent as does a change in temperature and c. d. Anodes of smooth platinum and iridium yield mostly ethane, while iron and palladium under identically the same conditions yield mostly oxygen and not a trace of ethane. Midway between these two extremes, platinized-platinum electrodes yield a mixture of oxygen, and larger amounts of oxidation products. In the following table the anodes and cathodes were of the same size in all cases; the cathode was in all cases platinized-platinum, in a solution containing 45 g. of potassium acetate in 100 cc. of solution, at 18°[37].

Table VI

Anode Material	Potential Drop in Volts	Current in Amperes	Current Density at Anode in Amp./cm 2	Portion of Anodic Current Used in		
				O_2 Evolution	C_2H_6 Formation	Oxidation Reactions
Smooth Pt.	4.3	0.4	0.18	1	76	23
Smooth Pt.	3.75	0.2	0.09	2	59	39
Iridium	4.6	0.9	0.072	....	74.3	24.7*
Platinized-Pt, previously cathodically polarized	3.62	0.4	0.18	43.6	....	51.9*
Same anode	3.1	0.2	0.09	54	....	45 *
Platinized-Pt, previously anodically polarized	4.1	0.4	0.18	2	22	74.5 *
Smooth Fe	3.15	0.4	0.18	83.6	....	16.4
Pd	3.8	0.9	0.072	70	....	28 *

* Some CO was present in these gases.

The different behavior of these electrodes is connected with the varying potential at which oxygen is liberated at them; the potential[38] required for the formation of ethane lies below that at which oxygen is evolved at platinum or iridium anodes but above the value for iron and palladium anodes. Both iron and palladium under similar conditions have almost the same potential drop through the bath, but it is very

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[36] See Nobili, Ann. chim. et phys., **34**, 280 (1827), on the electrolytic coloration of metals.

[37] Foerster and Piguet, Z. Elektrochem., **10**, 729 (1904).

[38] See G. Preuner, Z. physik. Chem., **59**, 670 (1907).

much below that for platinized-platinum; both metals are slightly soluble. At a platinized-platinum anode the oxidation increases with the increasing c. d., while the oxygen evolution, which requires a lower anode potential, decreases. Previous polarization of the electrode by strong oxygen evolution increases the oxidation to CO_2 while it allows a slight formation of ethane, eliminating practically all evolution of oxygen. Diluting the potassium acetate raises the anodic potential on a smooth platinum anode to such an extent that only oxygen evolution takes place. A high temperature requires a low potential, therefore warming decreases ethane formation. The presence of alkali in the electrolyte decreases the formation of ethane. At a smooth platinum anode with increasing alkali content the oxygen evolution increases, while at a platinized-platinum anode this decreases. It is a question whether the high voltage required for ethane formation proves that the discharged acetate ions, which are heavier than hydroxyl ions, separate and are then decomposed into ethane and carbon dioxide, or whether the high numbers are explained by the high resistance of the electrolyte due to the free acetic acid at the anode. Therefore the question is still unsettled whether or not the ethane is formed directly by the decomposition of the discharged acetate ion.

The acetates of different metals behave differently on being subjected to electrolysis. The acetates of metals such as Mg, K, Na, U, Zn, Ca, and Cu in general behave like the alkali acetates. The acetates of metals with a variable valence, such as Fe^{++}, Mn, Cr, and Pb, yield oxygen in place of ethane. An aqueous solution of lead acetate[39] yields at the anode not an evolution of oxygen but the formation of lead dioxide, PbO_2. A cool solution[40] of lead acetate acidified with free acetic acid[41] forms small amounts of lead tetraacetate. The electrolysis of cobalt and nickel diacetates in glacial acetic acid yields the corresponding triacetates.[42] A saturated solution of chemically pure zinc acetate,[43] electrolyzed between a mercury cathode and a platinum wire anode with 0.01 sq. dm. of surface, using a current of 0.7 amp., yielded 92–94 per cent of pure ethane.

Methanol, free from acetone, can be obtained by the electrolysis of potassium acetate, using the method of Hofer and Moest.[44]

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[39] Depretz, Compt. rend., **45**, 449 (1857); Smith, Am. Chem. Jour., **7**, 329 (1885). See also Tommasi, "Traite," page 747.

[40] W. Löb, Z. Elektrochem., **2**, 495 (1896).

[41] K. Elbs, Z. Elektrochem., **3**, 70 (1897).

[42] Schall and Markgraf, Trans. Am. Electrochem. Soc., **45**, 119 (1924).

[43] Bauer, Dissert., Giessen, 1897.

[44] H. Hofer and M. Moest, Ann., **323**, 284 (1902); D.R.P. 138442 (1902); Baker, Thesis, Cambridge, Mass., 1921.

Propionates.—The conditions under which solutions of the higher homologues in this series of salts have been electrolyzed are those under which potassium acetate yields ethane.

The electrolysis of aqueous solutions of alkali propionates yields at the anode oxygen, carbon dioxide, ethylene, butane, ethyl propionate. The reactions may be expressed by the following equations:[45]

$$2C_2H_5COO^- + 2F \rightarrow C_4H_{10} + 2CO_2$$

$$2C_2H_5COO^- + 2F \rightarrow C_2H_4 + C_2H_5COOH + CO_2$$

$$2C_2H_5COO^- + 2F \rightarrow C_2H_5COOC_2H_5 + CO_2$$

The addition of inorganic salts, as stated above, leads to the formation of smaller amounts of ethyl alcohol than in the analogous case of the formation of methanol from potassium acetate.[46]

Butyrates.—A concentrated solution of potassium butyrate yields at the anode a mixture of gases which, after the carbon dioxide has been removed, consists of propylene and only a trace of oxygen and hexane.[47] During the progress of the electrolysis an oily layer, which consists of the propyl ester together with the greater part of the hexane formed, collects on the surface of the electrolyte.

In the electrolysis of a potassium butyrate solution the expected ester is, of course, propyl butyrate, but considerable quantities of isopropyl butyrate are also formed.[48] The assumption is that the isopropyl alcohol is first formed by the hydrolysis of propylene, one of the primary products of the electrolysis:

$$CH_3 \cdot CH : CH_2 + H_2O \rightarrow CH_3CHOHCH_3$$

Whether this is really the mechanism is at present uncertain, because commercially the preparation of isopropyl alcohol from propylene is more complicated than the simple passage of propylene through water. The electrodes must have some catalytic action as there are no salts in solution.

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[45] Bourge, J. Russ. Phys. Chem. Soc., **21**, 551 (1889); Jahn, Ann. d. Phys., **37**, 430 (1889); Zimmermann, Dissert., Giessen (1899); J. Petersen, Z. physik. Chem., **33**, 110 (1900).

[46] H. Hofer and M. Moest, Ann., **323**, 288 (1902).

[47] Engelbach, Krit. Z. f. Chem., 653 (1864); Bunge, Jour. Russ. Phys. Chem. Soc., **21**, 525 (1889); J. Hamonet, Compt. rend., **123**, 252 (1896); J. Petersen. Z. physik. Chem., **33**, 110 (1900).

[48] Englebach, loc. cit.; Hamonet, Compt. rend., **123**, 254 (1896); J. Petersen, Z. physik. Chem., **33**, 116 (1900).

Besides these compounds there are formed certain alcohols [49] which remain dissolved in the electrolyte. On electrolyzing a cold aqueous solution of potassium butyrate (sp. gr. 1.09), 18 g. of isopropyl alcohol were obtained in twenty-two hours, but no hexane and no normal propyl alcohol were detected.

The electrolysis of the potassium salt of normal butyric acid in the presence of inorganic salts yields, according to the above results, isopropyl alcohol with a considerable amount of the normal alcohol.[50]

When $HClO_4$ is added the formation of hexane predominates, though propyl alcohol and propionaldehyde are also formed.

Why this normal alcohol is not formed in large quantities when these salts are absent has not been explained. There must be a catalytic influence that directs the course of the reaction. If the alkali is strong, there is an evolution of oxygen in place of the formation of alcohol.[51]

The electrolysis of potassium isobutyrate yields only a trace of the expected hydrocarbon, diisopropyl, some hexane with large amounts of isopropyl alcohol, and propylene.[52]

Alkali Valerates.—In his efforts to isolate free radicals, Kolbe [53] electrolyzed potassium valerate in a neutral solution between a platinum anode and a copper cathode. At the cathode only hydrogen was evolved, but at the anode a mixture of carbon dioxide, oxygen, and another gas was collected. The latter gas, after the removal of the oxygen and carbon dioxide, burned with a smoky flame. He suspected that he had isolated the radical valyl, as he called it. Now we know that the oil was normal octane, and the gas was butylene. The ethereal odor of the oil was shown to be due to esters (ethers as they were then called), of a four carbon atom acid, i.e., butyl ester.[54]

Higher oxidation products are more prominent here than in any of the preceding reactions. Considerable quantities of O_2, butyraldehyde and alcohols are formed, the latter remaining dissolved in the electrolyte. The salts of normal and isovaleric acid yield mostly octane according to equation (18*b*), but the secondary and tertiary acid salts yield mostly butylene according to equation (18*c*), with only a trace of octane.

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[49] Hamonet, Compt. rend., **123**, 252 (1896). Hamonet did not find a paraffin, but later Petersen found hexane.

[50] H. Hofer and M. Moest, Ann., **323**, 290 (1902).

[51] Bourgoin, Ann. chim. et phys., [4], **14**, 174 (1868).

[52] Hamonet, Compt. rend., **123**, 252 (1896); J. Petersen, Z. physik. Chem., **33**, 110 (1900).

[53] Kolbe, Quart. Jour. of the Chem. Soc., Vol. 2 (1850); Ann., **69**, 279 (1849).

[54] H. Kolbe, Ann., **69**, 257 (1849); J. Petersen, Z. physik. Chem., **33**, 295 (1900); Z. Elektrochem., **12**, 141 (1906).

The alkali salts of normal valeric acid yield the normal products with some iso-hydrocarbons. The current yield of octane is about 50 per cent of the theoretical value.

The salts of isovaleric acid, $(CH_3)_2CHCH_2COOH$, yields diisobutyl, $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$, corresponding to the constitution of the acid, besides a little isobutyl isovalerate, the trimethylcarbinol ester of isovaleric acid, trimethylcarbinol, two isomeric olefins, isobutylene $(CH_3)_2C : CH_2$ and β-butylene, $CH_3CH : CHCH_3$. Of the two olefins formed, only the former is soluble in dilute sulphuric acid.[55]

Potassium trimethyl acetate yields the corresponding unsaturated hydrocarbon isobutylene, in place of octane, according to the equation: The olefin combines with the elements of water to form trimethyl carbinol; no ester is formed, but some hexamethyl ethane and one of its isomers, together with two isomeric butylenes, are also formed. The iso predominates over the β-butylene.

The electrolysis [56] of the potassium salt of methyl ethyl acetic acid yields trimethylcarbinol, the trimethylethylcarbinol ester of methyl ethyl acetic acid, 3, 4-dimethyl hexane and β-butylene.

The Alkali Salts of the Higher Aliphatic Acids.—The salts of the higher fatty acids [57] of normal carbon chains react exactly like the lower members of the series and form mostly saturated hydrocarbons. As high as 77 per cent of the theoretical amount of normal decane with amylene, amyl alcohol, amyl caproate, and some aldehyde, probably $CH_3(CH_2)_3CHO$, have been obtained from the electrolysis of normal caproic acid salts. Potassium isobutyl acetate,[58] one of the isomers of caproic acid, yielded the isomeric decane, diisoamyl, but no ester or olefin. In an analogous manner, salts [59] of normal heptylic acid yield dodecane. Normal caprylic salts yield tetradecane.

Beginning with the acids containing ten carbon atoms, it is necessary to carry on the electrolysis in a dilute alcoholic solution because the aqueous solutions foam too much for easy manipulation. The gradual

[55] J. Petersen, Z. Elektrochem., **12**, 142 (1906); Z. physik. Chem., **33**, 295 (1900); Kolbe, loc. cit., found diisobutane, butylene, CO_2 and the butyl ester of valeric acid; Brester, Jahresb. f. Chem., 86 (1859); 757 (1866) got only CO_2, O_2 and butylene; Zimmermann, Dissert., Giessen (1899).

$$2(CH_3)_3C\cdot COO^- + 2F \rightarrow (CH_3)_2C : CH_2 + (CH_3)_3C\cdot COOH + CO_2$$

[56] J. Petersen, Z. Elektrochem., **12**, 142 (1906).

[57] Rohland, Z. Elektrochem., **4**, 120 (1897); Brazier and Goszleth, Ann., **76**, 265 (1850); J. Petersen, Z. physik. Chem., **33**, 317 (1900); Würtz, Ann. chim. et phys., [3], **44**, 291 (1855).

[58] Brazier and Goszleth, loc. cit.

[59] Brazier and Goszleth, loc. cit.; Rohland, loc. cit.; Schorlemmer, Ann., **161**, 277 (1872); Tommasi, "Traite," page 685.

addition of the solid acid to the electrolyte from time to time causes the yields of the corresponding hydrocarbon to be increased.

The following table explains itself: [60]

TABLE VII

Acid	Current, Ampere	Hydrocarbon	Per Cent Yield	
			Material	Current
Heptylic *	....	dodecane	....	....
Pelargonic*	....	dioctyl	....	....
Lauric †	0 84	docosane	90.	45.
Myristic †	0 96	hexacosane	89.1	33.7
Palmitic †	0.98	triacontane	88.1	30.
Stearic †	0.98	tetriacontane	73.6	27.6

* Rohland, loc. cit.
† Petersen, loc. cit.

Besides the docosane, lauric acid yields some ester which is probably $C_{11}H_{23}COOC_{11}H_{23}$, and possibly some ethyl laurate. Myristic acid salts yield an ester, probably the ethyl ester of myristic acid. Potassium palmitate yields some ethyl palmitate. As the number of carbon atoms increases, the percentage production of hydrocarbon decreases; the remainder of the anode current is probably utilized in oxidizing the solvent alcohol.

In the following table the portions of the current that are used for the stated reactions are given as percentages of the total current at the anode. In all cases the experimental conditions were identical with respect to the concentration of the alkali salts, acidity of the solution, condition of the smooth platinum electrodes, and c. d. (6 amp.) The percentage of the current that is indicated as not belonging to any particular reaction, is considered as used in side reactions of the nature of oxidations, or the evolution of oxygen.[61]

In prosecuting the study of the formation and decomposition of peracids and its accompanying theory, Fichter and Reeb investigated the electrolysis of cyclopropane carboxylic acid [62] (I). The product obtained was the allyl ester of cyclopropane carboxylic acid (IV); the cylcopropanol (III), which is first formed is evidently at once rearranged

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[60] J. Petersen, Z. Elektrochem., **12**, 143 (1906); see also Brester, Jahresb. f., Chem., **60** (1866).

[61] J. Petersen, loc. cit.

[62] Fichter and Reeb, Helv. Chim. Acta, **6**, 450 (1923).

to allyl alcohol.[63] On the basis of the peracid theory the equations for the reaction will be:

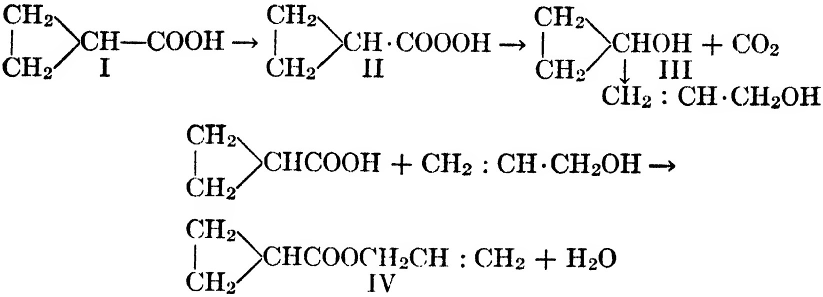

TABLE VIII

Acid	Per Cent Paraffin Formation	Per Cent Olefine Formation	Per Cent Ester Formation
Acetic	85	2	2
Propionic	8	66	5
Butyric	14.5	53	10
Isobutyric	trace	62	10
n-valeric	50	18	4
Isovaleric	43	42	5
Methyl ethyl acetic	10	42	10
Trimethyl acetic	13	52	0
Caproic	75	7	1.5
Lauric	45	....	......
Myristic	33.7	....	......
Palmitic	30	....	......
Stearic	27.6	. .	......

Fused Salts.— The electrolysis of the anhydrous fused salts of the aliphatic acids seems to proceed by a slightly different mechanism. Faraday[64] in 1833 stated: "Acetate of soda fused and anhydrous is directly decomposed, being, as I believe, a true electrolyte, and evolving soda and acetic acid at the cathode and anode. These however have no sensible duration, but are immediately resolved into other substances; charcoal, sodiuretted hydrogen, etc., being set free at the former, and, as far as I could judge under the circumstances, acetic acid mingled with carbonic oxide, carbonic acid, etc., at the latter." Lassar-Cohn[65]

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[63] M. Kishner, J. Russ. Phys. Chem. Soc., **37**, 304 (1905).

[64] Faraday, Exp. Res., vol. 1, page 228.

[65] Lassar-Cohn, Ann., **261**, 357 (1889).

subsequently obtained methane and hydrogen at the cathode with carbon dioxide at the anode.

In 1904 Berl[66] repeated the work of Faraday and Lassar-Cohn, using pure fused potassium acetate and also a fused mixture of sodium and potassium acetates. The results of previous work were verified, for the anode gases consisted of 44 per cent hydrogen, 26 per cent methane and 21 per cent carbon dioxide. The mechanism suggested by Berl is that the decomposition of the electrolyte is due to the action on the fused salt of metallic sodium liberated at the cathode. This mechanism is sustained by experimental evidence. Petersen,[67] with a fused eutectic mixture of lead and zinc acetates, obtained very little ethane but did get large yields of hydrogen and methane. Larger amounts of ethane were obtained from a fused mixture of lead and sodium acetates. Fused lead propionate and butyrate yielded very small amounts of the paraffin compounds which would be expected if the reaction were entirely analogous to the electrolysis of the aqueous solutions.

Without a doubt the course of the oxidation in the fused state is different from the course in aqueous solution. This however may be due to the fact that in the fused state the molecular condition is more complex (owing to molecular association) than in the aqueous solution (where there is dissociation).[68]

SALTS OF THE UNSATURATED ALIPHATIC ACIDS

Until Petersen[69] electrolyzed the salts of acrylic acid and other members of that series, no one had ever reported any investigations in the field of electrolysis of salts of unsaturated acids unaccompanied by oxidation or reduction reactions. A series of rearrangements entirely analogous to those in the electrolysis of the saturated fatty acids occurs in the case of acrylates:

$$(21a)\qquad 2CH_2:CHCOOH \rightarrow 2CH_2:CHCOO^- + H_2$$

$$(21b)\qquad 2CH_2:CHCOO^- + H_2O \rightarrow 2CH_2:CHCOOH + \tfrac{1}{2}O_2$$

$$(21c)\qquad 2CH_2:CHCOO^- + 2F \rightarrow CH_2:CHCOOH + CH:CH + CO_2$$

$$(21d)\qquad 2CH_2:CHCOO^- + 2F \rightarrow CH_2:CH\cdot CH:CH_2 + 2CO_2$$

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[66] Berl, Ber., **37**, 325 (1904).

[67] Z. Elektrochem., **20**, 328 (1914).

[68] See Walden, Nichtwässerige Lösungen, page 318, Barth, Leipzig, 1924.

[69] J. Petersen, Oversigt K. Danske Videnske Selsk. Forh., **1**, 25 (1912), Z. Elektrochem., **18**, 710 (1912).

Of these expected reactions only (21*b*) was realized to any great extent. On the electrolysis of the slightly acid solution reaction (21*b*) yielded very large percentages of gaseous oxygen. There was also the formation of about 1.55 per cent C_2H_2, according to (21*c*). Not sufficient CO_2 was evolved to indicate the completion of (21*d*). A small quantity of carbon monoxide was formed, probably according to the equation:

$$2C_2H_2 + 3O_2 = 4CO + H_2O$$

Instead of the formation of a butadiene according to (21*d*) (the analogue of the formation of ethylene from potassium acetate) there was an evolution of ethylene, probably formed by the reduction of a part of the acrylic acid. A small amount of acetaldehyde was formed, probably by the hydration of the acetylene of (21*c*).

Potassium crotonate gave reactions as indicated by equations (21*a*, *b* and *c*) for acrylic acid salts. Some acetone was detected in the electrolyte, having been formed by the addition of the elements of water to allylene. A reaction indicating the presence of an aldehyde was obtained.

Potassium undecenoate $C_{10}H_{19}COOK$ yielded mostly the diolefin $C_{10}H_{19}\cdot C_{10}H_{19}$ according to the equation (21*d*) above, and therefore behaved exactly like a saturated fatty acid. The corresponding acetylene hydrocarbon $C_{10}H_{18}$ as per (21*c*) above was also detected in the liquid. This hydrocarbon reacted like most of the unsaturated hydrocarbons in that it seemed to add the elements of water to form a mixture of primary and secondary alcohols of the unsaturated series, $C_{10}H_{19}OH$. There was practically no evolution of oxygen. Potassium oleate ($C_{17}H_{33}COOK$) acted like the potassium undecenoate, yielding mostly the diolefin $C_{17}H_{33}\cdot C_{17}H_{33}$, some $C_{17}H_{32}$ and some alcohols of the series $C_{17}H_{33}OH$.[70]

The difference in the action of the lower and higher members of the series may be due to the fact that the radical attached to the carboxyl group is much more negative in the case of the short-carbon-chain lower acids than in the long-carbon-chain higher acids. Under the influence of the current this great negativity may prevent the formation, in large quantities, of the acetylene and the diolefin hydrocarbons until the chain of the carbon atoms is long enough to reduce the negativity of the radical and allow two of them to unite. Rohland [71] obtained a series of unsaturated hydrocarbons of an undetermined nature in the electrolysis of an aqueous solution of potassium oleate.

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[70] See also Rohland, loc. cit.

[71] Rohland, loc. cit.

CHAPTER IV

THE ELECTROLYTIC OXIDATION OF IONIZED SUBSTANCES—PART II

THE ELECTROLYSIS OF THE ALKALI SALTS OF THE SUBSTITUTED ALIPHATIC ACIDS

A. Halogen-substituted Acids.—The substituted aliphatic acids do not react as expected but tend to decompose according to reactions of another order. After the anion is broken up, the smaller parts are more easily oxidized, yielding more carbon dioxide than usual. The sodium salt of monochloroacetic acid yields carbon dioxide, hydrochloric acid, and chlorine [1] and according to Troeger and Ewers yields also carbon monoxide and oxygen together with an unknown oil. Kaufler and Herzog [2] find that the electrolysis of alkali salts of monochloroacetic acid also yields methylene chloride and chloromethyl chloroacetate in small amounts. These compounds are very difficult to detect, because of their extreme dilution, in the presence of Cl_2, CO, CO_2 and O_2. The mechanism of the electrolysis of these acids seems to be similar to the electrolysis of the fatty acids. The discharge of the anion yields the residue CH_2ClCOO^- which eliminates CO_2 leaving $-CH_2Cl$. This residue can either react with the CH_2ClCOO^- to form monochloromethyl monochloroacetate, or two of them can unite to form ethylene chloride; but it is remarkable that not even a trace of ethylene chloride is detected. The main products of the reaction are, however, Cl_2, CO, CO_2 and HCl. Therefore the mechanism must be slightly different from that discussed in the previous chapter. Since even a very slight current at once produces chlorine, there may be a breaking down of the discharged anion into $-CH_2COO^-$ and Cl^-. The CO which is formed immediately by the passage of a very slight current, may be produced by the following decomposition:

$$CH_2ClCOO^- + F \rightarrow CH_2O + CO + Cl$$

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[1] Lassar-Cohn, Ann., **251**, 341 (1889); Troeger and Ewers, J. prakt. Chem., [2], **58**, 121 (1898); Bunge, J. Russ. Phys. Chem. Soc., 690 (1892); Ber., **26**, 380 (1893); Greszly, Dissert., Basel (1901); Kolbe, Ann., **69**, 279 (1849).

[2] F. Kaufler and C. Herzog, Ber., **42**, 3858 (1909); **43**, 266 (1910).

Then the hydrochloric acid is formed by the action of the chlorine on the formaldehyde or on the carbon monoxide; the carbon dioxide may be formed by the action of the carbon monoxide on the chlorine, followed by a reaction with water,

$$CH_2O + 4Cl \rightarrow 2HCl + COCl_2$$

$$CO + 2Cl \rightarrow COCl_2; \qquad COCl_2 + H_2O \rightarrow CO_2 + 2HCl$$

Formaldehyde may be detected in the electrolyte by the method of Rimini.[3] The absence of even a trace of ethylene chloride indicates that there is no tendency for the two halogenated residues to unite according to Kolbe's ethane synthesis. The oil of Troeger and Ewers evidently was the chloroester of the chloroacid.

The electrolysis of a solution of monobromoacetate [3a] causes the anodic formation of bromine, CO, CO_2 and O_2 as the primary products besides methyl bromide and probably some bromomethyl bromoacetate. Iodoacetates [3a] yields as the non-gaseous products only iodine and methylene iodide. In the case of the electrolyses of the latter two substituted acids the addition may be:

$$XCH_2COO^- \rightarrow X_2 + CO + CO_2 + HX$$

$$XCH_2COO^- \rightarrow XCH_2 + CO_2$$

$$XCH_2 + X \rightarrow X_2CH_2$$

in which X is the halogen atom.

The salts of dichloroacetic acid yield the usual products,[4] besides an oil not identified at the time but which Kaufler and Herzog have been able to identify as the dichloromethyl ester of dichloroacetic acid. Sodium or zinc trichloroacetate, besides CO_2, CO, Cl_2 and HCl, yields the usual compounds according to Kolbe's syntheses, that is, the trichloromethyl ester of trichloroacetic acid:[5]

$$2CCl_3COO^- + 2F \rightarrow CCl_3COOCCl_3 + CO_2$$

The sodium salt of α-dichloropropionic acid reacts just like the sodium salt of trichloroacetic acid, yielding oxygen, carbon dioxide, and a crystalline ester, the α-dichloroethyl ester of α-dichloropropionic acid.[6] The sodium salt of α, α, β-trichlorobutyric acid yields tetrachloro-

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[3] Rimini, Ann. di. Farmacol, **97** (1898).

[3a] Kaufler and Herzog, loc. cit.

[4] Troeger and Ewers, loc. cit.

[5] K. Elbs, J. prakt. Chem., [2], **47**, 101 (1893); Elbs and Kratz, ibid., **55**, 502 (1897); F. Kaufler and C. Herzog., loc. cit. See also F. M. Jaeger, Z. Elektrochem., **18**, 664 (1912); Elbs, "Übungsbeispiele," page 68.

[6] Troeger and Ewers, loc. cit.

hexyleneglycol[7] according to the following equation:

$$2CH_3CHClCCl_2COO^- + 2F \rightarrow CH_3CHClCCl_2 \cdot CCl_2CHClCH_3 + 2CO_2$$

$$CH_3CHClCCl_2CCl_2CHClCH_3 + 2H_2O \rightarrow CH_3CHOHCCl_2 \cdot CCl_2CHOHCH_3 + 2HCl$$

It could easily in the normal manner form a hexachlorohexane, the β-chlorine atom being unstable and easily removed by hydrolysis. β-Iodopropionate formed iodine and iodoform with a gas containing more CO_2 than CO.[8]

B. Amino Acids.—Lilienfeld[9] observed that the electrolysis of the copper salt of glycocoll yielded products that corresponded with the Kolbe ethane synthesis, forming at the anode ethylenediamine:

$$2NH_2CH_2COO^- + 2F \rightarrow NH_2CH_2CH_2NH_2 + 2CO_2$$

The ethylenediamine was isolated as the hydrochloride in 95 per cent yield. Formic acid was detected in the absence of oxalic and acetic acids.[10]

How deep-seated is the decomposition of the glycocoll at the anode, has been clearly shown by the recent work of Fichter and Schmidt,[11] in which the electrolysis was repeated with precautions to insure the careful identification of the products, and in which it was shown that the mechanism outlined above may be wrong. Instead of ethylenediamine the products were mono-, di-, and tri-methylamine. The error was discovered because the reaction, as given in the literature, was at variance with the peroxide theory which Fr. Fichter is developing.

7.6 g. of glycocoll were dissolved in 40 cc. of $N \cdot H_2SO_4$ in a clay cell and oxidized at a small platinum anode with a c. d. of 50 amperes until one-half of the glycocoll had been oxidized. After chemical treatment the amines were distilled, collected in HCl and identified. Since the electrolysis of a mixture of formaldehyde and ammonium sulphate gives the same products, the mechanism is probably that in sulphuric acid or in alkali sulphates glycocoll yields ammonia, carbon dioxide and formaldehyde according to the equation:

$$NH_2CH_2COOH + O + 2F \rightarrow NH_3 + HCHO + CO_2$$

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[7] Troeger and Ewers, J. prakt. Chem., [2], **59**, 464 (1899).

[8] Troeger and Ewers, J. prakt. Chem., [2], **58**, 121 (1898).

[9] D.R.P. 147 943 (1902), Lilienfeld.

[10] See also O. Kühling, Ber., **38**, 1638 (1905).

[11] Fichter and Schmidt, Helv. Chim. Acta, **3**, 704 (1920).

and then the ammonia and the formaldehyde unite to form the ammonia bases mentioned.[12] The following amino acids have been similarly oxidized: acetyl glycocoll, iminodiacetic acid, methylaminodiacetic acid, α-aminoisobutyric acid, α-*p*-tolylsulphamino-isobutyric acid, N-methyl-α-benzene-sulphaminoisobutyric acid, β-alanine, and α-alanine;[13] α-alanine was studied by Fichter and Kuhn.[14]

Fichter is not quite willing in the absence of definite proof of the formation of a peracid in the above cases, to assume that his peroxide theory explains the " oxidative deaminization " of amino compounds. But his work proves that Kolbe's hydrocarbon synthesis does not express the facts of the case.

C. Hydroxy Aliphatic Acids.—The alkali salts of the α-hydroxy aliphatic acids yield on the electrolysis of their concentrated solutions an aldehyde and an acid containing a smaller number of carbon atoms than the acid started with, also some CO_2, CO and H_2O.[15] Lactic acid (α-hydroxypropionic acid) yields acetaldehyde, acetic and formic acids, CO and CO_2.[16] The formation of the aldehyde can be expressed either as a primary or a secondary electrolytic reaction:

$$(1)\quad 2CH_3CHOHCOO^- + 2F \rightarrow CH_3CHO + CH_3CHOHCOOH + CO_2$$

$$(2)\quad 2CH_3CHOHCOO^- + O \rightarrow 2CH_3CHO + 2CO_2 + H_2O$$

The first equation is the analog of the formation of olefines; the first formed vinyl alcohol, being unstable, immediately rearranges into acetaldehyde:[17]

$$CH_2 : CHOH \rightarrow CH_3CHO$$

A most interesting oxidation of lactic acid to pyruvic acid has been accomplished by electrolytic means. Pyruvic acid, being rather rich in oxygen, is necessarily more or less unstable in the presence of electrolytic oxygen, is further oxidized to various degradation products. However by an ingenious use of electrolytes and experimental condi-

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[12] This is like the purely chemical oxidation of glycocoll with NaOCl according to Langheld, Ber., **42**, 2360 (1909), and like the enzymic decomposition of tyrosine according to Chodat and Schweitzer, Arch. Gen., [4], **35**, 140 (1913).

[13] Fichter and Schmidt, loc. cit.

[14] Fichter and Kuhn, Helv. Chim. Acta, **6**, 167 (1924).

[15] Kolbe, Ann., **113**, 244 (1860); Miller and Hofer, Ber., **27**, 469 (1894); J. Walker, J. Chem. Soc., **69**, 1278 (1896); Hamonet, Compt. rend., **132**, 259 (1901); Brester, Jahresb. f. Chem., 60 (1866).

[16] Miller and Hofer obtained formic acid, but when the solution was kept alkaline they found aldol and crotonaldehyde instead of acetaldehyde.

[17] Dextro lactic acid yields acetaldehyde and CO_2.

tions Smull and Subkow[18] were able to stop the electrolytic oxidation at pyruvic acid. Under normal conditions no pyruvic acid could be detected in their products of electrolysis. But when copper lactate in the presence of copper nitrate, so that the copper concentration of the system was not lower than 20 per cent, was electrolyzed with a c. d. of 0.04 ampere on a platinum foil anode, the pyruvic acid formed momentarily was removed from the solution by the copper ions as the insoluble precipitate of copper pyruvate. Lead acted about as well as copper in removing the pyruvic acid from the sphere of oxidation. Alkaline, neutral and acid solutions yielded no pyruvic acid. This is an excellent example of what can happen if an unstable or a transient compound can be removed from the sphere of depolarization as a means of protecting it from further action.[19]

Pyruvic acid is of importance in the manufacture of Atophan (Cincophen) and because of the expense connected with its preparation from tartaric acid by dry distillation, costs are very high. Probably the one reason for the high price of these drugs is the cost of the pyruvic acid. Lactic acid is not very expensive at present and if the method of preparation of pyruvic acid by the electrolytic method can be perfected on a large scale it will be a decided benefit.

Other hydroxy acids have been electrolyzed. In the case of glycolic acid the course of the oxidation is:

$$CH_2OH{\cdot}COOH \rightarrow CHO{\cdot}COOH \rightarrow COOH{\cdot}COOH$$

but even at that there is a splitting of the molecule with a deep-seated destruction of the residue to form formaldehyde.[20]

$$2H(R)COH{\cdot}COO^- \rightarrow 2 - H(R)COH \rightarrow$$

$$2 - H(R)COH + O \rightarrow 2RCOH + H_2O$$

Probably the compound is first oxidized to an aldehyde which is subsequently oxidized with the evolution of carbon dioxide. Similarly α-hydroxybutyric, α-hydroxyisobutyric and glyceric acids have been electrolyzed.

Whatever the mechanism may be, the results show that there is an elimination of carbon dioxide followed by a very deep-seated oxidation of the residue. The discharged anion may lose carbon dioxide to form a residue, such as an aldehyde, which is very sensitive to anodic oxygen.[21]

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[18] J. G. Smull and P. Subkow, Chem. and Met., **28**, 357 (1923).

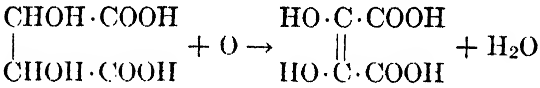
[19] This idea will also be applied later in the formation of aldehydes, etc.

[20] Miller and Hofer, loc. cit., and Ber., **27**, 2487 (1895); Walker, loc. cit. Methoxyglycolic acid yields HCHO, HCOOH, CO, CO_2, CH_3OH and methylal.

[21] E. Baur, Z. Elektrochem., **25**, 102 (1919).

The more dilute the electrolyte the more carbon monoxide is formed, less aldehyde remains in solution, and more oxygen is evolved. The aldehyde has a tendency to remain in solution because it is not as good a depolarizer as the hydroxy acid.

However the anode has a part to play in directing the oxidation. Tartaric acid [22] in a sulphuric acid electrolyte is unattacked by the anodic oxygen at a platinum anode, but a lead peroxide anode causes an oxidation to take place forming the aldehyde or keto acid with 3 carbon atoms, i.e., $CHO \cdot CHOH \cdot COOH$, which on continued electrolysis breaks down to tartronic acid ($CO_2H \cdot CHOH \cdot CO_2H$) and mesoxalic acid ($CO_2H \cdot CO \cdot CO_2H$), yielding finally also glyoxal ($CHO \cdot CHO$), and oxalic acid ($COOH \cdot COOH$). Platinized-platinum and lead peroxide anodes lead to the formation of dihydroxy maleic acid:



$$\begin{array}{l} CHOH \cdot COOH \\ \vert \\ CHOH \cdot COOH \end{array} + O \rightarrow \begin{array}{l} HO \cdot C \cdot COOH \\ \quad \Vert \\ HO \cdot C \cdot COOH \end{array} + H_2O$$

In an alkaline solution the above products are also found, together with much oxalic acid, formic acid, CO and CO_2. Since it has been shown that oxalic acid is not an intermediate in the formation of formic acid, these two compounds therefore must be formed by entirely different reactions.

As long as the chain of carbon atoms has not been broken by an oxidation, the reactions at the anode can be reversed by reduction at the cathode. If carbon dioxide has been eliminated, the reaction can not be cathodically reversed.

Neuberg [23] showed that the ethane formation from acetic acid had no counterpart in the case of hydroxy acids of the aliphatic series. He hoped to obtain a polyhydric alcohol of ten carbon atoms by electrolyzing the alkali salt of δ-gluconic acid, but instead obtained a decomposition reaction which formed δ-arabinose:

$$CH_2OH \cdot (CHOH)_3 \cdot CHOH \cdot COO^- + OH^- + 2F \rightarrow$$

$$CH_2OH \cdot (CHOH)_3 \cdot CH(OH)_2 + CO_2$$

$$CH_2OH(CHOH)_3 \cdot CH(OH)_2 \rightarrow CH_2OH(CHOH)_3 \cdot CHO + H_2O$$

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[22] Shivonen, Ann. acad. sci. Fennicae, 16A, No. 9, (1921) has found as oxidation products of tartaric acid the following additional compounds: $HCHO$, CH_3CHO, CH_2OHCHO, CH_3COOH, $CH_2OHCOOH$, $CHOCOOH \cdot H_2O$, $C_3H_5CH_2OH$, C_3H_5CHO, $CH_3COCOOH$, $CH_2OHCOCOOH$, $CHOCOCOOH$.

[23] C. Neuberg, Biochem. Zeit., 7, 527 (1908).

This electrolytic degradation method is applicable to the majority of the alkali salts of the carboxylic acids of the sugars. Melibionic acid forms a reducing sugar containing eleven carbon atoms; saccharic acid yields the dialdehyde of tartaric acid; tartaric acid forms glyoxal; serin and isoserin yield substances which with *p*-nitrophenylhydrazine give the corresponding osazones of glycolaldehyde; *l*-arabonic acid forms *l*-erythrose; *i*-erythric acid forms *i*-glyceraldehyde; *i*-glyceric acid yields glycolaldehyde; glycolic acid yields formaldehyde. There is every evidence that there is a trace of keto-acid of the type $CH_2OH(CHOH)_xCO \cdot COOH$ formed. In each of the above cases[23a], there is the elimination of one molecule of formic acid from the one molecule of the hydroxy acid:

$$CH_2OH(CHOH)_xCHO\ H \cdot COOH \rightarrow CH_2OH(CHOH)_xCHO + HCOOH$$

By this method glucose can be reverted step by step into formaldehyde.

In actual practice it has been found best to lead the slightly acid solution through the anode compartment in a slow stream so that the aldehyde as formed can be immediately removed from the anode to prevent its further oxidation.[24] Raising the concentration of the solution increases the rate of formation of the aldehyde; decreasing the concentration of the solution increases the evolution of oxygen and so increases the amount of oxidation of the aldehyde formed. On this same basis *d*-galactonic acid yields *d*-lyxose; *d*-*l*-erythronic acid yields *d*-*l*-glyceraldehyde; *d*-*l*-glyceric acid yields *d*-*l*-glycolaldehyde; and glycolic acid yields formaldehyde; while isoserine yields a product which when oxidized with mercuric chloride and sodium hydroxide yields pyrazine, indicating that aminoacetaldehyde is formed in the reaction. The calcium salt of melibionic acid yields a small quantity of sugar which may be isolated as the osazone with *p*-nitrophenylhydrazine. The alkaline earth salts work best in these degradations. According to the reaction given above, the successive degradation of glucoheptonic acid to HCHO may be accomplished.[25]

The *β*-hydroxy acids have a CH_2 group attached to the carboxyl group and obey Kolbe's reactions for the synthesis of hydrocarbons. The potassium salt of *β*-amoxypropionic acid on electrolysis gives 50 per cent yields of the diamyl derivative of 1, 4-butanediol, carbon dioxide, formic acid, and resin.[26]

$$2C_5H_{11}O \cdot CH_2CH_2COO^- + 2F \rightarrow$$
$$C_5H_{11}O \cdot CH_2 \cdot (CH_2)_2 \cdot CH_2 \cdot OC_5H_{11} + 2CO_2$$

[23a] Neuberg, loc. cit.

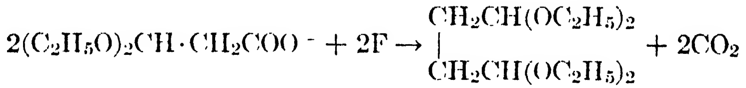
[24] W. von Miller and H. Hofer, Ber., **27**, 469 (1894).

[25] C. Neuberg, L. Scott, S. Lachmann, Bioch. Zeitschr., **24**, 152 (1910).

[26] J. Hamonet, Compt. rend., **132**, 259 (1901).

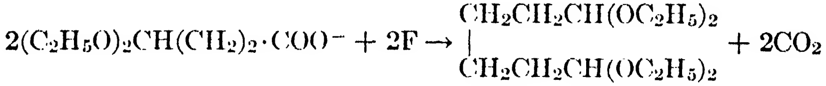
Similarly potassium ethoxyacetate yields the diethyl ether of ethylene glycol; the salts of ethoxypropionic and ethoxybutyric acids yield the diethyl ether of propylene glycol and butylene glycol respectively.[27] γ-Hydroxybutyric acid derivatives do not follow the above system but form crotonaldehyde, formic acid, carbon monoxide, and carbon dioxide together with unsaturated hydrocarbons probably from acetic acid as an impurity.[28] A very deep-seated oxidation takes place when a solution of β-methyl glyceric acid (α, β-dihydroxybutyric acid: $CH_3CHOHCHOHCOOH$) is electrolyzed. The products found to be present are carbon monoxide, carbon dioxide, formic acid, formaldehyde, acetic acid, and acetaldehyde, and other compounds which reduce Fehling's solution.[29] The anhydride of this acid, namely β-methylglycidic acid yields the same compounds.

D. Aldehyde Acids.—The free aldehyde acids, because of their instability in the presence of oxygen, are so easily oxidized that they cannot be electrolyzed with great success, but their ethers are stable under electrolyzing conditions. The electrolysis of the potassium salt of β-diethoxypropionic acid gives a 60 per cent yield of the double acetal of the dialdehyde of succinic acid:[30]



$$2(C_2H_5O)_2CH\cdot CH_2COO^- + 2F \rightarrow \begin{array}{l} CH_2CH(OC_2H_5)_2 \\ | \\ CH_2CH(OC_2H_5)_2 \end{array} + 2CO_2$$

Similarly the potassium salt of γ-diethoxybutyric acid[30] yields 35 per cent of the theoretical amount of the double acetal of the aldehyde of adipic acid:



$$2(C_2H_5O)_2CH(CH_2)_2\cdot COO^- + 2F \rightarrow \begin{array}{l} CH_2CH_2CH(OC_2H_5)_2 \\ | \\ CH_2CH_2CH(OC_2H_5)_2 \end{array} + 2CO_2$$

In the electrolysis of the potassium salt of diethoxybutyric acid[30] there are evidences of the formation of acrolein acetal in a 37 per cent yield according to the reaction:

$$2(C_2H_5O)_2CH(CH_2)_2COO^- + 2F \rightarrow$$
$$(C_2H_5O)_2CH(CH_2)_2COOH + (C_2H_5O)_2CH\cdot CH : CH_2 + CO_2$$

By purely chemical methods the dialdehydes of dicarboxylic acids are very difficult to prepare. The simplicity and the good yields of the

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[27] Mend, Dissert., Munich (1900).

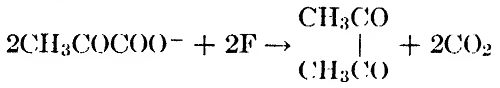
[28] Hamonet, Compt. rend., **136**, 96 (1903); Miller and Hofer, loc. cit.

[29] Pissarshenski, J. Russ. Phys. Chem. Soc., **29**, 289 and 338 (1897).

[30] A. Wohl and H. Schweitzer, Ber., **39**, 890 (1906).

electrolytic method make it a valuable addition to the methods of synthetic chemistry.

E. The Electrolysis of the Alkali Salts of Ketonic Acids.—Contrary to the action of the hydroxy acids it has been found that α- and γ-ketonic acids follow the Kolbe synthesis to form diketones[31] when a concentrated solution of their potassium salts is electrolyzed in a slightly alkaline solution. Pyruvic acid yields small amounts of diacetyl, CH_3COOH and CH_3CHO;

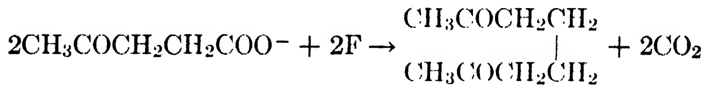


$$2CH_3COCOO^- + 2F \rightarrow \begin{array}{c} CH_3CO \\ | \\ CH_3CO \end{array} + 2CO_2$$

but the main course of the reaction is an oxidation on the same plan by which acetic acid yields methyl alcohol, i.e.:

$$CH_3COCOO^- + OH^- + 2F \rightarrow CH_3COOH + CO_2$$

Much better results are obtained in the case of levulinic acid, when the yields are as much as 50 per cent of 2, 7-octanedione:



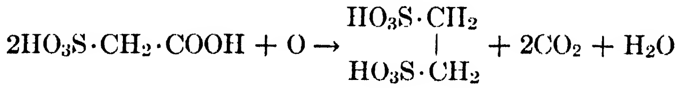
$$2CH_3COCH_2CH_2COO^- + 2F \rightarrow \begin{array}{c} CH_3COCH_2CH_2 \\ | \\ CH_3COCH_2CH_2 \end{array} + 2CO_2$$

though there is also an extensive oxidation of the residue

$$CH_3COCH_2CH_2—$$

to form large amounts of acetic acid and CO_2.

F. Aliphatic Sulphonic Acids.—According to Kolbe's ethane synthesis, the electrolysis of sulphoacetic acid should proceed according to the equation:



$$2HO_3S \cdot CH_2 \cdot COOH + O \rightarrow \begin{array}{c} HO_3S \cdot CH_2 \\ | \\ HO_3S \cdot CH_2 \end{array} + 2CO_2 + H_2O$$

Ethane disulphonic acid[32] has been isolated in small quantities as its Ba salt, though however the major part of the starting material is oxidized to sulphuric acid and CO_2. The other gases that are evolved are CO, ethane, formaldehyde, and sulphur dioxide. Some methane disulphonic acid has been detected.

At the start of the electrolysis the carbon dioxide removed from the dibasic acid dissolves in the electrolyte forming a bicarbonate and giving to the solution an alkaline reaction. This bicarbonate solution is a condition which favors "Hofer and Moest's formation of an alcohol"

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[31] H. Hofer., Ber., **33**, 650 (1900); Rockwell, J. Am. Chem. Soc., **24**, 719 (1902).

by the hydroxylation of the "Kolbe hydrocarbon residue." The product under these conditions should be methanol sulphonic acid:

$$HO_3S \cdot CH_2— + OH^- + F \rightarrow HO_3S \cdot CH_2OH$$

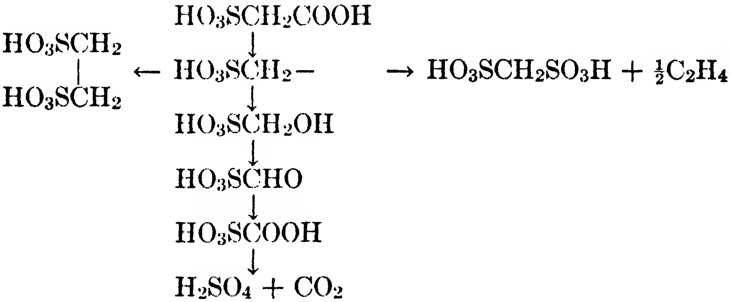
As this product could not be detected in the reaction mixture it was in all probability further oxidized at the anode according to the following set of equations:[32]

$$HO_3SCH_2OH \rightarrow HO_3SCHO \rightarrow HO_3SCOOH \rightarrow H_2SO_4 + CO_2$$

Kolbe[33] completely oxidized trichloromethane sulphonic acid. We have no check on the course of the oxidation in the case of the sulphoacetic acid because none of the intermediate products are stable. However, the fact that ethylene and methane disulphonic acid have been isolated leads to the conjecture that the following may be the means for their formation:

$$HO_3SCH_2^- + {}^-CH_2SO_3H \rightarrow =CH_2 + HO_3SCH_2SO_3H$$
$$2 =CH_2 \rightarrow C_2H_4$$

The removal of the SO_3H group from the hydrocarbon residue as the analog of the removal of the COO group is not very acceptable because the potassium salt of methane disulphonic acid yields no ethane but only carbon dioxide and sulphuric acid. The following mechanism has been proposed:



$$\begin{tikzcd}
 & HO_3SCH_2COOH \arrow[d] & \\
\begin{matrix} HO_3SCH_2 \\ | \\ HO_3SCH_2 \end{matrix} & HO_3SCH_2- \arrow[l] \arrow[r] \arrow[d] & HO_3SCH_2SO_3H + \tfrac{1}{2}C_2H_4 \\
 & HO_3SCH_2OH \arrow[d] & \\
 & HO_3SCHO \arrow[d] & \\
 & HO_3SCOOH \arrow[d] & \\
 & H_2SO_4 + CO_2 &
\end{tikzcd}$$

The electrolysis of the free acid yields CO_2, O_2, ozone, sulphuric and persulphuric acids.

Peculiarly sulphopropionic acid yields no butane disulphonic acid but only ethylene according to the equation:

$$HO_3SCH_2CH_2COOH \rightarrow H_2SO_4 + C_2H_4 + CO_2$$

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[32] F. Fichter and T. Lichtenhahn, Ber., **48**, 1949 (1915); F. Fichter, Z. Elektrochem., **20**, 471 (1914).

[33] Kolbe, J. prakt. Chem., [1], **41**, 138 (1847).

Other products of the oxidation are CO, $\mathrm{SO_2}$, formaldehyde and acetic acid. The scheme for this reaction has been suggested as being:

$$\begin{array}{l} \mathrm{HO_3SCH_2CH_2COOH} \\ \quad\downarrow \\ \mathrm{HO_3SCH_2CH_2-} \quad \rightarrow \mathrm{H_2SO_4 + C_2H_4} \\ \mathrm{HO_3SCH_2CH_2OH} \\ \quad\downarrow \\ \mathrm{HO_3SCH_2CHOH} \\ \quad\downarrow \\ \mathrm{CHO_3SCHOO_2} \end{array}$$

Isethionic acid has been oxidized to sulphoacetic acid:[34]

$$\mathrm{HO\cdot CH_2\cdot CH_2SO_3H \rightarrow HOOC\cdot CH_2SO_3H + H_2O}$$

In the case of the sulphonic acids in the benzene series the reaction cannot be stopped as easily and it goes on to a complete oxidation giving finally $\mathrm{CO_2}$ and sulphuric acid. Intermediately there are compounds which were not isolated but nevertheless gave the characteristic reactions for the polyhydroxy compounds of benzene as pyrocatechol, quinol, etc. 2, 5-phenol disulphonic acid, 2, 4-phenol disulphonic acid, and *m*-benzene disulphonic acid have been completely oxidized.[35]

Several substituted sulphuric acids have been oxidized, namely: methylsulphuric acid to formic acid, CO, $\mathrm{CO_2}$, sulphuric acid, and trioxymethylene;[36] trichloromethylsulphate[37] to $\mathrm{CO_2}$, $\mathrm{Cl_2}$, sulphuric and perchloric acids; ethyl sulphuric acid and its potassium salt[38] to formaldehyde, formic and acetic acids.

G. Aliphatic Acids which Contain Aromatic Groups.—These acids do not obey the rules which govern the properties of pure aliphatic acids. When the alkali salts of phenylacetic acid are electrolyzed there is no anodic evolution of $\mathrm{CO_2}$, but only a regeneration of the free acid in the electrolyte;[39] but Petersen[40] found an ester of the starting acid together with benzyl alcohol and benzaldehyde. Dibenzylacetic[41]

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[34] W. Wenk, Dissert., Basel (1912)

[35] Fichter, Brändlin and Hallauer, Helv. Chim. Acta, **3**, 410 (1920).

[36] Renard, Ann. chim. et phys., [5], **17**, 289 (1897).

[37] Bunge, Ber., **3**, 911 (1870).

[38] Renard, Tommasi, "Traite," 742. See Chapter V for the oxidation of aromatic sulphur compounds.

[39] Slawik, Ber., **7**, 1051 (1874).

[40] Petersen, Jahresber. f. Chem., **4**, 348.

[41] Heuser, Dissert., Munich (1901).

and phenylpropionic acid[42] do not form synthetic compounds. Mandelic acid[43] however is oxidized to CO_2, CO and benzaldehyde.

DICARBOXYLIC ACIDS

When the alkali salts of the dicarboxylic acids are electrolyzed, there is no reaction similar to the ethane formation, by the union of two discharged anions.

Oxalic acid, the first member of the series of dibasic acids is just as anomalous in its actions with respect to its homologues as formic acid is in the monobasic series; it contains no hydrocarbon residue.

The electrolysis of oxalates[44] varies with the electrodes used; at a platinum electrode there is an evolution of carbon dioxide with a trace of oxygen. A sharp increase in current density has no influence on the gases evolved, while at nickel and iron electrodes the oxygen evolution is the only reaction that takes place.[45] This indicates that the oxalate ion is less easily discharged than the hydroxyl ion yet more easily than acetate ion. A sulphuric acid solution of oxalic acid[46] electrolyzed with a low anodic potential is completely oxidized in theoretical quantities before any oxygen is evolved:

$$H_2C_2O_4 + O \rightarrow H_2O + 2CO_2$$

Higher Acids.—The alkali salts of malonic, isosuccinic (methylmalonic), ethylmalonic, and pyrotartaric acids (methyl succinic) on electrolysis with a low anodic potential yield only small amounts of unsaturated hydrocarbons. The predominating reaction at the anode being an oxygen evolution with a slight oxidation thereby of the acid residues to CO and CO_2. Bourgoin, with pyrotartaric acid, obtained a temporary deposit of the free acid at the anode, but this later disap-

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[42] Rohland, Z. Elektrochem., **4**, 120 (1897); β-phenyllactic acid yields benzaldehyde and a resin; Miller and Hofer, Ber., **27**, 461 (1874).

[43] Miller and Hofer, Ber., **27**, 461 (1894). More acids might be mentioned here but they are reserved for the discussion under the electrolysis and oxidation of aromatic acids later.

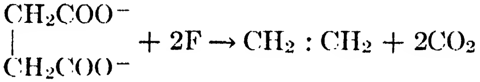
[44] Bourgoin, Ann. chim. et phys., [4], **14**, 157 (1868); Bourgoin, Compt. rend., **67**, 97 (1868); Brester, Jahresb. f. Chem., 87 (1866); Bourgoin, Ann. chim. et phys., [4], **21**, 264 (1870); J. Petersen, Z. Physik. Chem., **33**, 698 (1900); Bunge, Ber., **9**, 78 (1876); F. Oettel, Z. Elektrochem., **1**, 90 (1894); Renard, Ann. chim. et phys., [5], **17**, 289 (1878); T. Akerberg, Z. anorg. Chem., **31**, 161 (1902); F. Salzer, Z. Elektrochem., **8**, 893 (1902); Balbiano and Alessi, Gazz. chim. ital., **12**, 190 (1882); Ber., **15**, 2236 (1882); Bartoli and Papasogli, Gazz. chim. ital., **11**, 468 (1881); Ageno and Donini, ibid., **40**, i., 21 (1910).

[45] A. Bültemann, Dissert., Dresden (1905).

[46] Foerster, "Wässerige Lösungen," p. 861.

peared due to a partial oxidation to CO_2. Petersen, however, was able to detect propylene, primary and secondary propyl alcohol, propionaldehyde, CO and CO_2.[47]

Acetylmalonic and acetone dicarboxylic acids do not permit the union of their anions.[48] The electrolysis of potassium succinate at the positive electrode besides oxygen yields considerable amounts of ethylene, the formation of which is traced back to the decomposition of the discharged anion:[49]



$$\begin{matrix} CH_2COO^- \\ | \\ CH_2COO^- \end{matrix} + 2F \rightarrow CH_2 : CH_2 + 2CO_2$$

The quantities of ethylene increase with increasing current density and concentration of the organic salt. In the presence of inorganic salts such as chlorates, bicarbonates, etc., alkali succinate, at a platinum anode with a c. d. of 30–40 amperes yields large amounts of β-hydroxypropionic acid, but no glycol; acrylic, acetic, formic acids, acetaldehyde and methanol were found. It seems possible that the elimination of a COO group with the subsequent introduction of an OH^- group in its place is possible with only one carboxyl group of a dibasic acid.[50] Only one carboxyl group is replaced by a hydroxyl group, which adds additional evidence to the theory that in dibasic acids the carboxyl groups are of different value electrolytically.

On the above considerations, the electrolysis of the higher members of the dibasic acid series should yield cyclic hydrocarbons. Therefore in the hope of obtaining trimethylene, Vanzetti[51] electrolyzed a 20 per cent aqueous solution of potassium glutarate in an atmosphere of CO_2 with platinum electrodes at a temperature of − 5° C. Instead of trimethylene he was able to detect only the formation of propylene, carbon dioxide and oxygen.

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[47] Bourgoin, Ann. chim. et phys., [4], **14**, 157 (1868); Bourgoin, Compt. rend., **90**, 608 (1880); Bourgoin, Bull. Soc. Chim., **33**, 417 (1889); Miller, Jour. prakt. Chem., [2], **19**, 328 (1879); Lassar-Cohn, Ann., **251**, 349 (1889); Reboul and Bourgoin, Compt. rend., **84**, 1231 and 1395 (1877); J. Petersen, Z. physik. Chem., **33**, 700 (1900); Reboul and Bourgoin, Bull. Soc. Chim., [2], **27**, 545 (1877).

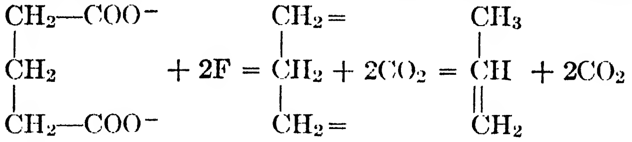
[48] Weems, Am. Chem. J., **16**, 569, (1894).

[49] H. Kolbe, Ann., **113**, 244 (1860); A. Kekule, Ann., **131**, 79 (1864); Bourgoin, loc. cit.; J. Petersen, loc. cit.; Clarke and Smith, J. Am. Chem. Soc., **21**, 967 (1899).

[50] H. Hofer and M. Moest, Ann., **323**, 291 (1902); M. Moest, D.R.P. 138442 (1902).

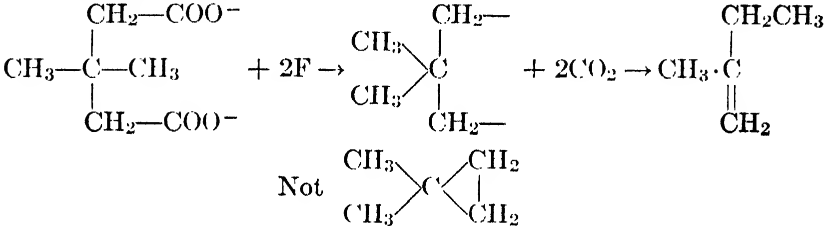
[51] B. L. Vanzetti, Atti. R. Accad. Dei Lincei, [5], **13**, ii, 112 (1904). See also Bourgoin and Reboul, Bull. Soc. Chim., [2], **27**, 545 (1877), and **28**, 51 (1877); Compt. rend., **84**, 1231 and 1395 (1877).

The propylene was produced by the migration of a hydrogen atom:



$$\begin{array}{l}CH_2—COO^-\\ |\\ CH_2\\ |\\ CH_2—COO^-\end{array} + 2F = \begin{array}{l}CH_2=\\ |\\ CH_2\\ |\\ CH_2=\end{array} + 2CO_2 = \begin{array}{l}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} + 2CO_2$$

When β, β-dimethyl glutarate was substituted for the glutarate in the electrolysis, such a transference of hydrogen was impossible, so that if in this case an open chain hydrocarbon was formed at all, it could only be by the migration of the hydrocarbon group as a unit. Walker and Wood[52] tried this and found that the hydrocarbon was an unsymmetrical methylethylethylene; not dimethyltrimethylene.



In the original acid, the maximum chain in the hydrocarbon radical was three carbon atoms; in the electrolytic hydrocarbon, there was a chain of four carbon atoms. There was evidently a fundamental rearrangement of the carbon atoms, most easily conceived as a transference of a methyl group. The main reaction at the anode was the formation of CO_2, CO and oxygen while the amounts of unsaturated hydrocarbon were small, most of the starting material being oxidized by the oxygen liberated.

The salts of adipic acid, according to Vanzetti,[53] on electrolysis yield an anode gas of which the mean and almost constant composition is 25 per cent CO_2, 1.5 per cent unsaturated hydrocarbons, 12 per cent O_2, 1.5 per cent CO, 60 per cent H_2. The unsaturated hydrocarbons are butylenes of the formulae $CH_2Me \cdot CH : CH_2$ and $CHMe : CHMe$. There is a characteristic ethereal odor which is due to the formation, by secondary reactions, of alcohols and ethereal salts. There is no trace of the cyclic hydrocarbon tetramethylene.

A 28.8 per cent aqueous solution of potassium acid suberate[54] electrolyzed between platinum electrodes at 45° with a c. d. of 0.5 amperes gives a vigorous evolution of carbon dioxide, some oxygen, and about 1 per cent of CO, but no hydrocarbons, saturated or unsaturated.

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[52] J. Walker and Wood, J. Chem. Soc., **89**, 598 (1906).

[53] B. L. Vanzetti, Atti. R. Accad. dei Lincei, [5], **15**, i, 574 (1906).

[54] B. L. Vanzetti, Atti. R. Accad. dei Lincei, [5], **16**, ii, 79 and 139 (1907).

The principal products isolated were the isomeric unsaturated alcohols of the general formula $C_6H_{12}O$; isomeric unsaturated acids of the formula $C_7H_{12}O_2$; saturated 7 carbon atom acids; neutral aldehydic compounds; keto- and aldo-acids; and a lactone, $C_7H_{13}O_3$, of an acid the barium salt of which was isolated and analyzed as having the formula $(C_7H_{13}O_3)_2Ba$; but no hexamethylene was found.

The lower members of the oxalic acid series yield hydrocarbons on electrolysis but as the number of carbon atoms increases, the reaction becomes more complicated and secondary products predominate.

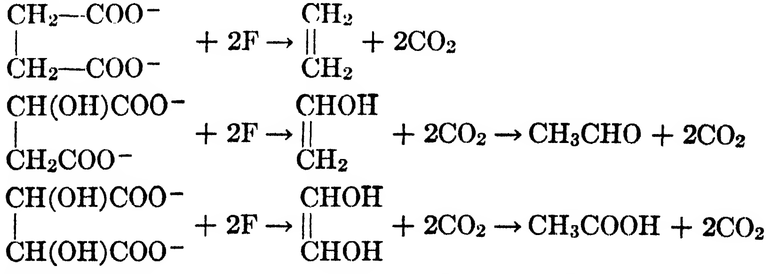
Pimelic acid alkali salts yield ethylene and propylene in approximately equal proportions along with compounds analogous to those from suberic acid,[55] but no cyclopentane is formed, even though according to the Baeyer strain theory the closing of the carbon atom ring should take place more readily with 5 carbon atoms than in the other cases.

These syntheses seem to be due to the demolition of the anion as it is discharged at the anode. A variation of the conditions of electrolysis never leads to the formation of the corresponding cyclic hydrocarbon tri-, tetra-, penta-, and hexamethylene as would be expected if the two COO groups of the anion leave the latter simultaneously on its discharge at the anode.

Substituted Acids.—The salts of malic acid yield first the aldehyde which is then further oxidized to acetic acid, CO_2 and CO.[56]

Tartrates [57] yield acetic acid and glyoxal besides CO, CO_2, O_2, ethane, ethylene, fomaldehyde, and formic acid. Miller and Hofer obtained no acetic acid nor ethylene. Racemic and ethyltartaric acids formed CO and CO_2 and an unknown aldehyde.

The formation of these substances from the respective alkali salts is the analog of ethylene formation and depends probably on the decomposition of the anion as it is discharged at the anode:



$$\begin{array}{l} CH_2{-}COO^- \\ | \\ CH_2{-}COO^- \end{array} + 2F \rightarrow \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2$$

$$\begin{array}{l} CH(OH)COO^- \\ | \\ CH_2COO^- \end{array} + 2F \rightarrow \begin{array}{l} CHOH \\ \| \\ CH_2 \end{array} + 2CO_2 \rightarrow CH_3CHO + 2CO_2$$

$$\begin{array}{l} CH(OH)COO^- \\ | \\ CH(OH)COO^- \end{array} + 2F \rightarrow \begin{array}{l} CHOH \\ \| \\ CHOH \end{array} + 2CO_2 \rightarrow CH_3COOH + 2CO_2$$

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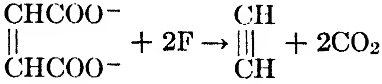
[55] Vanzetti, Atti. R. Accad. dei Lincei, [5], **17**, ii, 331 (1898).

[56] Brester, Bull. Soc. Chim., [2], **8**, 23 (1867); Bourgoin, ibid., [2], **9**, 427 (1868); W. von Miller and H. Hofer, Ber., **27**, 270 (1894).

[57] A. Kekule, Ann., **131**, 88 (1864); Bourgoin, Bull. Soc. Chim., [2], **11**, 405 (1869); W. von Miller and H. Hofer, loc. cit.; C. Neuberg, Biochem. Zeit., **7**, 528 (1908).

The first formed vinyl alcohol $CH_2 : CHOH$ is at once rearranged into acetaldehyde while the first formed glycol $(:CHOH)_2$ is rearranged into acetic acid.

Unsaturated Acids.—The alkali salts of the unsaturated dibasic acids also yield moderate amounts of unsaturated hydrocarbons. Maleates and fumarates[58] yield an anode gas containing oxygen, carbon dioxide and acetylene, the latter being formed according to the equation:

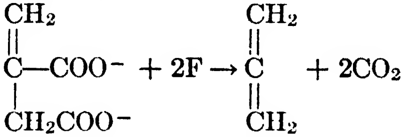


$$\begin{array}{l}CHCOO^-\\ \|\\ CHCOO^-\end{array} + 2F \rightarrow \begin{array}{l}CH\\ |||\\ CH\end{array} + 2CO_2$$

The application of the current to maleates transforms some of that acid into its isomer, fumaric acid.

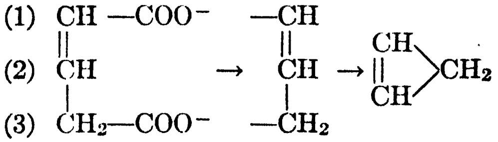
Henrich and Schenk[59] studied the electrolysis of the potassium salt of citraconic acid in an apparatus especially designed by them. Allylene, $CH_3C \vdots CH$, was detected in the anode gases.[60] Henrich and Schenk believed that the whole process was influenced by the alkali used and that the anodic decomposition of alkali salts to hydrocarbons was an oxidation reaction, according to Fichter and Krummenacher's theory, rather than merely an ionic reaction as explained by Brown and Walker.

Mesaconic acid salts[61] also yield allylene besides traces of acrylic and itaconic acids, while itaconic acid salts[62] in a solution containing alkali carbonate yield propylene and allene:



$$\begin{array}{l}CH_2\\ \|\\ C—COO^-\\ |\\ CH_2COO^-\end{array} + 2F \rightarrow \begin{array}{l}CH_2\\ \|\\ C\\ \|\\ CH_2\end{array} + 2CO_2$$

According to the above results the electrolysis of the alkali salts of glutaconic acid, which is isomeric with all three of the above acids, should progress according to the scheme:



$$\begin{array}{ll}(1) & CH—COO^-\\ & \|\\ (2) & CH\\ & |\\ (3) & CH_2—COO^-\end{array} \rightarrow \begin{array}{l}—CH\\ \|\\ CH\\ |\\ —CH_2\end{array} \rightarrow \begin{array}{l}CH\\ \|\\ CH\end{array}\!\!>CH_2$$

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[58] A. Kekule, Ann., **131**, 88 (1864); Bourgoin, Ber., **7**, 1039 (1874).

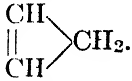
[59] F. Henrich and W. Schenk, Ber., **52**, 2120 (1919).

[60] Aarland., J. prakt. Chem., [2], **7**, 142 (1873).

[61] Aarland, J. prakt. Chem., [2], **7**, 142 (1873).

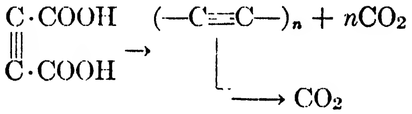
[62] Aarland and Carstanjen, J. prakt. Chem., [2], **4**, 376 (1871); Aarland, J. prakt. Chem., [2], **6**, 256 (1873); Chem. News, **24**, 317 (1872); Bull. soc. chim., [2], **19**, 258 (1873); Behal, Ann. chim. et phys., [6], **16**, 367 (1897).

At the negative pole there would be an evolution of hydrogen gas, while at the positive pole there would be the discharge of the anion and then secondarily, the decomposition of this into carbon dioxide and some hydrocarbon of the unsaturated series. It is conceivable that as two molecules of carbon dioxide are separated, one from each of the carbon atoms (1) and (3), the free valences so formed would unite to form cyclopropylene



Such a compound is to be expected from the great activity of the methylene grouping. Herzog[63] found that the electrolysis of a concentrated aqueous solution of potassium glutaconate yielded a hydrocarbon that burned with a yellow sooty flame and formed a precipitate not only in an ammoniacal silver nitrate but also in a cuprous oxide solution.

Acetylenedicarboxylic acid[64] yields an unknown hydrocarbon, fumaric acid, acetylene and some other unsaturated hydrocarbons. The C_2H_2 is probably formed by the decomposition of maleic and fumaric acids: The reaction may be expressed as



$$\begin{matrix} C\cdot COOH \\ ||| \\ C\cdot COOH \end{matrix} \rightarrow (—C\equiv C—)_n + nCO_2 \quad \rightarrow CO_2$$

Phenylpropiolic acid is difficult to electrolyze because of the formation of crusts on the surface of the anode. A very high c. d. is required to start the decomposition. The products are CO_2, some unsaturated compounds but no acetylene and no CO.[64]

THE ELECTROLYSIS OF THE ESTER ACID SALTS OF DICARBOXYLIC ACIDS

The alkali salts of the monoesters of dicarboxylic acids react on being electrolyzed just as if they were monobasic fatty acids. Since electrolytic action is due to the reactions of the parts of these compounds which form ions it is evident that the esterified part of the compound is inactive[65] and the synthetic action is possible only where there is a carboxyl group containing an alkali metal in combination. The portion separated from the alkali metal is reactive in the sense of the Kolbe ethane synthesis, two residues uniting to form a diester of a dibasic acid. Potassium ethyl oxalate cannot obey the scheme set forth below by Brown and Walker, but it does yield ethylene probably

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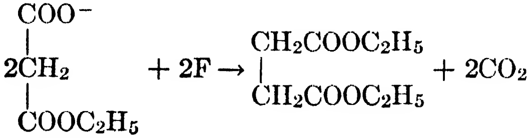
[63] A. Herzog, Diss., Erlangen, 1908; F. Henrich and Herzog, Ber., **52**, 2126 (1919).

[64] Vanzetti, Gazz. chim. ital., **46**, i., 49 (1916).

[65] Guthrie, Ann., **99**, 65 (1856).

by the saponification of the ethyl group.[66] The potassium salt of ethyl malonate yields primarily the diethyl ester of succinic acid: [67]

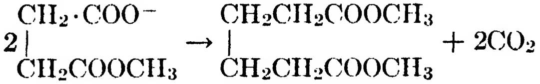


$$2\begin{matrix}\mathrm{COO^-}\\|\\\mathrm{CH_2}\\|\\\mathrm{COOC_2H_5}\end{matrix} + 2\mathrm{F} \rightarrow \begin{matrix}\mathrm{CH_2COOC_2H_5}\\|\\\mathrm{CH_2COOC_2H_5}\end{matrix} + 2\mathrm{CO_2}$$

Similarly the alkali salt of ethyl succinate yields the diethyl ester of adipic acid. [68]

This method had proven very valuable in the synthesis of the normal carbon chain dicarboxylic acids up to 18 carbon atoms; otherwise a great many of these acids are very difficult to synthesize.

The conditions for optimum yields are the same as in the ethane synthesis requiring high concentration of the solution, 1 to 1.5 part of salt to 1 part of water, a low temperature, and a high anodic current density. The electrolysis of 15 g. of potassium ethyl malonate in a platinum crucible as cathode and a piece of platinum wire as the anode yielded 4.5 g. of the diester of succinic acid; but when the current was reversed using the same solution and the same current and temperature, the yield was scarcely one-tenth of the amount.[69] The application of the method is very easy because the alkali alkyl esters are usually very soluble; the diesters are insoluble in the aqueous electrolyte which precludes any further oxidation. Since there is the formation of alkali hydroxide at the cathode there will be considerable saponification of the diester if it comes in contact with the alkali; a diaphragm therefore is very necessary. A stream of CO_2 passing through the electrolyte near the cathode will form potassium bicarbonate and decrease the loss due to saponification. Bouveault [70] found that a methanol solution of sodium methyl succinate furnished 70 per cent of the theoretical yield of methyl adipate. The equations for these reactions are:



$$2\begin{matrix}\mathrm{CH_2\cdot COO^-}\\|\\\mathrm{CH_2COOCH_3}\end{matrix} \rightarrow \begin{matrix}\mathrm{CH_2CH_2COOCH_3}\\|\\\mathrm{CH_2CH_2COOCH_3}\end{matrix} + 2\mathrm{CO_2}$$

The formation of the diester of the dicarboxylic acid is always accompanied by the formation of an ester of an unsaturated monobasic carboxylic acid, usually in smaller quantities than the saturated diester

[66] Brown & Walker, Ann., **274**, 75, (1893).

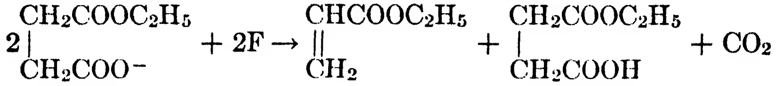
[67] C. Brown and J. Walker, Ann., **261**, 107 (1891).

[68] Elbs, "Übungsbeispiele," page 70.

[69] C. Brown and J. Walker, Ann., **261**, 107 (1891).

[70] Bouveault, Bull. Soc. Chim. [3], **29**, 1038–1048, (1903).

of a dicarboxylic acid. The sodium salt of ethyl succinate yields the ethyl ester of acrylic acid:[71]

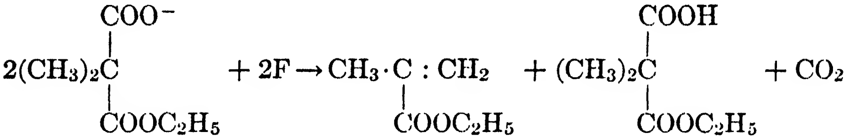


$$2\begin{array}{l}CH_2COOC_2H_5\\|\\CH_2COO^-\end{array} + 2F \rightarrow \begin{array}{l}CHCOOC_2H_5\\\|\\CH_2\end{array} + \begin{array}{l}CH_2COOC_2H_5\\|\\CH_2COOH\end{array} + CO_2$$

while the ethyl ester of normal pentenecarboxylic acid, 72

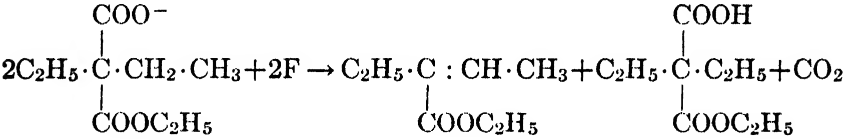
$$CH_2 : CH(CH_2)_3COOC_2H_5$$

is formed in the electrolysis of sodium salt of ethyl pimelate. The formation of unsaturated esters, corresponding to the formation of ethylene from acetic acid, assumes larger proportions when substituted dicarboxylic esters are employed. The potassium salt of the ethyl ester of dimethylmalonic acid, yields considerable quantities of the ethyl ester of α-methylacrylic acid amounting to one-fourth of the total reaction products formed:[73]



$$2(CH_3)_2\begin{array}{l}COO^-\\|\\C\\|\\COOC_2H_5\end{array} + 2F \rightarrow CH_3\cdot\begin{array}{l}\\\\C : CH_2\\|\\COOC_2H_5\end{array} + (CH_3)_2\begin{array}{l}COOH\\|\\C\\|\\COOC_2H_5\end{array} + CO_2$$

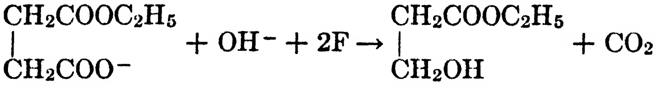
In the same manner the alkali salt of the ethyl ester of diethylmalonic acid yields the ethyl ester of α-ethylcrotonic acid.



$$2C_2H_5\cdot\begin{array}{l}COO^-\\|\\C\cdot CH_2\cdot CH_3\\|\\COOC_2H_5\end{array} + 2F \rightarrow C_2H_5\cdot\begin{array}{l}\\\\C : CH\cdot CH_3\\|\\COOC_2H_5\end{array} + C_2H_5\cdot\begin{array}{l}COOH\\|\\C\cdot C_2H_5\\|\\COOC_2H_5\end{array} + CO_2$$

The electrolysis of sodium ethyl succinate, sodium methyl succinate,[74] and potassium ethyl dipropylmalonate yield the corresponding compounds.

Analogous to the formation of alcohols from the fatty acids is the formation of esters of monobasic hydroxy acids. An aqueous solution of sodium ethyl succinate yields the ethyl ester of hydroxy-acrylic acid:[75]



$$\begin{array}{l}CH_2COOC_2H_5\\|\\CH_2COO^-\end{array} + OH^- + 2F \rightarrow \begin{array}{l}CH_2COOC_2H_5\\|\\CH_2OH\end{array} + CO_2$$

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[71] C. Brown and J. Walker, Ann., **261**, 107 (1891), and **274**, 41 (1893); Bouveault, Bull. Soc. Chim. [3], **29**, 1043 (1903).

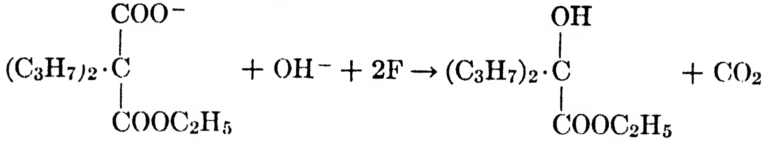
[72] J. Walker and Lumsden, J. Chem. Soc., **79**, 1197, (1901).

[73] C. Brown and J. Walker, Ann., **261**, 107 (1891), and **274**, 41 (1893).

[74] C. Brown and J. Walker, loc. cit.; Bouveault, loc. cit.

[75] Bouveault, loc. cit.

and the potassium salt of the ethyl ester of dipropylmalonic acid yields the ethyl ester of dipropylglycollic acid:[76]

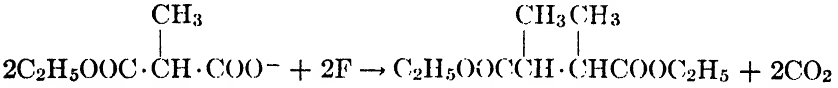


$$(C_3H_7)_2\cdot\overset{COO^-}{\underset{COOC_2H_5}{C}} + OH^- + 2F \rightarrow (C_3H_7)_2\cdot\overset{OH}{\underset{COOC_2H_5}{C}} + CO_2$$

However the main product of the electrolysis of these acids is the formation of the diesters of the dicarboxylic acids as indicated in the first set of these reactions: The acid esters yield the corresponding diesters of the higher acids as indicated below:

Glutaric acid[77] → suberic acid
Adipic acid[77] → sebacic acid
Pimelic acid[78] → *n*-decanedicarboxylic acid
Suberic acid[79] → *n*-dodecanedicarboxylic acid
Sebacic acid[79] → *n*-decahexanedicarboxylic acid
β, β-dimethylglutaric acid[80] → β, β, β′, β′-tetramethylsuberic acid.
Azelaic acid[81] → 1, 14-tetradecanedicarboxylic acid

The electrolysis of the ester salts of isosuccinic acid yields both the cis- and trans- forms of dimethylsuccinic acid simultaneously.[82]



$$2C_2H_5OOC\cdot\overset{CH_3}{CH}\cdot COO^- + 2F \rightarrow C_2H_5OOC\overset{CH_3}{C}H\cdot\overset{CH_3}{C}HCOOC_2H_5 + 2CO_2$$

and similarly the ester salts of the following acids yield the corresponding diesters as normal products corresponding to the formation of C_2H_6 from CH_3COOH:

Dimethylmalonic acid[83] → tetramethylsuccinic acid
Ethylmalonic acid[83] → diethylsuccinic acid
Dipropylmalonic acid[84] → tetrapropylsuccinic acid

[76] D. C. Crichton, J. Chem. Soc., **89**, 929 (1906).

[77] C. Brown and J. Walker, Ann., **261**, 107 (1891), and **274**, 41 (1893).

[78] Komppa, Ber., **34**, 900 (1901); Walker and Lumsden, J. Chem. Soc., **79**, 1197 (1901). Besides *n*-decanedicarboxylic acid there is also some ethyl ester of *n*-pentenecarboxylic acid.

[79] C. Brown and J. Walker, loc. cit.; sebacic acid also forms an ester (M. P. 121°) of the acid $CH_2 : CH\cdot(CH_2)_6\ COOH$.

[80] J. Walker and Wood, J. Chem. Soc., **89**, 598 (1906).

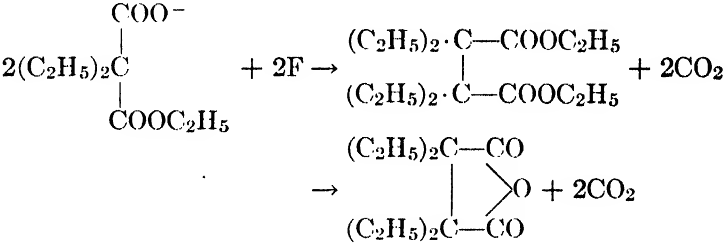
[81] K. Stosius and K. Wiesler, Biochem. Zeit., **108**, 75 (1920). Sir James Walker recently has by this method synthesized a dibasic acid containing $32CH_2$ groups. J. Soc. Chem. Ind., **40**, 169 R, (1921).

[82] C. Brown and J. Walker, loc. cit.

[83] C. Brown and J. Walker, loc. cit.

[84] D. C. Crichton, J. Chem. Soc., **89**, 929 (1906).

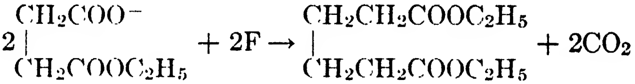
Brown and Walker [85] obtained an oil in the electrolysis of the sodium salt of the ethyl ester of diethylmalonic acid which they were unable to analyze. Later Walker and Walker [86] found this oil to be the anhydride of tetraethylsuccinic acid:



$$2(C_2H_5)_2\begin{array}{l}COO^-\\ |\\ C\\ |\\ COOC_2H_5\end{array} + 2F \rightarrow \begin{array}{l}(C_2H_5)_2\cdot C\text{—}COOC_2H_5\\ \qquad\quad |\\ (C_2H_5)_2\cdot C\text{—}COOC_2H_5\end{array} + 2CO_2$$

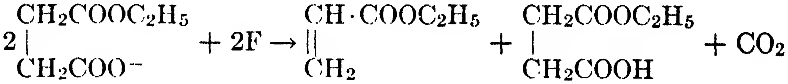
In the case of the electrolysis of the alkali salts of the monoesters of the dibasic acids there are, therefore, reactions entirely analogous to the reactions of the alkali salts of normal monobasic aliphatic acids. Taking succinic acid as the example we have:

(1) Similar to the ethane synthesis:



$$2\begin{array}{l}CH_2COO^-\\ |\\ CH_2COOC_2H_5\end{array} + 2F \rightarrow \begin{array}{l}CH_2CH_2COOC_2H_5\\ |\\ CH_2CH_2COOC_2H_5\end{array} + 2CO_2$$

(2) Similar to the formation of the unsaturated hydrocarbons, the saturated acid and CO_2:

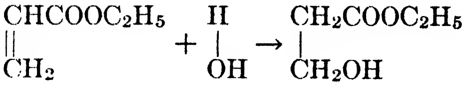


$$2\begin{array}{l}CH_2COOC_2H_5\\ |\\ CH_2COO^-\end{array} + 2F \rightarrow \begin{array}{l}CH\cdot COOC_2H_5\\ \|\\ CH_2\end{array} + \begin{array}{l}CH_2COOC_2H_5\\ |\\ CH_2COOH\end{array} + CO_2$$

(3) Similar to the formation of the ester and CO_2:

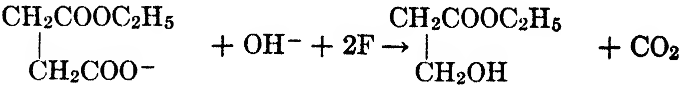
No parallel

(4) Similar to the addition of water to the unsaturated hydrocarbon:



$$\begin{array}{l}CHCOOC_2H_5\\ \|\\ CH_2\end{array} + \begin{array}{l}H\\ |\\ OH\end{array} \rightarrow \begin{array}{l}CH_2COOC_2H_5\\ |\\ CH_2OH\end{array}$$

which is also like that in which the COO-group is replaced by a hydroxyl group:



$$\begin{array}{l}CH_2COOC_2H_5\\ |\\ CH_2COO^-\end{array} + OH^- + 2F \rightarrow \begin{array}{l}CH_2COOC_2H_5\\ |\\ CH_2OH\end{array} + CO_2$$

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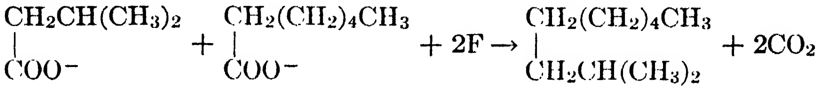
[85] C. Brown and J. Walker, Ann., **274**, 51 (1893).

[86] J. Walker and A. Walker, Proc. Chem. Soc., **21**, 210 (1905).

ELECTROLYSIS OF MIXTURES OF THE ALKALI SALTS OF DIFFERENT ACIDS

When a mixture of the calcium salts of different fatty acids is heated the result is the formation of a mixed ketone. When a mixture of the alkali salts of different fatty acids is electrolyzed there is the formation of a hydrocarbon by the union of the two residues. Thus the electrolysis of a mixture of the potassium salts of isovaleric and heptylic acids yields 8-methylnonane:[87]



$$\begin{matrix} CH_2CH(CH_3)_2 \\ | \\ COO^- \end{matrix} + \begin{matrix} CH_2(CH_2)_4CH_3 \\ | \\ COO^- \end{matrix} + 2F \rightarrow \begin{matrix} CH_2(CH_2)_4CH_3 \\ | \\ CH_2CH(CH_3)_2 \end{matrix} + 2CO_2$$

The electrolysis of a mixture of the potassium salts of acetic and heptylic acids yields small amounts of normal heptane.[88] These results are to be expected from the equation (1) above which is the hydrocarbon synthesis from the potassium salts of the saturated aliphatic acids. As the numbers of the carbon atoms in the two acids, become equal, the reaction is like the ordinary electrolysis of a single pure salt solution as explained above.

The esters of the higher monobasic acids are obtained by the electrolysis of mixtures of the alkali salts of monobasic fatty acids and an acid ester salt.[89] Potassium acetate with potassium ethyl succinate gives a 70 per cent material yield of the ethyl ester of normal butyric acid:

$$CH_3COO^- + {}^-OOCCH_2CH_2COOC_2H_5 + 2F \rightarrow CH_3CH_2CH_2COOC_2H_5 + 2CO_2$$

From the alkali salts of the first two acids we get the ester of the third acid in the table:

Glycollate + acetate → C_2H_5OH and an aldehyde
Ethyl succinate + propionic acid → valeric acid
Ethyl succinate + isobutyric acid → isobutylacetic acid
Ethyl malonate + acetic acid → propionic acid
Ethyl malonate + propionic acid → butyric acid
Ethyl malonate + butyric acid → *n*-valeric acid

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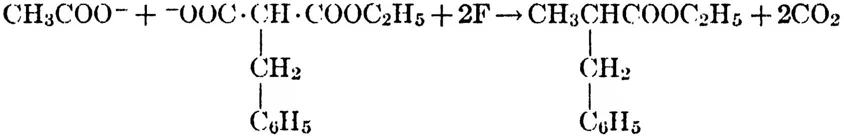
[87] Würtz, Ann. chim. et phys., [3], **44**, 291 (1855).

[88] Würtz., loc. cit.

[89] W. von Miller and H. Hofer, Ber., **28**, 2427 (1895).

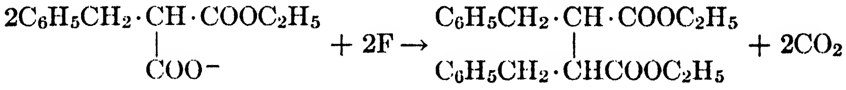
When the acid ester salts of two dibasic acids are electrolyzed a diester of a dibasic acid is formed. Potassium ethyl malonate [90] when electrolyzed with potassium ethyl succinate in molecular ratio yields diethyl glutarate with the ethyl esters of succinic, adipic acids and a small amount of an unsaturated ester, probably methyl acrylate. Similarly when 2 parts of potassium ethyl succinate are electrolyzed with 3 parts of potassium acetate, a material yield of 40 per cent of ethyl butyrate is obtained; but the use of a mixture of 1 part of succinate to 3 parts of acetate under the same conditions yields 70 per cent of ethyl butyrate.[91]

If one of the discharged anions is more easily broken down by anodic oxygen than the other the former will seldom combine.[92] This is especially true in the electrolysis of a mixture of potassium acetate and the potassium salt of the ethyl ester of benzylmalonic acid which yields the ethyl ester of methylhydrocinnamic acid, though the alkali salt of benzylmalonic acid ester on electrolysis yields no synthetic products, but only oxidation products.[93]



$$\begin{array}{lcll} CH_3COO^- + {}^-OOC\cdot & CH\cdot COOC_2H_5 + 2F \rightarrow CH_3 & CH & COOC_2H_5 + 2CO_2 \\ & | & | & \\ & CH_2 & CH_2 & \\ & | & | & \\ & C_6H_5 & C_6H_5 & \end{array}$$

In the presence of potassium acetate the two discharged residues unite to form the diethyl ester of dibenzylsuccinic acid, but also forms some cinnamic and hydrocinnamic acids,[94] in which the potassium acetate seems to be a catalyst:



$$\begin{array}{lcll} 2C_6H_5CH_2\cdot CH\cdot COOC_2H_5 & & C_6H_5CH_2\cdot CH\cdot COOC_2H_5 & \\ \qquad\quad | & + 2F \rightarrow & \qquad\qquad\quad | & + 2CO_2 \\ \qquad COO^- & & C_6H_5CH_2\cdot CHCOOC_2H_5 & \end{array}$$

Ketones may be formed by the electrolysis of a mixture of the potassium salts of a keto-acid and a fatty acid.[95] Potassium pyruvate and potassium butyrate mixed, yield methylpropyl ketone:

$$CH_3COCOO^- + {}^-OOCCH_2CH_2CH_3 + 2F \rightarrow CH_3COCH_2CH_2CH_3 + 2CO_2$$

[90] B. L. Vanzetti and A. Coppadoro, Gazz. chim. ital., **34**, 1, 154 (1904). Also in Atti. R. Accad. d. Lincei, [5], **12**, ii, 209 (1903).

[91] W. von Miller and H. Hofer, Ber., **28**, 2427 (1895).

[92] Miller, Z. Elektrochem., **4**, 55 (1897).

[93] C. Brown and J. Walker, Ann., **274**, 67 (1893).

[94] See Mend, Dissert., Munich (1900); also Bloch, Dissert., Munich (1902); Hauser, Dissert., Munich (1901).

[95] H. Hofer, Ber., **33**, 656 (1900); Mayr, Dissert., Munich (1904).

From the alkali salts of the first two acids the corresponding ketone is obtained as the product of electrolysis:

Pyruvic acid + acetic acid → acetone
Levulinic acid + acetic acid → methylpropyl ketone + 2, 7-octanedione
Levulinic acid + butyric acid → methylheptyl ketone
Benzoylpropionic acid + acetic acid → propylphenyl ketone

A diketone is the result of the electrolysis of a mixture of two keto-acids. Levulinic acid and pyruvic acids yield acetonyl-acetone and 2, 7-octanedione,

$$CH_3COCOO^- + {}^-OOCCH_2CH_2COCH_3 + 2F \rightarrow CH_3COCH_2CH_2COCH_3 + 2CO_2$$

When a mixture of organic and inorganic salts is electrolyzed there is only a very slight coupling of the organic residue with the discharged inorganic anion. Only traces of ethyl nitrite are formed when potassium nitrite and potassium propionate are electrolyzed together, but when the iodide is used in place of the nitrite there is a small amount of ethyl iodide formed, while most of the iodine appears at the anode in the solid form.[96] This reaction shows that the iodine carries most of the current to the anode while the organic anion carries but little of the current. Chloride ions are much more difficult to discharge than iodide ions and therefore in the presence of a chloride, such as potassium chloride, the electrolysis of potassium caproate yields considerable quantities of chloropentane.[97]

$$C_5H_{11}COO^- + Cl^- + 2F \rightarrow C_5H_{11}Cl + CO_2$$

The introduction of the OH group has been discussed above.

THE ELECTROLYSIS OF THE SALTS OF TRIBASIC ACIDS

The first record of the electrolysis of a tribasic acid is that of Berthelot [98] who obtained O_2, CO, and acetylene, but no CO_2 from the potassium salt of aconitic acid. Very much later this work was repeated using a solution of aconitic acid, one-half of which was neutralized by sodium hydroxide with the result that 60 per cent yields of tricarballylic acid were obtained.[99]

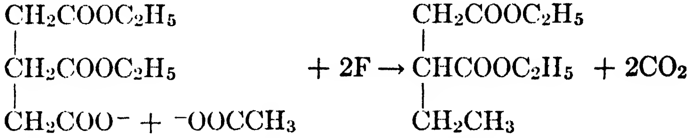
[96] Miller and Hofer, Ber., **28**, 2436 (1895).

[97] H. Hofer and M. Moest, Ann., **323**, 286 (1902).

[98] See Bourgoin, Bull. soc. chim., [2], **9**, 103 (1868).

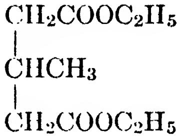
[99] Marie, Compt. rend., **136**, 133 (1903).

The mono-potassium salt of the diethyl ester of tricarballylic acid yields no synthetic products unless some potassium acetate is present, then it yields the diethyl ester of ethylsuccinic acid by the union of the two acid residues.[100]



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \\ | \\ CH_2COO^- + {}^-OOCCH_3 \end{array} + 2F \rightarrow \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CHCOOC_2H_5 \\ | \\ CH_2CH_3 \end{array} + 2CO_2$$

But its isomer, i.e., methylglutaric diethyl ester,



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CHCH_3 \\ | \\ CH_2COOC_2H_5 \end{array}$$

is not formed under these conditions since a partial saponification of the tri-ester yields a potassium salt in which the potassium atom is attached to an end carboxyl group.

THE ELECTROLYSIS OF THE ALKALI SALTS OF AROMATIC ACIDS

The products yielded by the electrolysis of aqueous solutions of the alkali salts of the aromatic acids differ greatly from those yielded by the electrolysis of the same salts of the aliphatic acids. There are in general no Kolbe hydrocarbon syntheses; only an evolution of hydrogen and oxygen with the liberation of the free acid. In other words there is merely an electrolysis of the solvent water.

At the anode potassium benzoate yields[101] under all conditions only oxygen and free benzoic acid, the latter being insoluble in the electrolyte makes itself evident by crystallizing from the liquid,

$$2C_6H_5COO^- + H_2O + 2F \rightarrow 2C_6H_5COOH + \tfrac{1}{2}O_2$$

The benzoic acid residues are evidently not very easily oxidized because there is the formation of only very minute traces of CO_2, CO and acetylene. The aromatic acids with the COOH groups attached to the side chain behave similarly; the alkali salts of phenylacetic acid[102] and phenylpropionic acid[103] (hydrocinnamic acid) yield at the anode only

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[100] Miller, Z. Elektrochem., **4**, 55 (1897).

[101] Matteuci, Ann. chim. et phys., [2], **74**, 99 (1840); Bull. soc. chim., [2], **10**, 209 (1868); Bourgoin, Bull. soc. chim., [2], **9**, 431 (1867); W. Löb, Z. Elektrochem., **2**, 663, and **3**, 3 (1896). See also later under oxidations.

[102] Slawik, Ber. **7**, 1051 (1874).

[103] Rohland, Z. Elektrochem., **4**, 120 (1897).

the free acid and the usual anodic oxygen. According to Petersen[104] the potassium salt of phenylacetic acid yields the corresponding ester of phenylacetic acid according to a secondary electrolytic reaction, along with benzyl alcohol and its oxidation product benzaldehyde:

$$2C_6H_5CH_2COO^- + 2F \rightarrow C_6H_5CH_2COOCH_2C_6H_5 + CO_2$$

Kaufler and Herzog[105] have also made a study of the regeneration of the aromatic acids in the electrolysis of such salts to determine whether this be due to the strongly acid character of the carboxyl group bound to the phenyl radical, or to a specific chemical influence of the phenyl residue. The potassium salt of *p*-dimethylaminobenzoic acid regenerates the acid quantitatively on electrolysis. The corresponding acid is also regenerated in the electrolysis of the salts of phenylacetic and acetylmandelic acids. The former acids yield no dibenzyl. Walker has obtained hydrobenzoin from the salts of mandelic acid[106]

$$\text{I. } 2C_6H_5CH(OH)COO^- + 2F \rightarrow C_6H_5CH(OH)\cdot CH(OH)C_6H_5 + 2CO_2$$

$$\text{II. } 2C_6H_5CH(OH)COO^- + \underset{\text{anodic}}{O} \rightarrow 2C_6H_5CHO + 2CO_2 + H_2O$$

$$2C_6H_5CHO \rightarrow C_6H_5CO\cdot CH(OH)C_6H_5$$

$$\text{III. } C_6H_5COCH(OH)C_6H_5 + \underset{\text{cathodic}}{2H} \rightarrow C_6H_5CH(OH)\cdot CH(OH)C_6H_5$$

But this formation can easily be understood when it is remembered that Walker worked without a diaphragm, so that there was probably a diffusion of the anode products to the cathode. Miller and Hofer[107] obtained at the anode some benzaldehyde in the electrolysis of phenyl β-lactic acid and salts of phenylglyceric acids. Acetylmandelic acid salts were electrolyzed only to have the free acids regenerated. After two hours of electrolysis the sodium salt of acetylmandelic acid yielded only the odor of benzaldehyde, but chemically there could be no benzaldehyde detected.

The salts and ester salts of the dibasic aromatic acids behave just like the salts of the monobasic aromatic acids in that they do not yield the expected synthetic products, but only the free acid or acid esters, as in the cases of phthalic acid and benzylmalonic acid.

There is a slight disruption of the molecule of phthalic acid when electrolyzed in an alkaline solution, which is indicated by the evolution

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[104] J. Petersen, Jahrb. f. Elektrochemie, **4**, 348.

[105] Kaufler and Herzog, Ber., **42**, 3858 (1909).

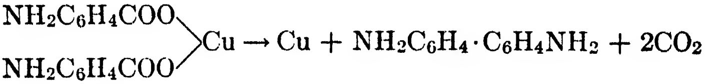
[106] J. Walker, J. Chem. Soc., **69**, 1279 (1896).

[107] Miller and Hofer, Ber., **27**, 461 (1894).

of CO and CO_2.[108] The potassium salt of the monoethyl ester of phthalic acid under the influence of electrolysis turns dark colored due to the formation of a resin which has not yet been identified.[109]

A mixture of the potassium salt of *o*-nitrobenzoic acid with the free acid dissolved in acetic anhydride yields at the anode nitrobenzene and *o*-nitrobenzyl alcohol with some *o*-nitrophenyl ester of *o*-nitrobenzoic acid. However an aqueous solution of the same salt in the presence of potassium acetate yields nitrobenzene, *o*-nitrobenzyl alcohol and the methyl ester of *o*-nitrobenzoic acid.[110]

Only the alkali salts of the aromatic acids show this peculiar reaction. The copper salts of some of the aromatic acids do yield the ordinary synthetic products according to the Kolbe reaction, splitting out CO_2 and forming the analog of ethane.[111] On electrolysis with a c. d. of 1.0 ampere, 8 g. of the copper salt of *p*-aminobenzoic acid, probably as the sulphate to insure complete solubility in the electrolyte, yields 3.5 g. of benzidine according to the reaction:



$$\left.\begin{array}{l}NH_2C_6H_4COO\\ NH_2C_6H_4COO\end{array}\right\rangle Cu \rightarrow Cu + NH_2C_6H_4\cdot C_6H_4NH_2 + 2CO_2$$

plating out copper at the cathode.

Analogously the copper salt of *p*-nitrobenzoic acid gives a 71 per cent yield of di-*p*-nitrodiphenyl:

$$2NO_2C_6H_4COO^- + 2F \rightarrow NO_2C_6H_4\cdot C_6H_4NO_2 + 2CO_2$$

The reduction of the nitro groups does not take place as long as copper is being plated out on the cathode. As soon as all the copper has been deposited, the passage of more current causes the evolution of hydrogen which of course will have a reducing action on the nitro groups. Haber and Moser[112] criticize this work because of the very slight solubility of these copper salts which allows only a very small anion concentration under optimum conditions, permitting the formation of the stated synthetic product with only the lowest conceivable current efficiency. At the present time the question is still open for convincing proof either way.

The electrolytic oxidation of aromatic hydroxycarboxylic acids leads to the formation of a yellow mordant dye in an aqueous sulphuric acid solution. Among the acids so studied are salicylic, *m*-dihydroxy

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[108] Bourgoin, Jahresb., f. Chem., 631 (1831).

[109] Brown and Walker, Ann., **274**, 67 (1893).

[110] Schall, Z. Elektrochem., **24**, 154 (1918).

[111] Lilienfeld, D.R.P. 147943 (1893).

[112] Haber and Moser, " Elektrolytische Prozesse," page 47.

benzoic, gallic, tannic, and gallaminic acids; the esters of *m*- and *p*-trihydroxybenzoic acids.[113]

Fused Salts.—The use of non-aqueous solutions leads to different results. A solution of sodium benzoate in molten benzoic acid on electrolysis yields a small amount of diphenyl. The conductivity of the mixture is very low at best and requires a voltage of about 100 volts to begin electrolytic action.[114] The thermal effect concomitant with the electric current seems to cause the reaction to take place.

When the potassium salt of *o*-nitrobenzoic acid in molten *o*-nitrobenzoic acid is electrolyzed between platinum electrodes with a current of 1 ampere and 25 volts, a small amount of nitrobenzene is formed instead of the expected dinitrodiphenyl, which would be formed by the union of two acid residues after the CO_2 is removed.[115] The formation of nitrobenzene is considered as due to a secondary action of the potassium liberated at the cathode [116] because the use of a porous cup to separate the anolyte from the catholyte prevents the formation of the nitrobenzene. The substances formed in the anolyte and catholyte have never been identified. Schall considers that there might have been a trace of the *o*-dinitrodiphenyl formed in each case. When the potassium salt of *p*-nitrobenzoic acid is electrolyzed in a hot solution of pure acetic anhydride a small quantity of the expected *p*-dinitrodiphenyl is formed and may be recognized by its conversion to benzidine. The formation of this substance is assumed to occur through a composite electrolysis of the potassium nitrobenzoate and acetate in the acetic anhydride solution, the acetate being formed by a primary thermal decomposition. The application of thermal effect alone does not form an aromatic hydrocarbon.[117]

Berl [118] claims that the formation of these substances is not due to the primary electrolytic action on the salt but is due to the action of the discharged alkali metal on the molten solvent or to the thermal effects of the very high temperature. Metallic potassium reacts with molten *o*-nitrobenzoic acid potassium salt to form nitrobenzene, and with potassium benzoate to give benzene. He also cites the pyrogenic decomposition of salicylic and anthranilic acids to a rather large extent and benzoic acid to a less extent, in all cases to form some of the corresponding hydrocarbon. The use of the high voltage in the electrolysis of sodium benzoate in molten benzoic acid could easily over-heat the

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[113] D.R.P. 85390 (1895), Badische.

[114] C. Schall and Klein, Z. Elektrochem., **6**, 102 (1899).

[115] C. Schall and Klein, Z. Elektrochem., **5**, 256 (1898).

[116] Berl, Ber., **37**, 325 (1904).

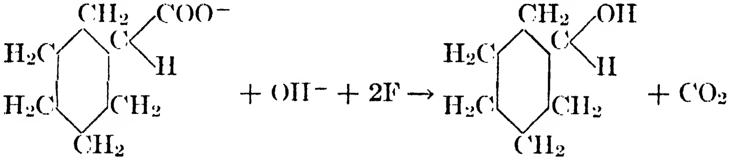
[117] C. Schall, Z. Elektrochem., **21**, 69 (1915).

[118] Berl, Ber., **37**, 325 (1904).

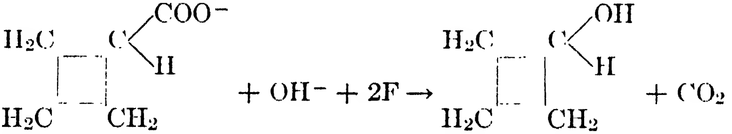
electrodes locally and so form the diphenyl pyrogenically instead of by primary electrolytic action.

THE ALKALI SALTS OF HYDROAROMATIC ACIDS

The hydroaromatic acid salts react like the aliphatic acid salts, rather than like their congeners the ordinary aromatic acids. An aqueous solution of potassium hexahydrobenzoate (hexamethylenecarboxylic acid), made alkaline by the addition of K_2CO_3 yields the corresponding alcohol of cyclohexane, i.e., cyclohexanol:[119]



This reaction is the analog of the reaction for the formation of alcohol from the salts of fatty acids in the presence of the inorganic salts, potassium carbonate, chlorate, etc. The potassium salt of tetramethylene carboxylic acid similarly yields cyclobutanol together with some of the corresponding ester:[120]



The acid ester salts of the camphor series react as if they were members of the dicarboxylic acids of the aliphatic series, yielding the diester of a saturated dicarboxylic acid of double the number of carbon atoms less two, together with an unsaturated monobasic acid: A concentrated aqueous solution of the potassium salt of the ethyl ester of allo-camphoric acid[121] (I), yields besides other products at the anode the ethyl ester of allo-campholytic acid (γ-lauronolic acid) (II), together with the diester of allo-camphotetic acid (III) and the free acid of (I).

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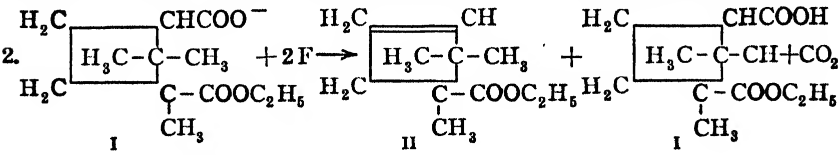

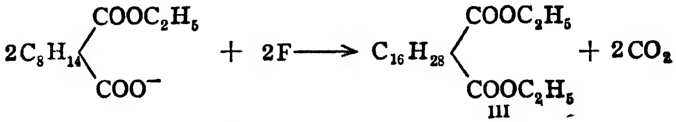

$$2C_8H_{14}\left\langle\begin{matrix}COOC_2H_5\\ COO^-\end{matrix}\right. + 2F \longrightarrow C_{16}H_{28}\left\langle\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix}\right. + 2CO_2$$

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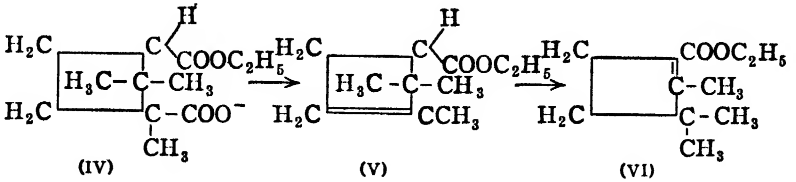
[119] Demjanoff, Jour. Russ. Phys. Chem. Soc., 314 (1904).

[120] Demjanoff and Dojarenko, Ber., **40,** 2596 (1907).

[121] J. Walker and Henderson, J. Chem. Soc., **67,** 337 (1895), and **68,** 748 (1896), Chem. News, **73,** 254 (1896).

The alkali salt of ortho-camphoric acid ethyl ester [122] (IV), (prepared by heating camphoric acid with absolute alcohol and sulphuric acid) under similar conditions yielded mostly the ester of ortho-campholytic acid (V), which by rearranging the double bond and a methyl group during the electrolysis, was partially transformed into the ester of β-campholytic acid (VI) (iso-lauronolic acid), an α-β-unsaturated acid.



When a solution of sodium ethyl camphorate is submitted to electrolysis, one of the products is the ester of an unsaturated acid.[123] This acid, now known as isolauronolic acid, was recognized later as being an α-β-unsaturated acid, a view confirmed by its subsequent synthesis.[124] This migration of the methyl group has been found to occur in another instance as explained above in the case of the electrolysis of β, β-dimethyl glutaric acid.[125]

THE ELECTROLYSIS OF ACID COMPOUNDS WHICH ARE NOT CARBOXYLIC ACIDS

Sodium malonic ester and other similar compounds which contain a methylene group having acid properties are fairly good conductors of electricity when in alcoholic solution. On being subjected to electrolysis they react just as if they were the salts of aliphatic acids in that two discharged anions couple. Thus by the electrolytic method, a series of compounds can be made which are the same as those formed when iodine reacts with sodium malonic ester and its homologues.

Sodium diethyl malonate [126] in alcoholic solution at a platinum wire anode yields the symmetrical ethanetetracarboxylic ester:

$$2HC(COOC_2H_5)_2^- + 2F \rightarrow \begin{array}{l} HC(COOC_2H_5)_2 \\ | \\ HC(COOC_2H_5)_2 \end{array}$$

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[122] Walker, Chem. News, **67**, 129 (1893); Walker and Cormack, J. Chem. Soc., **77**, 374 (1900); Proc. Chem. Soc., **16**, 58 (1900).

[123] Walker, J. Chem. Soc., **63**, 495 (1893).

[124] Perkin and Thorpe, J. Chem. Soc., **85**, 128 (1904).

[125] Walker and Wood, J. Chem. Soc., **89**, 598 (1906).

[126] Mulliken, Am. Chem. Jour., **15**, 323 (1893).

In an analogous manner the sodium salts of the following compounds yield the respective products:[127]

Methanetricarboxylic ethyl ester[128] → ethanehexacarboxylic ester
Methylmalonic acid diester[128] → dimethylethanetetracarboxylic ester
Ethylmalonic acid ester[128] → diethylethanetetracarboxylic ester
Nitromalonic acid ester[129] → dinitroethanecarboxylic acid ester
Cyanomalonic acid ester[130] → dicyanoethanetetracarboxylic acid ester
Acetylacetone[131] → tetraacetylethane
Acetoacetic ester[132] → diacetylsuccinic acid ester

The potassium salts[133] of the oximino compounds of malonic acid and several other acids also react on electrolysis to form synthetic compounds. Platinum electrodes with a current of 0.2 to 0.25 ampere give fairly good yields. From the sodium or potassium salts of the following compounds the respective synthetic products are obtained:

Oximinomalonate → *sym*-dinitrosoethanetetracarboxylic acid ester

$$2^{-}ON = C(COOC_2H_5)_2 + 2F \rightarrow \begin{array}{l} ON \cdot C(COOC_2H_5)_2 \\ \quad\;\;\; | \\ ON \cdot C(COOC_2H_5)_2 \end{array}$$

Oximinopropionate → *sym*-dinitrosodimethylethanedicarboxylic acid diester,

$$2^{-}ON = C(CH_3)COOC_2H_5 + 2F \rightarrow \begin{array}{l} ON(CH_3) \cdot C \cdot COOC_2H_5 \\ \qquad\qquad\;\; | \\ ON(CH_3) \cdot C \cdot COOC_2H_5 \end{array}$$

α-Oximinobutyrate → *sym*-dinitrosodiethylethanedicarboxylic acid di-ester,

$$2CH_3CH_2(NO^{-})C \cdot COOC_2H_5 + 2F \rightarrow \begin{array}{l} CH_3CH_2(NO) \cdot C \cdot COOC_2H_5 \\ \qquad\qquad\qquad\;\; | \\ CH_3CH_2(NO) \cdot C \cdot COOC_2H_5 \end{array}$$

When the sodium compounds of the mercaptans and other compounds containing sulphur are electrolyzed the product is the same as

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[127] Weems, Am. Chem. Jour., **16**, 569 (1894); Mulliken, loc. cit.

[128] Weems, Am. Chem. Jour., **16**, 569 (1894).

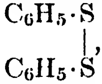
[129] Ulpiani and Gasparini, Gazz. chim. ital., **32**, ii, 235 (1902).

[130] Ulpiani and Rodano, ibid., **35**, ii, 365 (1905).

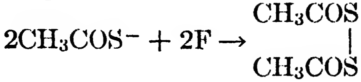
[131] Mulliken, loc. cit.

[132] Weems, loc. cit.

[133] Ulpiani and Rodano, Atti. R. Accad. d. Lincei, [5], **14**, ii, 601 (1905).

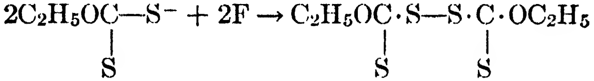
if the original compound had been treated with iodine.[134] An alcoholic solution of sodium phenylmercaptan C_6H_5SNa yields at the anode diphenyldisulphide,  $\begin{array}{c} C_6H_5\cdot S \\ | \\ C_6H_5\cdot S \end{array}$,while sodium ethylmercaptan yields diethyldisulphide, $2C_2H_5SNa \rightarrow C_2H_5SSC_2H_5$. The sodium methylmercaptan acted similarly.

The sodium salt of thioacetic acid,[135] CH_3COSNa, in aqueous solution yields diacetyldisulphide:



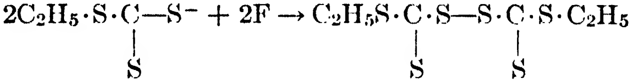
$$2CH_3COS^- + 2F \rightarrow \begin{array}{c} CH_3COS \\ | \\ CH_3COS \end{array}$$

In an aqueous solution Schall [136] has found that the alkali salts of compounds of the type RCSSH react according to the Kolbe ethane synthesis, and on discharge, two anion residues unite to form compounds of the general type RCSS—SSCR. Thus potassium xanthogenate yields xanthogen supersulphide (ethyl dioxythiocarbonate),



$$2C_2H_5O\underset{\underset{S}{|}}{C}-S^- + 2F \rightarrow C_2H_5O\underset{\underset{S}{|}}{C}\cdot S-S\cdot\underset{\underset{S}{|}}{C}\cdot OC_2H_5$$

This is also true of the methyl, isobutyl, and isoamyl esters of xanthogenic acid. Potassium ethyl trithiocarbonate yields the corresponding dithiodisulphide:



$$2C_2H_5\cdot S\cdot\underset{\underset{S}{|}}{C}-S^- + 2F \rightarrow C_2H_5S\cdot\underset{\underset{S}{|}}{C}\cdot S-S\cdot\underset{\underset{S}{|}}{C}\cdot S\cdot C_2H_5$$

Ammonium dithiocarbamate yields thiuramdisulphide,

$$(H_2N\cdot C\cdot S)S-S(SC\cdot NH_2)$$

while the diethylammonium-diethyl-dithiocarbamate forms tetraethylthiuram disulphide,

$$[(C_2H_5)_2NCS]S-S[SCN(C_2H_5)_2]$$

The metallic compounds of the nitro bodies also yield synthetic products on electrolytic oxidation.[137] Unless the reaction is carried out in a palladium vessel there is a great deal of trouble with the formation of undesirable by-products. A concentrated aqueous solution of

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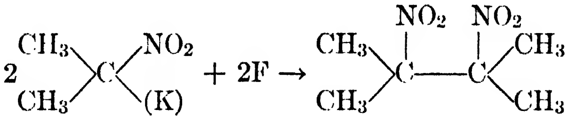
[134] Bunge, Ber., **3,** 911 (1870).
[135] Bunge, Ber., **3,** 297 (1870).
[136] C. Schall, Z. Elektrochem., **2,** 475 (1896); **3,** 83 (1896); **5,** 226 (1898).
[137] Zelinsky and Schilow, J. Russ. Phys. Chem. Soc., **26,** 608 (1894).

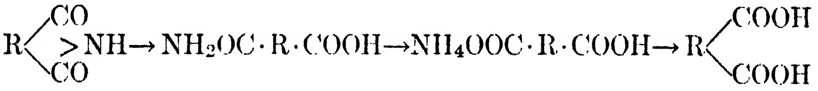
the potassium salt of nitro isopropane at the anode forms a heavy oil which on purification yields dinitrodiisopropyl melting at 209–210° C:



$$2\,\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NO_2\\(K)\end{matrix} + 2F \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\underset{}{\overset{NO_2}{C}}\!-\!\!-\!\!\overset{NO_2}{C}\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

When an alkali derivative of an imide is electrolyzed the imide is first transformed into the corresponding acid amide.[138] The ammonium salt is then resolved by the current into ammonia at the negative pole and the free acid at the positive pole. The potassium which discharges at the cathode reacts with the free acid to form the potassium salt. As the electrolysis progresses the electrolyte in the case of phthalimide turns brown at the anode and becomes acid, while, at the cathode, ammonia gas is evolved. After all the ammonia is evolved the catholyte assumes an acid reaction. At the anode the potassium salt of phthalic acid separates.

The electrolysis of a solution of the potassium salt of succinimide at once yields ammonia gas at the cathode, but only after the reaction has been in progress for some hours is solid succinic acid separated at the anode. The amount of acid formed increases with the acidity of the anolyte.



$$R\!<\!\!\begin{matrix}CO\\CO\end{matrix}\!\!>\!NH \rightarrow NH_2OC\cdot R\cdot COOH \rightarrow NH_4OOC\cdot R\cdot COOH \rightarrow R\!<\!\!\begin{matrix}COOH\\COOH\end{matrix}$$

The sodium salt of acetamide yields acetic acid, etc.

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[138] Weems, Am. Chem. Jour., **16,** 569 (1894); Pannain, Gazz. chim. ital., **35,** ii 95 (1905).

CHAPTER V

THE ELECTROLYTIC OXIDATION OF NON-IONIZED SUBSTANCES—PART I

THE OXIDATION OF CARBON AND THE ALIPHATIC COMPOUNDS

Under most conditions carbon electrodes are more or less easily attacked in reactions in which anodic oxygen is evolved. Arc lamp carbons are corroded without the evolution of any oxygen when used as the electrodes in a cell, the electrolyte of which is a 1 : 1 solution of sulphuric acid in water at room temperature at a c. d. of 0.75 ampere; at the same time a metallic-like substance is plated out on the cathode.[1] On the other hand in dilute acid solutions anodes of retort and wood carbon are mostly oxidized to carbon dioxide and a black amorphous substance "Mellogen," $C_{11}H_2O_4$, which settles out of solution.[2] This substance when dissolved in hot water or alkalies and oxidized by means of bleaching powder yields graphitic acid (benzenehexacarboxylic acid) and also pyrographitic acid (benzenetetracarboxylic acid). This black material is insoluble in acids, and so, when formed in an acid solution, settles out, thus being removed from any possibility of being further attacked by the anodic oxygen. In an alkaline solution these carbon anodes are directly oxidized to graphitic and pyrographitic acids because the intermediate substance is soluble in the alkali and so may be subjected to a further oxidation. The final product of the reaction is hydromellitic acid, $C_{12}H_{12}O_{12}$, which is undoubtedly formed by the graphitic acids diffusing to the cathode, and there being reduced by the cathodic hydrogen. By purely chemical methods, graphite and other forms of carbon may be oxidized to graphitic acid by a mixture of potassium chlorate, nitric acid and sulphuric acid.[3]

For several years past acetylene has been oxidized by purely chemical methods to form acetaldehyde. A large variety of methods have been patented. Electrolytic methods have now been applied with

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[1] Coehn, Z. Elektrochem., **3**, 424 (1897).

[2] Bartoli and Papasogli, Gazz. chim. ital., **11**, 468 (1881); **12**, 113 (1882); **14**, 90 (1884); **15**, 461 (1885); Compt. rend., **102**, 363 (1886).

[3] V. Kohlschütter and P. Haenni, Z. anorg. allgem. Chem., **105**, 121 (1919).

great success to the regeneration of the catalyst used. A method[4] has been described in which the acetylene is passed through an aqueous solution of sulphuric acid containing mercury salts together with some ferric and vanadic compounds. The mercury catalyst is regenerated electrolytically while the ferric and vanadic compounds act as carriers. The aldehyde is carried off as a vapor with the excess of the acetylene. The former is then polymerized to the paraldehyde by passing it through 15 to 20 per cent sulphuric acid. Anodes of platinum, lead dioxide, or Fe_3O_4 may be used.[5] Platinum anodes may be used on the bottom of the cell with a mercury catalyst and ferrous, cerium, or chromium salts as oxygen carriers; the carriers are regenerated electrolytically with an auxiliary anode which makes contact with the mercury, the anode acting as the stirring device. The cathode of copper is surrounded by a clay cell to prevent diffusion.[6]

Glycols [7] may be made from ethylene or gases containing ethylene, using a solution of sodium cholride which is sufficiently conductive for industrial uses with or without a diaphragm and electrolyzing between electrodes which may be of platinum, carbon, or lead with an oxide catalyst of chromium, manganese, or cerium.

Instead of ethylene alone the apparatus may be fed with oil gas containing from 40–50 per cent of various hydrocarbons. The catalyst may be platinum-black or palladium-black. If no diaphragm is used the resulting solution is a neutral salt solution containing the glycol.

Acetic acid may be formed [8] by oxidizing acetylene at a platinum or lead anode in a 30 per cent sulphuric acid solution containing 1 to 2 per cent of mercury salt at 30–40° C., using a clay cell as a diaphragm and a platinum or copper cathode in a 30 per cent sulphuric acid catholyte. These results are similar to those obtained by a purely chemical method described by the same men.[9]

OXIDATION OF ALCOHOLS

When an alkaline solution of an aliphatic alcohol is subjected to electrolysis no definitely predominating reaction seems to take place,

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[4] See also K. A. Hoffmann, Ber., **32**, 874 (1899); Soc. des Aciers et Forges de Firming, Brit. Pat. 132529 and 124194, (1919).

[5] U.S.P. 1315543 and 1315543 (1919); many patents for similar methods have been assigned to H. W. Matheson.

[6] Brit. P. 155775 (1920), Stockholm Superfosfat Fab. Akt.; Brit. P. 156147 (1920), H. Plauson and J. A. Vielle; Brit. P. 155838, ibid.; Brit. P. 143891 (1920); Brit. P. 130138 (1918).

[7] U.S.P. 1308797 (1919), K. P. McElroy.

[8] U.S.P. 1156376 (1915), C. Hauser and A. Weindel.

[9] U.S.P. 1129270 (1915).

though the formation of an aldehyde may at times be rather large These aldehydic compounds usually polymerize to form resins and other condensation products.[10]

Methanol.—The earlier work on the electrolytic oxidation of methanol in an aqueous sulphuric or phosphoric acid solution showed an evolution of H_2 with the formation of acetic acid, methylal, methyl acetate, methyl formate, methylsulphuric acid, a little CO and CO_2 but no formaldehyde. By itself or in an alkaline solution the products[11] are chiefly potassium carbonate, H_2, O_2, CO, and CO_2. According to Jaillard, the presence of the acetic acid is due to the interaction of methanol with the CO,

$$CH_3OH + CO \rightarrow CH_3COOH,$$

though Jahn[12] has ascribed it to a contamination of the methanol by ethyl alcohol. Habermann found some potassium methylcarbonate when the electrolysis was carried out in the presence of potassium acetate. However it does seem that the concentration of the acid or the alkali in the electrolyte determines to some extent the course of the reaction.

A solution of methanol[13] in 1 liter of twice normal sulphuric acid at a plain platinum anode in a divided cell at 30° C., and a c. d. of 3.75 amperes forms an 80 per cent current yield of formaldehyde besides small quantities of formic acid, carbon monoxide and carbon dioxide. At a platinized-platinum anode the yield of formaldehyde drops to about one-half. Thus increasing, by the further oxidation of the primarily formed aldehyde, the amount of CO_2 formed. At a lead dioxide anode the oxidation is carried almost completely to carbon dioxide. After the passage of 14.2 ampere hours at 30° C. these results have been recorded:

TABLE IX

Anode of	Grams Formaldehyde	Grams Formic Acid	Grams CO	Grams CO_2
Pt.	7.1	0.24	0.05	0.19
Ptd-Pt.	3.4	0.17	0.00	2.09
PbO_2.	1.4	0.09	0.00	2.91

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[10] Habermann, Sitzungsber. d. Wien. Akad., **94**, ii, 583 (1886).

[11] Renard, Compt. rend., **80**, 105 and 236 (1875); Ann. chim. et. phys., [6], **17**, 289 (1879); Almeida and Deherain, Compt. rend., **59**, 214 (1865); Jaillard, ibid., **58**, 203 (1864); Habermann, Monatsch., **7**, 259 (1886); Connell, Pogg. Ann., **36**, 487 (1835); Dony-Henault, Z. Elektrochem., **6**, 533 (1900).

[12] Jahn, Grundriss der Elektrochemie, 291 (1894).

[13] Elbs and Brunner, Z. Elektrochem., **6**, 604 (1900).

In all three cases the oxygen consumed was 100 per cent, that is, there was no evolution of oxygen.

A more careful study of the electrolytic oxidation of methanol has been made by Müller [14] according to which the anodic evolution of hydrogen with time is as follows:

TABLE X

Hours after beginning	cc. of H_2 evolved at Pt.
2	4.4
4	10.4
6.5	24.0
7.5	31.5

The anodic potential was compared with a normal calomel electrode as a standard, the gas volumes measured and analyzed for their content of H_2, methane, ethylene, O_2 and CO.

To explain this evolution of hydrogen Müller has developed a mechanism in which the hydrogen comes directly from the methanol just as it does in the case of formaldehyde (which see), i.e., it is also a " dehydroxidation." [15]

1. $CH_3OH \rightleftarrows H_3C{-}O^- + H^+$

2. $H_3CO^- + F \rightarrow H_3C=O$ (oxy-alcohol)

3. $H_3C = O \rightarrow H_2C = O + H\ ;\ 2H \rightarrow H_2$

The primary product of the oxidation is the oxy-alcohol which then breaks down into the aldehyde and hydrogen.

Ethyl Alcohol.—Hydrogen is also evolved in the electrolytic oxidation of ethyl alcohol. The other products are CO_2, methane, etc., and the scheme is like that for methanol, i.e., the products are H_2, methane, and ethane, but the latter appears only in very small quantities probably because the —CH_3 reacts more easily and rapidly with H than

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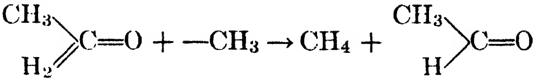
[14] E. Müller and A. R. y Miro, Z. Elektrochem., **27,** 54 (1921); Müller and Hochstetter, Z. Elektrochem., **20,** 367 (1914).

[15] Müller and Hochstetter, Z. Elektrochem., loc. cit.; Müller, Ann., **420,** 241 (1920).

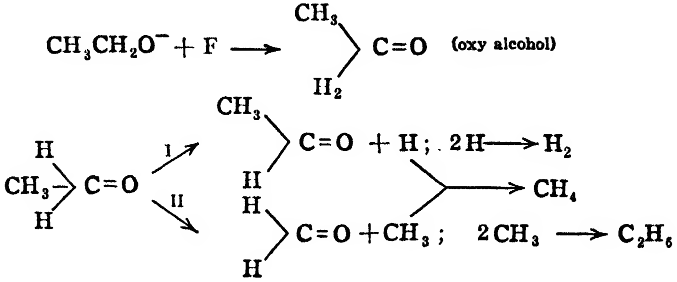
with itself, for if reaction 1 is depressed, the —CH_3 group reacts with the oxy-alcohol:



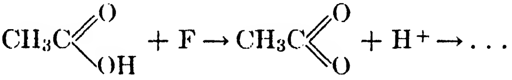
$$\begin{matrix}CH_3\\ H_2\end{matrix}\!\!>C=O + -CH_3 \rightarrow CH_4 + \begin{matrix}CH_3\\ H\end{matrix}\!\!>C=O$$

The general scheme for the oxidation of any alcohol will therefore be:

$$CH_3CH_2OH \rightleftarrows CH_3CH_2O^- + H^+$$

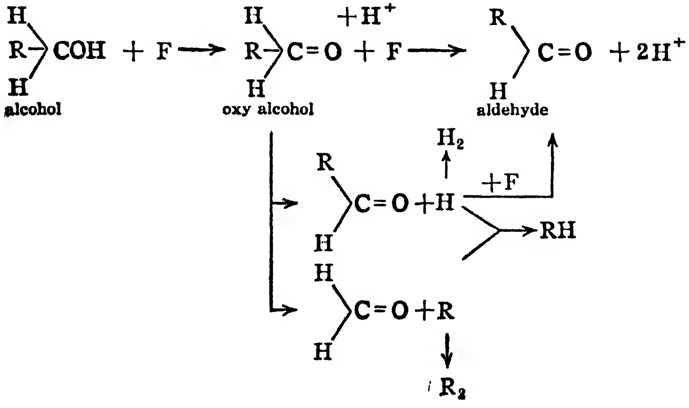


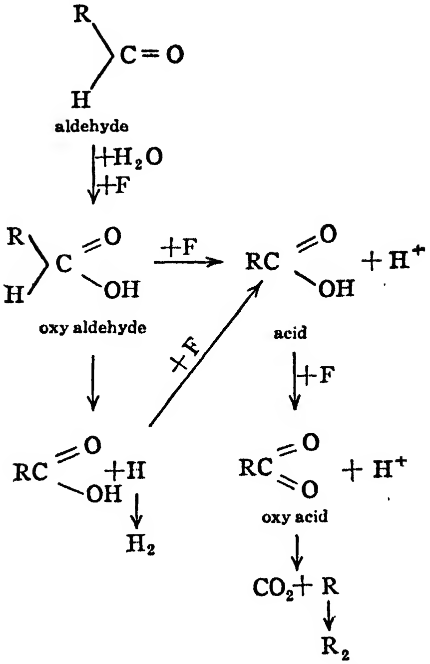
An acid is also oxidized to an oxy- acid:



$$CH_3C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + F \rightarrow CH_3C\begin{matrix}\nearrow O\\ \searrow O\end{matrix} + H^+ \rightarrow \ldots$$

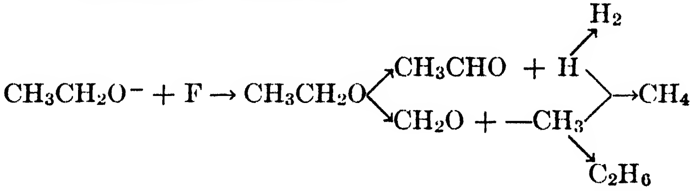
which by the elimination of —CH_3 can form ethane but at the same time evolving no hydrogen so fulfilling the Kolbe synthesis of hydrocarbons from acids.





Briefly the electrolytic oxidation of ethyl alchol may be expressed when a platinum anode is used:[16]

$$CH_3CH_2OH \rightleftarrows CH_3CH_2O^- + H^+$$



$$CH_3CH_2O^- + F \rightarrow CH_3CH_2O\left\langle\begin{matrix}\nearrow CH_3CHO + H \xrightarrow{} H_2 \\ \searrow CH_2O + -CH_3 \xrightarrow{} C_2H_6\end{matrix}\right. \qquad H + -CH_3 \rightarrow CH_4$$

The products of the electrolysis of ethyl alcohol in various acids are not always the same.[17] In sulphuric acid solution the products are acetaldehyde, ethyl acetate, ethyl formate, ethylidenehydroxyethyl ether $CH_3CH\left\langle\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$, and ethylsulphuric acid. In a nitric acid solution the products are the above, to which may also be added the carbon

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[17] E. Müller, Z. Elektrochem., **27**, 563 (1921); O. Hauffe, Dissert., Dresden (1921); Müller and Miro, loc. cit.

[18] Schönbein, Tomassi, " Traite," 726; Becquerel, Compt. rend., **81**, 1002 (1875); Bartoli and Papasogli, Wieder. Beiblätter, **7**, 121 (1882); Renard, Compt. rend., **80**, 105 and 236 (1875); Ann. chim. et phys., [5], **17**, 289 (1879); Connell, Phil. Mag., [3], **17**, 353 (1840).

derivatives of ammonia.[18] In an HCl solution [19] chloroacetic acids and their derivatives are formed. In an alkaline solution Habermann obtained CO_2 and an aldehyde resin, but Connell [20] obtained a body closely resembling coumarinic aldehyde. In an aqueous solution containing potassium acetate Connell found ethane, CO_2, ethyl acetate and potassium ethyl carbonate.

Under the same circumstances which yield formaldehyde from methanol, ethyl alcohol is nearly completely oxidized to acetic acid so that the acetaldehyde formed amounts to only one-twentieth of the acetic acid, with the evolution of CO_2 but not CO.[21] The necessity of stopping a reaction at a certain point is dependent on whether the product formed first is a good depolarizer or not. Acetaldehyde is an excellent depolarizer at a voltage of 1.66.[22] It has been shown that aldehyde is formed almost quantitatively when the voltage is 1.3 with a very small c. d. Alcohol is as good a depolarizer as acetaldehyde therefore if an excess of alcohol is present there is a better opportunity for the amount of aldehyde formed to be larger than if there was a deficiency in alcohol. Jaillard [23] electrolyzed a solution of alcohol containing only 1 per cent of sulphuric or acetic acids and so obtained only acetaldehyde. A low c. d. and an excess of alcohol form only a small amount of aldehyde in comparison with the alcohol present; by diffusion this aldehyde is removed from the electrode beyond the sphere of oxidation influences. On the other hand, if the c.d. is high the amount of oxygen discharged is large and the aldehyde cannot diffuse away from the electrode fast enough to get out of the way of the oxygen and undergoes a further oxidation to the acid. Hence, with dilute solutions and a high c. d. the main product is acid and not aldehyde. This thoroughly agrees with the results of Dony-Henault, who used platinized-platinum electrodes at room temperature:

TABLE XI

Current Density in Amperes	Anode Potential toward a Hydrogen Electrode	Per Cent Current Yield of Aldehyde
0.012	0.93 to 1.	99.1
0.025	0.95	85.
0.06	1.5 to 1.7	39.

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[18] Almeida and Deherain, Compt. rend., **51**, 214 (1865).

[19] Lüdersdorff, Pogg. Ann., **19**, 77 (1830); Riche, Tomassi, 728.

[20] Connell, loc. cit. and Phil. Mag., [3], **18**, 47 (1841).

[21] Elbs and Brunner, Z. Elektrochem., **6**, 604, (1900).

[22] Dony-Henault, Z. Elektrochem., **6**, 533 (1900); Elbs and Foerster, ibid., **7**, 341 (1900).

[23] Jaillard, Compt. rend., **58**, 203 (1864). See also Habermann, loc. cit.

The remainder of the anodic current was used to oxidize further the aldehyde to acid. For equivalent concentrations acetaldehyde is a better depolarizer than ethyl alcohol.[24]

Under the present conditions of development this method of formation of aldehydes cannot be used commercially, because of the uncertain yields and the exceeding low current densities which are required for the formation of aldehydes, making enormous electrolyzing tanks necessary for the production of even small quantities. However Schlötter[25] was able to obtain current yields of about 80 per cent of the theoretical, by working at high temperatures, thus causing the aldehyde as formed to be distilled out and so be removed from the sphere of oxidation. No diaphragm was necessary because the aldehyde is not reduced at a platinum cathode.

A method for the oxidation of ethyl alcohol to acetic acid had been developed.[26] When a solution of 250 g. of alcohol in 1 liter of water, containing 37 g. of sulphuric acid is electrolyzed at 35° C. on a platinum wire gauze anode with a c. d. of 0.2 ampere at a potential of 4 volts, the current yield of acetic acid is 72 per cent and the material yield is 80 per cent. Of course some provision must be made for the retention in the solution of the intermediate product, acetaldehyde. A good condenser is sufficient for this purpose. The current yields are not steady but rise and fall with the concentration of the depolarizer. There is also an intermediate formation of ethyl acetate,

$$C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O,$$

but this ester is subsequently oxidized and is not found at the end of the electrolysis.

Higher Alcohols.—The higher alcohols[27] for the most part are oxidized to the corresponding acids. Propyl alcohol when electrolyzed in a dilute sulphuric acid solution at Pt or PbO_2 anodes gives a 90 per cent yield of propionic acid with very little aldehyde, except at very low c. d. Practically no CO and CO_2 are found.[28] On the other hand isopropyl alcohol yields mostly acetone in 70 per cent current yields together with acetic acid, CO_2 and formic acid. In an alkaline solution a resin results.

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[24] W. Slaboszcwiez, Z. physik. Chem., **42**, 343 (1903); also E. Baur, Ber., **34**, 3723 (1901).

[25] Schlötter, Dissert., Munich (1902).

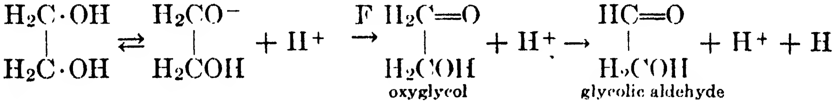
[26] P. Askenasy, R. Leiser and N. Grünstein, Z. Elektrochem., **15**, 843 (1909).

[27] Elbs and Brunner, Z. Elektrochem., **6**, 604 (1900); Brunner, Dissert., Giessen (1899).

[28] Elbs, "Übungsbeispiele," page 135.

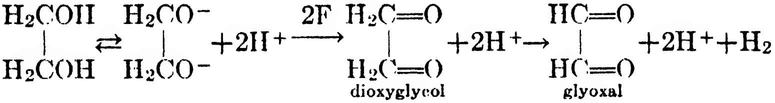
The oxidation of isoamyl alcohol[29] leads to the formation of isovaleric aldehyde at lead dioxide and nickel anodes, when the c. d. is less than 1 ampere in a sulphuric acid solution. When the c. d. exceeds this value the aldehyde is always contaminated with acid. At a c. d. of 2 amperes the acid is the main product. The addition of the sulphates of cerium or iron or the oxide of vanadium as carriers increases the efficiency of the cell, when an acid anolyte is used. An alkaline anolyte always leads to the formation of both isovaleric aldehyde and isovaleric acid.

About 5 per cent of hydrogen was obtained by the anodic oxidation of propyl and isopropyl alcohols, and about 1.8 per cent in the case of benzyl alcohol but in no case was a hydrocarbon obtained. The slight solubility of these alcohols in the alkali does not permit this fact to be used as proving or disproving the theory. Increasing the solubility by the addition of acetone, etc., did not increase the yields.[30] In the case of the polyatomic alcohols the reactions are supposed to be:



$$\begin{array}{c}H_2C\cdot OH\\ |\\ H_2C\cdot OH\end{array} \rightleftarrows \begin{array}{c}H_2CO^-\\ |\\ H_2COH\end{array} + H^+ \xrightarrow{F} \underset{\text{oxyglycol}}{\begin{array}{c}H_2C{=}O\\ |\\ H_2COH\end{array}} + H^+ \rightarrow \underset{\text{glycolic aldehyde}}{\begin{array}{c}HC{=}O\\ |\\ H_2COH\end{array}} + H^+ + H$$

or



$$\begin{array}{c}H_2COH\\ |\\ H_2COH\end{array} \rightleftarrows \begin{array}{c}H_2CO^-\\ |\\ H_2CO^-\end{array} + 2H^+ \xrightarrow{2F} \underset{\text{dioxyglycol}}{\begin{array}{c}H_2C{=}O\\ |\\ H_2C{=}O\end{array}} + 2H^+ \rightarrow \underset{\text{glyoxal}}{\begin{array}{c}HC{=}O\\ |\\ HC{=}O\end{array}} + 2H^+ + H_2$$

Complex secondary alcohols are oxidized by electrochemical methods just as easily as by purely chemical processes. Tropine yields tropinone without much secondary oxidation.

The higher monoatomic alcohols, because of their very slight solubility in aqueous sodium hydroxide, evolve very little hydrogen gas at the anode. On the other hand the polyatomic alcohols such as glycol, glycerol, mannitol yield much hydrogen in a strongly alkaline medium, but in an excessively strong alkaline solution they are practically completely oxidized to CO_2.

The knowledge of the reactions of the polyatomic alcohols with anodic oxygen is for the most part very fragmentary. Until recently only some of the end products were known. Glycol in sulphuric acid

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[29] Shunzo Koizumi, J. Chem. Soc., Japan, **42**, 928 (1921); Elbs and Brunner, loc. cit., used a high c. d. to obtain only isovaleric acid in 80 per cent yields.

[30] The purely chemical dehydroxidation of methly, ethyl and isopropyl alcohols, glycol, glycerine and mannite with potassium ferricyanide gave results similar to those obtained in the electrolytic oxidation; isopropyl, sec. butyl, tert. butyl and benzyl alcohols gave no hydrocarbon gases; Müller, loc. cit.

yielded CO, CO_2, trioxymethylene, glycolic and formic acids, O_2, H_2, and a sugar which was not a pentose, but which formed an osazone melting at 184–185°. In phosphoric acid the results were similar.[31] The scheme suggested for the oxidation of glycol is:

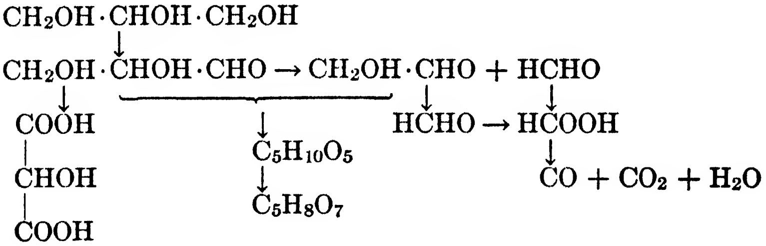
$$\begin{array}{l} CH_2OH\cdot CH_2OH \\ \quad\downarrow \\ CH_2OH\cdot CHO \\ \quad\downarrow \\ \quad 2HCHO \rightarrow 2HCOOH \rightarrow CO + CO_2 + H_2O \end{array}$$

Glycerol in 5 per cent sulphuric acid similarly yielded H_2, O_2, CO, CO_2, glyceraldehyde, trioxymethylene, formic, acetic, acrylic, propionic acids, acrolein and a compound the barium salt of which was $(C_3H_3O_4)_2Ba$, much formaldehyde together with a syrup which contained no glycolaldehyde, dioxyacetone, nor a hexose but which probably did contain a pentose such as arabinose.[32]

Glycolaldehyde in the presence of colloidal barium carbonate has been shown to yield a pentose by a reaction which is probably:[33]

$$CH_2OH\cdot CHOH\cdot CHO + CH_2OHCHO \rightarrow CH_2OH(CHOH)_3\cdot CHO$$

The scheme which has been suggested for the oxidation of glycerol may be indicated as follows: [34]



Glucose [35] has also yielded a variety of products from a sulphuric acid solution: CO, CO_2, acetaldehyde, formic, and acetic acids. While

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[31] Renard, Ann. chim. et phys., [5], **17**, 303 and 313 (1897); Compt. rend., **81**, 188 (1875); **82**, 562 (1876); Löb and Pulvermacher, Biochem. Zeit., **17**, 343 (1909); Löb, ibid., **16**, 1 (1910).

[32] Renard, loc. cit.; Stone and McCoy, Am. Chem. J., **15**, 656 (1893); Wertha, J. prakt. Chem., [1], **88**, 151 (1863); Voigt, Z. angew. Chem., 107 (1894); Löb, Z. Elektrochem., **16**, 1 (1910); Perls, J. prakt. Chem., [1], **88**, 151 (1863); Bartoli and Papasogli, Gazz. chim. ital., **13**, 287 (1883).

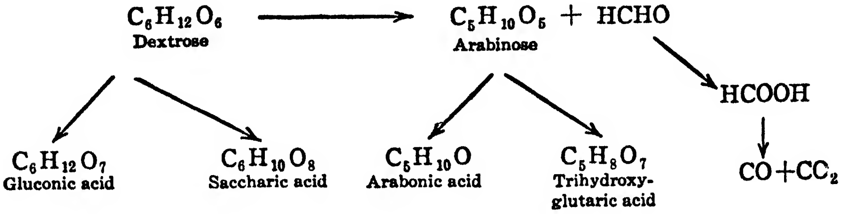
[33] Neuberg, Biochem. Zeit., **12**, 337 (1908).

[34] Löb and Pulvermacher, Biochem. Zeit., **17**, 343 (1909); **16**, 1 (1910); see also Bartoli and Papasogli, Gazz. chim. ital., **13**, 287 (1883).

[35] Brown, Chem. News, **25**, 249 (1872).

Renard[36] was able to identify formic acid, trioxymethylene, saccharic acid, other compounds that have been identified are an alcohol,[37] lactic acid;[38] and mannitol,[39] a compound that gave the iodoform test,[40] and some δ-glucosone.[41]

The first serious study of these oxidations was attempted by Löb.[42] The electrolysis of dextrose was carried on at a lead anode in dilute sulphuric acid in an apparatus suitable for preventing a rise in temperature during the passage of the current. After the electrolysis, in addition to some unaltered dextrose, the solution contained formaldehyde, formic acid, δ-arabinose, δ-arabonic acid, trihydroxyglutaric, gluconic and saccharic acids. Löb then suggested the following scheme in which the primary reaction is the decomposition of the dextrose and the secondary process is the oxidation of these fragments to their respective acids:[43]



The arabinose is probably formed by a degradation of the dextrose,[44]

$$C_6H_{12}O_6 \rightleftarrows C_5H_{10}O_5 + CH_2O,$$

that is the equilibrium between glucose on the one hand with arabinose and formaldehyde on the other is disturbed not only by electrolytic oxygen but also electrolytic hydrogen. Other compounds that have been identified[45] are mannitol and a pentose which forms an osazone melting at 170–172° C. Similarly *l*-arabinose yields formaldehyde with a sugar from which a tetrose (expected according to the theory) has not yet been isolated. Some very valuable conjectures co-relating the mechanism of these oxidations with those which take place biologically have been developed by Löb and his collaborators, in which it is claimed

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[36] Renard, Ann. Chim. et phys., [5], **17**, 303, 313 (1879).
[37] Berthelot, Compt. rend., **87**, 949 (1881).
[38] Maumené, ibid., **101**, 1156 (1895).
[39] O'Brien Gunn, D.R.P. 140318 (1900).
[40] Gladstone and Tribe, Chem. News, **47**, 277 (1883).
[41] C. Neuberg, Biochem. Zeit., **7**, 527 (1908).
[42] W. Löb, Biochem. Zeit., **17**, 132 (1909).
[43] See also Lawrence, Dissert., Cambridge, Mass. (1921).
[44] Löb, Biochem. Zeit., **22**, 103 (1909); Z. Elektrochem., **16**, 1 (1910).
[45] Löb and Pulvermacher, loc. cit.

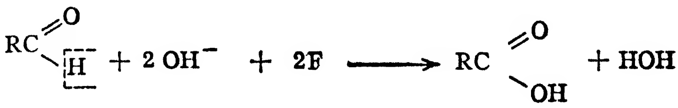
that sugar synthesis is a reversible reaction taking place best in an alkaline solution corresponding to the pH value of the blood.[46]

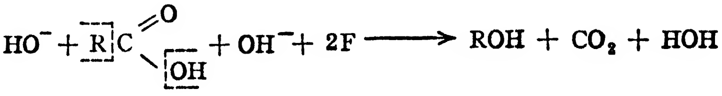
Mannitol[47] and erythritol[48] have been oxidized; the former yielding HCOOH, trioxymethylene, HCHO, a sugar isomeric with glucose and an acid $C_6H_8O_8$ (probably an aldehyde of saccharic acid), but no mannonic acid.

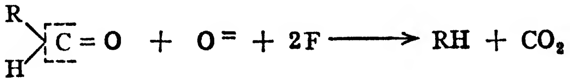
Cane sugar is electrolytically oxidized to a strong acid that has a reducing action. Very little CO_2 and practically no formic nor acetic acids are formed. Dextrin, starch, gum arabic, and collodion produce no noticeable results. These oxidations seem to be stepwise but the steps have not been determined.[49]

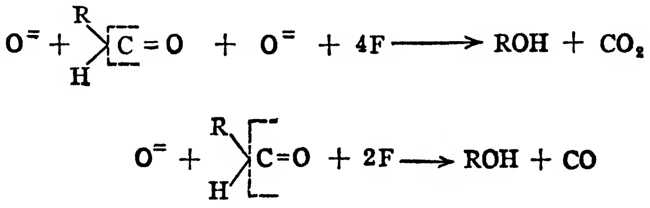
THE OXIDATION OF ALDEHYDES

The lower aldehydes except formaldehyde and isobutyraldehyde when electrolyzed in a dilute sulphuric acid solution at a platinum cathode are oxidized to the corresponding acid, with the evolution of CO and CO_2. The higher aldehydes on the other hand yield some saturated hydrocarbons. Law[50] explains these formations as follows:

1.

$$RC\begin{matrix}\nearrow O\\ \searrow \boxed{H}\end{matrix} + 2\,OH^- + 2F \longrightarrow RC\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + HOH$$

2.

$$HO^- + \boxed{R}C\begin{matrix}\nearrow O\\ \searrow \boxed{OH}\end{matrix} + OH^- + 2F \longrightarrow ROH + CO_2 + HOH$$

3.

$$\begin{matrix}R\searrow\\ H\nearrow\end{matrix}\boxed{C}=O + O^= + 2F \longrightarrow RH + CO_2$$

4.

$$O^= + \begin{matrix}R\searrow\\ H\nearrow\end{matrix}\boxed{C=O} + O^= + 4F \longrightarrow ROH + CO_2$$

$$O^= + \begin{matrix}R\searrow\\ H\nearrow\end{matrix}\boxed{C=O} + 2F \longrightarrow ROH + CO$$

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[46] Löb and Pulvermacher, Biochem. Zeit., **23**, 10 (1909).

[47] Renard, Ann. chim. et phys., (5), **17**, 289 and 316 (1879).

[48] Bizzarini and Campani, Gazz. chim. ital., **13**, 490 (1889).

[49] Brester, Bull. soc. chim., (2), **8**, 23 (1866); Ulsch, Z. Elektrochem., **5**, 539 (1899). See Tommasi, "Traite," 734.

[50] H. D. Law, J. Chem. Soc., **87**, 198 (1905).

From the alcohol the oxidation takes place in the following stages:

$$\begin{tikzcd}
RCH_2OH \arrow[r] \arrow[d] & RCHO \arrow[r] & RCOOH \arrow[d] \\
RCOOH \arrow[rr] & & CO_2
\end{tikzcd}$$

By reactions 2, 3, 5, the alcohols formed would be too small to be detected. But these alcohols are formed during the oxidation of aliphatic acids, as in equation 2,[51] and from this point of view the oxidation would go as in the above scheme. Law thinks that in the oxidation of compounds of the aliphatic series there is a gradual breaking down into compounds containing less and less carbon, till the final stage, CO_2, is reached. Only one step is missing; so far the saturated hydrocarbons have given no oxidation products.[52]

The postulation that formic acid was formed in the electrolytic oxidation of acetaldehyde found verification at the hands of Heimrod and Levene[53] when they electrolyzed the aldehyde in 0.9 normal sodium hydroxide. The percentage of oxygen consumption was 922 per cent according to the equation:

$$2CH_3CHO + 3O_2 \rightarrow 4HCOOH$$

In a neutral salt or an acid solution only acetic acid could be detected. The higher aldehydes as butyraldehyde and isobutyraldehyde in normal sodium hydroxide solution formed only CO_2 with a very little fatty acid because of the slight solubility of the starting material in the electrolyte used.

It has been shown[54] that when a solution of equal volumes of 1 to 4N·NaOH and methanol is electrolyzed in a divided cell using a platinum anode and a c. d. of 0.6 ampere, the products at the anode are formic acid, formaldehyde and 135 cc. of a gas consisting of 97.4 per cent hydrogen, 1.2 per cent oxygen, and 1.4 per cent CO. The amount of gas increased as the electrolysis proceeded. When copper is substituted for the platinum anode no gas evolution takes place. On the other hand, with the platinum anode and formaldehyde no gas is evolved. But with the copper anode and formaldehyde pure hydrogen is evolved in equal amounts at the anode and cathode. The data from the work show that the whole current can be used in effecting the reaction:

$$HCHO + O + 2F = H_2 + CO_2$$

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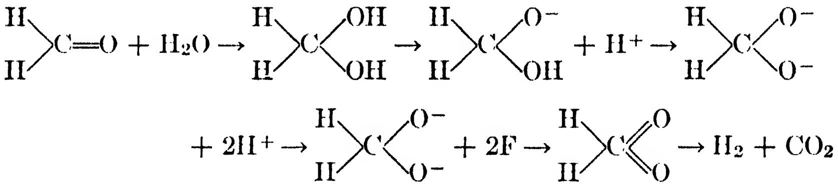
[51] Hofer and Moest, Ann., **323**, 304 (1902); Foerster and Piguet, Z. Elektrochem., **10**, 729 (1904).

[52] Law and Perkins, Trans. Farad. Soc., **1**, 31 (1905).

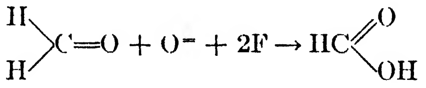
[53] Heimrod and Levene, Ber., **41**, 4443 (1908).

[54] E. Müller and F. Hochstetter, Z. Elektrochem., **20**, 367 (1914).

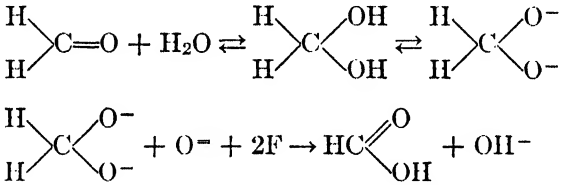
and that this reaction probably consists in the discharge of the ion $H_2CO_2^=$, since formaldehyde in alkaline solution behaves as a dibasic acid. The following scheme may be used to represent the changes:



The other equations according to which no hydrogen is evolved at the anode may be:



or



$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2$$

Another set of potential measurements was made in 100 cc. of 2N·NaOH containing 20 cc. of formaldehyde at a freshly prepared copper anode:

TABLE XII

Minutes.	Potential Toward Normal Electrode.
1	−0.24 volt
2	+0.33
4	0.34
12	0.35
26	0.36
65	0.40
240	0.56

As the electrolysis proceeds the evolution of hydrogen at the anode gradually ceases. Müller [55] has shown that the rate of evolution of hydrogen can be made irregular, but in the ratio of one molecule of hydrogen per faraday used, if the anode is made of copper foil which

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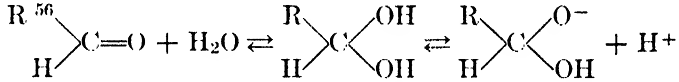
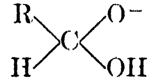
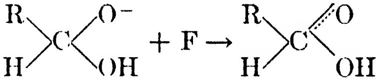
[55] E. Müller, Ann., **420**, 241 (1920).

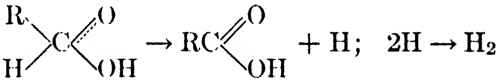
has been covered with molten cuprous chloride and subsequently cathodically reduced in a sodium hydroxide solution. A silver foil anode treated in a similar manner yields the same results. This action also takes place in the presence of certain metallic oxides, such as the oxides of silver and copper, but in these cases there is a period of incubation. The reaction has been extended to acetaldehyde and benzaldehyde, which are also converted into the corresponding acid and gaseous hydrogen. Gaseous hydrogen is evolved in small quantity from alkaline solutions of formaldehyde in the presence of certain metals and in the absence of particular oxidizing agents; the metals, i.e., Cu, Ag, Pt, Pd, Rh, etc., which accelerate the Cannizzaro reaction may be used. The reaction may be:

(6) 

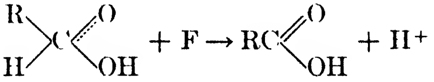
The anion  is discharged forming an unstable compound probably an oxy-aldehyde:

(7) 

which may react in two different ways:

(8) 

i.e., to yield an acid and gaseous hydrogen, or it may also react

(9) 

to form the acid and hydrogen ions. This scheme indicates the formation of an unstable oxyaldehyde, that is one containing an over-saturated carbon atom. If this superoxide decomposes more rapidly according to (8) than according to (9) dehydroxidation is observed. The transformation of aldehyde to acid without the evolution of hydrogen proceeds according to the scheme (6) to (9). Whether the oxidation of the aldehyde in the presence of catalysts causes the evolution of the hydrogen depends on whether the catalyst accelerates reaction (8) more than (9).

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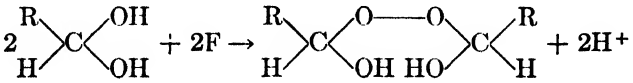
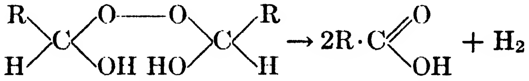
[56] R is an alkyl radical or hydrogen.

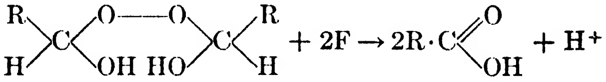
Then too, there may be the formation of an intermediate peroxide (10) whereupon the catalytic effect of the electrode is to decompose the peroxide according to (11) with the evolution of hydrogen at the anode, while the electrolytic oxidation takes place according to (12).

(10) 

$$2\,\begin{matrix}R\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OH\\OH\end{matrix} + 2F \rightarrow \begin{matrix}R\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}O\!-\!\!-\!\!-\!O\\OH\quad HO\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}R\\H\end{matrix} + 2H^+$$

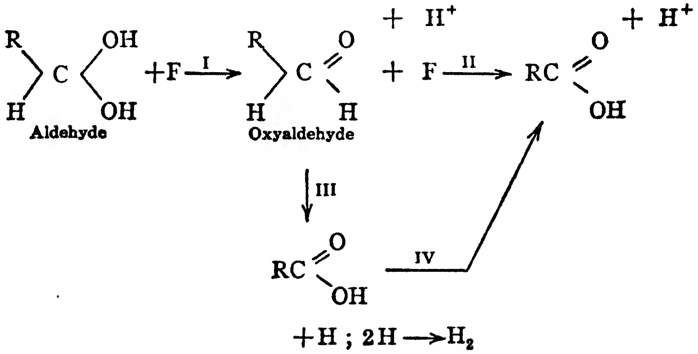
(11) 

$$\begin{matrix}R\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}O\!-\!\!-\!\!-\!O\\OH\quad HO\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}R\\H\end{matrix} \rightarrow 2R\cdot C\!\begin{matrix}\nearrow\!\!\!\!\!\!/\,O\\ \searrow OH\end{matrix} + H_2$$

(12) 

$$\begin{matrix}R\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}O\!-\!\!-\!\!-\!O\\OH\quad HO\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}R\\H\end{matrix} + 2F \rightarrow 2R\cdot C\!\begin{matrix}\nearrow\!\!\!\!\!\!/\,O\\ \searrow OH\end{matrix} + H^+$$

We may therefore write the scheme as being:



I + II = Oxidation and I + III = Dehydroxidation

The oxidation of the aldehyde to acid without hydrogen evolution can go I to II or I to III to IV. Whether the oxidation of the aldehyde in the presence of the catalyst evolves hydrogen depends on whether the catalyst accelerates III more than IV.[57]

An extensive series of potential measurements was made by Müller,[58] which seem to bear out the theory of dehydroxidation. The two reac-

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[57] Acetaldehyde at a Cu anode in alkaline solution did not yield a combustible gas, and at a specially prepared Ag anode gave less than the quantitative amount of combustible gases; less in quantity than HCHO. Benzaldehyde reacted qualitatively like HCHO and CH_3CHO but evolved still less H_2. Without the passage of an electric current Ag_2O in an alkaline solution will evolve H_2 from acetaldehyde and benzaldehyde but in quantities less than the electrolytic method. Müller, loc. cit.

[58] Müller, Z. Elektrochem., **29**, 264 (1923).

tions, i.e., the formation of formic acid alone or formic acid + hydrogen, probably take place under slightly different conditions. The second or dehydroxidation probably requires the formation of an oxyaldehyde which decomposes or is further oxidized as described above. The potential measurements were made with copper and platinum anodes against a standard electrode. The curves are similar to those of methanol and ethyl alcohol, containing breaks and maximum points very much alike but in different positions.

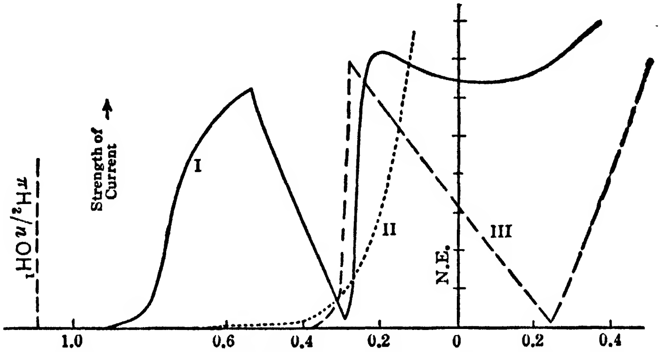
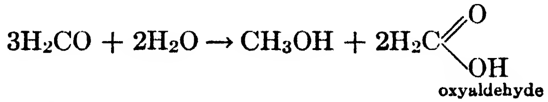


FIG. 5.—Current Potential Curves for Formaldehyde in Alkaline Solution.

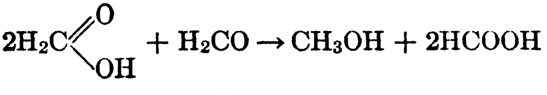
These reactions correspond to the purely chemical oxidations:

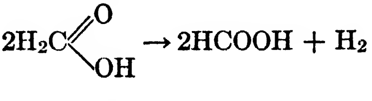
$$2RCHO + H_2O + CuO \rightarrow 2RCOOH + H_2 + Cu$$
$$2RCHO + 2H_2O + Cu^{++} \rightarrow 2RCOOH + H_2 + Cu + 2H^+$$
$$2RCHO + 2CuO \rightarrow 2RCOOH + 2Cu$$

And on this basis Müller[59] studied the catalytic dehydroxidation of formaldehyde by rhodium in an alkaline solution to obtain H_2, formic acid and methanol. The equations which he has set up are:


$$3H_2CO + 2H_2O \rightarrow CH_3OH + 2H_2C\begin{matrix}{\nearrow}O \\ {\searrow}OH\end{matrix}$$

oxyaldehyde


$$2H_2C\begin{matrix}{\nearrow}O \\ {\searrow}OH\end{matrix} + H_2CO \rightarrow CH_3OH + 2HCOOH$$


$$2H_2C\begin{matrix}{\nearrow}O \\ {\searrow}OH\end{matrix} \rightarrow 2HCOOH + H_2$$

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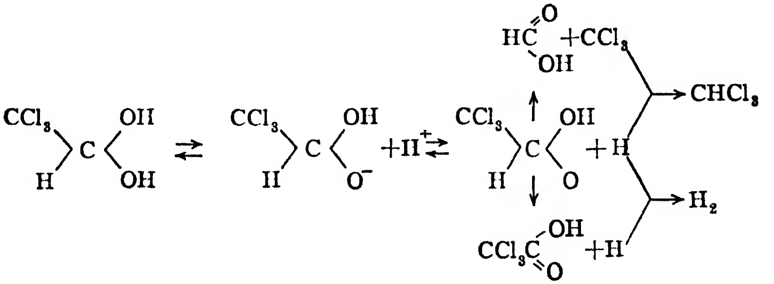
[59] E. Müller, Z. Elektrochem., **27**, 558 (1921).

Peculiarly Pd, Pt, Ag, Cu, do not cause this kind of a decomposition of formaldehyde. The auto-oxidation of trichloroacetaldehyde in the absence of a catalyst has been shown to be along the same lines:[60]



Paraldehyde[61] may be oxidized to acetic acid in dilute (10 per cent) sulphuric acid. The paraldehyde floats on an acid of this strength. The electrolyte may contain oxygen carriers such as the salts of manganese, cerium, molybdenum, vanadium, etc., to the amount of several thousandths of one per cent. A magnetite or platinum anode is used with a porous cathode of retort carbon to decrease the amount of alcohol formed unless it is desired to make ethyl acetate. The acetic acid is distilled off at a rather high concentration or an equal amount of ethyl alcohol is added and the ethyl acetate distilled off in a rectifying apparatus. The residual electrolyte is always available for re-use.

THE OXIDATION OF SOLUTIONS CONTAINING AMMONIA OR AMMONIUM SALTS

The electrolytic oxidation of ammonia and ammonium salts has been carried out by several investigators,[62] but in no case was there a formation of an organic derivative as a carbamide. A variety of electrodes, current densities and other experimental conditions were used. The only compounds found were always ammonium nitrate, nitrous oxide and nitrogen but no organic compounds were obtained. With low concentrations of ammonia along with a good evolution of oxygen the formation of the nitrate predominated. As the concentration of ammonia

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[60] See E. Müller and F. Hochstetter, Z. Elektrochem., **12**, 367 (1914); E. Müller, Ber., **54**, 3214 (1921); Z. physik. Chem., **107**, 347 (1923).

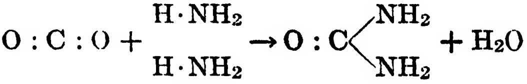
[61] Brit. Pat. 124295, 1919, assigned to Soc. des Acier and Forges de Firming.

[62] Traube and Biltz, Ber., **37**, 3130 (1904); **39**, 166 (1906); E. Müller and F. Spitzer, Ber., **38**, 778 (1905), Z. Elektrochem., **11**, 917 (1905); A. Brochet and G. Boiteau, Bull. soc. chim., [4], **5**, 667 (1909); G. Oesterbeld, Z. anorg. Chem., **86**, 105 (1914); H. B. Seebolm, Dissert., Dresden (1920); Fichter and Kappler, Z. Elektrochem., **15**, 937 (1909).

increased, gaseous oxidation products were evolved in larger quantities together with nitrogen. Current density and temperature have very little influence on the course of the reaction.

In an alkaline solution ammonia is oxidized at a Pt electrode to nitrogen, nitrous oxide and nitrate, but at anodes of Cu, Ni, Co, and Fe, besides nitrogen, some nitrite is formed especially at the copper anode. When copper oxide is present the oxidation goes completely to nitrite without the formation of gaseous compounds. It will not be necessary to go any further into the formation of inorganic nitrogen compounds at this point. We are interested only in the organic derivatives.

In 1885 and 1886 Millot [63] electrolyzed a concentrated solution of ammonia between a cathode of platinum and an anode of retort carbon for several days and was able to isolate from the resulting solution considerable amounts of urea, biuret, and guanidine. The urea was purified by recrystallization from an aqueous alcohol solution, analyzed and identified by conversion to the nitrate and oxalate. The formation of the urea was supposed to have taken place by the union of the ammonia of the solution with the carbon dioxide formed by the oxidation of the carbon anode:



$$O:C:O + \begin{matrix} H\cdot NH_2 \\ H\cdot NH_2 \end{matrix} \rightarrow O:C\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix} + H_2O$$

This work did not receive much credit for the reason that Bartoli and Papasogli [64] were not able to give it the necessary confirmation when an ammoniacal solution of sodium chloride was electrolyzed.

It seems peculiar that all the intervening investigators should not have thoroughly confirmed the work of Millot, but it was not until 1912 that organic compounds could be synthesized from ammonia derivatives by the electrolytic method.[65] It is well known that formamide can be oxidized in an ammoniacal solution to carbamide by purely chemical means, which fact gave Fichter the key to the starting point. The series of compounds primarily formed in the oxidation of ammonia may be indicated as the reverse of the reduction of nitro compounds, i.e.,

$$HNH_2 \rightarrow HNHOH \rightarrow HNO \rightarrow NO_2^- \rightarrow NO_3^-$$

in which scheme HNO has not been isolated.

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[63] Millot, Compt. rend., **101**, 432 (1885); **103**, 153 (1886).

[64] Bartoli and Papasogli, Compt. rend., **102**, 363 (1886).

[65] F. Fichter, Z. Elektrochem., **18**, 647 (1912).

Evidence points to the fact that only those organic compounds, which first form formamide as an intermediate product may be electrochemically oxidized in an ammoniacal solution. The reaction then will be:

$$2NH_2COOH + 2NH_2OH \rightarrow HCONH_2 + H_2N_2O_2 + H_2O$$

and the $HCONH_2$ is further oxidized to carbamide in the presence of an excess of ammonia. Fichter explains the failure to detect hydroxylamine and hyponitrous acid in the reaction mixture as being due to their immediate reduction. Müller and Spitzer[66] found that the gaseous and dissolved products of the oxidation were less by 20–30 per cent than that calculated from the current used, which would be accounted for by the escape of nitrous oxide. Explosion experiments also seem to indicate the presence of nitrous oxide among the gaseous products of the oxidation of an ammonium carbamate solution.

Dry ammonium carbamate, NH_2COONH_4, reacts with dry hydroxylamine, NH_2OH, to form formamide, $H \cdot CONH_2$. Carbamide is formed in the electrolytic oxidation of ammonium formate in aqueous solutions and in liquid ammonia, and also in the electrical oxidation of ammonium acetate. An aqueous solution of formamide yields small quantities of urea on electrolysis. When a saturated solution of ammonium carbonate containing ethyl alcohol is electrolyzed the solution yields, on evaporation, acetamidine nitrate, $CH_3C(:NH)NH_2 \cdot HNO_3$. These facts indicate the direction of the course of the oxidation. The highest yields of urea, though small at best, are obtained when a solution of 12 gram equivalents of ammonia and 8 gram equivalents of ammonium carbamate is oxidized with an anodic c. d. of 13.3 to 55.5 amperes. The yield being about 0.6 gram per 100 ampere hours of current passed, and increases with the concentration of the carbamate and also free ammonia, though the concentration of the latter has more influence than the concentration of the former. The low yields are due to the further oxidation of the carbamide to ammonium nitrate; the yield increasing as the amount of free ammonia in the solution increases. Under these conditions Fichter, Stutz and Greishaber[67] collected the anode gases and analyzed them. At 18° C. with an anodic c. d. of 4.4 amperes the per cent of free oxygen slowly decreases, while the nitrogen increases with the concentration of the free ammonia up to 7 g. equivalents per liter; on further increasing the free ammonia content the amount of nitrogen in the anode gas increases rapidly till at 12 g.

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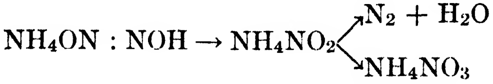
[66] Müller and Spitzer, loc. cit.

[67] Verhand. Naturfors. Ges., Basel, **23**, 222 (1912).

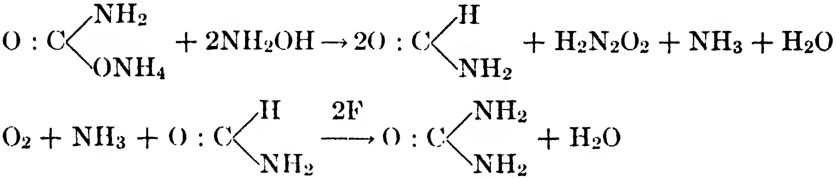
equivalents of ammonia it is 100 per cent of the gas. The scheme of oxidation is:



$$NH_4ON : NOH \rightarrow NH_4NO_2 \left\langle \begin{array}{l} N_2 + H_2O \\ NH_4NO_3 \end{array} \right.$$

$$NH_3 \rightarrow NH_2OH \rightarrow N_2O_2H_2 \rightarrow N_2O + H_2O$$

These steps are confirmed by the analysis of the electrode gases. The scheme for the formation of carbamide by the electrolytic oxidation of ammonium carbamate is:

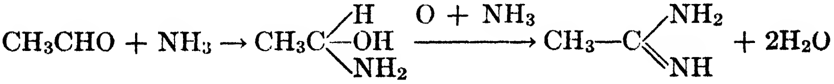


$$O : C \left\langle \begin{array}{l} NH_2 \\ ONH_4 \end{array} \right. + 2NH_2OH \rightarrow 2O : C \left\langle \begin{array}{l} H \\ NH_2 \end{array} \right. + H_2N_2O_2 + NH_3 + H_2O$$

$$O_2 + NH_3 + O : C \left\langle \begin{array}{l} H \\ NH_2 \end{array} \right. \xrightarrow{2F} O : C \left\langle \begin{array}{l} NH_2 \\ NH_2 \end{array} \right. + H_2O$$

At first Fichter, Stutz and Greishaber[68] considered that formamide is produced by the interaction of hydroxylamine of electrochemical origin with ammonium carbonate, and then it in turn is oxidized electrolytically in the presence of ammonia to carbamide. There seems to be ample evidence that the formamide was an intermediate product. By purely chemical methods, i.e., by the action of ammoniacal potassium permanganate on oxyacids, ketones, and ketonic acids, and other compounds that yield CO on oxidation, a certain amount of urea may be formed. When in the oxidation of ammonium carbamate the electrodes are noticeably attacked, especially in the case of a mercury cathode, a compound, $OHg_2NH_2CO_3$, may be isolated. The best yields of urea are obtained with carbon electrodes in which case the formamide is markedly attacked, with the formation of oxidation products. The addition of methanol prevents the formation of these decomposition products in large quantities. A good part of the ammonia is oxidized to hyponitrite, nitrite, nitrogen, and nitrate when methanol is added; but on the addition of ethyl alcohol to the aqueous ammoniacal solution a small quantity of acetamidine nitrate may be isolated. The yield is increased by the addition of ammonium nitrate; though sometimes without this addition there is no yield at all:

$$CH_3CH_2OH \rightarrow CH_3CHO;$$



$$CH_3CHO + NH_3 \rightarrow CH_3C \left\langle \begin{array}{l} H \\ OH \\ NH_2 \end{array} \right. \xrightarrow{O + NH_3} CH_3{-}C \left\langle \begin{array}{l} NH_2 \\ NH \end{array} \right. + 2H_2O$$

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[68] Fichter, Stutz and Greishaber, loc. cit.

This latter compound is obtainable by purely chemical methods when acetamide is heated with ammonium nitrate in liquid ammonia for 12 hours in a sealed tube; it can also be made by oxidizing acetaldehyde ammonia with calcium permanganate, ammonium persulphate, or hydrogen peroxide, and can be isolated only after an excess of ammonia and ammonium salts have been used. When propyl alcohol is electrolytically oxidized in aqueous ammoniacal solution as above, some propionamidine nitrate, $CH_3CH_2C(NH)NH_2 \cdot HNO_3$, may easily be isolated. It is readily crystallized from alcohol (being soluble in water and alcohol) and melts at 126–127° C., being identical with Primer's compound.[69] Similar compounds are obtained from butyl alcohol though the amount of amidine nitrate formed decreases as the number of carbon atoms in the alcohol increases; the aromatic alcohols form no amidine compounds at all.

Renewing the work of Fichter et al. in 1916 [70] it was believed that formamide is not an intermediate product in the formation of urea from ammonium carbamate for the reason that the latter is not reduced chemically by hydroxylamine. However CO_2 reacts with hydroxylamine as it does with ammonia, and, according to the conditions, forms either the hydroxylamine carbamate or the dihydroxylamine salt of hydroxycarbamic acid, respectively:

$$NH_2COOH \cdot NH_2 \quad \text{or} \quad HONH \cdot COOH \cdot NH_2OH$$

When ammoniacal solutions of ammonium carbamate are electrolyzed with a diaphragm to separate the anolyte from the catholyte, urea is formed only at the anode, without any traces of some reduction products as formic acid or formamide. This is considered as evidence that the formation of formamide is not a necessary intermediate step.

Drechsel [71] obtained urea by the electrolysis of a solution of ammonium carbonate with an alternating current, and considered that the reaction was possible only with an alternating current. However, if certain conditions are fulfilled, a direct current may be used to convert the ammonium carbonate into urea, the reaction being an anodic oxidation reaction.[72] The volatilization of the ammonia is prevented by strong cooling with an ice bath, the heat of reaction set free at the anode must be removed rapidly by local cooling of the electrode, under which conditions some urea is formed. The reaction is also possible by purely chemical means; by oxidizing an ice cold solution of a mixture of ammo-

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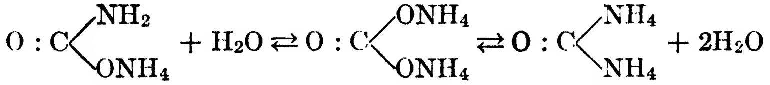
[69] Primer, Ber., **17**, 178 (1884).

[70] Fichter, Steiger and Stannisch, Verh. Nat. Ges., Basel **28**, ii, 66 (1916); an excellent discussion of all reactions involved is given in this paper.

[71] Drechsel, J. prakt. Chem., [2], **22**, 476 (1880).

[72] Fichter, Z. Elektrochem., **24**, 41 (1918).

nium carbonate and ammonium carbamide with calcium permanganate, hydrogen peroxide, or ozone. It seems that the reaction is entirely similar to that occuring in the living organism and an anodic oxidation:



$$O : C\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown ONH_4} + H_2O \rightleftarrows O : C\genfrac{}{}{0pt}{}{\diagup ONH_4}{\diagdown ONH_4} \rightleftarrows O : C\genfrac{}{}{0pt}{}{\diagup NH_4}{\diagdown NH_4} + 2H_2O$$

So it is shown that this field in general is still open for more conclusive work in the development of a theoretical background.

THE ELECTROLYTIC OXIDATION OF CYCLIC AMMONIUM BASES

In only a few cases in which the electrolytic methods of oxidation have been tried, have better results been obtained than in the purely chemical oxidation. A tar sometimes forms which causes much trouble in isolating the oxidation product. In other cases the yields are very much more satisfactory. N-methyl-α-pyridone and N-methyl-α-quinolone have been prepared by the electrolytic oxidation of the respective pyridinium and quinolinium sulphates at an iron anode in a sodium hydroxide catholyte using a divided cell. The sodium hydroxide had a specific gravity of 1.15; the current was 3 amperes at 28 volts. Without the addition of an oxygen carrier there was only an evolution of gaseous oxygen at the anode; when a carrier such as potassium ferricyanide was added there was no evolution of oxygen and no formation of tar.[73] This method was later revised so as to allow the formation of larger amounts of the desired compounds.[74] The potassium hydroxide solution used as catholyte had a sp. gr. of 1.7. The same catalyst was used but in some cases the sodium hydroxide was replaced by potassium or barium hydroxides with equally good results. If a tar started to form during the course of the oxidation it could be prevented from causing further damage by adding to the catholyte some concentrated sodium hydroxide solution. The following compounds have been studied: N-methyl-o-toluquinolinium hydroxide to N-methyl-o-toluquinolone; N-methyl-naphthoquinoline to N-methyl-naphthoquinolone; N-methylacridine to N-methylacridone. The method has been further improved by changing the preparation of the starting materials a little and working in a more dilute solution.[75] The following oxidations were accomplished: N-methyl-8-methoxyquinoline to 8-methoxy-1-methyl-2-quinolone; N-methyl-6-methoxyquinoline to 6-methoxy-1-methyl-2-quinolone.

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[73] O. Fischer and K. Neundlinger, Ber., **46**, 2544 (1913).

[74] K. Neundlinger and M. Chur, J. prakt. Chem., [2], **89**, 466 (1914).

[75] O. Fischer and M. Chur., J. prakt. Chem. [2], **93**, 363 (1916).

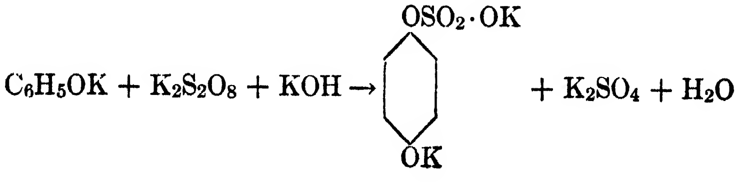
CHAPTER VI

THE ELECTROLYTIC OXIDATION OF NON-IONIZED SUBSTANCES—PART II

OXIDATION OF AROMATIC COMPOUNDS

OXIDATION OF THE NUCLEUS

THE definite oxidation of the ring in cyclic compounds is a difficult task for the reason that the oxidation either does not touch the nuclear carbon atoms or else it breaks the ring. Under certain conditions either the ring or the side chain may be oxidized electrolytically with very excellent results. In the oxidation of the ring, the first step is usually the introduction of a hydroxyl group followed by the oxidation of this to quinone, etc. The oxidation of benzene in a sulphuric acid solution yields at the anode hydroquinone; aniline is oxidized to *p*-aminophenol, azobenzene to tetrahydroxybenzene, anthraquinone to alizarine, etc. Elbs[1] concludes that the formation of the above hydroxyl derivatives may be due to the action of nascent persulphuric acid electrolytically formed at the anode. He makes this assumption because many organic compounds, especially the aromatic series, are changed in this manner by the action of persulphates. For example, nitrophenol yields nitrohydroquinone on oxidation with ammonium persulphate or on electrolytic oxidation in acid, neutral or alkaline solution. Potassium persulphate in alkaline solution reacts on phenol, which has its *p*-position free, to form the potassium salt of the sulphuric acid ester of *p*-dihydroxybenzene, i.e., the potassium salt of hydroquinone sulphuric ester:



$$C_6H_5OK + K_2S_2O_8 + KOH \rightarrow C_6H_4(OSO_2\cdot OK)(OK) + K_2SO_4 + H_2O$$

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[1] Elbs. J. prakt. Chem., [2], **48**, 179 (1893); E. Schering, D.R.P. 81068, 81297, 81298 (1894).

which is readily hydrolyzed by acids into hydroquinone and sulphuric acid.

The Oxidation of Compounds Containing a Single Ring.—With an alternating current between platinum electrodes, E. Drechsel [2] was able to isolate from a solution of phenol in weak sulphuric acid a large variety of oxidation products among which were hydroquinone, catechol, *p*-biphenol, oxalic acid, formic acid; as reduction products, cyclohexanone, succinic acid; as dehydration products: phenyl hydrogen sulphate besides which were detected butyric, *n*-valeric and malonic acids. It is well understood now that these products of Drechsel are not strictly the results of the alternating current, but that they are formed by oxidation and reduction reactions, and may be also obtained by the use of a direct current.

Benzene.—Gattermann and Friedrichs [3] electrolyzed a mixture of 20 g. of benzene, 65 cc. of alcohol and 15 cc. of 50 per cent sulphuric acid for two days at a potential of 6 volts and obtained 2 g. of hydroquinone. Since the solvent alcohol is in itself an excellent depolarizer, the low yield of hydroquinone probably was due to the oxidation of the solvent. Kempf [4] was able to obtain quinone directly from benzene by using a lead peroxide anode without the use of an alcoholic solvent. He worked with a suspension of benzene in 10 per cent sulphuric acid, stirring violently during the passage of the current. The quinone formed at the anode diffused to the cathode and there in the same cell at a cathode of Pb or Zn was easily reduced to hydroquinone.

In an atmosphere of carbon dioxide a solution of benzene in twice normal sulphuric acid at 60° yielded at a platinum anode a small quantity of phenol together with some *o*- and *p*-dihydroxy benzene and a residue insoluble in sulphuric acid but soluble in benzene, being probably $(HO)_2C_6H_3COOH$.[5]

Technical methods have been developed for the preparation of quinone and hydroquinone with 70 per cent yields.[6]

Still better yields of quinone are claimed by Inoue and Shikata [7] when 10 g. of benzene in 100 cc. of 4 per cent sodium sulphate are electrolyzed on a Pb anode with a c. d. of 2–3 amperes at 3–5 volts,

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[2] E. Drechsel, J. prakt. Chem., [2], **29**, 229 (1884); **34**, 135 (1886); **38**, 65 (1888).

[3] Gattermann and Friedrichs, Ber., **27**, 1942 (1894); see also Renard, Compt. rend., **91**, 175 (1880); Liebmann, Z. Elektrochem., **2**, 497 (1896); D.R.P. 117129 (1900), Boehringer. Renard did not identify a compound melting at 171°.

[4] Kempf, D.R.P. 117251 (1899); W. Lang, D.R.P. 189178.

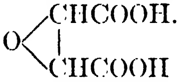
[5] Fichter and Uhl, Helv. Chim. Acta, **3**, 22 (1920).

[6] U.S.P. 1322580 (1919), Kitchen; C. Claudius, Rev. prod. chim., **21**, 219 and 288 (1918); U.S.P. 808095 (1905).

[7] H. Inoue and M. Shikata, J. Chem. Ind., Japan, **24**, 567 (1921).

keeping the temperature below 20° C. If only 1 per cent of sodium acetate is added to the anolyte the yields are increased to 81.5 per cent, and the product is not contaminated by anything which can not be removed by simply washing with water.

In the electrolytic oxidation of benzene the first product formed is probably phenol, but this cannot be isolated because it is a better depolarizer than benzene, due to its greater solubility in the electrolyte. Quinol on further oxidation forms the relatively stable *p*-benzoquinone which is the main product of the reaction together with some maleic acid when a diaphragm is used. However, if no diaphragm is used this quinone is continually changed back to quinol at the cathode.[8]

p-Benzoquinone.—Kempf [9] oxidized a solution of *p*-benzoquinone in 10 per cent sulphuric acid with a current of 4–5 amperes. The results were the formation of maleic, formic, racemic and tartaric acids, CO and CO_2 with sometimes an acid of the molecular formula, $C_4H_4O_5$ melting at 141.5°–145.5° (corr.) the barium salt being $C_4H_2O_5Ba \cdot 2H_2O$. The free acid is probably maleglycidic acid:  $\mathrm{O}\left\langle\begin{array}{l}\mathrm{CHCOOH.}\\ |\\ \mathrm{CHCOOH}\end{array}\right.$ These products are similar to those obtained [10] by the oxidizing action of H_2O_2 and Ag_2O_2, which leads Kempf to the conclusion that in all electrochemical oxidation processes, the actual oxidizing agent is a metallic oxide formed by the action of nascent oxygen on the electrode. But this is hardly in accordance with the work of Fichter and Stocker,[11] who were able to obtain the same products using either platinum, lead, or graphite electrodes in a dilute sulphuric acid suspension of benzene. The results show that the use of a lead electrode increases the amount of quinol and quinone formed, but qualitatively the results are the same with all the electrodes. It may be that the lead dioxide formed changes the equilibrium in favor of the quinol and quinone, as well as the primary oxidation of the benzene. In the case of the graphite electrodes the conception of an intermediately formed catalytic superoxide is impossible. Elbs [12] considered that the electrochemical oxidation of aromatic compounds in many cases depended on the formation of intermediate persulphuric acid, but Fichter and Stocker have found that the same qualitative results are obtained when the electrolyte is aqueous phosphoric acid, or aqueous persulphuric acid. It is unlikely that genuine

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[8] An excellent bibliography on the oxidation-reduction potential of the system quinol-quinone is given by E. Biilmann, Trans. Faraday Soc., **19**, 690–691 (1924).

[9] Kempf, J. prakt. Chem., [2], **83**, 329 (1911).

[10] Kempf, Ber., **38**, 3963 (1905); **39**, 3715 (1906).

[11] Fichter and Stocker, Ber., **47**, 2003 (1914).

[12] Elbs, loc. cit. See page 102.

peracids are produced under such conditions from either of these acids. A peracid of the former is more improbable than a peracid of the latter.

In the case of benzene, on account of its slight solubility even in organic solvents, the anode reaction is very slow and incomplete. The oxidation products resulting from the passage of the current, however, dissolve much more readily in the solvent, so that some of the benzene is completely oxidized long before all of the benzene has been attacked by anodic oxygen. Such conditions are exceedingly unfavorable from an electrochemical point of view. To oxidize benzene a certain oxidation potential is necessary, which could be closely regulated if it were possible to get a larger amount of benzene in solution and so bring up the concentration of benzene available as a depolarizer. Since this has not yet been accomplished it is practically impossible to observe the first step in the electrolytic oxidation of benzene. It is however probable that the first step is the formation of phenol which then undergoes a further immediate oxidation.[13]

Phenols.—In the first study of the electrolytic oxidation of phenol the results were not interpreted; they were only stated as experimental data.[14] It was found that salts of phenol behaved as if they were the salts of aromatic acids; they regenerated the free acid and evolved oxygen. At coke, graphite, or Pt anodes in an alkaline solution a compound, $C_7H_6O_4$ melting at 93° C. and having acid properties, was isolated. With the first mentioned anode there was a deep-seated oxidation of the phenol with the formation of a resin. A neutral solution of phenol such as potassium phenolate, gave a compound, $C_{65}H_{48}O_{22}$, which was soluble in alkali but insoluble in acids. Neutral sodium phenolate yielded a compound, $C_{29}H_{20}O_8$.

A more complete study has been made in which the conditions of c. d. and concentration of depolarizer were regulated carefully. The first two compounds obtained were diphenols: *o,p′*-diphenol and *p, p′*-diphenol which are intermediate in the formation of catechol and hydroquinone.[15]

The electrochemical oxidation of *p, p′*-diphenol on Pb electrodes was very slow owing to its very small solubility in H_2SO_4, but the final product was quinol. Under similar conditions the *o,p′*-diphenol was more readily oxidized to catechol and quinol. The scheme for these reactions has been indicated as: [16]

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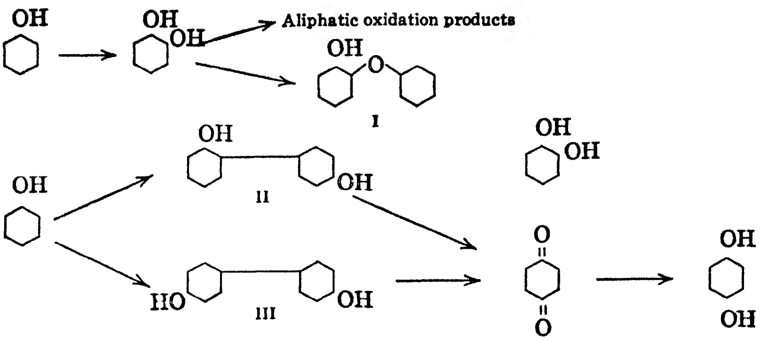
[13] See F. Fichter, Trans. Am. Electrochem. Soc., **45**, 107 (1924).

[14] Bartoli and Papasogli, Gazz. chim. ital., **14**, 1-3 (1884); Bunge, Ber., **3**, 296 (1870).

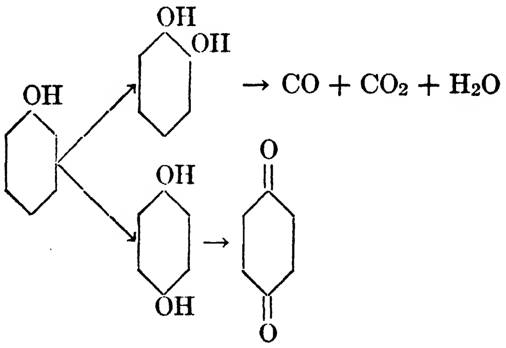
[15] Fichter and Stocker, loc. cit.

[16] Fichter and Brunner, Bull. soc. chim., (4), **19**, 281 (1916).



Pyrocatechol always appears in such small quantities, that, although it can be identified by its typical color reactions with ferric chloride, and by being precipitated by lead acetate, its quantitative determination yields no trustworthy values. Owing to its greater depolarizing power it can never accumulate in large quantities in the presence of hydroquinone. When subjected to further oxidation (just as in the case of hydroquinone) it finally has its nucleus disrupted to form fumaric acid; or if the anode and cathode are not separated by a diaphragm to succinic acid. As to the original exact proportions of hydroquinone and pyrocatechol, no definite statement can be made. Possibly they are formed in the same amounts, or even the pyrocatechol may predominate as in the purely chemical oxidation with hydrogen peroxide by Cross, Bevan and Heidberger.[17]

Fichter [18] was able to change the yield but not the product by changing the anode material from platinum to lead dioxide or graphite. He found the products to be similar to those obtained by the oxidation of benzene with hydrogen peroxide, in both cases being:



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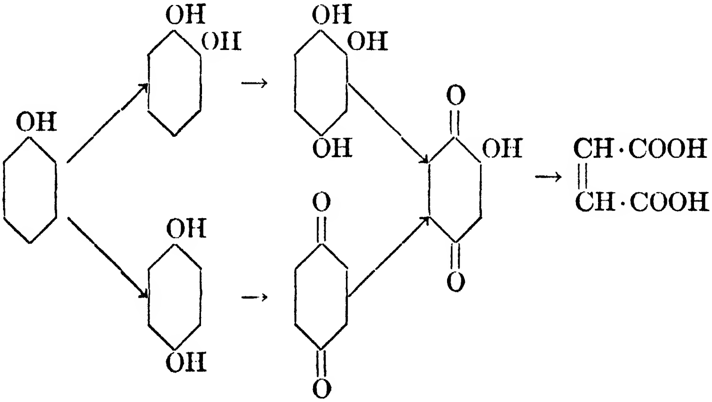
[17] Cross, Bevan and Heidberger, Ber., **33**, 2015 (1900).
[18] Fichter, Z. Elektrochem., **19**, 781 (1914).

Continuing their study of the oxidation of phenol Fichter and Ackermann [19] oxidized a solution of catechol in 0.5 normal sulphuric acid at lead electrodes with a c. d. of 2.0 amperes without a diaphragm to form the products CO, CO_2, and a volatile liquid having the odor of butyric acid which was really a mixture of butyric acid with lower homologues, particularly formaldehyde and succinic acid. When a diaphragm was used the products contained some fumaric acid. (Succinic acid by the way is rather stable toward electrolytic oxygen.) These results are in perfect accord with the results of both Drechsel and of Kempf,[20] though the latter obtained maleic and racemic acids instead of fumaric acid. It may be that the maleic acid is the oxidation product of the system hydroquinone-quinone while the fumaric acid is the product of the oxidation of catechol. Butyric acid is only obtained in the electrochemical oxidation of catechol and not from the oxidation of quinol which shows that catechol is present in the oxidation of phenol. The only conclusion about the formation of this acid is, that it is formed by the oxidation of a first formed reduction product of catechol. If it were formed by the reduction of an oxidation product of catechol we should have the formation of butyric acid from quinol which is an oxidation product of catechol. On a well prepared lead, but even more rapidly on a thickly and freshly platinized-platinum cathode, catechol is reduced to cyclohexanol. The further oxidation of cyclohexanol yields the odor of butyric acid and also some maleic acid,



Without a diaphragm the cathodic action protects the system quinone-quinol, the former not being attacked by anodic oxygen, while the catechol is attacked so that after electrolyzing for some time a considerable amount of quinol is formed with corresponding loss of catechol.

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[19] Fichter and Ackermann, Helv. Chim. Acta, **2**, 583 (1919).

[20] Drechsel, loc. cit.; Kempf, J. prakt. Chem., [2], **83**, 329 (1911).

Hydrogen peroxide reacts with phenol to form catechol.[21] The electrode potential values which showed that at low concentrations quinol is a more active depolarizer of a platinum electrode in twice normal sulphuric acid than catechol but at concentrations above 0.05 normal acid the reverse is true.[22]

TABLE XIII

Cell: Pt | $2N \cdot H_2SO_4$ | $N \cdot KCl$ | Hg_2Cl_2 | Hg

E.M.F. = 0.286 volt, of the Pt electrode = + 0.571 volt

Concentration in Mols per Liter	Pyrocatechol		Hydroquinone	
	E.M.F., Volt	ϵ_h Volt	E.M.F., Volt	ϵ_h Volt
0.0015	0.277	+0.562	0.270	+0.555
0.003	0.272	0.558	0.266	0.551
0.006	0.269	0.554	0.265	0.550
0.0125	0.266	0.551	0.263	0.548
0.025	0.263	0.548	0.260	0.545
0.05	0.259	0.545	0.259	0.544
0.1	0.256	0.541	0.257	0.542
0.2	0.253	0.538	0.256	0.541
0.4	0.249	0.534	0.254	0.539

In a neutral solution phenol is no longer a depolarizer, though catechol is a stronger depolarizer than quinol. From this work it is very evident that no conclusions can be drawn as to the relative amounts of the substances which are to be formed. However by determining the amount of CO_2 formed in the electrolytic oxidation of phenol, quinol, and catechol, we must come to the conclusion that equal amounts of catechol and quinol are formed in the oxidation of phenol.

TABLE XIV

5.5 g. pyrocatechol in 60 cc. $0.5N$ H_2SO_4, Pb anode with c. d. = 0.02 amp.

Current in Ampere-hours	Without a Diaphragm		With a Diaphragm	
	G. of CO_2	G. of CO_2 per Ampere-hour	G. of CO_2	G. of CO_2 per Ampere-hour
1	0.1566	0.1566	0.1712	0.1712
6	1.3326	0.2221	1.4514	0.2419
13.4	3.1961	0.2385	3.3234	0.2480

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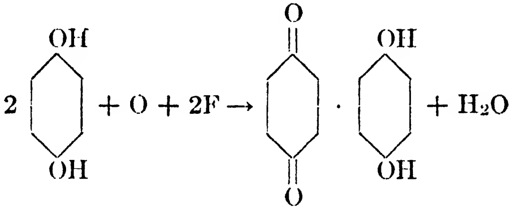
[21] C. F. Cross, E. J. Bevan, T. W. Heidberg, Ber., **33**, 2015 (1900); Martinon, Bull. soc. chim., (2), **43**, 156 (1885).

[22] Fichter and Ackermann, loc. cit.

Besides the products already mentioned as the results of the oxidation of phenol a number of complex substances have been isolated, such as: *o*-hydroxyphenyl ethers, diphenyl, tetrahydroxydiphenyl, and dihydroxydiphenyl ester, $HO \cdot C_{12}H_8OC_{12}H_8 \cdot OH$, and a reduction product cyclohexanol.

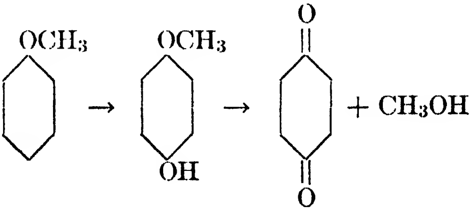
The oxidation of hydroxyquinol yielded succinic acid but no odor of butyric acid. It was first assumed that catechol was oxidized to *o*-quinone but on oxidizing pure *o*-quinone only formic acid was obtained.

Quinol, when oxidized at a platinum or carbon anode[23] in an aqueous solution of sulphuric acid yields, even without a diaphragm, quinhydrone almost quantitatively,



as an intermediate product between quinone and quinol with only traces of quinol. An alternating current produces excellent yields of quinhydrone since at both electrodes there is an evolution of hydrogen. The reason why Drechsel[24] isolated with an alternating current so much catechol in the electrolysis of phenol must be due to the fact that the alternating current tended to check the increase in oxidation potential of the electrodes. The presence of oxygen carriers such as manganese salts or nitric acid leads to the formation exclusively of quinone.[25]

Phenol ethers have also been studied to some extent.[26] Anisole in twice normal H_2SO_4 at a lead dioxide anode without a diaphragm yields hydroquinone and quinhydrone; but with a diaphragm yields 29 to 71 per cent material and 23 to 87 per cent current yields of quinone and methanol.



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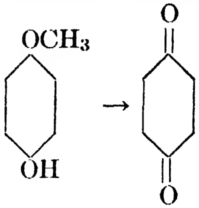
[23] Liebmann, Z. Elektrochem., **2**, 497 (1896).

[24] Drechsel, loc. cit.

[25] Boehringer, D.R.P. 117129 (1900).

[26] Fichter and Dietrich, Helv. Chim. Acta, **7**, 131 (1924).

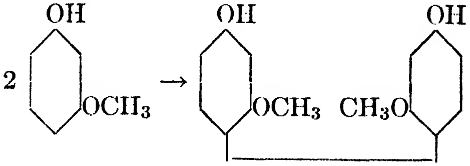
This was supported by the oxidation of *p*-hydroxyanisole to quinone:



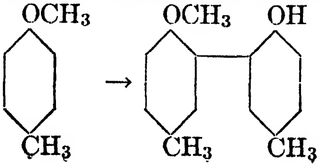
There is a disruption of the nucleus shown by the evolution of small amounts of CO_2. No guaiacol nor pyrocatechol have been detected. At a Pt anode a little quinone and formaldehyde with much CO_2 are formed. Phenetole and phenol isoamyl ether have similarly been oxidized. All three ethers give as the main product quinone, by the splitting off of the alkyl residue; in the case of anisole to form the alcohol but in the other two cases to form the corresponding acid and CO_2. The yields are less with the increase in the molecular weight probably due to the decrease in their solubility so that the required potential is too high for a maximum formation of quinone without a further destruction of the molecule.

The dimethyl ether of hydroquinone yields methylquinone besides methanol and CO_2, but the yields are low. Guaiacol with a diaphragm yields pyrocatechol, CO_2 and fumaric acid but without a diaphragm yields succinic acid in place of fumaric acid. The yields of this latter acid are larger from guaiacol than from catechol.

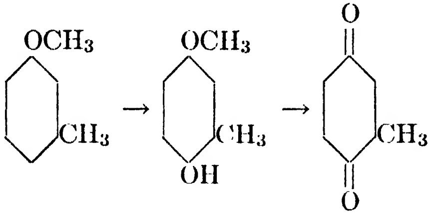
When the duration of the oxidation is short, diphenol[27] derivatives are formed in large amounts as an oily layer; but as the anodic action continues these diphenols are oxidized and destroyed. On this basis a short time oxidation of guaiacol yields some diguaiacol. Veratrole yields diveratrole, catechol and succinic acid, showing that the compound is practically demethylated. Resorcin monomethyl ether yields diresorcin dimethyl ether, etc.,



The methyl ether of *p*-cresol is partially demethylated as follows:



and the same ether of *m*-cresol does not form a double molecule,[27] but the oxidation is:



Of the triphenols hydroxyquinol (see above) and pyrogallol have been studied [28] and the latter substance yields purpurogallin in 45 per cent current yields which is very much better than any present chemical method. It was hoped to discover some intermediate products between pyrogallol and purpurogallin and so partially clear up the constitution of the latter, but no intermediate products could be obtained. The purpurogallin prepared electrolytically is the same as that prepared by Gerard [29] by the action of potassium permanganate and sulphuric acid on pyrogallol. A naphthalene derivative was also formed which is rather remarkable though not unique, for Zincke and Branke [30] prepared dibromo-β-naphthaquinone carboxylic acid by the action of nitric acid on bromoprotocatechuic acid. During the formation of these substances, it appears likely that a certain quantity of the phenol is converted by oxidation into an open chain compound, which then condenses with the phenyl residue. The highest yields were 46.4 per cent of the theoretical amount based on material used. Peroxidized lead anodes do not give good results probably because the potential at which oxygen is yielded is too high causing a too vigorous oxidation of the ring.

It might be well to mention here the oxidation of a derivative of pyrogallol namely, gallic acid, 3,4,5-trihydroxybenzoic acid. The chemical oxidation gives very pure yields of purpurogallincarboxylic acid which led A. G. Perkin and F. M. Perkin [31] to study its electro-chemical oxidation.

The homologues of benzene are sometimes attacked in the nucleus and sometimes in the side chain, and sometimes in both places. The oxidation of toluene being as follows: [32]

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[27] Fichter, Trans. Am. Electrochem. Soc., **45**, 107 (1924).

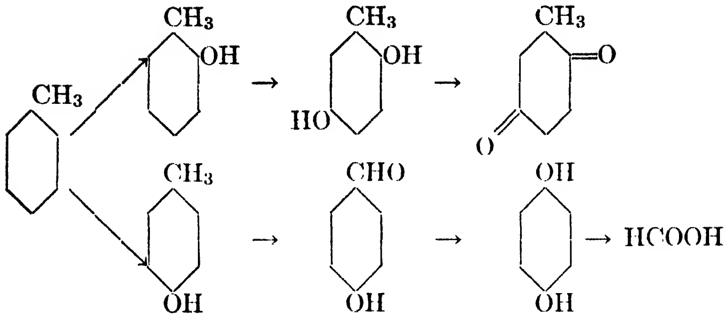
[28] Rotondi, Jahresber. f. Chem., 223 (1883); A. G. Perkin, J. Chem. Soc., **83**, 192 (1903); A. G. Perkin and F. M. Perkin, ibid., **85**, 243 (1904).

[29] Gerard, Ber., **2**, 562 (1869).

[30] Zincke and Branke, Ann., **293**, 120 (1896).

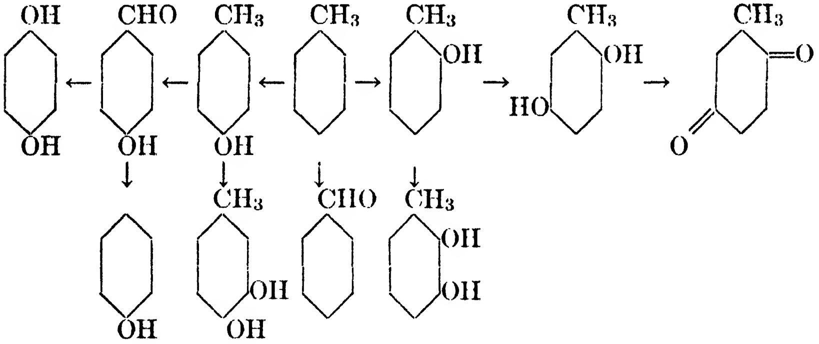
[31] A. G. Perkin and F. M. Perkin, J. Chem. Soc., **85**, 243 (1904).

[32] F. Fichter, Z. Elektrochem., **19**, 781 (1914). However, Perkin, "Practical



This set of reactions is not the same as those obtained by Law and Perkin as described later under the heading of the oxidation of side chains (page 122, et. seq.)

Fichter and Stocker [33] were able to detect compounds formed in the electrolytic oxidation of toluene which indicated that the course of the oxidation might be:



This scheme has been corroborated by the results obtained with *o*- and *p*-cresol [34] (which see). In the products of the oxidation the following were isolated: toluoquinone (by reduction with sulphur dioxide to toluoquinol), some small amounts of phenol, benzaldehyde, and quinol. The products isolated from the oxidation of *p*-xylene were *p*-toluic aldehyde (the only one obtained by Law and Perkin),[35] *p*-xyloquinol, *p*-xylylenedioxide, and a material melting at 160–161° C., which gave no reaction for a phenol but was probably identical with the

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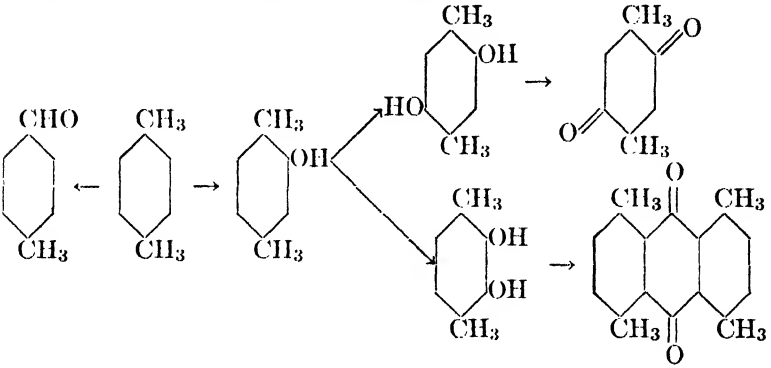
Methods," p. 280, obtained only an aldehyde and a resin with no oxidation of the nucleus.

[33] Fichter and Stocker, Ber., **47**, 2003 (1914).

[34] The oxidation of *p*-hydroxybenzaldehyde to quinol and formic acid has also been accomplished by purely chemical oxidation by Dakin, using hydrogen peroxide; Dakin, Am. Chem. J., **42**, 477 (1909).

[35] Law and Perkin, J. Chem. Soc., **91**, 258 (1907).

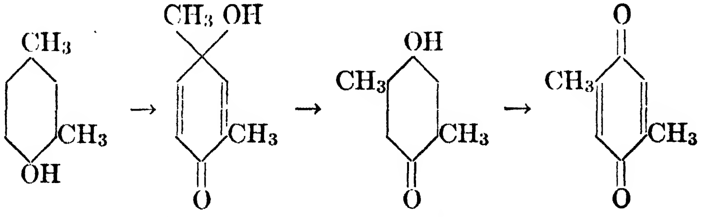
diphenylene dioxide of Ullmann and Stein[36] and which was probably formed by dehydration of two molecules of dimethyl catechol and the subsequent coupling of the residues. The scheme for the electrolytic oxidation of *p*-xylene will therefore be:



The electrolytic oxidation of *p*-xylene is very unsatisfactory because of its insolubility in the electrolyte. The greater part of the electrolytic oxygen does not attack the dissolved material but is evolved as gaseous oxygen.

p-Xylene has yielded an aldehyde, an alcohol and a resin[37] while later *p*-xyloquinone, *p*-xylenedihydroxide and the aldehyde were obtained.[38] Then the oxidation of the methyl group was investigated with the result[39] that 6.4 per cent *p*-toluic acid and 26 per cent of *p*-toluic aldehyde were obtained at a platinum anode using a c. d. 1.5 ampere.

On the other hand *m*-xylene is oxidized to *p*-xyloquinone which was[40] thought at first to be due to the inevitable presence of *p*-xylene even in the purest *m*-xylene. But when especially prepared pure *m*-xylene was used the formation of *p*-xyloquinone was even more pronounced. The scheme is probably:



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[36] F. Ullmann and A. Stein, Ber., **39**, 622 (1906).

[37] Law and Perkin, J. Chem. Soc., **91**, 258 (1907).

[38] Fichter and Stocker, Ber., **47**, 2018 (1914).

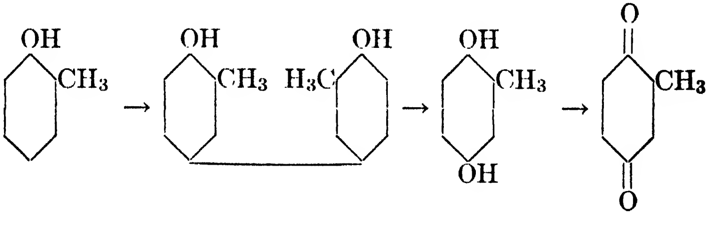
[39] Fichter and Grisard, Helv. Chim. Acta, **4**, 928 (1921).

[40] Fichter and Meyer, Trans. Am. Electrochem. Soc., **45**, 107 (1924.)

Several substituted phenols have also been studied. Trichlorophenol electrolyzed at a Pt anode in a suspension in twice normal sulphuric acid at 70° yielded small amounts of 2,6-dichloroquinol, which is also formed by the purely chemical action of nitric acid [41] or nitrous acid [42] on trichlorophenol.

Since, by electrolytic oxidation, benzene is easily hydroxylated to form quinol and then the quinol is further oxidized to quinone it seems possible that toluene should be first hydroxylated to cresol which is then further oxidized in the same manner as the quinol above. The products of the oxidation of toluene indicated that this is true. Cresol and toluene however should yield the same products if cresol is an intermediate product. A solution of *o*-cresol yields 5.4 per cent of toluquinol. On the other hand when *p*-cresol is used in place of the *o*-cresol the product is not a toluoquinol but is a mixture of phenol and quinol. That is, when the *p*-position is closed by a methyl group, this group is attacked rather than a nuclear carbon atom.[43]

In later work on the oxidation of the cresols [44] there were found unattacked *o*-cresol, toluoquinol (by reduction of the toluoquinone with sulphur dioxide), *o*-dicresol similar to that of Geuther [45] and Hobbs,[46] which was further identified by conversion to the diacetate; contrary to the expectations no isohomocatechol was detected. The following is the scheme for the electrolytic oxidation of *o*-cresol:



In a similar manner *p*-cresol was oxidized and the products formed were toluoquinol, quinol, *p*-dicresol, and a material containing one oxygen atom more than *p*-dicresol and melting at 196° which was probably 2, 2′-dihydroxy- 5,5′-dimethylphenyl ether. The *p*-dicresol predominated here more than did the *o*-dicresol. The scheme for this oxidation therefore is:

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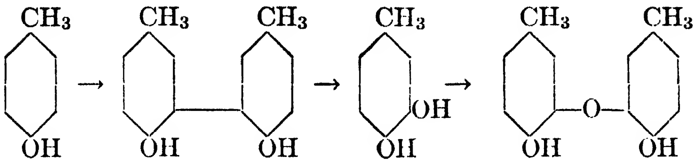
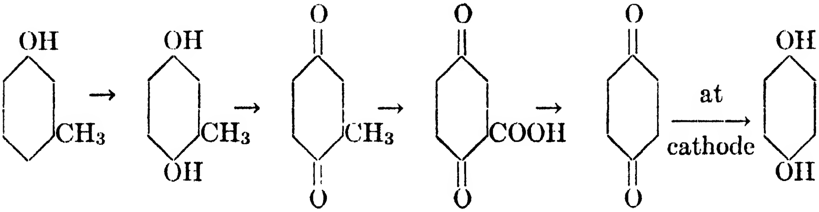
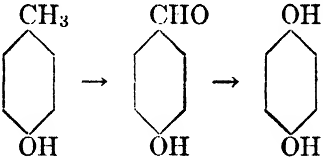
[41] E. Faust, Ann., **149**, 153 (1869).
[42] Weselsky, Ber., **3**, 646 (1870).
[43] Fichter and Stocker, loc. cit., p. 2007.
[44] Fichter and F. Ackermann, Helv. Chim. Acta, **2**, 583 (1919).
[45] Geuther, Ber., **21**, 749 (1888).
[46] Hobbs, Ber., **21**, 1067 (1888).



The *p*-cresol contained some *m*-cresol (detected by the method of Raschig)[47] from which the quinone may have been formed according to the scheme:



instead of from the *p*-cresol by going through the stage of *p*-hydroxy benzaldehyde, etc.:



m-Xylene is oxidized electrolytically to dixylenol in 33 per cent yields when the reaction is not too energetic.[48] In an analogous manner thymoquinone formed thymoquinol in a current yield of about 6 per cent, together with a great deal of resin which was impure bithymol.

For the oxidation of benzaldehyde a platinum anode is required instead of the expected lead dioxide anode, which oxidizes benzaldehyde by catalysis to benzoic acid. In order to get even fairly good results a strong stirring is required in order to counteract the very low solubility of the aldehyde in the solution.

At an iron anode in an alkaline solution aniline is oxidized to azobenzene in very unsatisfactory amounts,[49] while in an acid or neutral

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[47] F. Raschig, Z. angew. Chem., **13**, 759 (1900).

[48] Fichter and Meyer, Trans. Am. Electrochem Soc., **45**, 107 (1924). The purely chemical oxidation is very difficult.

[49] Rotondi, Jahresber. f. Chem., 270 (1884); Christeller, Dissert., Basel (1900); Klein, Dissert., Munich (1902); Rotondi used an ammoniacal solution and electrolyzed it for three days after which he found the following compounds to be present: benzene diazonium nitrate, azobenzene, nitric and nitrous acids.

solution good yields of aniline black are obtained without a further oxidation to quinone even at platinum anode.[50] However with a lead dioxide anode in the presence of oxygen carriers such as chromium, manganese and vanadium salts, a sulphuric acid solution of aniline forms quinone when subjected to electrolytic oxidation.[51]

When the aniline is dissolved in concentrated sulphuric acid the oxidation takes a slightly different direction. When two parts of aniline sulphate in three parts of concentrated sulphuric acid are electrolyzed at a platinum anode with a c. d. of one ampere at a potential of 15 volts, the predominating reaction is the formation of *p*-aminophenol.[52] The yields are poor when based on the current used because the conductivity of the solution is so very low that it requires too high a potential for the passage of the current and too much energy is required to be applicable as a technical method. The presence of the concentrated sulphuric acid protects the *p*-aminolphenol from further oxidation; but if water is present the aminophenol reacts with the excess of the aniline used to form *p*-aminohydroxydiphenylamine which is further oxidized to aniline black.

No results of any great value have been obtained from the study of the oxidation of aniline and its derivatives to form dyes, though several investigators have done work along this line.[53]

Dimethylaniline at a platinum anode in sulphuric acid to which has been added some chromic acid is oxidized to tetramethylbenzidine.[54] The necessity for the addition of the chromic acid could not be proven [55] because the oxidation goes at both platinum and lead dioxide anodes without the addition of a carrier.

The purely chemical oxidation of dimethylaniline by lead dioxide in sulphuric acid does not result in good yields,[56] but the electrochemical oxidation at a lead dioxide anode yields good amounts of tetramethylbenzidine, tetramethyl-diaminodiphenylmethane with traces of tri-

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[50] Goppelsröder, Ding. Polyt. Jour., **221**, 75 (1876); **223**, 317 and 634 (1877); **234**, 92 and 209 (1879); Compt. rend., **81**, 944; **82**, 331 and 1199 (1875); Coquillion, ibid., **81**, 408; **82**, 228 (1875).

[51] Elbs, Chem.-Ztg., **17**, 210 (1895); D.R.P.117129 (1900), Boehringer; D.R.P. 172654 (1903), Meister.

[52] Vidal, Eng. Pat. 573 (1902).

[53] Goppelsröder, Ueber die Darstellung der Farbstoffe mit Hilfe der Elektrolyse, Reichenberg (1885); Voigt, Z. angew. Chem., 107 (1894); Foelsing, Z. Elektrochem., **2**, 30 (1895); Szarvasy, ibid., **6**, 403 (1900). An excellent review of the work of Goppelsröder together with a bibliography is given by Fichter, Verhand. Naturfors. Ges., Basel, **31**, 133 (1920).

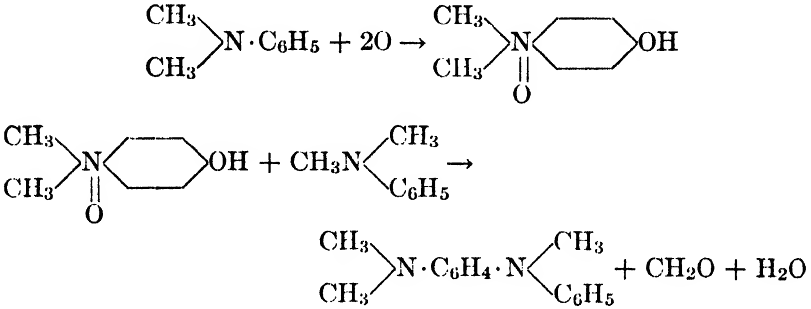
[54] W. Löb, Z. Elektrochem., **7**, 608 (1901).

[55] See J. Müller, Dissert., Basel (1918).

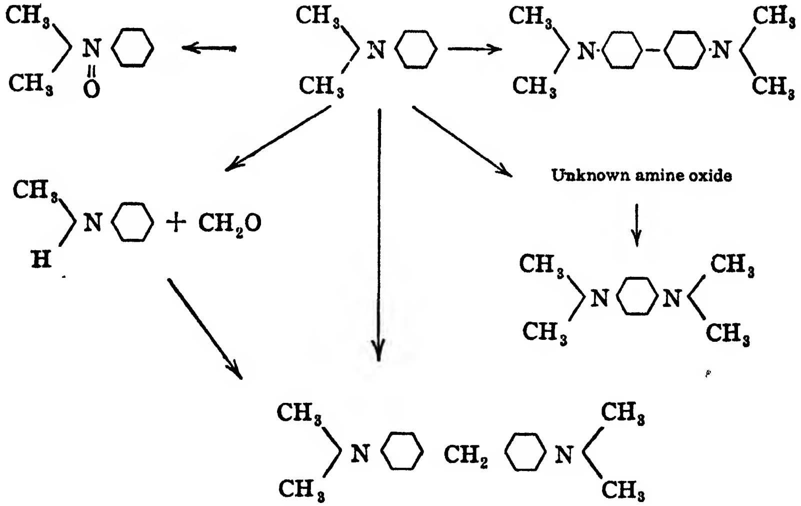
[56] See Michler and Pattinson, Ber., **14**, 2163 (1891).

methyl-phenyl-*p*-phenylenediamine; at a platinum anode the first and third compounds are the main products and the second appears in traces.[57]

In developing the mechanism for the formation of these compounds Fichter has some very good evidence for the intermediate formation of an amine oxide the formation and reactions of which are probably:



The scheme for the whole oxidation has been suggested as being:



A very unsatisfactory report of some work on the oxidation of azobenzene claimed that the product was tetrahydroxy-azobenzene, a dye (?) stable to light, water and acids,[58] but no record of current density, or electrodes was given:

$$C_6H_5 \cdot N = N \cdot C_6H_5 \rightarrow (HO)_2C_6H_3 \cdot N = N \cdot C_6H_3(OH)_2$$

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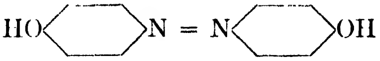
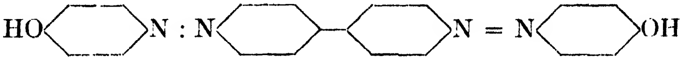
[57] Fichter and Rothenberg, Helv. Chim. Acta, **5**, 166 (1922).

[58] Heilpern, Z. Elektrochem., **4**, 89 (1897).

This work recently was repeated by Fichter and Jaeck [59] who found that the tetrahydroxy-azobenzene of Heilpern could not be isolated; but two new compounds were discovered, namely, *p*-dihydroxy-azobenzene (*p*-azophenol),

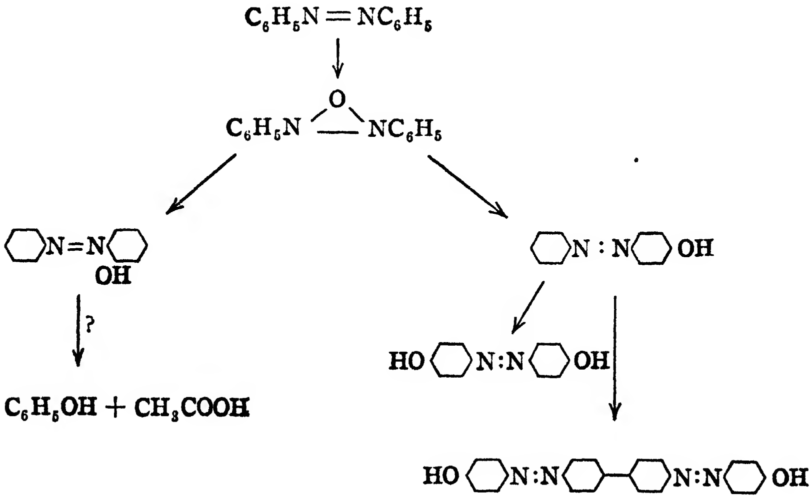


and diphenyl-bisazo-phenol,



with other compounds which defied identification; the most that can be said of these unknown products is that they have a very high molecular weight.

The scheme for the formation of these compounds is suggested as:



In this scheme the fate of the *o*-hydroxyazobenzene is unknown. Possibly it is further oxidized to phenol and acetic acid which always could be detected in every experiment.

In view of this work it is doubtful whether the patent of the Badische Company will be proven to be correct.[60] The claim of this patent is that azobenzene dyes are changed into the corresponding benzidine

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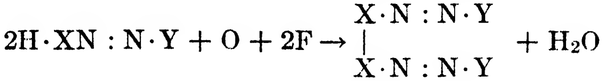
[59] Fichter and Jaeck, Helv. Chim. Acta, 4, 1000 (1921).

[60] D.R.P. 88597 (1895) Badische.

dyes by the removal of two nuclear hydrogen atoms and a subsequent linking of the two residues:



$$2\mathrm{H{\cdot}XN : N{\cdot}Y} + \mathrm{O} + 2\mathrm{F} \rightarrow \begin{array}{l} \mathrm{X{\cdot}N : N{\cdot}Y} \\ | \\ \mathrm{X{\cdot}N : N{\cdot}Y} \end{array} + \mathrm{H_2O}$$

in which X is an aniline residue as *o*-toluidine, *o*-anisidine, or any other base with a free *p*-position, and Y is a residue of α- or β-naphthol or salicylic acid, etc. If the method works, it is to be desired rather than the purely chemical oxidation with manganese dioxide.

The Electrolytic Oxidation of Compounds Containing More than One Ring.—Naphthalene has been electrolyzed in sulphuric acid-acetone-acetic acid solution with platinum and lead anodes to yield naphthaquinone and phthalic acid in only small amounts because the solvent is as good a depolarizer as is the solute. At a platinum anode in a suspension in glacial acetic and sulphuric acid naphthalene yields phthalic acid.[60a] A suspension of naphthalene in dilute sulphuric acid in the presence of an oxygen carrier, for example 2 per cent cerium sulphate, with a current density of 0.01–0.02 ampere yields naphthaquinone or phthalic acid according to the duration of the electrolysis. Similarly phenanthene is oxidized first to phenanthraquinone, then to diphenic acid and finally to benzoic acid.[61] K. Ono[62] has made a rather complete study of the oxidation of naphthalene with respect to the effects of different anodes, the nature of the electrolyte, current density, temperature, mode of production of oxygen and the use of catalyzers. In an acid solution anodes of platinum and lead work better than nickel, lead or iron electrodes, probably due to their efficiency in oxygen evolution and also to the catalytic effect. The reaction does not take place in alkaline solution. The order of activity of catalyzers is as follows: ceric nitrate, vanadic acid, potassium chlorate, dichromate, or ferrocyanide, manganous sulphate, and chrome alum. From the products of the oxidation, which seem to be very numerous, there have been isolated the following: α-naphthol; a red compound, which seems to be a compound of α-naphthol and naphthaquinone, produced in the electrolytic oxidation, was obtained by steam distillation of the α-naphthol solution; a dark brown resinous matter containing phenolic hydroxyl groups which yielded (*a*) phthalic acid and an insoluble black substance when fused with potassium hydroxide; (*b*) a large quantity of phthalic acid on oxidation with alkaline potassium permanganate; (*c*) α-α- and β-β-dinaphthyls by distillation with

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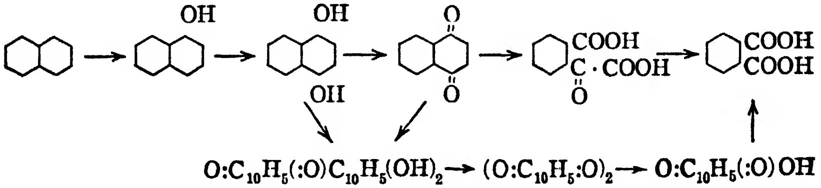
[60a] P. de Bottens, Z. Elektrochem., **8**, 673 (1902).

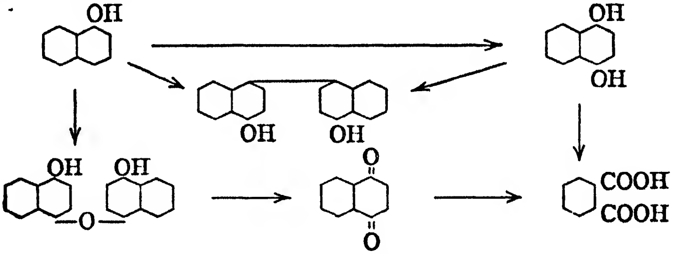
[61] D.R.P. 152063 (1902), Meister. Heat favors the reaction; a diaphragm is not required.

[62] K. Ono, J. Chem. Soc., Japan, **42**, 38 (1921).

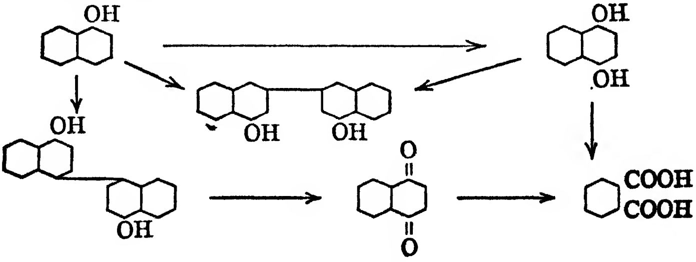
zinc dust; and (*d*) α-naphthaquinone, β-β-dinaphthyl-α-diquinone, and a violet brown substance when acted on by nitric acid. Therefore Ono believes that the scheme of oxidation of naphthalene may be indicated as follows:



The oxidation of α-naphthol proceeds[63] most satisfactory in an acid electrolyte which contains about 10 per cent of sulphuric acid when a c. d. of 1 ampere is used with a lead dioxide anode rather than anodes of platinum, nickel or lead. The products vary with the current applied; with a large c. d. a compound of α-naphthol and α-naphthaquinone known as α-naphthol-α-naphthaquinone, a red crystalline product is obtained. There is also a ring cission by which phthalic acid is formed. The indication is that α-naphthol on oxidation yields first α-α-dinaphthol which is further oxidized to α-naphthaquinone. The scheme suggested is as follows:



It is interesting to compare the action of purely chemical oxidizing agents on α-naphthol; ferric chloride yields α-α-binaphthol; chromic acid yields α-naphthaquinone and phthalic acid; potassium permanganate forms phthalic and phthalonic acids.



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[63] K. Ono, J. Chem. Soc., Japan, **42**, 559 (1921).

Lead dioxide is better as the anode material than platinum or graphite for the oxidation of α-naphthylamine to α-naphthaquinone and α-naphthylamine violet; the yields being proportional[64] to the quantity of current passed. The most efficient carriers are potash, alum, potassium chromate, potassium chlorate, and ferrous sulphate, and $K_4Fe(CN)_6$. Thus the oxidation of the amino derivatives of the naphthalene series differs from the oxidation of aniline in that aniline is oxidized to aniline black. If α-naphthaquinone were soluble in the anolyte it might also be completely oxidized. The intermediate formation of 4-amino-α-naphthol has not been proven. Similarly *ar*-tetrahydro-α-naphthylamine can be oxidized to *ar*-tetrahydro-α-naphthaquinone.[64]

A suspension of anthracene in 40 per cent sulphuric acid containing as an oxygen carrier 2 per cent K_2CrO_4, 5 per cent $MnSO_4$ or 15 per cent $CeSO_4$ (2 per cent $CeSO_4$ according to Meister),[65] when electrolyzed between an anode of lead, which is the retaining vessel, and a platinum plate as a cathode which also acts as the stirrer and without the use of a diaphragm, forms anthraquinone in very good current and material yields, without losing much efficiency by cathodic reduction; however the surface of the cathode must be very small compared with the surface of the anode.[66] The solubility of anthracene in the electrolyte is very small and so the best conditions are obtained when the hydrocarbon is suspended in a mixture of acetone and sulphuric acid. As the anthracene is oxidized, more of it goes into solution. With the lead anode vessel the best yields were 55 per cent, but the product was dark colored; when oxygen carriers were added the yield increased to 80 per cent. If a permanganate carrier is used the electrolyte may be made alkaline though the results in this case are very low. Manganous sulphate in acid solution gives the best product which is clear yellow and easily purified. After the anthraquinone has been filtered off, the electrolyte is available for another electrolysis. The yields are about 1 g. of anthraquinone per ampere hour of current used. Vanadium salts[67] are excellent oxygen carriers and permit a more rapid depolarization of the anode.

When anthraquinone is electrolyzed in concentrated sulphuric acid (10 g. in 35 cc. of 92 per cent acid) as anolyte in a clay cell with a platinum anode also acting as stirrer about 90–96 per cent material yield of dihydroxyanthraquinones are formed, namely, quinizarin (II), and

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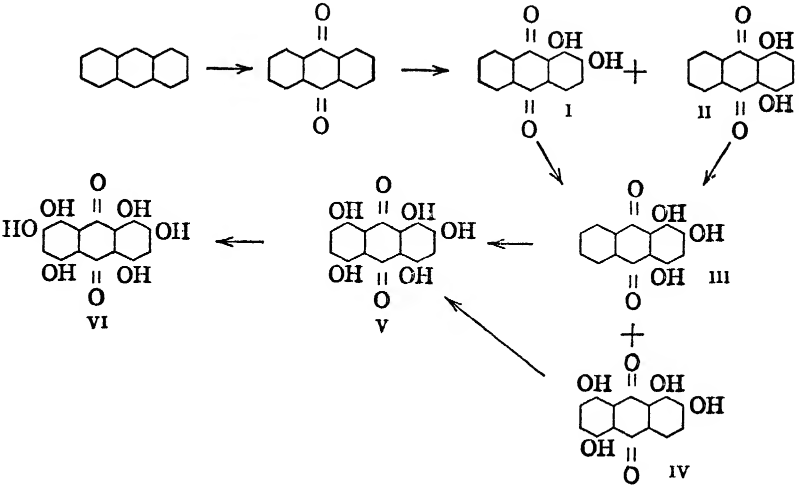
[64] K. Ono, Mem. Coll. Sci. Kyoto Imp. Univ., **5**, 345 (1922).

[65] D.R.P. 152063 (1902), Meister.

[66] A. Fontana and F. M. Perkin, Z. Elektrochem., **11**, 99 (1904).

[67] D.R.P. 172654 (1903), U.S.P. 823435 (1905), Meister.

alizarin (I), besides a small amount of trihydroxyanthraquinone (III), (Purpurin).[68] These high yields of dihydroxyanthraquinone are doubtful because alizarin, purpurin and alizarin bordeaux, (IV), are further oxidized to penta-, (V), and hexa- (VI), hydroxyanthraquinone.[69]



Phenanthrene[70] yields phenanthraquinone besides some diphenic and benzoic acids; the quantities of the latter two products varying with the duration of the reaction. The temperature must remain below 60° C. and the current density must be less than that used for the oxidation of anthracene. Phenanthraquinone on further oxidation yields a mixture of mono- and tri-hydroxyphenanthraquinone when substituted for anthraquinone in the above method.

The Oxidation of the Aliphatic Side Chains of Aromatic Compounds

Ordinarily the aliphatic side chain of an aromatic compound is oxidized to a greater or less degree by purely chemical oxidation, which as a rule is very difficult to stop at a definite intermediate point, so that the result is the formation of practically quantitative amounts of acid. For a long time it was thought that electrolytic oxygen attacked only the side chain, the methyl groups being oxidized to the aldehyde with

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[68] Perlin, Dissert., Berlin (1899); see Weizmann, F. P., 265,291 (1897); Goppelsröder, Ding. Polyt. J., **224**, 209 (1877).

[69] D.R.P. 74353 (1893), Bayer & Co.

[70] D.R.P. 152063 (1902), Meister.

great smoothness. The aldehydes are more or less stable to electrolytic oxygen; hence, in the majority of cases the aldehyde is the final product of an electrolytic oxidation.[71]

An acetone-sulphuric acid solution of toluene at platinum electrodes yields benzaldehyde and perhaps some benzylalcohol but no benzoic acid as long as any of the toluene remains unoxidized, as the hydrocarbon seems to be a better depolarizer than the aldehyde. In some cases the electrolytic oxidation stops at the intermediately formed alcohol, as in the oxidation of *p*-nitrotoluene which at platinum electrodes yields almost completely *p*-nitrobenzylalcohol without any traces of the corresponding aldehyde or acid.[72] However, other results have been obtained which seem to indicate almost conclusively that the oxidation of these hydrocarbons under certain conditions leaves the side chain intact though a nuclear carbon atom may be attacked. It has been shown that toluene yields *o*-, and *p*-cresols which are in turn oxidized to toluoquinol and toluoquinone before the methyl group is attacked. *p*-Cresol finally yields quinol, though at all times some of the side chain is attacked and lower homologues are also obtained.[73]

The Oxidation of the Side Chain of Benzene Homologues.—Law and Perkin have done a great deal of excellent work on the oxidation of the homologues of benzene and their derivatives. The solvent plays an important role in these oxidations, for if an alcoholic sulphuric acid suspension of toluene is used, most of the oxygen at a Pt anode attacks the solvent without touching the toluene, and only small amounts of benzaldehyde, benzoic acid and the ethyl ester of benzoic acid are formed. With a high c. d. some sulphobenzoic acid is formed. In a dilute solution [74] of sulphuric acid a toluene suspension is completely oxidized to CO_2 and H_2O at platinum and lead dioxide electrodes.

When the solvent is acetone in a sulphuric acid solution the oxidation goes a great deal more smoothly. After 20 per cent excess of current has been passed the benzaldehyde is isolated by steam distillation and purified as usual, but the material yield is only 15 per cent. Some resin, and a little benzyl alcohol but no benzoic acid are formed. Toluene is a very poor depolarizer and so most of the electrolytic oxygen is evolved as a gas. Strange to say in the case of these hydrocarbons the addition of an oxygen carrier seems to have no effect on the speed of the

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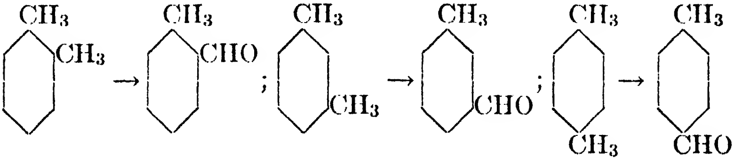
[71] See Fichter *et al.*, page 112 et seq.

[72] H. D. Law and F. M. Perkin, Trans. Farad. Soc., **1**, 31 (1905).

[73] Fichter, Z., Electrochem., **19**, 781 (1914), etc.

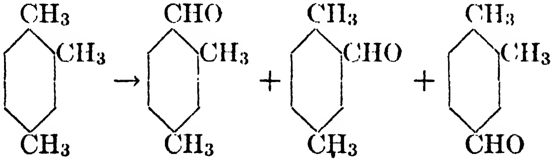
[74] Merzbacher and Smith, J. Am. Chem. Soc., **22**, 723 (1900); Puls, Chem. Ztg., **25**, 263 (1901); Renard, Compt. rend., **91**, 175 (1880); H. D. Law, and F. M. Perkin, Chem. News, **91**, 54 (1905); **92**, 69 (1905).

oxidation nor on the amount of oxidation products formed. Chromium, manganese, and cerium salts have been tried as oxygen carriers without success.[75] Where there is more than one methyl group in the nucleus the monoaldehyde is the chief product, though in some cases after the first methyl group is attacked, the second group undergoes oxidation, but never the two at the same time.[76] The oxidation of the three isomeric xylenes similarly yield the corresponding tolualdehyde as the main product:

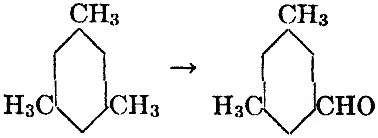


After passing twice the calculated amount of current the material yield of the *o*- and *p*-tolualdehyde are respectively 35 per cent and 30 per cent. The *m*-xylene yields only 10-15 per cent of *m*-tolualdehyde at best.

Pseudocumene (1, 2, 4-trimethylbenzene) yields 10-12 per cent of dimethylbenzaldehyde, but peculiarly this substance is a mixture of the three dimethyl aldehydes:



Mesitylene (1, 3, 5-trimethylbenzene) yields the corresponding dimethylbenzaldehyde in 10-15 per cent material yields. These facts bear out the statement that only one methyl group is oxidized at a time.



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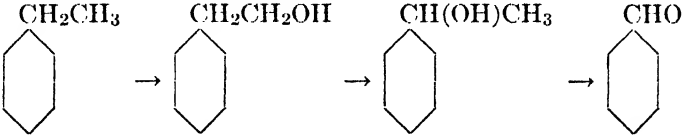
[75] F. M. Perkin, "Practical Methods," page 297; D.R.P. 189178, Lang, claims good yields of benzaldehyde by the electro-chemical oxidation of toluene in the presence of manganous ammonium sulphate. U.S.P. 808095 (1905) uses Pb anode with 70 per cent H_2SO_4 containing Mn_2O_3.

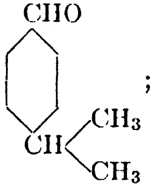
[76] Law and Perkin, Trans. Farad. Soc., 1, 31 (1905).

Law and Perkin[77] studied the oxidation of the homologues of benzene which had long side chains such as ethylbenzene, *p*-cymene, and cumene. With ethylbenzene, the secondary alcohol

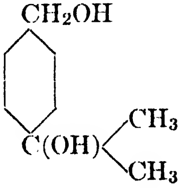
$$C_6H_5 \cdot CH(OH) \cdot CH_3$$

was obtained in considerable quantities together with a small amount of what was probably the primary alcohol, $C_6H_5CH_2CH_2OH$, but this was not obtained in sufficient quantity to be analyzed accurately. Benzaldehyde was obtained only after the bulk of the hydrocarbon had been oxidized to the alcohol. After passing 80 ampere hours of electricity, which was one third less than the theoretical amount required by the reaction to oxidize the ethylbenzene completely to benzaldehyde; when the electrolysis was stopped, phenyl methyl carbinol and phenyl ethyl alcohol with some benzaldehyde were isolated:

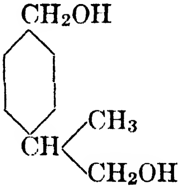




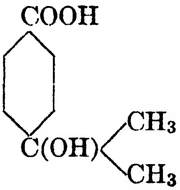
Cymene was oxidized to cumic aldehyde ; besides this there were also obtained two higher boiling fractions, the upper one of which was shown by analysis to be a new but impure di-alcohol probably of the constitution:



or



The lower fraction seemed to be a mixture of a mono- and di-alcohol. Hydroxyisopropylbenzoic acid,



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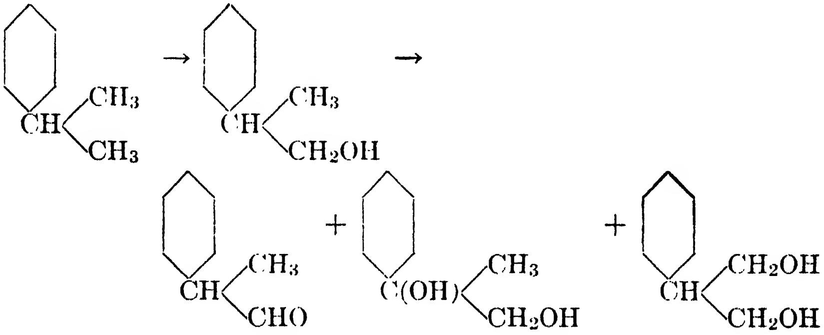
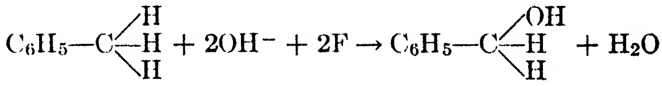
[77] Law and Perkin, Chem. News, **92**, 66 (1905).

was produced when cymene was oxidized with potassium permanganate, but on further oxidation it was converted to terephthalic acid. Cold nitric acid yielded *p*-methyl tolyl ketone but the hot acid gave *p*-toluic acid; in this last case the isopropyl group was attacked before the methyl group.

When cumene was oxidized in a sulphuric acid-acetone solution much cumene remained unattacked, but there was some aldehyde, some acid, and some resin formed. The aldehyde on examination was found to be a mixture of cuminaldehyde and hydratropaldehyde. There seems to be evidence that some small quantity of monohydric and dihydric alcohols were also formed, though whether the monohydric alcohol is a primary or tertiary alcohol is unknown. The presence of the aldehyde group seems to indicate that the alcohols are primary in each case:

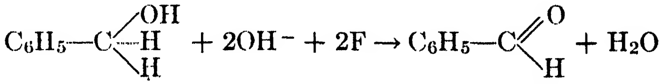


Assuming that the oxidation in the above three cases is due to the action of discharged hydroxyl groups, the following equations will suffice to explain the reaction which takes place. With the toluene and xylenes the primary alcohol is first formed thus:

(1) 

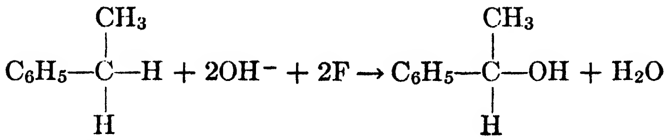
$$C_6H_5{-}\overset{H}{\underset{H}{C}}{-}H + 2OH^- + 2F \rightarrow C_6H_5{-}\overset{OH}{\underset{H}{C}}{-}H + H_2O$$

and the alcohol is then further oxidized as follows:

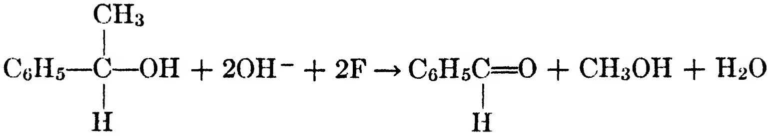
(2) 

$$C_6H_5{-}\overset{OH}{\underset{H}{C}}{-}H + 2OH^- + 2F \rightarrow C_6H_5{-}\overset{O}{\underset{H}{C}} + H_2O$$

In the case of ethyl benzene, the hydrogen in the β-position is the most easily attacked and therefore no aldehyde is formed; further oxidation could only produce acetophenone, which however has never been detected, although a portion is further oxidized to benzaldehyde:

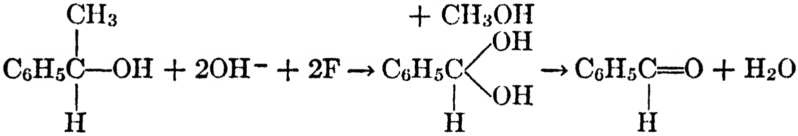
(3) 

$$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-H + 2OH^- + 2F \rightarrow C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH + H_2O$$

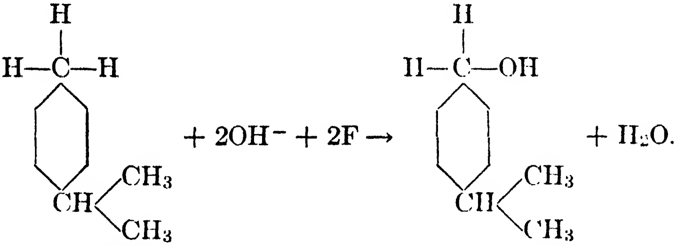
(4) 

$$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH + 2OH^- + 2F \rightarrow C_6H_5\underset{\underset{H}{|}}{C}{=}O + CH_3OH + H_2O$$

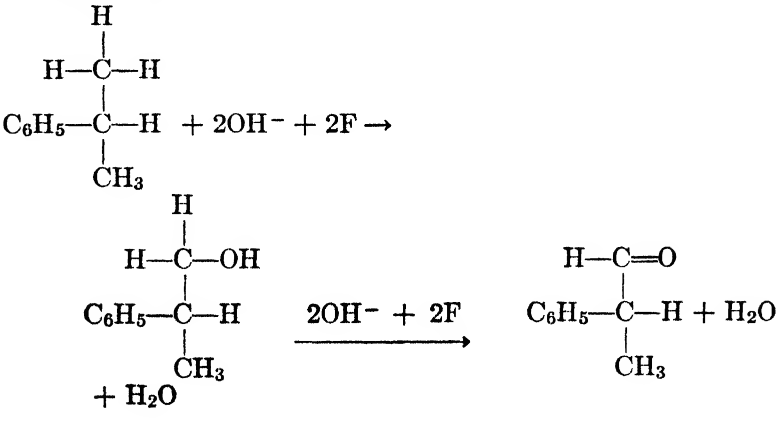
Methanol has never been detected in the oxidation products of ethyl benzene, but this would be very hard to detect in the large quantity of acetone which is used as the solvent for the depolarizer:

(5) 

With cymene the case is simply one in which the methyl group is the first one attacked; and then the reaction goes on to the formation of aldehyde:

(6) 

The alcohols are formed by reactions similar to those written out above. In the case of cumene the main reaction seems to be:

(7) 

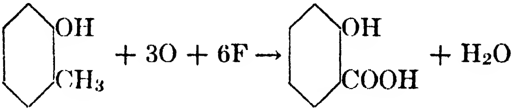
$$C_6H_5-\overset{\overset{\displaystyle H-\overset{\overset{H}{|}}{C}-H}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + 2OH^- + 2F \rightarrow$$

$$C_6H_5-\overset{\overset{\displaystyle H-\overset{\overset{H}{|}}{C}-OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \quad \xrightarrow{2OH^- + 2F} \quad C_6H_5-\overset{\overset{\displaystyle H-C{=}O}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + H_2O$$

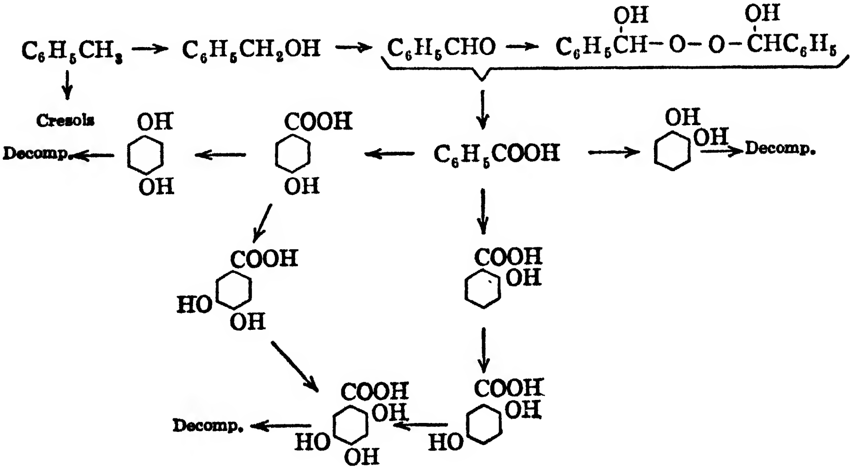
$$+ H_2O$$

The dihydric alcohol is formed by a similar oxidation of the second methyl group, or possibly by the oxidation of the tertiary hydrogen atom.

When *o*-cresol is oxidized in small amounts in fused caustic alkali containing a little water at a temperature of 110 to 120° C. and finally at 230 to 235° C., the methyl group is oxidized to the acid and salicylic acid is the result.[78] A previous patent [79] gives a good description of the method in which the electrodes may be of copper, lead, iron, nickel, or nickel-steel. All cresols may be oxidized in this manner:



Fichter and Uhl [80] believe that the reason for the formation of the oxidation products of toluene lies in the fact that at a platinum anode in the presence of an excess of benzaldehyde (a primary oxidation product of toluene) the passage of the electric current leads to the formation of a peroxide of benzaldehyde which immediately reacts with the excess aldehyde to form benzoic acid. But owing to the great polarization of the platinum the benzoic acid is immediately oxidized further to hydroquinone carboxylic acid, hydroquinone, pyrocatechol, etc., according to the scheme:



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[78] U.S.P. 1265378 (1918), Pomilio.

[79] Brit. Pat. 103739 (1916), Pomilio.

[80] F. Fichter and E. Uhl, Helv. Chim. Acta, 3, 22 (1920).

The Oxidation of Compounds with Unsaturated Side Chains.—Eugenol (1-propylene-3-methoxy-4-hydroxy-benzene) in the form of its acetic ester is oxidized by potassium permanganate to vanillin, vanillic acid and homovanillic acid.[81]

An alkaline 15 per cent solution of eugenol yields, it is claimed, first isoeugenol and then vanillin. The alkali transforms the eugenol to the isoeugenol and then the anodic oxygen acts on the latter.[82] The current must be broken before all the isoeugenol is oxidized. This work has been discredited by Lowy;[83] vanillin itself is very susceptible to anodic oxygen.

The Oxidation of Cyclic Compounds Containing a Nitro Group on the Ring.—Electrolytic oxygen has very little effect on nitrobenzene, but once the oxidation has started, it takes an unexpected direction, yielding only maleic acid.[84] The removal of the diaphragm to permit the reduction of a quinone to a quinol gives no results, for it has been shown that a nitroquinone does not exist.[85] Maleic acid is the only product which can be detected after the oxidation of both *o*-nitrophenol and *m*-nitrophenol while *p*-nitrophenol is entirely decomposed.

A sulphuric-glacial acetic acid solution of *p*-nitrotoluene yields a small amount of *p*-nitrobenzyl alcohol without the formation of any of the corresponding aldehyde or acid. The toluene derivative is a very poor depolarizer and so most of the anodic oxygen is evolved as a gas from the anolyte. To get even a fairly good yield, at least three times the theoretical amount of current must be passed.[86] The addition of 0.1 g. of manganous sulphate to 1000 cc. of anolyte or the use of lead dioxide anodes, leads to the formation of *p*-nitrobenzoic acid.[87]

A systematic study of the oxidation of *p*-nitrotoluene has been reported by Dunbrook and Lowy[88] in which they used platinum, lead and lead dioxide anodes in acetone-sulphuric acid and glacial acetic acid anolytes with very poor results. At best, the current yields were only 7 per cent. They however did find that a 20 per cent nitric acid solution with a platinum anode at a temperature of 100° C. with a current density of 4 amperes gave current yields of 34.1 per cent of

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[81] Meyer-Jacobson, Lehrb. d. org. Chem. II, 1, 434, edit. (1902).

[82] D.R.P. 92007 (1895), F. F. von Heyden Nachf.; see F. P. 244680 (1895), Kolbe.

[83] Moore and Lowy, Trans. Am. Electrochem. Soc., **42**, 273 (1922).

[84] F. Fichter and R. Stocker, Ber., **47**, 2003 (1914).

[85] F. Kehrmann and M. Idzkowska, Ber., **32**, 1065 (1899).

[86] Elbs, Z. Elektrochem, **2**, 522 (1896); Elbs, "Übungsbeispiele," page 96. Labhardt and Zschoche, Z., Electrochem., **8**, 93 (1902), obtained some aldehyde and when an excess of current was used some nitro acid.

[87] Coehn, Z., Elektrochem., **9**, 643 (1903); D.R.P. 117129, Boehringer (1900).

[88] R. F. Dunbrook and A. Lowy, Trans. Am. Electrochem. Soc., **45**, 82 (1924).

p-nitrobenzoic acid. At lower temperatures than this the yields were correspondingly lower. A very desirable condition in this work is the elimination of the diaphragm because *p*-nitrobenzoic acid is not attacked by cathodic hydrogen. This is the first instance on record where a nitric acid solution has been used in an electrolytic oxidation in the true sense of the word.

Under the conditions described by Boehringer and also by Coehn [89] at a platinum anode *o*-nitrotoluene yields first small amounts of *o*-nitro benzyl alcohol. Pierron obtained the alcohol, a great deal of resin,[90] and much unchanged starting material when he electrolyzed *o*-nitrotoluene. *m*-Nitrotoluene is oxidized in only very small amounts to the corresponding aldehyde.

At an electrolytically prepared lead anode dinitrotoluene and trinitrotoluene are oxidized very smoothly and quickly to the corresponding acid, which is the exact parallel of the purely chemical oxidation of Sachs and Kempf.[91]

Fichter and Benhote [92] have found that electrolytic oxygen attacks both the ring and the side chain of *p*-nitrotoluene; in the latter case the reaction proceeds normally from the alcohol through the aldehyde to the acid, while in the former case the nitro group is oxidized (as nitric acid) probably forming toluene which, as shown previously, is oxidized to a cresol and finally is lost as a resin. The complete oxidation yields oxalic acid, CO_2 and H_2O. As the oxidation proceeds the amount of nitric acid increases in the electrolyte with harmful influences; therefore the solvent should be glacial acetic acid if satisfactory yields of side chain oxidation products are desired. The nitrotoluene is soluble in glacial acetic acid and so can be brought to the anode in sufficient quantities to permit a regular oxidation. Since the nitrohydrocarbon, the nitroaldehyde, and nitroalcohol, and the nitro acid are all very excellent depolarizers the yields of nitro oxidation products necessarily decrease from step to step, so the final yield of any one nitro derivative is very small as the electrolysis proceeds. One nitro group on the ring does not protect the ring from the action of anodic oxygen, whereas two nitro groups do protect it. Accordingly 2, 4-dinitrotoluene yields only 2, 4-dinitrobenzoic acid in 25 per cent yields, which means that neither of the nitro groups is oxidized to nitric acid. With *p*-nitrotoluene the ready formation of resinous compounds of phenolic nature, which are excellent depolarizers, protects the alcohol formed in the first oxidation

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[89] Boehringer, loc. cit.; also Coehn, loc. cit.

[90] Pierron, Bull. soc. chim., [3], **25**, 852 (1901)

[91] Sachs and Kempf, Ber., **35**, 2704 (1902).

[92] Fichter and Bonhote, Helv. Chim. Acta, **3**, 395 (1920).

of the methyl group from further oxidation making the final yield *p*-nitrobenzyl alcohol. However in the oxidation of *m*-nitrotoluene the aldehyde is the first product which can be detected. The small quantity of phenolic resins has insufficient depolarizing power to prevent the formation of new product, by further oxidation of the alcohol group. In the case of *o*-nitrotoluene some aldehyde but mostly the alcohol is obtained. To these authors it seems that the stability of the alcohols with a nitro group in the *o*- or *p*-position may be due to the formation of peroxides as in the case of the oxidation of benzaldehyde, which polarize the anode to such an extent that benzoic acid is formed and then further oxidized. Though the peroxide of *p*-nitrobenzyl alcohol has never been prepared, its formation has been detected by measuring the anode potential by the method of Fichter and Uhl.[93] Another reason why the peroxide theory is the more plausible, is that the nitro-alcohol can be obtained at a platinum anode but not at a lead dioxide anode, for peroxides are not possible at the latter anodes. If a thin film of *p*-nitrobenzyl alcohol peroxide forms on the surface of a platinum anode the oxygen liberated there could escape without coming in contact with the unchanged *p*-nitrotoluene. The aldehyde is formed by the interaction of the peroxide with the unchanged alcohol, and il the aldehyde is the starting material, the acid is regularly and easily formed, because the aldehydes have very little tendency to form peroxides.

The Oxidation of Benzene Derivatives which Contain an Acid Group.—As stated above in the discussion of the electrolysis of aromatic acids, benzoates [94] are supposed to yield only the free acid and oxygen, but Löb showed that benzoates undergo a deep-seated decomposition of an undetermined nature which prevents the oxidation from paralelling the Kolbe hydrocarbon synthesis; the products were CO, CO_2, C_2H_2, and benzaldehyde, but no diphenyl or aliphatic derivatives.[95] A study of the oxidation of benzoic acid has shown that the evolution of CO_2 is scarcely one-twelfth that required by the equation:

$$C_6H_5COOH + 15O + 30F \rightarrow 7CO_2 + 3H_2O$$

which means that CO_2 is not the only oxidation product. On this assumption a detailed study of the oxidation with a smooth platinum anode has been made.[96] In the solution remaining at the end of the

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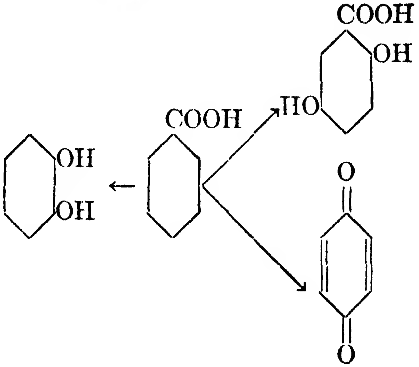
[93] Fichter & Uhl, Helv. Chim. Acta, **3**, 22 (1920).

[94] Matteuci, Bull. soc. chim., [2], **10**, 209 (1868); Bourgoin, ibid., **9**, 431 (1867); Brester, Jahresber. f. Chem., 87 (1866); Berthelot in Tommasi, "Traite," page 760; several salts were electrolyzed by Bourgoin.

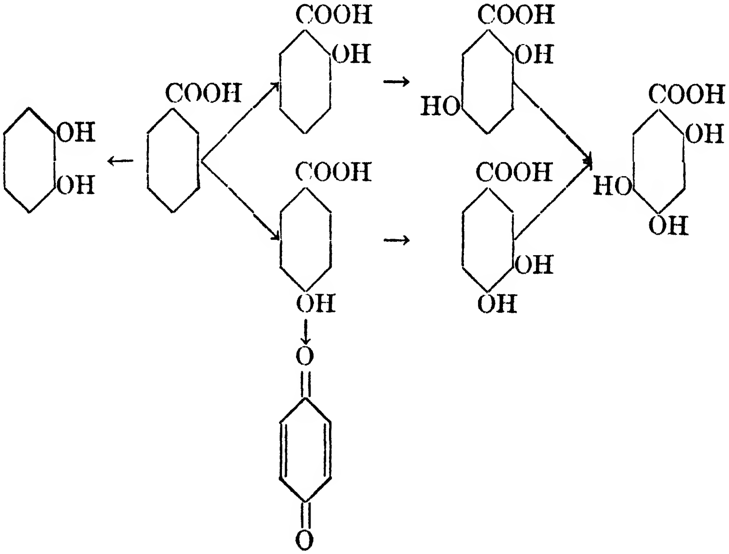
[95] Löb, Z. Elektrochem., **2**, 663 (1896); **3**, 3 (1896).

[96] Fichter and Uhl, Helv. Chim. Acta, **3**, 22 (1920).

oxidation there are unattacked benzoic acid, pyrocatechol, hydroquinone, hydroxyhydroquinone carboxylic acid, and hydroquinone carboxylic acid. The scheme suggested is:



Under similar conditions salicylic acid produces hydroquinone carboxylic acid, hydroxyhydroquinone carboxylic acid, but no pyrocatechol nor hydroquinone. *p*-Hydroxybenzoic acid forms protocatechuic acid and hydroquinone. These facts taken together have led Fichter to assume that the scheme for the anodic oxidation of benzoic acid is:



In a concentrated sulphuric acid solution *o*-nitroanthraquinone is oxidized to nitrohydroxyanthraquinone.[97]

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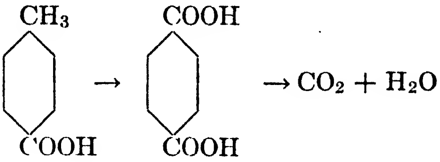
[97] Weizmann, F. P. 265292 (1897).

At a platinum or lead dioxide anode in alkaline solution *p*-toluic acid yields small amounts of terephthalic acid.[98]



A large current density oxidizes some of the phthalic acid to carbon dioxide and water as in the case of benzoic acid. But with a small current density the greater part of the electrolytic oxygen is evolved as a gas unused. The yields of terephthalic acid are never very high.

Even the addition of acetone to increase the solubility of the starting material has no effect on the yields. Similarly the *o*-toluic acid in an acetone-sulphuric acid solution, gives only 5 per cent yields of the phthalic acid; in this case there is a strong evolution of CO_2.

p-Chlorotoluene also has been oxidized in a nitric acid solution to *p*-chlorobenzoic acid. Yields of 64 per cent are obtained when the oxidation is carried out in 20 per cent nitric acid with a current density of 0.5 ampere at a temperature of 100° C., and if some acetic acid is added to the system the yields increase to 96 per cent on the quantity of current used. The *o*-chlorobenzoic acid is not sensitive to cathodic hydrogen therefore the diaphragm may be eliminated.[99]

The Electrolytic Oxidation of Aromatic Nitriles.—Electrolytic oxidation in the case of aromatic hydrocarbons may be directed more or less toward the destruction of the nucleus or toward the oxidation and ultimate removal of the side chain. As we have seen, the constituent groups have a regulating influence on the point of attack. A nitrohydrocarbon is oxidized to the nitroalcohol not to the nitroaldehyde,[100] while in the absence of water the nitro group is removed as nitric acid and a strong oxidation of the compound follows.[101] The sulphonic acid group is readily replaced by a hydroxyl group.[102] Now the influence of the cyanogen group has been investigated with a view toward studying the possibility of saponification which might effect the course of the oxidation. At a platinum anode in 0.5 normal sulphuric acid, benzonitrile yields carbon dioxide, ammonia, nitrogen,

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[98] Labhard and Zschoche, Z. Eleketrochem., **8** (1902);
Fichter and Grisard, Helv. Chim. Acta, **4**, 928 (1921).

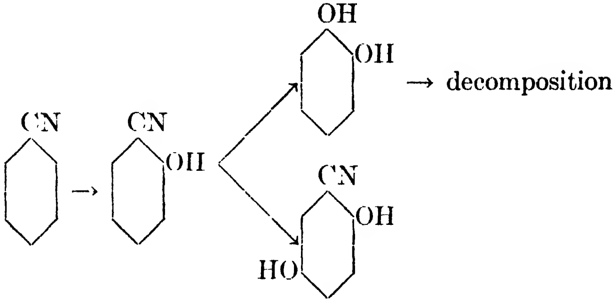
[99] Lowy and Dunbrook, Trans. Am. Electrochem. Soc., **45**, 82 (1924).

[100] Elbs, Z. Elektrochem., **2**, 522 (1896).

[101] Fichter and Bonhote, Helv. Chim. Acta, **3**, 395 (1920).

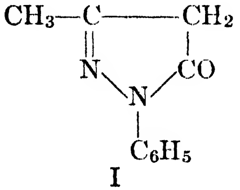
[102] Fichter, Brändlin and Hallauer, ibid., **3**, 421 (1920).

benzoic acid, pyrocatechol, and dihydroxybenzonitrile. Some of the starting material is evidently saponified and some completely oxidized to CO_2. The scheme suggested is:

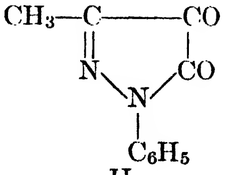


p-Tolunitrile similarly yielded at a platinum anode *p*-cyanobenzoic acid and terephthalic acid but no other compounds. The course of this reaction therefore is different from the oxidation of toluene. *o*-Tolunitrile yields phthalic acid, *o*-cyanobenzoic acid and some *o*-toluic acid. *m*-Tolunitrile yields large amounts of tar. Benzyl cyanide yielded benzoic acid, benzaldehyde and ammonia; in fact it was more strongly attacked at platinum than at lead dioxide anodes.[103]

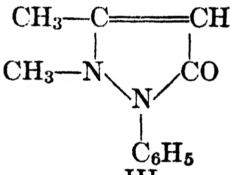
Heterocyclic Compounds. — Electrolytic oxidation methods have also been applied recently to heterocyclic compounds. In most cases the products obtained by the purely chemical oxidation of pyrazol derivatives are not the same as those obtained electrochemically.[104] 1-phenyl-3-methylpyrazolone-5 (I) has been oxidized to methylenediphenyl-methylpyrazolone; 1-phenyl-3-methyl-4-ketopyrazolone-5 (II) to 1-phenyl-3-methyl-4-oxypyrazolone 5; 1-phenyl-2,3-dimethylpyrazolone-5 (antipyrine) (III) to form only decomposition products; 1-phenyl-3, 4-dimethylpyrazolone-5 (IV) to bis-1-phenyl-3,4-dimethylpyrazolone-5; 1-phenyl-3-methylpyrazol (V) to quinone; 1, 3-dimethylpyrazol (VI) to pyrazol-3-carboxylic acid. These reactions have been carried out in an acid or neutral solution:



I



II



III

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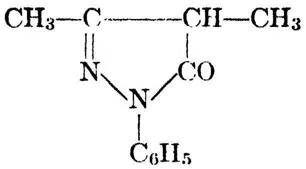
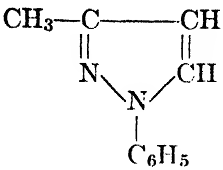
[103] Fichter and Grisard, Helv. Chim. Acta, 4, 928 (1921)

[104] Fichter and Montmollin, Helv. Chim. Acta, 5, 256 (1922).


IV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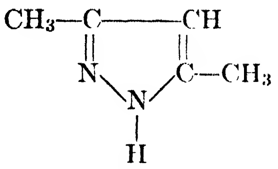

VI

In an alkaline solution 1-phenyl-3-methylpyrazol yields pyrazol-3-carboxylic acid.

THE OXIDATION OF SULPHUR COMPOUNDS

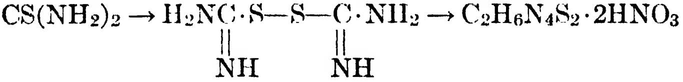
With but very few exceptions the electrolytic oxidation of organic sulphur compounds has received very little attention. Practically all of the work has been reported by Fichter and his collaborators.

The electrolytic oxidation of ethyl thiocyanate in an acid solution at a platinum anode causes a regular evolution of carbon dioxide and the formation of ethylsulphonic acid. The oxidation of diethylsulphide in a mixture of hydrochloric and acetic acids yields 70 per cent of ethylsulphoxide, which may be further oxidized in a hydrochloric acid solution by the passage of the theoretically required amount of current to the corresponding sulphone:

$$(C_2H_5)_2S \rightarrow (C_2H_5)_2SO \rightarrow (C_2H_5)_2SO_2$$

The mercaptol, $(CH_3)_2C(SC_2H_5)_2$, in a solution of dry acetic acid saturated with dry hydrochloric acid gas and containing some acetic anhydride is oxidized at a graphite anode to 2, 2′-diethylthionyl propane,[105] $(CH_3)_2C(SOC_2H_5)_2$, and an oil having the constitution, $(C_2H_5)_2S_2O_2$.[106]

The oxidation of thiourea in an acid solution (preferably nitric acid, because it facilitates the isolation of the nitrate of the final compound), at a platinum anode forms dithioformamidine dinitrate:[107]



$$CS(NH_2)_2 \rightarrow H_2N\underset{\underset{NH}{\|}}{C}\cdot S—S—\underset{\underset{NH}{\|}}{C}\cdot NH_2 \rightarrow C_2H_6N_4S_2\cdot 2HNO_3$$

Similarly acetylthiocarbamide yields dithiomonoacetyl-formamidine,[108] In most of these oxidations there is a side reaction which destroys some

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[105] Fichter and W. Wenk, Ber., **45**, 1373 (1912).

[106] Fichter and Braun, Ber., **47**, 1526 (1914.)

[107] Fichter and W. Wenk, Ber., **45**, 1373 (1912); M. Matsui and E. Ashida. Jour. Tokyo Chem. Soc., **40**, 147 (1919); Fichter and Braun, Ber., **47**, 1526 (1914).

[108] Matsui and Ashida, loc. cit. In this paper there is a discussion of the constitution of the thio-amide grouping.

of the carbamide to form ammonia and sulphuric acid which may be expressed by the equation:

$$CH_4N_2S + 4O + 2H_2O \rightarrow CO_2 + (NH_4)_2SO_4 + H_2O$$

Diethylthiourea similarly yields *sym*-diethylformamidine disulphide. Allylthiourea yields the corresponding formamidine disulphide, while phenyl formamidine disulphide was formed from phenylthiourea. β-trithioacetaldehyde has been studied under similar conditions.[109]

In the oxidation of these organic sulphur compounds it is necessary to be sure that the acid which is used to acidify the anolyte is not more easily oxidized than the sulphur compound, and also that the sulphur compound is entirely stable in the presence of the acid used. Sometimes sulphuric acid has a deleterious effect on the starting material.

The study of the oxidation of aromatic sulphur compounds is more limited than in the case of the aliphatic sulphur compounds. The electrolytic oxidation of benzyl sulphide in an acetic acid solution at a platinum anode does not require the use of a diaphragm for the reason that the oxidation products formed are very poor depolarizers for cathodic hydrogen. This is a distinct advantage. In the cold, a solution of benzyl sulphide in acetic acid containing some HCl is readily oxidized to benzyl sulphoxide in 92 per cent yields:[110]

$$(C_6H_5CH_2)_2S \rightarrow (C_6H_5CH_2)_2SO$$

The use of a warm solution for the electrolytic oxidation leads to the formation of benzyl disulphoxide:[111]

$$(C_6H_5CH_2)_2S \rightarrow (C_6H_5CH_2)_2S_2O_2$$

The electrolysis of benzyl sulphide in a strong sulphuric acid solution forms tribenzylsulphonium sulphate as the main product:

$$(C_6H_5CH_2)_2S \rightarrow (C_6H_5CH_2)_3S \cdot SO_4H$$

Using acetic acid with hydrobromic, hydrofluoric, nitric, or phosphoric acids or an oxygen carrier such as a cerium salt, also using acetone with acids, neutral salts, or alkalies there is the formation of a third compound namely benzaldehyde. The best solutions for obtaining this benzaldehyde are the mixture of acetic and phosphoric acids or the acetone with a cerium salt. In no case has the formation of a sulphone from benzyl sulphide been detected. On the other hand diphenyl sulphide in concentrated HCl solution at a platinum anode with an

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[109] Fichter and Braun, loc. cit.

[110] Fichter and P. Sjöstedt, Ber., **43**, 2422 (1910); Fromm and Raiziss, Ann., **347**, 90 (1910).

[111] See Fromm and Achert, Ber., **36**, 544 (1903); Smyth, J. Chem., Soc., **95**, 349 (1909).

excess of current readily forms diphenyl sulphone. With a very low anodic current density some diphenyl sulphoxide may be obtained but only in a very impure form:

$$(C_6H_5)_2S \rightarrow (C_6H_5)_2SO \rightarrow (C_6H_5)_2SO_2$$

o-Nitrobenzyl sulphide similarly is oxidized in an acetic acid solution containing preferably HCl (though nitric or phosphoric acids may also be used) to *o*-nitrobenzyl sulphoxide. If the temperature rises very high some *o*-nitrobenzyl disulphoxide will be formed: [112]

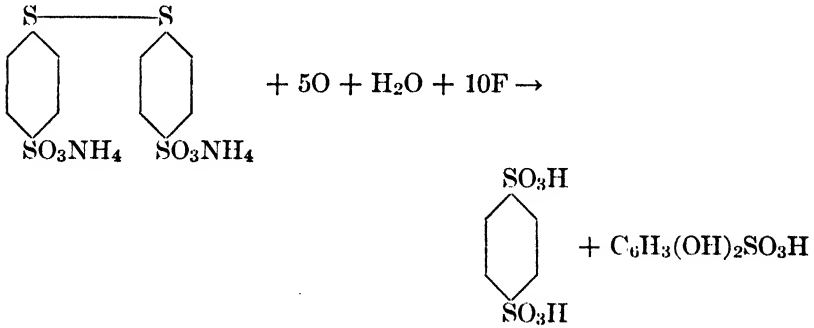
$$(O_2N \cdot C_6H_4CH_2)_2S \rightarrow (O_2N \cdot C_6H_4CH_2)_2S_2O_2.$$

p-nitrobenzyl sulphide is oxidized with similar results.

Symmetrical compounds as diethyl- or diphenyl sulphides are normally oxidized to the corresponding sulphoxide or sulphone. A mixed sulphide such as phenyl ethyl sulphide is split and yields benzene sulphonic acid and acetic acid.

Benzyl disulphide yields benzyl disulphoxide [113] but phenyl disulphide under similar conditions yields only benzenesulphonic acid.[114] This action seems to be characteristic of the phenyl grouping even when there are substitutions in the ring.

When a normal solution of the ammonium salt of the *p,p'*-disulphide of benzenesulphonic acid is oxidized at a platinum gauze anode with an amount of current as calculated from the equation, 80 per cent of the theoretical quantity of barium salt of *p*-benzenedisulphonic acid is formed:



Some of the disulphonic acid is further oxidized to compounds mostly of an uncertain composition, but catecholsulphonic acid has been identified together with an acid of the formula $C_{12}H_8O_{16}S_5$ (isolated as the barium and ammonium salts).

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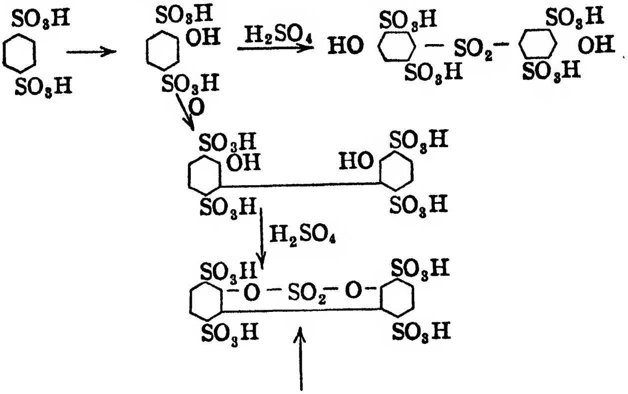
[112] Fichter and Wenk, Ber., **45**, 1373 (1912).

[113] Fichter and Sjöstedt, loc. cit.

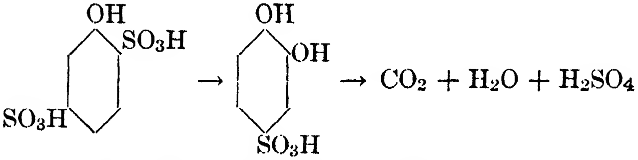
[114] Fichter and Wenk, loc. cit.

The scheme of the oxidation of benzene-*p*-disulphonic acid is:

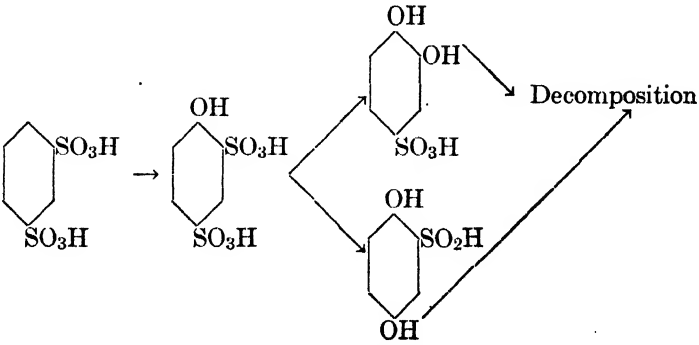


$C_{12}H_8O_{16}S_5$

The ammonium salt of 2, 5-phenoldisulphonic acid was electrolytically oxidized in a neutral solution and in a sulphuric acid solution to carbon dioxide and sulphuric acid with the intermediate formation of catechol-4-sulphonic acid.



The ammonium salts of *m*-benzenedisulphonic acid and 2, 4-phenol disulphonic acid were completely decomposed by electrolytic oxygen though the former during the electrolysis yielded a reaction for catechol (green color with ferric chloride) together with an odor of *p*-benzoquinone which indicated the intermediate formation of catechol-4-sulphonic acid and quinol sulphonic acid.[115]



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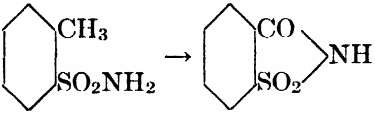
[115] F. Fichter, R. Brändlin, and E. R. Hallauer. Helv. Chim. Acta, 3, 410 (1920).

Saccharin, an important modern pharmaceutical product, may also be made by the electrolytic oxidation of *o*-toluenesulphonamide:



The anolyte is a solution of 10 equivalents of *o*-toluenesulphonamide in 100 equivalents of 2 per cent aqueous sodium hydroxide solution; the catholyte is a 15 per cent sodium carbonate solution; the anodic c. d. is 6–9 amperes at a potential difference of 4 volts. After the current has been discontinued the electrolyte is treated with hydrochloric acid to precipitate the hydrochlorides which are filtered and then further treated with a sodium carbonate solution; this allows the insoluble unchanged amide to separate out from the soluble saccharin. The saccharin crystallizes from the soda solution after the addition of hydrochloric acid.[116]

Such is the preparation of saccharin on paper. However the value of the method has been seriously questioned by the work of later investigators,[117] who were able to detect only mere traces of the desired compound under the conditions described in the first patent. That the methyl group can be oxidized to the carboxyl group, and that the amide can be oxidized to the imide group is not questioned. The trouble lies in the simultaneous oxidation of these groups so that the desired ring closure takes place. The amide grouping seems to be a better depolarizer than the methyl group. Therefore during the oxidation of the methyl group the amide group must be protected by some means. These investigators found that an ammoniacal electrolyte did the work with some degree of satisfaction. The presence of four normal ammonium hydroxide and some ammonium sulphate in the suspension of *o*-toluenesulphonamide permitted the formation of saccharin in 75 per cent material and 42 per cent current yields. In a weakly alkaline suspension the oxidation is favored by the addition of salts of ammonia, lead, cerium and manganese; 75 per cent yields are claimed on a continuous basis.[118]

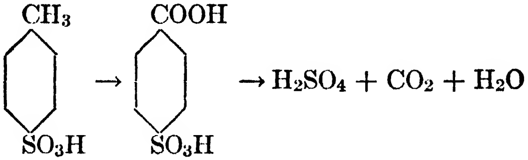
The *p*-sulphonic acid of toluene in a sulphuric acid solution at an electrolytically prepared lead anode is readily oxidized by a c. d. of

[116] D.R.P. 85491 (1895), Hyden, Friedländer, 4, 1263; Sebor, Z. Elektrochem., 9, 370 (1903); Barbier, B. P. 9322 (1903); Klages, Swiss, P. 78277 (1918).

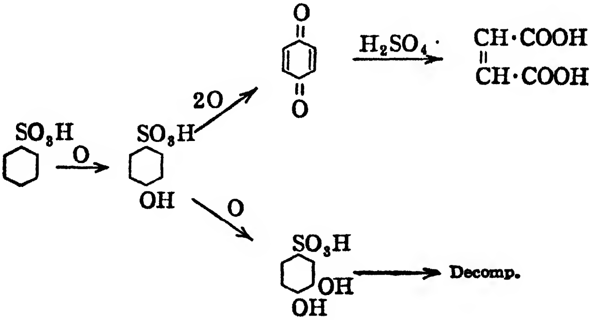
[117] A. V. Pamfilov, Bull. Inst. Polyt. Ivanovo-Voznesewsk, 4, 167 (1921); F. Fichter and H. Löwe, Helv. Chim. Acta, 5, 60 (1922); H. Löwe, Die Elektrochemische Oxidation des *o*-toluolsulphamide zu Saccharin, Basel (1921).

[118] Brit. P. 174913 (1922), H. Löwe.

3.7 amperes to *p*-sulphobenzoic acid.[119] The current yield is about 34 per cent. The oxidation is so violent that a portion of the products are oxidized to CO_2, water and sulphuric acid, at a lead electrode, while at a plain platinum anode most of the oxygen is evolved unused, allowing only about 2 per cent to be used in the electrolytic oxidation. This oxidation is the analogue of the action of *p*-toluic acid:



In the hope of discovering a benzene sulphoperacid Tonoli[120] oxidized benzene sulphonic acid with a very high current density at platinum electrodes, obtaining only phenol and sulphuric acid. That is, the oxidation was complete. In repeating this work but with a lower current density Fichter and Stocker isolated from the electrolyte the following compounds: benzoquinone, fumaric acid, and pyrocatechol sulphonic acid. The formation of these compounds may be expressed in the form of a series of equations as follows:[121] (The *p*-phenol sulphonic acid cannot yet be traced with certainty.)



The work was done with platinum anodes using a current density of 4.0 amperes. The anolyte was a twice normal solution of benzenesulphonic acid in a clay cell.

By an admirable bit of work in the field of peroxides, etc., Fichter has been able to develop the following hypothesis concerning the electrochemical oxidation of benzenesulphonic acid: "Benzenesulphonic acid is oxidized to benzene sulphoperacid at the anode, at current

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[119] Sebor, Z. Elektrochem., **9**, 371 (1903); Löwe, Dissert., Basel, 1921.

[120] R. Tonoli, Rend. soc. chim. ital. fasca., **2** (1912).

[121] Fichter, Trans. Am. Electrochem., Soc., **45**, 131 (1924).

densities which are low. The sulphoperacid is very unstable, and insoluble in ether; it lasts but a short time in a dilute aqueous solution and then rapidly decomposes into pyrocatechol sulphonic acid:

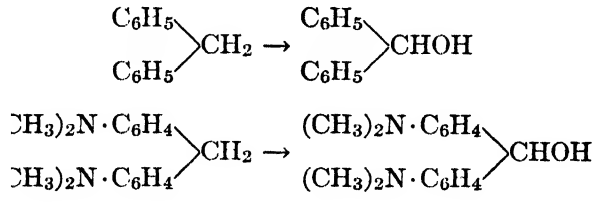
$$C_6H_5SO_3H + O \rightarrow C_6H_5SO_4H$$

$$2C_6H_5SO_4H \rightarrow C_6H_3(OH)_2 \cdot SO_3H + C_6H_5SO_3H$$

The first product of the rearrangement to be expected would be *p*-phenol sulphonic acid. The fact that it is not detected may be due to its having been further oxidized by the peracid to pyrocatechol sulphonic acid. It will be possible to elucidate these matters more clearly, if we once succeed in isolating the benzene sulphoperacid." [122]

THE OXIDATION OF THE METHYLENE GROUP IN DIPHENYLMETHANE DERIVATIVES

Chromic acid and the ordinary oxidizing agents, except lead dioxide, oxidize the methylene group of diphenylmethane to the ketonic group, yielding benzophenone.[123] The electrolytic oxidation is much more gentle than the purely chemical oxidation and so permits the isolation of the intermediate compound benzohydrol (the corresponding secondary alcohol), in fact, this compound is the final product of the electrolytic oxidation.[124] By the same reaction tetramethyl-diamino-diphenylmethane yields the corresponding benzohydrol without any difficulty,



$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CH_2 \rightarrow \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CHOH$$

$$\begin{matrix} CH_3)_2N \cdot C_6H_4 \\ CH_3)_2N \cdot C_6H_4 \end{matrix} > CH_2 \rightarrow \begin{matrix} (CH_3)_2N \cdot C_6H_4 \\ (CH_3)_2N \cdot C_6H_4 \end{matrix} > CHOH$$

and tetramethyl-diamino-ditolylhydrol is formed from tetramethyl-diamino-ditolylmethane in quantitative yields after the passage of twice the calculated amount of current.[125]

These compounds are of great interest in the color industry because they may be condensed with various benzene derivatives to form leucobases of the triphenylmethane series.

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[122] Fichter, Trans. Am. Electrochem., **45**, 131 (1924).

[123] Meyer and Jacobson, Lerb. d. org. Chem., II, **2**, 55 (1903).

[124] Escherich and Moest, Z. Elektrochem., **8**, 851 (1902), and D.R.P. 133896 (1901); Elbs, "Übungsbeispiele," page 134.

[125] F. Reitzenstein and O. Runge, J. prakt. Chem., [2], **71**, 113 (1905).

An effort has been made to apply these methods technically. The first case studied was the electrolytic oxidation of the leuco-base of malachite green.[126] The results of this work show that in this particular case there is no appreciable oxidation in the absence of a catalyst; uranyl sulphate is the best catalyst; a higher temperature than that required by the chemical oxidation method using lead peroxide is necessary; low concentration of the starting material favors high yields; sulphuric acid is the only solvent that allows the oxidation to proceed.

OXIDATION OF HYDROAROMATIC COMPOUNDS

The electrolytic oxidation of hydroaromatic compounds is also possible. The reaction between isoborneol and nitric acid (sp. gr. 1.43) is started by a momentary passage of an electric current. As soon as the reaction is proceeding at normal speed the circuit is broken and the purely chemical oxidation is allowed to complete the reaction.[127]

Borneol, isoborneol and camphene oxide are readily oxidized to form camphor in an electrolyte of 5 per cent sodium chloride in a divided cell with a c. d. of 100 amperes.[128]

FORMATION OF RESINS

Very often in the course of a reaction there are formed by-products which in most cases are extremely undesirable. However the by-product may be made the main product with very valuable properties. Such is the case in electrolytic oxidations. Very often there are resinous contaminations that complicate the isolation of a desired product. But if the resin is of any value the direction of the reaction may be changed to yield these resins in larger amounts. The resinification of aromatic compounds during electrolytic oxidations is made the basis of a patent for the preparation of resins.[129] A mixture of phenol, cresol, xylenol, derivatives with aldehydes or substituted aldehydes in an electrolyte of sodium acetate, etc., yields artificial resins together with intermediate condensation products which are hard, but yet easily removable from the anode. The yields are good and mechanical difficulties are few, though a divided cell is necessary. Excellent results

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[126] A. Lowy and Haux, Trans. Am. Electrochem. Soc., **40**, 123 (1921).

[127] U.S.P. 1324140 (1919); R. L. Andreau; see also U.S.P. 1225052 (1917), Piguet.

[128] U.S.P. 875062 (1907), Glaser.

[129] Brit. P. 130608 (1919); Resan Kunstharz- Erzeug.- Gesell.

are obtained if the catholyte is a sodium chlorite solution, because during the electrolysis the chlorite ions are carried into the anolyte, there assisting in the condensation.

ELECTROLYTIC OXIDATION OF ORGANIC COMPOUNDS OF ARSENIC

Cacodylic acid in an alkaline solution is oxidized at the anode to arsenic acid. An alkaline solution is best because the cacodylic acid is not attacked at the cathode under these conditions and the use of a diaphragm is eliminated. In the course of the oxidation it was found[130] that 8.6 mols of CO_2 were formed per mol of arsenic acid instead of the expected 2 mols as required by the equation:

$$(CH_3)_2AsO_2H + 8O \rightarrow 2CO_2 + H_3AsO_4 + 2H_2O$$

so some other oxidation product also yielded CO_2 without increasing the amount of arsenic acid in the solution. Such a product may be formed according to the equation:

$$(CH_3)_2AsO_2H + 4O \rightarrow CO_2 + CH_3AsO_3H_2 + H_2O$$

that is, monomethylarsenic acid is formed. This accounts for the high yields of CO_2 in proportion to the arsenic acid formed. The current yield in the formation of the monomethylarsenic acid is 10.8 per cent while in the total oxidation to arsenic acid the yield is 3.06 per cent. The monomethyl acid can be oxidized to arsenic acid in 5.15 per cent yields.

THE PREPARATION OF CHLOROHYDRINS

Several variations of methods for the preparation of chlorohydrins by the addition of chlorine and a hydroxyl group to an unsaturated hydrocarbon molecule have been recorded in the patent literature. The hydrocarbon or an oil-gas rich in ethylene is passed into the anode chamber of an electrolytic cell very close to the anode at which chlorine is being liberated. A temperature sufficient to volatilize the chlorohydrin is maintained by the passage of steam, using an apparatus suitable for condensing the vapors which distil over as the reaction proceeds. The electrolyte should be an aqueous solution of hydrochloric acid or sodium chloride.[131]

A catalyst may be added to the anolyte to speed up the reaction. Such a catalyst may be platinum-black, charcoal, or bone-black. Solvents for the ethylene, while increasing the ethylene in the solution

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[130] Fichter and Elkind, Ber., **49**, 239 (1916).

[131] Brit. P. 140831 (1917), R. Haddon; U. S. P. 1253615 (1918), K. P. McElroy.

and also the amount of ethylene in contact with the anode, will probably increase the speed of the reaction but will also to some extent decrease the conductivity of the system to such a point that their use will not be economical; such solvents are turpentine and mineral oil, etc.[132]

Temperature regulation is absolutely necessary, because at low temperatures olefine chlorides and not chlorohydrins are formed. The optimum temperature is about 97–100° C., at which temperature the chlorohydrins are easily volatile. Bromohydrins are also made in this manner.[133] The chlorohydrins are valuable solvents.

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[132] U.S.P. 1253617 (1918), K. P. McElroy.
[133] U.S.P. 1264538 (1918), K. P. McElroy.

CHAPTER VII

SUBSTITUTION

GENERAL

ELECTROCHEMICAL substitution differs from electrochemical oxidation or reduction in that there is no change in electrons in the substituted material. As a rule, a hydrogen atom is replaced by another atom and the only oxidation or reduction is with respect to the atom that is freed from the solution and allowed to act on the solute. Thus there are two different kinds of reaction possible but both may be called substitution reactions. The first is due to the oxidation of a material in the solution to another form which attacks the organic compound used. An example of this type of reaction is the oxidation of the hydracids of the halogens and their salts in the presence of a reactive organic material. Thus, if a solution of acetone containing hydrobromic acid or sodium bromide is electrolyzed, the bromide ions discharged at the anode react with the acetone to form bromacetone:

$$CH_3COCH_3 + 2Br^- + 2F \rightarrow CH_3COCH_2Br + HBr$$

Or this reaction may be written in two parts:

$$2Br^- + 2F \rightarrow Br_2$$

$$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + Br^- + H^+$$

That is, the reaction is not dependent on the passage of the current except for the liberation of the halogen at the electrode. The question is still open for further proof as to whether in these substitution reactions the introduction of the substituting group is or is not really dependent on the passage of the current. Examples will be cited later in which there has been a disagreement concerning the exact mechanism.

If the substitution is a function of the passage of the current, only one equation is necessary to express the results. However, if the substitution is a function of the discharge of the ions at the electrode and from this point is merely a chemical reaction, then the two equations must be written. In many cases there is very little relation between the current and the percentage yields, while in others there is a good evidence that the reaction is strictly due to the depolarizing action of the organic compound. The conditions which effect the substitutions are very uncertain. The electrode potential, and the formation of intermediate compounds may influence the introduction of the new group. Not very much is known of the real mechanism because the reaction is too rapid in most cases to be followed with ease. In the halogenation of cyclic compounds, it is possible to determine whether the reaction is due to direct depolarization or to the action of molecular halogens, by determining the point of the attack; that is, whether the reaction is one that goes with molecular halogens, without the application of the electric current, or whether the reaction is different from that of ordinary halogenation. If the electrolytic substitution is different from the ordinary substitution, there is ample evidence for the assumption that the passage of the current has a direct influence on the resulting product.

There is another type of substitution reaction which may be mentioned at this point. When a suspension of naphthalene in water is mixed with very dilute nitric acid there is no sign of any action. On the other hand when the dilute nitric acid suspension of the naphthalene is subjected to electrolysis, nitronaphthalene is separated at the anode. A study of the reaction shows that it is not due to the mere discharge of the NO_3^- ions at the anode, and then a secondary action of these ions on the naphthalene. There must be a certain concentration of NO_3^- ions in the neighborhood of the anode before the reaction starts. The progress of the reaction depends firstly on the original concentration of the materials, and secondly on the conditions under which the diffusion of the ions may take place, and finally also on any chance conditions which cause a favorable circulation of the liquid so that the concentration of the substituting material is increased about the anode. Of course, the current density and the form and arrangement of the electrodes have a great influence on the speed of the substitution, though not so much as in the case of the oxidation reactions of the previous chapter.

One of the most important reactions of this second class is the electrolysis of a solution of an aromatic amine in the presence of sodium nitrite in which there is a diazotization with a subsequent coupling with an acid to form a dye.

THE INTRODUCTION OF HALOGENS

According to Le Blanc, " Those ions separate first which give up their electric charges most easily. The other ions must wait their turn in the order of their ease of deposition." In the electrolysis of an aqueous solution of any halogen acid or salt there is a chance that several reactions may take place. That is, there might be a discharge of hydroxyl ions at the anode which would be substituted in the organic compound; or there might be an evolution of oxygen with the accompanying oxidation of the organic material, as is often the case. Acetone in fuming hydrochloric acid yields, on the passage of an electric current, large amounts of chloracetone; while aniline on the other hand in a normal hydrochloric acid solution is almost entirely oxidized to aniline black, the oxidation product of aniline; but in a hydrobromic acid solution the product is mostly tribromaniline.

With a proper regulation of the anode potential there is in most cases little danger of getting a mixed reaction. While several values for the decomposition voltage of water have been found,[1] a steady evolution of oxygen and hydrogen is only obtained when the potential is 1.7 volts. This value is taken as the decomposition of value of water. At this voltage the hydroxyl ions are discharged at the anode with the formation of water and the evolution of oxygen gas.

There is a gradation of potential among the members of the halogen hydracids as follows for the decomposition of the hydracid: [2]

$$\begin{aligned}\text{Normal } HCl &= 1.31 \text{ volt;}\\ \text{Normal } HBr &= 0.94 \text{ volt;}\\ \text{Normal } HI &= 0.52 \text{ volt.}\end{aligned}$$

From this it is recognized that, according to the decomposition voltages, the reaction may be controlled by regulating the potential, but there is always a danger that an evolution of oxygen will take place at a lower potential, or that something may cause a rise in the potential. Thus it is very difficult to predict just where there will be an oxidation or a substitution reaction.

The condition of the electrolyte has a great influence on the course of the reaction. For instance in an alkaline solution the discharge of the halogen takes place just as easily as in a neutral solution, but if the organic depolarizer is not present in sufficient quantities to react at once with the halogen, the latter reacts with the hydroxyl ion according to the equation:

$$OH^- + X^- + 2F \rightarrow HOX$$

forming hypohalogen acids which are capable of acting not only as a halogenating agent but also as an oxidizing agent. An example of the different action in acid and alkaline solution is found in the electrolysis

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[1] Le Blanc, "Textbook of Electrochemistry," pp. 305, et seq. (1907).

[2] Le Blanc, Z. Phys. Chem., **8**, 299 (1891); **12**, 333 (1893); E. Bose, Z. Elektrochem., **5**, 159 (1898).

of solutions of acetone. In dilute hydrochloric acid monochloracetone results, while in alkaline solution the reaction does not stop at the mono substitution product but goes on to form trihalogen acetone derivatives.[3] In acid solution the equation is:

$$CH_3COCH_3 + 2X \rightarrow CH_3COCH_2X + HX$$

While in alkaline solution the trihalogen acetone reacts with the excess of alkali to form alkali acetate and trihalogenated methane:

$$CH_3COCH_3 + 3NaOX \rightarrow CH_3COCX_3 + 3NaOH$$

$$CH_3COCX_3 + NaOH \rightarrow CHX_3 + CH_3COONa$$

Substitution in Acid Solution.—The first record of the introduction of a halogen in place of hydrogen is found in the work of Lüdersdorf,[4] who electrolyzed a mixture of ethyl alcohol and concentrated hydrochloric acid with the result that a heavy oily layer possessing a sweet ethereal odor separated.

In the electrochemical method for the preparation of chloral on a technical scale [5] an acid solution of alcohol and potassium chloride is electrolyzed at 100° C. in an apparatus equipped with a condenser so that the chloral formed may be distilled out of the electrolyte from time to time, and so removed from the danger of further attack. Since the anolyte is separated from the catholyte by a diaphragm, the anolyte always remains acid in reaction. Glucose, starch or sugar may replace the alcohol.[6] The purely chemical action of chlorine or bromine on acetone yields usually a mixture of products which are very difficult to separate. With platinum electrodes the electrolysis of a solution of acetone in water containing some hydrochloric or hydrobromic acids, a chloride, or a bromide yields a smooth reaction with the formation of only one product, the monohalogen acetone.[7] The insolubility of the monochloracetone causes the product to separate as an oily layer on the surface of the electrolyte and so is removed from further action. Equal volumes of acetone and 22° Bé. HCl are best electrolyzed at room temperature between platinum electrodes without a diaphragm. Since the monochloracetone is not very easily reduced at a platinum cathode the yields are about 80 per cent based on the current used.

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[3] (See later).

[4] Pogg. Ann., **19**, 83 (1830).

[5] E. Schering, Z. Elektrochem., **1**, 70 (1894); "?," Lum. elec., **52**, 226 (1894); Z. Elektrochem., **1**, 70 (1894).

[6] Tommasi "Traite," page 741.

[7] A. Richard, Compt. rend., **133**, 878 (1901); Richard, "Contribution a l'étude d. deriv. hal. d. acetone d. l. ser. grasse," Bordeaux (1904); Riche, Compt. rend., **49**, 176 (1859); Mulder, Jahresb. f. Chem., **339** (1859).

If the temperature rises, the yields are low; therefore cooling is necessary. There are always losses due to some oxidation of the acetone and to the evolution of gaseous chlorine. Monobromacetone has also been prepared in 74 to 93 per cent yields.[8]

The homologues of acetone, i.e., methyl ethyl ketone, methyl propyl ketone, diethyl ketone, etc., yield only the mono-substituted ketones by the electrolytic methods. However a variety of compounds are also formed whose constitution has never been worked out.

Substitution in Alkaline or Neutral Solution.—In the purely chemical methods iodoform is prepared by the action of iodine on water solutions of alcohol or acetone in the presence of sodium carbonate. The reaction is supposed to be as follows:

$$CH_3CH_2OH + 3I_2 + 2HIO \rightarrow CHI_3 + CO_2 + H_2O + 5HI$$

From this equation it is observed that 8 atoms of iodine yield one molecule of iodoform, which means that 5 out of every 8 atoms of iodine are not available in the iodoform. This iodine must be recovered in practice by the use of chlorine or hypochlorite solutions to oxidize them back to free iodine.

In the electrolytic method for the preparation of iodoform the starting materials are an alkaline solution of alcohol in which is dissolved some potassium iodide. In this case the free iodine of the purely chemical method is replaced by the potassium iodide, and the passage of the current liberates iodide ions at the anode to produce the required free iodine. The sodium iodide formed by the reaction is again electrolyzed and split up into iodide ions. This makes the process more or less continuous and eliminates the side reactions which take place when impure iodine is used. The first electrolytic method for the preparation of iodoform was described by E. Schering,[9] but was very quickly modified.[10] Probably the best and most efficient method for the preparation of iodoform is that described by Erich Müller.[11]

The reaction at the anode is supposed to be:

$$CH_3CH_2OH + H_2O + 10I^- + 10F \rightarrow CHI_3 + CO_2 + 7HI$$

and at the cathode,

$$10K^+ + 10H_2O + 10F \rightarrow 10KOH + 5H_2$$

$$10KOH + 5H_2O + 5CO_2 \rightarrow 5K_2CO_3 + 10H_2O$$

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[8] Richard, loc. cit.

[9] E. Schering, D.R.P. 29771 (1884); Kempf., U.S.P. 372940 (1885).

[10] K. Elbs and W. Herz, Z. Elektrochem., **4**, 113 (1897); F. Foerster and W. Meves, ibid., **4**, 268 (1897); Dony-Henault, ibid., **7**, 57 (1900).

[11] E. Müller, "Elektrochemisches Praktikum," p. 193; Elbs, "Übungsbeispiele," p. 131.

That the alcohol is not a depolarizer for the iodide ions is shown by the fact that the addition of alcohol to an aqueous solution of potassium iodide does not cause a decrease in the decomposition voltage. The above equations also show that in all, 10 atoms of iodine are required while 7 of them are used to form 7 equivalents of acid; these 7 molecules of acid neutralize 7 molecules of the 10 of alkali set free at the cathode in the same time, and 2 of these are necessary to produce the hypoiodous acid required by the equation above. Therefore for every molecule of iodoform produced there are set free 10 equivalents of potassium hydroxide at the cathode of which only 9 are combined, leaving 1 free equivalent of potassium hydroxide which will increase the concentration of the hydroxyl groups to such an extent that the hypoiodous acid reacts with itself to form an iodate and so lower the yield of iodoform. To remove this free alkali as it is formed is the function of the slow stream of carbon dioxide which is passed through the electrolyte just under the cathode. The stream of this gas must be so regulated that the alkali is changed to the carbonate; but if too much carbon dioxide is passed the carbonate is further changed to the bicarbonate which then increases the concentration of the hydroxyl ions above that value required for a maximum yield of iodoform. The amount of gas passed must be so regulated that there is always the amber yellow color in the electrolyte which indicates that the ratio I_2 : HIO is correct. When the yields are low the cause is the formation of iodates or the reduction of the hypoiodite to iodine at the cathode. Elbs and Herz have found that the amount of iodate formed may be decreased by increasing the concentration of the potassium iodide in the electrolyte, and with it, an increase in the amount of iodoform as shown by the table:[11a]

TABLE XV

Amp.-Hrs.	G. of KI	G. HIO_3 Formed	Yield of CHI_3	
			In grams	In per cent, theoretical
1.5	5	0.379	1.238	56.2
1.5	10	0.0866	1.710	77.7
1.25	15	0.0288	1.701	93.0

[11a] Elbs and Herz, Z. Elektrochem., **4**, 113 (1897).

The yield [12] of iodoform on the basis of current efficiency is dependent to a great extent on the current density at the anode:

1 amp./sq. dm. yielding 95–97 per cent iodoform
2 amp./sq. dm. yielding 80–93 per cent iodoform
3 amp./sq. dm. yielding 73–79 per cent iodoform

The process may be made continuous by adding from time to time the required amounts of potassium iodide, alcohol and alkali carbonate as indicated by the number of ampere hours of current passed according to the above equations. The iodoform settles out on the bottom of the cell, for it is insoluble in the electrolyte and is removed as conditions require.

If the reaction is carried out with a diaphragm the potential required for the passage of the current is higher than without the diaphragm. Merely wrapping the cathode in parchment paper will increase the yields without increasing the potential requirements as much as if a clay diaphragm were used.

The chemical reaction in which the free iodine, and not potassium iodide, is the starting material gives yields of only 20 to 30 per cent of iodoform, calculated on the iodine used, the rest of the iodine going to form potassium iodide and iodate. On the other hand the electrolytic method yields up to 98 per cent of the theoretical amounts of iodoform. The difference in yields is due to the fact that the discharge of iodide ions is so regulated that the amount of hypoiodous acid is only sufficient to react with the alcohol without allowing the accumulation of an excess which would react with itself to form iodic acid and so lower the yield of iodoform.

According to the wording of the Schering [13] patent for the preparation of iodoform from ethyl alcohol, the latter may be replaced by acetone without affecting the quality of the resulting product. Particulars of the method and the reaction, however, are not given, but it may be expected that the reaction goes something like this:

$$CH_3COCH_3 + 3I^- + H_2O + 6F \rightarrow CHI_3 + 3H^+ + CH_3COOH$$

The use of acetone in place of ethyl alcohol has several advantages, one of which is that 1 mol of iodoform as shown above is produced by the passage of only 6 faradays of electricity, which is 4 faradays less than the amount of current required in the use of alcohol. On the other hand at the cathode there are 6 equivalents of potassium hydroxide liberated,

[12] Foerster and Meves, Z. Elektrochem., 4, 268 (1897).

[13] D.R.P. 29771 (1884), E. Schering.

of which only 4 are neutralized by the acid liberated at the anode. The two free equivalents of potassium hydroxide are neutralized according to Abbot [14] by the addition of acetone in small portions during the course of the electrolysis using a cell with a reflux condenser. There are usually large losses when acetone is used, due to the formation of by-products from side reactions between iodine and acetone, the nature of which has not been definitely determined. Much better results may be obtained if the reaction is carried out in an almost neutral solution without a diaphragm not above 25° C.[15] The use of a very small cathode and therefore a very large cathodic current density, as described by Oettell,[16] lowers very considerably the losses due to cathodic reduction. The theoretical amount of iodoform by the passage of 1 ampere hour will therefore be 3.67 g. Teeple [17] obtained 3.34 g., which is 91 per cent of the theoretical yield for one ampere hour of electricity.

An excellent method has been developed by G. A. Roush [18] in which the reaction of the electrolyte is kept neutral by electrochemical means.

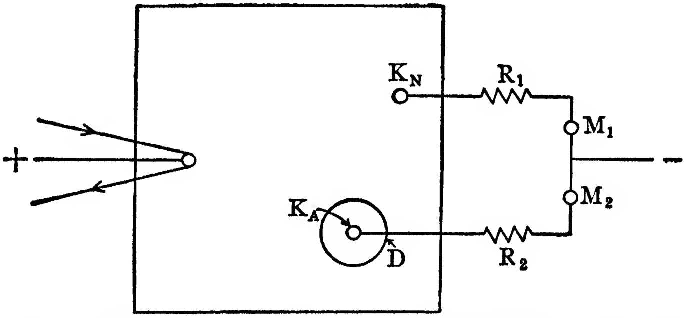

FIG. 6.—Sketch of a Cell with a "Roush Neutralization Cathode."

In the glass cell of about 350 or 400 cc. capacity is a clay cell, *D*, in which is placed one cathode, K_A, formed from copper foil which is the auxiliary cathode. A second cathode K_N, the neutralization cathode, is free in the electrolyte and is made from platinum wire. The glass cell contains a solution of 20 g. of potassium iodide and 1.5 cc. of acetone in 250 cc. of water. The clay cell contains an 8 per cent solution of potassium iodide. The two cathodes are connected in parallel with the supply current and to each cathode is connected a resistance, R_1 and R_2, and an ammeter, M_1 and M_2, in series so that the current in each can

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[14] H. Abbot, J. Phys. Chem., 7, 84 (1903).

[15] J. E. Teeple, J. Am. Chem. Soc., 26, 170 (1904).

[16] Oettel, Z. Elektrochem., 1, 90 (1894).

[17] Loc. cit.

[18] G. A. Roush, Trans. Am. Electrochem. Soc., 8, 283 (1905).

be regulated independently of the other. The object is to permit the passage of only sufficient current through the cathode K_N to neutralize the acid liberated at the anode in the reaction. The equations above show that in the reaction there are 4 equivalents of acid liberated at the anode for every 6 faradays of electricity passed. Therefore 4 faradays must be passed through the cathode K_N in order to keep the electrolyte neutral. The remainder of the current must pass through the cathode K_A, which is 2 faradays. This means that the current in the direction of the cathode K_A must be $\frac{1}{2}$ of the current in the direction of the cathode K_N. Practice has shown that when the current ratios are $K_A : K_N :: 2 : 3$ the electrolyte remains neutral. The diffusion of some of hydroxyl ions through the clay cell can hardly be prevented, with a corresponding increase in alkalinity of the electrolyte. At best this increase is not sufficient to cause great damage to the efficiency of the system. When the platinum anode A has an area of 20 sq. cm. and the current through K_N is added to the current through K_A and this total divided by the area of the anode, i.e., 20 sq. cm., the result is the anodic current density, because the current which is divided at the cathode is united at the anode. By this method yields of 95 per cent based on current used have been obtained.

The preparation of bromoform by the electrolysis of an alcoholic solution of a bromide is impossible [19] because the reaction of the bromide and hypobromous acid, freed at the cathode by the discharge of the bromine ions, on the alcohol is so very slow that the hypobromous acid molecules interact to form bromic acid, and also act so rapidly as an oxidizing agent that the alcohol is entirely oxidized to aldehyde and acetic acid and finally to carbon dioxide and water. Trechzinsky [20] gives an incomplete description of a method of preparing bromoform from alcohol by using calcium bromide as the electrolyte and source of bromine.

On the other hand the electrolysis of a bromide solution in the presence of acetone yields almost the theoretical quantities of bromoform, probably because acetone is more difficult to oxidize than ethyl alcohol. The bromoform is probably formed by a secondary action of the bromine ions discharged at the anode according to the equation:

$$CH_3COCH_3 + 6Br + H_2O \rightarrow CHBr_3 + CH_3COOH + 3HBr$$

Coughlin has developed a method [21] for the preparation of bromoform in 100 per cent yields, when the anolyte is a solution of 25 g. potas-

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[19] K. Elbs and W. Herz, Z. Elektrochem., **4**, 118 (1897); Dony-Henault, ibid., **7**, 65 (1900).

[20] J. Russ. Phys. Chem. Soc., **38**, 734 (1906).

[21] P. Coughlin, Am. Chem. Jour., **27**, 63 (1902).

sium bromide, 10 cc. of acetone and 75 cc. of water with an anode of platinum foil. During the progress of the reaction a solution of sodium carbonate must be introduced into the anolyte to neutralize the acid formed by the reaction.

In the absence of a diaphragm the cathodic reduction may be greatly diminished by the addition of small amounts of potassium chromate, the effects of which are shown in the following table. The solution used contained 125 g. potassium bromide, 50 cc. acetone, 4 g. sodium carbonate, in 375 cc. of water. This solution was electrolyzed between platinum foil electrodes with a current of 2 amperes, that is, a c. d. of 3.0 amperes. In the course of the reaction a current of CO_2 was passed through the electrolyte about the anode.[22]

TABLE XVI

Time, in Hours, After the Start of the Electrolysis	Per Cent Current Used in Reduction	
	Without K_2CrO_4	With 1 g. K_2CrO_4
1	12.4	3 8
2	13.5	3.1
3	14.8	5.4
4	44.8	4.6
4.5	58.6	4.0
4.75	69.5	4.2

An excellent method for the preparation of bromoform is that devised by Müller and Loeb.[23]

According to the equation, or the reaction at the anode:

$$CH_3COCH_3 + 6Br^- + H_2O + 6F \rightarrow CHBr_3 + CH_3COOH + 3HBr$$

the passage of 6F means the deposition of 190.8 g. of copper in the coulometer and the formation of 252.9 g. of bromoform in the cell, from which data the current yield may be calculated.

The reaction at the cathode is:

$$6H_2O + 6K^+ + 6F \rightarrow 6KOH + 3H_2$$

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[22] Müller and Loeb, Z. Elektrochem., **6**, 40 (1899); Z. Elektrochem., **8**, 230, and 909 (1902); Z. Elektrochem., **7**, 389 (1901); Z. Elektrochem., **10**, 49, and 409 (1904).

[23] E. Müller and R. Loeb, Z. Elektrochem., **10**, 409 (1904); also E. Müller, Elektrochemisches Praktikum, pages 196–198; Elbs, "Übungsbeispiele," page 132.

The passage of the 6F frees 2 equivalents of potassium hydroxide so that the reaction for the cell may be written:

$$6KBr + 3H_2O + CH_3COCH_3 + 6F \rightarrow 2KOH + CHBr_3 + CH_3COOK + 3KBr + 3H_2$$

and the reaction of the electrolyte becomes alkaline as the electrolysis proceeds. Although the formation of bromoform requires hydroxyl ions, the concentration of these ions must not become too great lest the reaction for the formation of bromates take place:

$$3Br_2 + 6KOH \rightarrow 5KBr + KBrO_3 + 3H_2O$$

the speed of which is greater than the speed of the reaction for the bromoform production. The function of the potassium bicarbonate added at the start is to limit the numbers of hydroxyl ions:

$$KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O$$

But still the hydrolysis of a potassium carbonate solution produces too many hydroxyl ions for the equilibrium to be correct. Consequently there seems to be a direct oxidation of the acetone by the bromine to form acetic acid, carbon dioxide and hydrobromic acid:

$$4Br_2 + 3H_2O + CH_3COCH_3 \rightarrow CH_3COOH + CO_2 + 8HBr$$

Therefore the CO_2 must be passed through the anolyte just over the surface of the anode which prevents the concentration of hydroxyl ions from exceeding that of a bicarbonate solution. By this method pure bromoform containing some dissolved bromine is easily obtained in large yields. According to the above reactions, yields of 90 per cent of the theory are claimed on the basis of the current used. Besides the bromoform the reaction yields bromate, free oxygen, and small traces of other oxidation or bromine substitution products of acetone, the amounts of which increase if the hydrogen-ion concentration of the electrolyte becomes too small.

The presence of the free bromine in the electrolyte as an accelerator of the bromination has been criticized[24] on the ground that the action of bromine on acetone (purely chemical) goes in three steps, requiring considerable time for completion:

$$2Br + CH_3COCH_3 \rightarrow CH_2BrCOCH_3 + HBr$$

$$4Br + CH_3COCH_3 \rightarrow CHBr_2COCH_3 + 2HBr$$

$$6Br + CH_3COCH_3 + H_2O \rightarrow CHBr_3 + CH_3COOH + 3HBr$$

[24] Feyer, Z. Elektrochem., **25**, 115 (1919).

All these end products are insoluble in water and so the bromoform will be contaminated by them.

For a long time the preparation of chloroform by electrolytic methods was a failure. When an alcoholic solution of an alkali chloride was electrolyzed, some chloroform, but mostly other oxidation products of alcohol were formed. As stated above, the decomposition voltage of a chloride is much greater than the decomposition voltage of either a bromide or an iodide. Even in a dilute acid solution the high voltage required for the separation of the chloride ion causes the chlorination to go on as far as the production of carbon tetrachloride. In an alkaline solution it is utterly impossible to expect that the hypochlorous acid formed would not have a greater oxidizing than chlorinating power. The electrolysis of a solution of 6 g. of sodium carbonate, 10 g. of KCl, 20 cc. of alcohol, in 100 cc. of water with a c. d. of 0.5 ampere between platinum electrodes at a temperature of 60° yields no chloroform but only higher oxidation products of alcohol.[25] There is a discharge of hydroxyl ions rather than a discharge of chloride ions at the anode. On raising the concentration of the chloride and also the current density in the solution there is a discharge of chloride ions, and when the concentration of the alcohol is decreased some chloroform is formed.[26]

The lowering of the hydroxyl-ion concentration by the carbonate-bicarbonate method as in the preparation of iodoform is not applicable here, because the regulation is not sufficiently close to prevent oxidation reactions. The method of Roush [27] is to be preferred. By this method [28] the electrolysis of an alcoholic solution gives current yields of 77 per cent and material yields of 82 per cent.

The reaction for the formation of chloroform is:

$$CH_3CH_2OH + 10Cl^- + H_2O + 10F \rightarrow CHCl_3 + CO_2 + 7HCl$$

Another method of preventing an increase in the alkali content of the electrolyte is to start with a solution of calcium chloride instead of sodium or potassium [29] chloride. The very slight solubility of the calcium hydroxide causes it to be precipitated. The platinum cathode is soon covered with a very impervious membrane possessing so high a resistance that the current ceases to pass. A method of preventing this has not been developed. Nickel or copper cathodes previously dipped in nitric acid, to thoroughly clean and smooth them, show very little

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[25] K. Elbs and W. Herz, Z. Elektrochem., **4**, 118 (1897); see also Dony-Henault, ibid., **7**, 65 (1900).

[26] Trechzinsky, Jour. Russ. Phys. Chem. Soc., **38**, 734 (1906).

[27] Roush, loc. cit.

[28] F. Foerster, "Wässerige Lösungen," p. 800; J. Feyer, loc. cit.

[29] Teeple, J. Am. Chem. Soc., **26**, 556 (1904); Trechzinsky, loc. cit.

increased resistance even after 20 hours of continuous use. An alcoholic solution which contains 500 g. calcium chloride to the liter gives a much larger yield of chloroform than does a solution in which sodium chloride is the electrolyte.[30]

The calcium chloride electrolyte may also be replaced by a solution of 80 g. of barium hydroxide and 1 g. of barium chloride in 300 cc. of H_2O to which 30 cc. of alcohol are slowly added during the electrolysis while the temperature rises gradually from 50° to 70°. From this electrolyte the chloroform and the alcohol distill off together in 35 per cent current yields. The production of barium formate as a by-product has not been explained.[31] The barium salts used must, in all cases, be free from $BaCO_3$, and the calcium salt must be free from contamination by iron salts. Magnesium chloride gives a lower yield than barium chloride.[32] The higher homologues of ethyl alcohol do not yield pure chloroform by the electrolytic method. Other chlorinated products interfere with the easy working up of the solution. In fact the chlorination products of propyl alcohol are unknown.

The formation of chloroform from acetone was studied by Teeple.[33] He obtained the best results with a solution of 120 g. of NaCl, 25 cc. of acetone in 700 cc. of water electrolyzed at room temperature between a platinum foil anode, which also acted as a stirrer, and a platinum wire cathode. The electrolyte had to be kept neutral, or at best very slightly alkaline, but the neutral point could not be detected in this case by a color change as was the case in the production of iodoform and bromoform. The indicator chosen to show the neutral point was trinitrobenzene. The neutralization was effected by hydrochloric acid, the amount of which may be calculated from the equation:

$$6NaCl + 3H_2O + CH_3COCH_3 + 6F \rightarrow$$
$$2NaOH + CHCl_3 + 3NaCl + CH_3COONa + 3H_2$$

The carbonate-bicarbonate method of neutralization gives 9 per cent yields when acetone is electrolyzed in the presence of NaCl between platinum electrodes. The Roush modification for neutralization gives yields of 65 and 80 per cent based on current and material used respectively.[34]

Methyl ethyl ketone also yields chloroform when electrolyzed in a solution containing an alkali chloride.[35]

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[30] J. Feyer, Z. Elektrochem., **25**, 115 (1919), who claims 82 per cent yields.

[31] B. Waeser, Chem. Ztg., **34**, 141 (1910).

[32] J. Feyer, loc. cit.

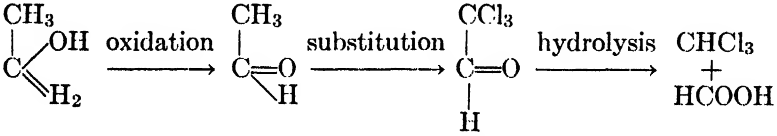
[33] Teeple, J. Am. Chem. Soc., **26**, 536 (1904).

[34] J. Feyer, loc. cit.

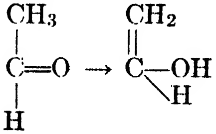
[35] J. Feyer, loc. cit., 41.2–44.4 per cent current and 31.7–47.5 per cent material yields.

The hypochlorous acid formed by the discharge of the chloride ions at the anode has a possibility of two reactions: that is, it may either form chloroform by its action on the alcohol and the acetone or it may react with itself to form a chlorate or chloric acid. An analysis of the conditions shows that in a neutral solution a rather high concentration of hypochlorous acid must be obtained before these molecules interact to form chloric acid, which condition is obtained with a high c. d. and a low temperature. The best temperature for working practice is either at, or very little above room temperature, at least not above 25°, for an increase in temperature lowers the yield of chloroform.[36] Chloroform has a tendency under the influence of the passage of the current to become negatively charged and migrate toward the anode where it is decomposed with the formation of HCl.[37]

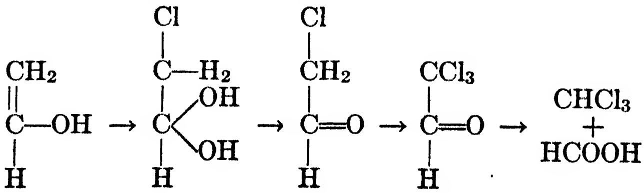
Schering patented a process on the assumption that electrolytic chlorination proceeds by the same mechanism as chemical chlorination, i.e., that there is a direct substitution of chlorine for hydrogen.



That is, the chloral is hydrolyzed in alkaline solution to the above products and the reaction is simply a case of the alcohol being a depolarizer. Dony-Henault [38] showed that the iodine in the preparation of iodoroform does not act directly but rather as hypoiodous acid, and that the alcohol is first oxidized to the aldehyde. Feyer considers that the aldehyde may assume an " enol " form:



this latter adds HOCl and splits out H_2O, the process continuing till trichloracetaldehyde is finally formed:



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[36] Feyer, loc. cit.

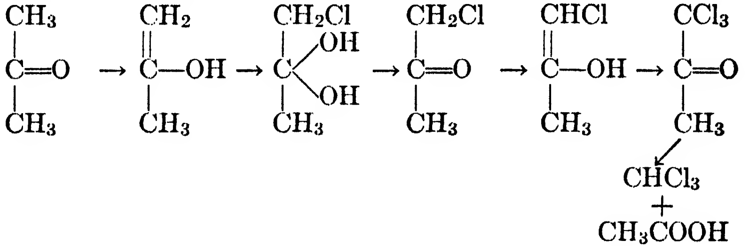
[37] F. Bottazzi, Atti. R. Accad. Lincei, [5], 18, ii, 133 (1909).

[38] Dony-Henault, loc. cit.

Then the formic acid is oxidized to CO_2 and we get the equation:

$$CH_3CH_2OH + 5HOCl \rightarrow CHCl_3 + CO_2 + 2HCl + 4H_2O$$

Richard [39] and Reich [40] have shown that chloracetone is the main end product with a little dichloracetone. Direct substitution reactions do not explain the reaction so well as an addition reaction. It is known that in an acid solution, acetone has a ketonic structure, but in alkaline solution it is enolic. Assuming that the enol form is present in alkaline solution we may have addition reactions as with the aldehyde above:



The reaction does not go to perchloracetone because trichloracetone is readily hydrolyzed by dilute alkali to chloroform.

In case of methyl ethyl ketone the methyl group evidently is not attacked, because if it were, propionic acid would result, but this acid has not yet been detected among the products of the reaction.

INTRODUCTION OF HALOGENS INTO AROMATIC COMPOUNDS

The electrolytic introduction of chlorine into aromatic compounds has been in a state of confusion for many years. Various results indicate that the reaction may proceed in two possible directions: the formation of addition products and the formation of substitution products. There are also two ways in which the mechanism of the reaction may be explained: (*a*) by a strictly electrolytic process, confined to the surface of the electrode, as in the case of electrolytic oxidation; or (*b*) by the secondary action of the dissolved chlorine gas as it is set free by the current and more or less distributed through the liquid. The determination of the exact mechanism is of great importance because both primary and secondary reactions may occur together, each yielding different results; but in any case, where the products are the same, and the latter process predominates, the use of the electric current is, for practical purposes, unnecessary because the same results can be obtained by the use of chlorine gas with a purely chemical method of chlorination.

Under the usual experimental conditions there seems to be no cor-

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[39] Loc. cit.

[40] Loc. cit.

relation between the amperage used and the yield of the products. In general, however, it may be said that suspensions of the aromatic hydrocarbons and their derivatives are not chlorinated with very good yields. On the other hand a clear solution in glacial acetic acid yields very satisfactory amounts of chlorinated products though the result is not a single compound but a mixture of several. Mülhofer[41] electrolyzed a suspension of benzene in concentrated HCl and obtained an oily chlorinated product which boiled between 100° and 140° C., but the greater part of the benzene remained unchanged. The addition of iodine as a catalyst had no effect on the reaction, which is contrary to the results obtained by Lowy and Frank.[42] Later Schleuderberg[43] in studying some actinochemical reactions found that, in the chlorination of benzene and similar hydrocarbons, the reaction of nascent chlorine resembles the action of chlorine in the presence of a halogen carrier rather than that of chlorine in sunlight, since the latter gave addition compounds. Benzene in ether saturated with $ZnCl_2$ was chlorinated electrolytically to about 70–80 per cent of the theoretical amount based on the combined chlorine, though the product was not a single substance. While the experimental data were not conclusive evidence, he was of the opinion that the chlorination in the case of benzene was due to the anodic depolarizing action of the benzene and therefore was a strictly electrochemical process.

The halogenation of benzene was rather carefully studied by Van Name and Maryott,[44] who investigated the effects produced by the electrolysis on graphite electrodes of a homogeneous solution of benzene together with an inorganic chloride in a non-aqueous solvent. Quantitative measurements were carried out with two solvents. In one case the solvent was acetic acid in which lithium chloride, previously dehydrated by fusion, was dissolved. In the second case anhydrous $ZnCl_2$ was dissolved in ether. The following is the summary with which they closed their paper:

1. Electrolysis of benzene in a solution of LiCl in glacial acetic acid gave chlorinated benzenes with current yields, under favorable conditions of 50–70 per cent. But addition and substitution chlorine were present in the product, the latter predominating. There was nothing to show that the effects were not due to the secondary action of chlorine previously set free by the current and dissolved in the liquid.

2. Benzene, dissolved in the same solution, is readily chlorinated

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[41] H. Mülhofer, Dissertation, Munich (1905).

[42] A. Lowy and H. S. Frank; Trans. Am. Electrochem. Soc., **43**, 107 (1923).

[43] C. G. Schleuderberg, Jour. Phys. Chem., **12**, 574 (1908).

[44] R. G. Van Name and C. H. Maryott, Am. Jour. of Science, **35**, 153 (1913).

by direct treatment with chlorine gas in the dark, yielding addition and substitution compounds in proportions which vary with the conditions.

3. The addition of benzene to the acetic acid-lithium chloride solution during the electrolysis raised the anode potential, and by an amount equal to or greater than that produced by a similar amount of carbon tetrachloride. This indicated that benzene has little or no depolarizing power toward chlorine, at least in this case. Phenol, added under similar conditions, produced a decided lowering of the anode potential.

4. The rate of chlorination of benzene, when dissolved in the same medium saturated with chlorine, was measured at 10.2°. Simultaneous electrolysis did not accelerate the chlorination perceptibly under conditions where a 10 per cent current yield could have been evident. The current yield, if appreciable, was therefore below 10 per cent.

5. The products of 4 above contained addition and substitution chlorine in the ratio of about 2 to 3, this ratio increasing slowly as the reaction progressed. The reaction velocity, calculated on the assumption that monochlorobenzene and benzenehexachloride were the sole products, showed a steady rise, but the rate of chlorination of monochlorobenzene, separately determined, appeared to be sufficient to account for this effect.

6. No positive evidence of strictly electrolytic (i.e., anodic), chlorination of benzene was obtained.

In 1916 Fr. Fichter and L. Glantzstein [45] reported some work on the electrolytic chlorination of benzene and its homologues. They suggest that the discordant results previously obtained are due to the lack of homogeneity in the electrolyte. In their opinion the electrolysis of clear glacial acetic acid solutions leaves no room for doubt but that the chlorination of benzene takes place as a truly electrochemical process. Under suitable conditions the chlorination can be pursued to its utmost limits, though the products are always contaminated by the presence of oxidation products. They were able in the case of benzene to isolate monochlorobenzene, *p*-dichlorobenzene, *sym*-tetrachlorobenzene, hexachlorobenzene, pentachlorophenol and chloranil. The formation of these products is sufficient evidence that the reaction is very complex, which accounts for the fact that there is no relation of any great consequence between the work done and the quantity of current of the duration of the reaction. The chlorination of benzene seems to follow in a general manner the law of mass action. Platinum electrodes give the best yields of chlorinated products and hexachlorobenzene but

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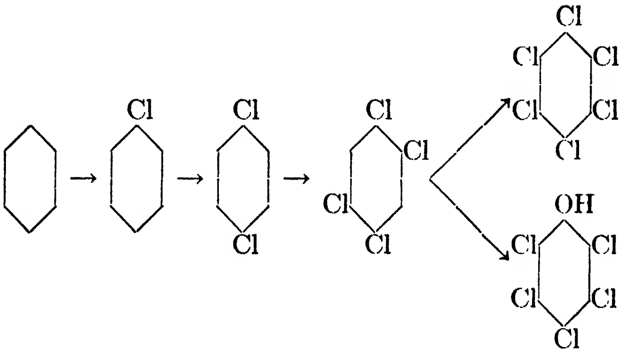
[45] Ber., **49**, 2473 (1916); also L. Glantzstein, Dissert., Basel (1916); C. Stehelin, Dissert., Basel (1914).

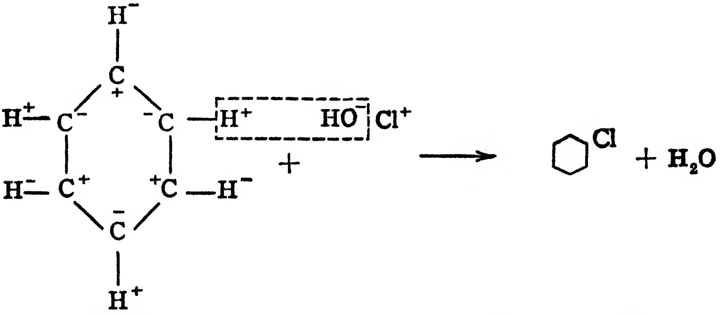
oxidation products are also present; at least one half of the product being soluble in alkali hydroxides. Electrodes of graphite and magnetic iron oxide give lower yields than platinum. The best current for the production of chlorination products in general is when 3 atoms of chlorine are liberated for each molecule of benzene in the solution, that is, when the current is 3 faradays. No conclusion can be drawn from this work as to the nature of the mechanism of the reaction (that is whether it is of strictly electrochemical origin or not). The scheme suggested for the chlorination of benzene is:



The electronic conception of valence developed by Fry[46] assumes that in the chlorination of benzene and its homologues, a carrier acts as a source of positive halogen, and, in the case of water being present, the chlorine first reacts with the water:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

The hypochlorous acid formed then acts as a source of positive chlorine which replaces positive hydrogen in the benzene.



An attempt[47] has been made to verify this mechanism. With chlorine and benzene in the presence of water, substitution was obtained.

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[46] Fry, "Electronic Conception of Valence," Longmans.

[47] A. Lowy and H. S. Frank, Trans. Am. Electrochem. Soc., **43**, 107 (1923).

Under identical conditions, with anhydrous materials, no substitution took place, but a considerable amount of benzene hexachloride was produced. As the results with water were duplicated when light was excluded from the system, there was, obviously, no photochemical action, and the effect was due entirely to water, which probably acts as suggested by Fry. The yields were nearly doubled by allowing the charge to stand over night at the conclusion of the experiment, i.e., the chlorine in solution caused additional chlorination. This theory gains some support from the work of Bruner and Czarnecki[48] who claim that substitution is independent of electrolysis; that it is due to atomic halogen when the substitution is on the nucleus, and to molecular halogen when in the side chain,[49] and further that nuclear substitution is influenced by the presence of ionized media.[50] That the reaction is partly an electro-chemical phenomenon is evidenced by the fact that the electrolytic method forms the more highly chlorinated products which the non-electrolytic reaction does not produce under the same conditions. However, the question is still undecided. Both reactions take place.

The work on the chlorination of toluene is a little more conclusive than the work on benzene. Mülhofer[51] electrolyzed a suspension of toluene in concentrated hydrochloric acid at a platinum wire gauze anode at room temperature, with the result that good yields of monochlorotoluene were obtained, the product being a mixture of 30 per cent para- and 70 per cent ortho-chlorotoluene. There was no evidence that the side chain was attacked and higher chlorination products were not detected in the reaction products. A halogen catalyst, such as iodine, did not change the halogenation product. When a mixture of toluene and strong hydrochloric acid was electrolyzed at the boiling point between carbon electrodes mostly the *p*-chlorotoluene was formed.

When pure toluene was electrolyzed at the boiling point between carbon electrodes in a flask fitted with a reflux condenser the rate of chlorination was greater than by the purely chemical method using pyrolusite and hydrochloric acid, but the carbon electrodes were without action on the chlorination process.[52] The chlorine entered the ring and the products were a mixture of *o*- and *p*-chlorotoluenes. The ratio of chlorination was in most cases from 10 to 30 per cent in the ortho- and 70 to 90 per cent in the para-position.

Schleuderberg,[53] found that electrolytic chlorine in the presence of

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[48] Bruner and Czarnecki, Anzeig. Akad., Krakow, 322 (1909).

[49] Bruner and Dluska, ibid., 691 (1909).

[50] Bruner and Vorbrodt, ibid., 221 (1909).

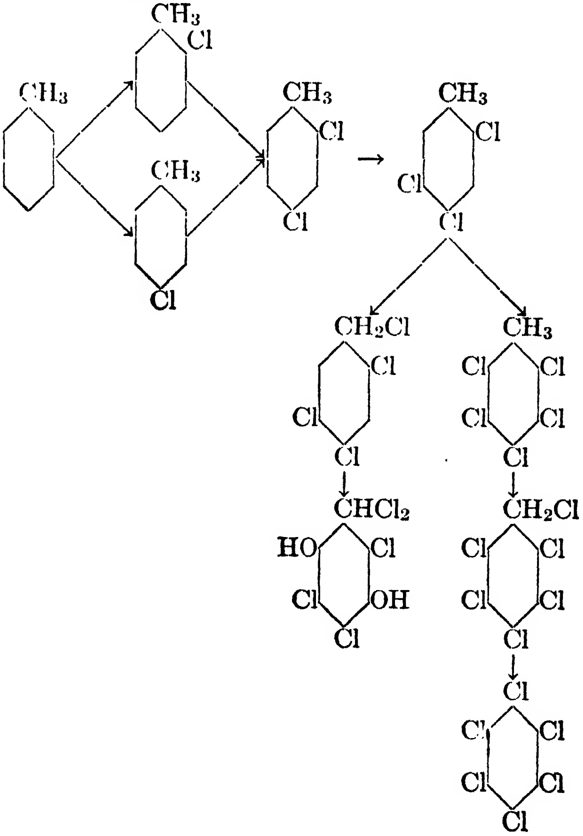
[51] Loc. cit.

[52] J. B. Cohen, H. M. Dawson, P. F. Crosland, J. Chem. Soc., **87**, 1034 (1905).

[53] Loc. cit.

dilute acids or alkalies yields some addition products besides substitution products.

Fichter and Glantzstein[54] continued this work on toluene but encountered a great difficulty in separating the complex compounds formed by the reaction. In the dark, at least three chlorine atoms were introduced into the molecule before the methyl group was attacked. By various methods they were able to identify the following products in the reaction mixture; *o*- and *p*-chlorotoluene, 2, 4-dichlorotoluene, 2, 4, 5-trichlorotoluene, pentachlorotoluene, pentachlorobenzyl chloride, hexachlorobenzene, 2,4,5-trichlorobenzyl chloride, 2,4,5-trichlor-3-6-dihydroxybenzal chloride. With very low current densities the sole products were mono and di-chlorotoluenes. As the current density increased the trichlorotoluene was formed. Quinol derivatives were formed and caused trouble in isolating the products of the reaction. The scheme is probably:



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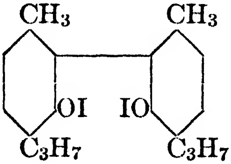
[54] Loc. cit.

m-Xylene in concentrated hydrochloric acid solution at room temperature between platinum wire gauze electrodes yields chlor-*m*-xylene by a reaction which is similar to the chlorination of *m*-xylene in the presence of an iodine carrier.[55]

Naphthalene, under the conditions for the electrolysis of xylene, yields only small amounts of an addition product, naphthalenedichloride, while anthracene has never been attacked by electrolytic chlorine.

The products formed by the electrolysis of phenol in hydrochloric acid or hydrobromic acid depend on the concentration of the acid used.[56] In normal acid solution mostly oxidation products are formed because the discharge of hydroxyl ions is easier than the discharge of the chloride or bromide ions. As the concentration of the acid increases more halogen ions are discharged and they attack the phenol. In 1901 Zehrlant,[57] by electrolyzing 4N hydrobromic acid containing phenol, obtained a 20 per cent yield of bromophenol. He also showed that there was a decided depolarizing action of the phenol toward the bromine which led to a marked depression of the anode potential. Tribromophenol may be produced under suitable conditions of electrolysis.[58] If the phenol is in excess, monobromophenol is produced instead of the tribromophenol, though this product is not the only one.

Peculiarly, iodine has no action in acid solution. The electrolysis of phenol in a hydriodic acid solution causes the separation of only iodine at the anode.[59] On the other hand, in alkaline solution there is a substitution reaction in which a hydrogen of the phenolic group is replaced to form an iodoxy compound.[60] A solution of 3 parts of thymol, 0.8 parts of sodium hydroxide, 7 parts of potassium iodide in 200 parts of water on electrolysis yields dithymoldiiodide:



The product is insoluble in the electrolyte and so separates as the reaction proceeds. Dithymoldiiodide is a substitute in medicine for iodoform and is commercially known as Aristol. Other substitution products, such as derivatives of phenol, β-naphthol, salicylic and cresotinic

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[55] Mülhofer, loc. cit.

[56] Zehrlant, Z. Elektrochem., 7, 501 (1901).

[57] Zehrlant, loc. cit.

[58] Mülhofer, loc. cit.

[59] Zehrlant, loc. cit.

[60] D.R.P. 64405 (1891), addendum to D.R.P. 49739, Bayer & Co.

acid, carvacrol, *p*-isobutylphenol, *o*-, *m*-, *p*-isobutyl cresol, etc., may be made by electrochemical methods, or by the action of iodine in alkaline solution.

The decomposition voltage of aniline in hydrochloric or sulphuric acid is 0.95 volt, which is lower than that of any of the other acids, and accordingly no chloraniline is formed.[61] The only product is aniline black, formed by an oxidation reaction. However, if the concentration of the aniline in the region of the electrode surface is made sufficiently small, the oxidation reaction can be depressed and the anode potential rises to that required for the steady evolution of chlorine (the decomposition voltage of hydrochloric acid), and chloraniline is formed by the diffusion and subsequent reaction of these discharged ions which are rather soluble in the electrolyte. On the other hand the oxidation potential of aniline is higher, by but a very small amount, than the decomposition voltage of hydrobromice acid and consequently the electrolysis of aniline in hydrobromi acid, solution yields bromaniline without the formation of any aniline black. The bromaniline, being insoluble, crystallizes from the anolyte. Without giving any details, Elbs and Brunnschweiler[62] have reported that the electrolysis of an hydrochloric acid solution of aniline or *o*- and *p*-toluidine always yields small amounts of chlorinated quinones.

In a divided cell potassium benzenesulphonate yields in a potassium chloride solution at a carbon anode a mixture of mono-, di-, tri-, and tetra-chloro-*p*-benzoquinones; the latter especially at the boiling temperature. Potassium bromide solutions act the same but potassium iodide solutions give no reaction except the separation of free iodine at the anode. Without a diaphragm no chloroquinones are formed.[63]

A combination reduction-substitution reaction was discovered by Löb[64] when he reduced nitrobenzene in the presence of concentrated hydrochloric acid at a platinum cathode. From the products he isolated a mixture of *o*- and *p*-chloraniline. The formation of these products is supposed to follow the equation:

$$1. \qquad C_6H_5NO_2 = C_6H_5NHOH + H_2O$$

$$2. \quad C_6H_5NHOH + HCl = \underset{p-}{\overset{o-}{}}\,Cl\cdot C_6H_4NH_2$$

However this is not a true electrolytic reaction, though it goes better in the presence of an electric current.

An electrochemical reaction which does not seem to have received

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[61] L. Gilchrist, J. Phys. Chem., **8**, 539 (1904).

[62] Elbs and Brunnschweiler, J. prakt. Chem. [2], **52**, 599 (1895).

[63] J. H. K. Ingliss and F. Wooten, J. Chem. Soc., **93**, 1592 (1908)

[64] W. Löb, Z. Elektrochem., **3**, 46 (1896); Ber., **29**, 1894 (1896).

its just dues is the bromination of the indigoid dyes. When indigo is electrolyzed with rapid stirring, in a 40 per cent hydrobromic acid suspension or in a solution of sulphuric acid containing a bromide, a bromindigo is formed at a carbon anode; the amount of bromination depends on the duration of the reaction and the current. A diaphragm is not necessary because these indigoid substitution products are not reduced cathodically in acid suspensions. By the purely chemical method the bromine is introduced into the molecule by the direct action of bromine in the presence of aqueous solutions of hydrochloric acid or sulphuric acid, but for each atom of bromine introduced, an atom of bromine is lost as hydrobromic acid.[65] If concentrated sulphuric acid or chlorosulphuric acid be employed in the chemical method,[66] five or six atoms of halogen may be introduced into the molecule. The advantage of the electrochemical method is in the fact that all the bromine or bromide ions in the solution are available directly for bromination and no bromide is evolved in the form of HBr by the reaction. Therefore instead of requiring two atoms for every bromine atom introduced, only one atom of bromine (one-half as much) is required to produce the same quantity.

Similarly there are possibilities of the introduction of bromine into the fluorescein molecule.[67] The eosin produced is of sufficient purity to be used directly in commerce. By replacing the bromine by iodine, erythrosine may be produced from fluorescein. In each of these reactions no halogen is lost as halhydric acid and so only the halogen actually required for introduction into the molecule need be added to the system. The one unfortunate factor of the electrochemical reaction is that the c. d. required is so very low that very large platinum electrodes must be used. This precludes the application of the method to very large batches of material on the industrial scale. Tetraiodophenolphthalein has been prepared by the electrochemical method from phenolphthalein.[68]

According to the method outlined by Mülhofer,[69] almost quantitative material and current yields of *p*-chlorohydrocinnamic acid are obtained by the electrolysis of hydrocinnamic acid, in 30 per cent HCl between platinum wire gauze electrodes. As the reaction proceeds, the chlorinated product separates from the electrolyte as a white solid which contains about 99 per cent of the *p*- and 1 per cent of the *o*-compound. Even high current densities permit the reaction to

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[65] D.R.P. 149941 (1902), Meister.

[66] Brit. P. 2609 (1909).

[67] D.R.P. 108838 (1899), Soc. Chim. des Usines du Rhone.

[68] A. Classen and W. Löb, Ber., **28**, 1603 (1895).

[69] Mülhofer, loc. cit.

proceed in a quantitative manner and as the reaction reaches completion the excess of chlorine is evolved as a gas from the anolyte. Cinnamic acid in the presence of potassium bromide yields bromostyrene [70]

SUBSTITUTION BY MEANS OF CONCENTRATION

As stated above on page 146, there is a second class of substitution reaction, i.e., the reaction which is due to the accumulation of the anion of an oxy-acid at the anode and a subsequent interaction with the organic compound in the electrolyte. The reaction only begins when the anion concentration reaches a certain value as determined by the current density and the inherent nature of the added groups. There may therefore be sulphonation, nitration, diazotization, etc., depending on the system of reacting substances chosen.

Unfortunately there has been no systematic investigation of this particular field and there are but few results which can be considered as coming under this group of reactions. By carefully controlling the conditions of electrolysis there should be a possibility of regulating the introduction of one or more sulphonic acid or nitro groups in various positions on the ring in the case of cyclic compounds.

The case of the nitration of naphthalene has been discussed above, the products being mono and dinitro-naphthalene.[71]

An example of the sulphonating action of sulphuric acid is found in the work of Merzbacher and Smith,[72] who electrolyzed an alcoholic solution of toluene in sulphuric acid and obtained, finally, *p*-sulphobenzoic acid.

Esters of organic alcohols and inorganic acids may also be prepared by this substitution reaction. An interesting preparation [73] is that of methylsulphuric, in which a mixture of two parts by volume of methanol and one part of 10 per cent sulphuric acid are electrolyzed to form at the anode about a 60 per cent material yield of methylsulphuric acid according to the equation:

$$CH_3OH + H_2SO_4 + F \rightarrow CH_3O \cdot SO_3H + H_2O$$

The most important reaction in this second group of substitution reaction is that of diazotization and coupling of an amine with another compound with the formation of a dye.[74] If a mixture of a nitrite and

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[70] Brester, Jahresb. f. Chem., 87 (1866); Löb, Z. Elektrochem., **3**, 46 (1896).

[71] See page 146; see also Tryller, D.R.P. 100417 (1897).

[72] Merzbacher and E. F. Smith, J. Am. Chem. Soc., **22**, 723 (1900); also Z. Elektrochem., **7**, 455 (1901); K. Puls, Chem. Ztg., **25**, 263 (1901).

[73] Renard, Ann. chim. et phys. [5], **17**, 289 (1879); see also Schlötter, Dissert., Munich (1902).

[74] W. Löb, Z. Elektrochem., **10**, 237 (1904); D.R.P. 152926 (1902); U.S.P. 761310 (1903), Boehringer.

a salt of an aromatic amine is electrolyzed at room temperature, the action at the anode forms the corresponding diazo compound of the amine. The reaction is the migration of the nitrite ions to the anode and there under the conditions of the experiment they react with the solvent water to form free nitrous acid, HNO_2, liberating gaseous oxygen. The free nitrous acid diazotizes the amine. The diazo compound may be coupled, if to the electrolyte in the very beginning of the reaction there is added some compound which will react quickly with the diazo compound as soon as it is formed, and so protect it from the oxidizing action of the current and other decomposing influences. The most desirable material according to Löb is a soluble phenol which forms the corresponding azo dye. Amines are not applicable because they undergo further action in the presence of the free nitrous acid at the anode. The results of Löb's investigation of the reaction show that the amine should be suspended in the aqueous anolyte together with a soluble coupling agent as the phenol and the soluble nitrite, all in the ratio of molecule for molecule. Examples are given in the following table. The first two dyes are soluble in the anolyte, but the second two separated from the anolyte during the course of the reaction:

TABLE XVII

Parts	Anolyte	Resulting Dye
195 144 69 700	Sodium sulphanilate β-naphthol $NaNO_2$ Water	Orange II
184 636 138 700 40	Benzidine Sodium naphthionate + $4H_2O$ $NaNO_2$ Water NaOH	Congo red
244 288 138 700	Dianisidine β-naphthol $NaNO_2$ Water	Dianisidine blue
184 320 138 700	Benzidine Sodium salicylate $NaNO_2$ Water	Chrysamine G.

Löb considered that only phenols could be used as the second component which must be present in the solution so that the diazo compound formed should be coupled and removed from the zone of action as quickly as possible. Krauss[75] extended the work of Löb and came to the conclusion that a phenol is not the only compound that can be used as the coupling agent.

In two instances the use of the electric current as a means of protection in the preparation of explosives has been recorded. Nitroglycerin and nitrocellulose[76] are formed in their nitration mixtures by the passage of an electric current with very little loss of acids and very little danger of explosion during the reaction.

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[75] R. B. Krauss, J. Am. Chem. Soc., **39**, 1427 (1917).

[76] U.S.P. 880373 (1908), Escales and Novak; U.S.P. 874564 (1907), Brialles.

PART II

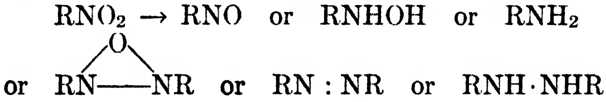
REACTIONS AT THE CATHODE

CHAPTER VIII

INTRODUCTION TO ELECTROLYTIC REDUCTION

GENERAL

THE reactions which take place at a cathode are reduction reactions, as opposed to the oxidation reactions which take place at an anode. The passage of an electric current through an electrolyte either deposits a metal on the cathode or evolves hydrogen. The electrolytic hydrogen may add to an organic compound or it may remove oxygen or both. An example of the addition of hydrogen to a molecule is found in the case of the reduction of cinnamic and nitrocinnamic acids. The best example of the removal of oxygen and in its place the substitution of hydrogen is the reduction of nitrobenzene, the various steps in the process being outlined as follows:



$$\mathrm{RNO_2} \rightarrow \mathrm{RNO} \quad \text{or} \quad \mathrm{RNHOH} \quad \text{or} \quad \mathrm{RNH_2}$$

$$\text{or} \quad \mathrm{RN}\overset{\mathrm{O}}{\overline{\qquad}}\mathrm{NR} \quad \text{or} \quad \mathrm{RN:NR} \quad \text{or} \quad \mathrm{RNH{\cdot}NHR}$$

What has been said in the introduction to electrolytic oxidation is for the most part applicable in the case of reductions, though there are some factors which are not of equal importance in both cases.

SPEED OF REDUCTION

Elbs was the first to study the speed of reduction by a reliable method.[1] He inserted a gas coulometer into the circuit with the reduction cell in order to measure the volume of hydrogen evolved by the current passing through the system. He compared this volume with

[1] Elbs, J. prakt. Chem., [2], **43**, 39 (1891); Z. Elektrochem., **7**, 119 (1900).

the volume of hydrogen evolved from the reduction cell containing nitrobenzene (i.e., with the volume of hydrogen not used in the reduction). This ratio gave an insight into the reducibility of various nitro compounds. The results indicate that nitro compounds were reduced more rapidly in alkaline than in acid solution; that mono-nitro were more rapidly reduced than poly-nitro compounds. In fact he found that the rate of reduction increased from member to member in the following series: picric acid, 2,4-dinitrophenol *p*-nitrophenol, *o*-nitrophenol. Picric acid was reduced half as fast as *o*-nitrophenol.

Elbs and Illig[2] attacked the problem from a slightly different angle. They reduced nitrobenzene and its homologs in an alcoholic-alkaline solution varying the current in such a manner that at first there was some hydrogen evolution at the cathode, then by a gradual reduction of the current strength finally no hydrogen was evolved. By careful measurements the exact "maximum current strength," at which value no more hydrogen was evolved for a given system, could be determined; that is, all the hydrogen evolved was used in the reduction of the nitrobenzene. At this point the speed of reduction was proportional to the current strength. This work of Elbs and Illig was carried a little farther by Zehrlant.[3]

In carrying out a similar study of the "maximum current strength" for nitrobenzene, the three nitrotoluenes, azoxy and azobenzene, Goldschmidt encountered difficulties.[4] He found the relation between the "maximum current strength" I_m and the concentration of the depolarizer C to be:

$$I_m = C^{2/3} + K \tag{1}$$

This relation was not the same for all temperatures, but the change was not very great even for 10° variations.

On the basis of Nernst's work, this equation did not seem to express correctly all the conditions.[5] Nernst's work applied both to anodic and cathodic depolarization though it was by no means a complete solution of the problem.

The theory which Nernst developed is known as the diffusion theory of depolarization. At the interface where the reaction takes place an equilibrium must be established with an extraordinarily great speed

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[2] Elbs and Illig, Z. Elektrochem., **5**, 111 (1898).

[3] Zehrlant, Dissert., Giessen (1901).

[4] Goldschmidt, Z. Elektrochem., **7**, 263 (1900).

[5] Nernst, Z. Elektrochem., **7**, 267 (1900); Z. physik. Chem., **47**, 52 (1904); also Noyes and Whitney, ibid., **23**, 689 (1897); Brunner, ibid., **47**, 56 (1904). See Ageno and Donini above on page 12.

because, if this did not happen, opposing forces would develop between the extremely close points where the reaction is occurring. The reaction velocity depends on the speed with which the mobile compounds reach the reaction interface. If the thickness of the contact interface between the reacting phases be represented by δ (while this thickness is measurable it is at the same time very slight, but all reactions occur here), C is the concentration of the diffusing substance at the surface of the fixed phase, c the concentration in the solution, D the diffusion constant, F the surface of the solid body, then in time dt the quantity of substance $dx = \mathrm{DF}\frac{\mathrm{C} - c}{\delta}dt$, will diffuse to the contact surface and immediately react. The reaction speed will be:

$$\frac{dx}{dt} = \mathrm{DF}\frac{\mathrm{C} - c}{\delta}, \tag{2}$$

and the speed is proportional to the concentration of the different substances. In most cases the reaction velocity depends only on the quantity of depolarizer getting to the electrode; but when ions are to be involved then the transfer number must also be included. The current strength is a measure of the reaction velocity except in two cases, i.e., when side reactions are encountered and when the discharge velocity is smaller than the reaction velocity so that the ions are not supplied with sufficient rapidity. When the current strength is such that all the liberated ions are just able to react then, and then only, is the current strength a measure of the reaction velocity. When the current strength is above this value there is usually an evolution of a gas at the electrode as a primary or a secondary reaction.

Therefore if we are to suppose that the adjustment of the equilibrium takes place with this extreme rapidity, the reaction velocity will on this basis be dependent solely on the diffusion velocity with which the depolarizer comes to the reaction interface and instead of the Goldschmidt equation $\mathrm{I}_m = \mathrm{C}^{2/3} + \mathrm{K}$ the equation will be $\mathrm{I}_m = \mathrm{KC}$. Just wherein this disagreement arises is unknown.

THE FUNCTION OF THE ELECTRODE POTENTIAL

Haber and Russ have developed a theory that is very much more in accord with the experimental work than the theories of Nernst and Goldschmidt. The theory[6] is applicable not only at unattackable electrodes but also at much lower current strengths than are permitted by the Goldschmidt assumptions. Hydrogen is the active principle in the reduction and it is liberated at the cathode according to the tenets

[6] Haber, Z. physik. Chem., **32**, 193 (1900); Haber and Russ, ibid., **47**, 263 (1904).

of Faraday's Law, which also permits the use of the ordinary gas laws. The foundation of the whole theory is that at the surface of the electrode there is a chemical equilibrium between the hydrogen ions and the gaseous H atoms either alloyed with or dissolved in the material of the cathode. This permits considering the hydrogen as the only active reducing agent, so that using Nernst's electrode potential formula we get

$$E = RT ln \frac{C_H}{C_{H^+}} \tag{3}$$

in which E is the electrode potential, R the gas constant, T the absolute temperature, C_H the concentration of the hydrogen gas absorbed in the surface of the electrode, C_{H^+} the concentration of the H^+ ions at the surface of the cathode.

The reactions which take place at the cathode are

$$(a) \quad 2H^+ + 2F = 2H$$

$$(b) \quad RO + 2H = R + H_2O$$

or

$$(c) \quad R + 2H = RH_2$$

On the basis of the Law of Mass Action the speed with which either one of these two reaction proceeds is expressed by the equation

$$\frac{-dC_{RO}}{dt} = kC_{RO}(C_H)^2S \tag{4}$$

in which C_{RO} is the concentration of RO in the electrolyte; if the current is not too strong the concentration of RO at the surface will be the same as the concentration all through the electrolyte. C_H is the concentration of H in the electrode, S is the area of the surface of the electrode and k is a proportionality constant. The equation means that the rate of change of the concentration of RO in an infinitely small period of time, i.e., $\frac{-dC_{RO}}{dt}$ is equal to $kC_{RO}(C_H)^2S$. Since the experimental conditions are such that 100 per cent of the theoretical yield is obtained we can assume that the rate of reduction of RO is proportional to the current I; that is

$$\frac{-dC_{RO}}{dt} = k'I \tag{5}$$

combining (5) and (4) we get

$$I = \frac{k}{k'}C_{RO}(C_H)^2S \tag{6}$$

but by using a standard electrode with the same area in each case the area S can be eliminated giving the equation;

$$I = k''C_{RO}(C_H)^2 \tag{7}$$

solving the equation for $(C_H)^2$ and inserting this value in the potential equation (1) above we get

$$E = \frac{RT}{2} ln \frac{I}{k''C_{RO}(C_{H^+})} \tag{8}$$

but in order to make measurements, the value of C_{H^+} must be held constant during the reaction, the equation then becomes

$$E = \frac{RT}{2} ln \frac{I}{kC_{RO}} \tag{9}$$

or

$$E = \frac{RT}{2} ln \frac{I}{C_{RO}} - K \tag{10}$$

The logarithmic relation between the current and the concentration of the depolarizer on the one hand with the potential on the other hand was proven, but the constant $\frac{RT}{2}$ was found to be slightly in error so that Haber and Russ[7] introduced into the potential equation a multiplying factor x which as a rule is slightly larger than 1; this makes the final equation for the potential:[8]

$$E = x\frac{RT}{2} ln \frac{I}{C_{RO}} - K \tag{11}$$

At first there was a great deal of uncoordinated data concerning the reduction of aromatic nitro compounds. Häussermann[9] and Elbs[10] had shown that the reduction of nitrobenzene in alcoholic H_2SO_4 solution was not as complete at a platinum as at lead or zinc cathodes. Elbs laid the stronger reducing power of the two latter metals to their chemical nature, i.e., zinc reduced nitrobenzene in the presence of dilute sulphuric acid by dissolving and so sending zinc ions into solution. These ions by the passage of the current were discharged at the cathode and deposited there as zinc-black. By the reduction of further quanti-

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[7] Loc. cit.

[8] The factor x is a function of the electrode condition and the constitution of the electrolyte, etc. For a discussion of the meaning of x see the work of Russ, Z. physik. Chem., **44**, 641 (1903).

[9] Häussermann, Chem. Ztg., **17**, 129 and 209 (1893).

[10] Elbs, ibid., **17**, 209 (1893); Z. Elektrochem., **2**, 472 (1896).

ties of nitrobenzene this zinc-black on the cathode was dissolved as zinc ions and then redeposited on the cathode by the current as before. This alternate solution and deposition of the zinc was continued until all of the nitrobenzene in the solution was reduced to aniline, when the zinc was permanently deposited on the cathode and the solution was free from zinc salt. The theory was the basis of the Boehringer patents which will be described later.

It is evident from the fact that there are so many different compounds which may be formed in the reduction of nitrobenzene that the experimental conditions for the definite preparation of any one of them must be decisive and accurately controlled. Very definite and conclusive evidence has been submitted that in the case of the electrolytic reduction of nitrobenzene the cathode potential is of primary importance.[11] Experiment has shown that a certain value of a cathodic reduction potential corresponds to the formation of a certain definite reduction product; and this reduction product may indifferently be the result of a primary or secondary reaction at the cathode. Whenever a compound acts as a depolarizer it acts concomitant with the value of the reduction potential; what happens after the reduction has taken place is immaterial so far as the course of the first reaction is concerned. Either a rearrangement or a condensation or precipitation may remove the reduced compound from the sphere of reduction. The value of the reduction potential shows itself in the first product formed in the reaction with the depolarizer.

By holding the cathodic potential under a certain fixed value, Haber was able to produce azoxybenzene from an alkaline solution of nitrobenzene; a slight increase above this value changed the final product to hydrazobenzene. This was done with unattackable cathodes at which the cathodic potential could be regulated carefully. Later Löb[12] showed that at any cathode which could give the same cathodic reduction potential the products would be the same both qualitatively and quantitatively; but a neglect of the cathodic potential permitted the formation of the most varied kinds of products. The potential is a measure of the cathodic reduction energy only when the greatest portion of the current is used in performing a certain definite reaction; but if the current is used in local overheating, etc., the results will vary within wide limits.[13] The material from which the cathode is prepared is of major importance in the maintaining a definite value for the cathodic poten-

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[11] F. Haber, Z. Elektrochem., **4**, 510 (1898); Z. physik. Chem., **32**, 193 (1900).

[12] W. Löb and Moore, Z. physik. Chem., **47**, 418 (1904).

[13] See Russ, Z. physik. Chem., **44**, 641 (1903); Haber and Russ, ibid., **47**, 257 (1904); Russ, Dissert., Karlsruhe (1903).

tial; besides this we must consider the kind of surface and the previous treatment which the cathode has received. A cathode which has been used as an anode previously is usually more active; this pre-polarization seems to convert the electrode into a most labile, active condition which is not at all understood.

Panchaud de Bottens [14] detected and determined the drop in potential to which a hydrogen electrode is subjected on the addition of compounds of the aromatic series. The depolarization values so obtained when measured under exactly similar conditions are a function of the chemical nature of the depolarizer and are closely related to their composition and constitution. He studied 53 compounds included in the series of nitroso, nitro, nitroso-amine, isodiazo, and diazonium compounds. Among other facts which he accumulated he found that *o*-nitro compounds are the easiest to reduce, that is, are the best depolarizers.

These facts are in entire accord with the differential electrolytic separation of metals from their solutions. The pressure under which the ion is changed into the gaseous form depends essentially on the potential with which the solution is electrolyzed. It is entirely reasonable to assume that the greater the pressure with which the hydrogen is liberated at the cathode, the more active it will be as a reducing agent. However it is usually much easier to work with a certain fixed cathode potential and with an empirically determined choice of experimental conditions (i.e., the condition of current density, temperature, and solution, or other variable) which will produce the desired result.

The electrode potential seems to play a more important part in the process of reduction than was suspected at first. There was an accumulation of data that was without explanation; for instance, nitrobenzene in an acid solution is reduced more easily at zinc or lead cathodes than at platinum to form aniline. The latter electrode yields phenylhydroxylamine.[15] Similarly the metals that on the one hand by the electrochemical method reduce nitrobenzene to aniline, by the purely chemical methods on the other hand reduce phenylhydroxylamine to aniline.[16] There are many cases of this partial reduction by one cathode and a more complete reduction by another cathode to be found in inorganic chemistry.

Thanks to the work of E. Müller [17] we now have the theoretical background which coordinates these facts, especially in inorganic chem-

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[14] Panchaud de Bottens, Z. Elektrochem., **8**, 305 and 332 (1902).

[15] K. Elbs, Z. Elektrochem., **2**, 473 (1896).

[16] A. Chilesotti, Z. Elektrochem., **7**, 718 (1901).

[17] E. Müller, Z. anorg. Chem., **26**, 1 (1900).

istry. He showed that for the same solution different electrodes led to the building up of different electrode potentials.

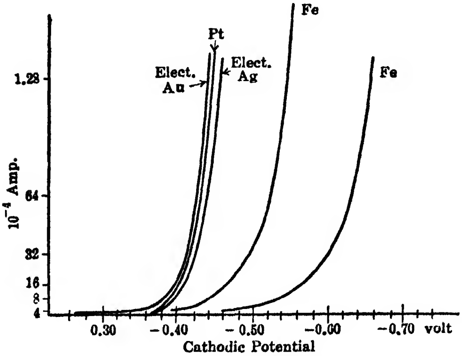

FIG. 7.—Nitrobenzene in Alcoholic Alkaline Solution.

The curve for the reduction of nitrobenzene in alcoholic sodium hydroxide is due to Russ.[18] It shows that for a given current each electrode has a different voltage at which the curve starts to rise rapidly, and also that there is a different maximum electrode potential for different metals. The higher the cathode potential the more complete is the reduction of the depolarizer.

The function of intermediately formed metallic hydrides has claimed some attention. The speed of reduction therefore seems to be dependent on more than one electrode property.[19]

Chilesotti tried to coordinate the specific chemical activity theory of Elbs[20] with the potential theory of Haber, Löb and others[21] by assuming the reduction to be due to the simultaneous activity of the chemical and electrolytic phenomena.[22]

To prove this, Chilesotti studied the purely chemical action of metals in the reduction of nitrobenzene and β-phenylhydroxylamine. He tried to show that the electrolytically prepared metallic sponge as the cathode was responsible for a chemical reaction wholly independent of the passage of the electric current.

THE FUNCTION OF OVERVOLTAGE

The voltages at which gaseous hydrogen is evolved at different electrodes varies somewhat from the potential of a reversible hydrogen electrode in the same solution, this difference being known as the overvoltage. The various values which different methods give to the metals are in many cases by no means consistent, and in fact, the accepted values are practically useless except for comparison. The only point

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[18] R. Russ, Z. physik. Chem., **44**, 641 (1900).

[19] K. Kindler, Ber., **56**, 2063 (1922).

[20] See above.

[21] See above.

[22] Chilesotti, Z. Elektrochem., **7**, 768 (1901); Tafel, Z. anorg. Chem., **21**, 219 (1902).

which has been settled is that the overvoltage values for the different metals are different. Caspari [23] determined some values and so did Tafel.[24]

These determinations are recorded in the table:

TABLE XVIII

Metal	H-overvoltage	
	Caspari	Tafel
Platinized-Pt	0.005 volt	0.07
Smooth Pt	0.09	....
Gold	0.02	0.95
Silver	0.15	....
Nickel	0.21	0.74
Copper	0.23	0.79
Palladium	0.48	....
Tin	0.53	1.15
Cadmium	....	1.22
Lead	0.64	1.23
Lead, polished	....	1.30
Zinc	0.70	....
Mercury	0.78	1.30

The following table giving the best accumulation of data concerning hydrogen overvoltage values is taken from Creighton's text on Electrochemistry.[25]

TABLE XIX

HYDROGEN OVERVOLTAGE OF METALS AND THEIR POSITION IN THE PERIODIC SYSTEM

Group in the Periodic Table	Metal	Typical Overvoltage
1	Na, Cu, Ag, Au	0.35 volt
2	Mg, Zn, Cd, Hg	0.70
3	Al, Tl	0.50
4	C, Sn, Pb	0.45
5	Sb, Ta, Bi	0.42
6	Cr, Mo, W	0.32
7	Mn	0.25
8	Fe, Ni, Rh, Pt, Ir	0.18

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[23] Caspari, Z. Physik. Chem., **30**, 89 (1899).

[24] Tafel, ibid., **50**, 641 (1905).

[25] Creighton, "The Principles of Electrochemistry," Wiley, New York, 1924.

Tafel was the first to recognize the relation between the phenomenon of overvoltage with the high reducing property of zinc and lead cathodes as compared with the low reducing capacity of a platinum cathode.[26]

The meaning of overvoltage is that the higher the overvoltage value of any cathode (and the absolute value from the above tables, means very little), the easier and more complete will be the reduction of the organic depolarizers which resist reduction at the electrodes which have the lower overvoltage values.[27]

The overvoltage effect is not the only factor which varies the course of a reaction from electrode to electrode. The electrode material itself often has an influence which is very difficult at times to regulate. For instance, platinized-platinum and palladium-black electrodes cause a more complete reduction in the majority of cases than smooth platinum or palladium cathodes, in either acid or alkaline solutions. For alkaline solutions copper is the metal which gives the most complete reduction, while zinc, tin and lead cathodes allow the reaction to stop before it is complete. These electrodes will be discussed later in the reduction of nitrobenzene. In many cases lead peroxide cathodes also give excellent results. It has been shown that for given conditions platinized, plain, rolled and electrolytically deposited platinum cathodes act very differently. The rough and spongy surfaces cause the reduction to be, as a rule, quicker and smoother.[28] Then too, previous polarization with a very strong current increased twenty-six fold the speed of the reduction of an alcoholic alkaline solution of nitrobenzene at a nickel cathode. The influence of this pre-polarization varies with electrodes of different metals. So the action of any particular cathode is dependent not only on its "history" but also on its "environment." The relation between the catalytic influence of the cathode material and the phenomenon of overvoltage has not been studied with the view toward determining just how much of any one reaction is due to the former and how much is due to the latter influence. This clarification must come sooner or later as the theoretical background of electrochemistry is developed.

THE FUNCTIONS OF ADDED CARRIERS AND CATALYSTS

Some substances are not very readily reduced by electrolytic hydrogen, but on the other hand they are easily reduced by purely chemical

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[26] Tafel, Z. physik. Chem., **34**, 187 (1900).

[27] Of course, in general, the data of c.d. and potential as well as overvoltage values refer to "mean values" over the entire electrode surface; actually, these values are usually unlike at different points on the surface, since the number of discharging current lines is at best uneven.

[28] R. Russ, Z. physik. Chem., **46**, 641 (1903).

means. If a compound is electrolytically reduced with little trouble and in this reduced state reacts chemically with the organic depolarizer in the solution, the speed of the whole reduction will be increased. The field of catalysts available is at present limited to the salts of those metals which possess more than one valence. The best known salts are those of titanium,[29] vanadium,[30] iron, copper, lead, mercury, and tin.[31]

Large amounts of these catalysts need not be added. The theory is that in the case of the titanic chloride in an acid solution with a platinum cathode the passage of the current reduces the titanium to the titanous state. In this condition it is able to reduce very rapidly the organic compound in the solution, and at the same time is itself oxidized back to the titanic state. The electric current reduces this again so the reaction is continuous. Examples of the use of these catalysts will be mentioned from time to time.

The exact nature of the action of these added salts is uncertain. In some cases the added salt is decomposed by the electric current and the metal deposited on the cathode. Therefore if an unattackable cathode such as platinum is used with a copper salt in solution, the passage of the current will change the surface of the cathode from platinum to a very thin layer of copper, so that the cathode acts as if it were a pure copper cathode.[32] The problem of added catalysts in solution has not been studied from the quantitative standpoint. It seems strange how 0.05–1 per cent of a metallic salt in an electrolyte can by chemical means alone cause so great an increase in the speed of a reaction.[33]

THE FUNCTION OF TEMPERATURE

That temperature should have some influence on the course of an electrolytic reduction follows from the fact that on a purely chemical basis many slow chemical reactions are speeded up very considerably by an increase in temperature. The individual examples of the influence of temperature will be discussed under the separate reductions later.

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[29] D.R.P. 168273 (1903); F.P. 338934, Meister; U.S.P. 742797; E.P. 15700. By the use of a Ti salt the complete reduction of nitro and carbonyl groups is possible. With Titanium sulphate the diaphragm may be eliminated, but not so with the chloride .

[30] D.R.P. 172654 (1904), Meister.

[31] D.R.P. 116942, 117007 (1900), Boehringer; Elbs and Silbermann, Z. Elektrochem., 7, 589 (1900); Chilesotti, ibid., 7, 768 (1900).

[32] D.R.P. 116942 (1900), Boehringer.

[33] However, see "Chemical dehydroxidation" in Chapter III.

CONCENTRATION

The influence of concentration of the depolarizer has been discussed in the chapters on Oxidations. Up to a certain point increasing the concentration of the depolarizer has a good influence on the speed of the reduction, but beyond this point it has no influence. The matter is entirely empirical.

THE FUNCTION OF CURRENT DENSITY

Another problem that is of an entirely empirical nature is the evolution of gaseous hydrogen simultaneously with the reduction reaction. Whether all the hydrogen discharged at the cathode is absorbed by the depolarizer depends on the activity of the depolarizer and the intensity of the current. In the presence of a very difficultly reducible material even a low c. d. will probably be accompanied by an evolution of gaseous hydrogen. An easily reducible material will absorb all the hydrogen, leaving none to be evolved. An electrolytic reduction can be carried out with theoretical current yields at high c. d. only when the compound is an excellent depolarizer; any factors which tend to increase the depolarizing action of a compound, such as temperature or catalysts, permit the use of a correspondingly higher c. d. Weak depolarizers as a rule must be reduced with very low c. d. if good yields are to be obtained.

THE USE OF A DIVIDED CELL

In the carrying out of an electrolytic process it is of foremost importance to prevent the anodic oxidation both of the starting material and of the reduction product. The parallel of the addition of a chromate to prevent cathodic reduction in the case of oxidation reactions has not been discovered. There is no one compound that may be added in the neighborhood of the anode to prevent oxidation reactions. The addition of Turkey Red Oil or a calcium salt will decrease oxidations to some extent by forming a membrane over the anode when it is platinum. The use of iron and nickel anodes in alkaline solution at ordinary current densities will decrease oxidations very much because these electrodes are only good for oxidations at a high current density.[34]

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[34] D.R.P. 297019 (1900), 141343 (1902), Meister.

CHOICE OF CATHODE

The choice of the cathode depends on the nature of the starting material and the kind of reduction reaction which is desired. For easily reducible compounds, or for the formation of intermediate compounds (that is incomplete reduction products), the best cathodes are made of plain platinum, nickel or carbon. Metal cathodes are best made from perforated plates or wire gauzes because these allow a large electrode surface and easy circulation of the catholyte. This latter property is very important. For energetic reductions zinc or tin cathodes are very good. When a large overvoltage is not necessary the best electrode is made of platinized-platinum or a palladium cathode covered with palladium-black.[35] Sometimes freshly prepared nickel or copper cathodes are very good. However any electrode may be used in case carriers or when catalysts as zinc or tin are added to an alkaline catholyte, or a copper salt is added to an acid solution. For the reduction of very inert compounds as pyridine or the uric acid derivatives, cathodes at which high overvoltages are developed are necessary. Mercury cathodes give a more complete reduction of these compounds than do lead electrodes, but the latter are much easier to handle and so predominate throughout the work.

An electrode should be made from the purest metal obtainable. It is astonishing what disastrous results even the smallest amounts or foreign materials in an electrode may have on the course of a reduction. The heavy metals have high overvoltages as a rule, yet only traces of the noble metals will so far lower the overvoltage values at these electrodes that their reducing powers are almost the same as if the noble metal had been used in the start.[36] Tafel found that the addition of 3 mg. of copper, 0.5 mg. of silver, or 0.04 mg. of platinum per square decimeter of a lead cathode surface submerged in 200 cc. of solution brought the reduction to a complete standstill, only gaseous hydrogen being evolved. What probably happened was that at the points where the noble metals were concentrated on the surface of the cathode there was a point of high current density set up locally which caused an evolution of hydrogen too rapid to be absorbed by the depolarizer. The evolution of hydrogen was not uniform over the whole surface of the cathode.

Lead cathodes must be prepared rather carefully. They should be cast in the form in which they are to be used, with the connecting tabs in place. Soldering is impossible because it contaminates the electrode

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[35] Fokin, Z. Elektrochem., **12**, 749 (1906); D.R.P. 187788 and 189332, Boehringer (1907).

[36] J. Tafel, Z. physik. Chem., **34**, 187 (1900); Ber., **33**, 2209 (1900).

with metals other than lead. Commercial lead must be especially treated in order to purify it. The methods of preparation are suggested by Tafel[37] and Löb.[38]

The relative position of the electrodes has a great deal to do with getting an even distribution of current over the surfaces. When flat sheets of metal are used they should be parallel to one another and of the same size if possible, though there are conditions when this is not advisable as will be seen later. By far the best position and shape is to use concentric cylindrical electrodes.

THE CHOICE OF SOLVENT

The ease and simplicity of a reduction and the recovery of the products from the reduced solution after the reaction is completed depends to a large extent on the choice of the solvent, if one is required. Indifference may not be shown in the choice of the proper solvent or electrolyte. For ordinary purposes a good solution is an aqueous-alcoholic solution acidified with sulphuric acid; on the other hand aqueous alkali solutions work very well in some cases. For neutral reduction medium an alcoholic aqueous solution of acetic acid containing sufficient sodium acetate to insure decreased H^+ concentration is the best.

It is necessary to use a solvent which will not be reduced by the passage of the current. This, of course, eliminates the use of acetone. When a very low overvoltage cathode is used the solution may contain pyridine as a solvent, but great care must be exercised in its use because pyridine is reduced in some instances and its reduction products complicate the recovery of the desired compounds from the solution. The use of a solvent is not absolutely necessary. With a good stirring apparatus a suspension of the organic compound in the electrolyte often serves to bring the necessary quantities of the depolarizer into contact with the cathode to keep the yields high. The absence of a solvent not only cuts down the expenses involved in the work but also simplifies the recovery of the reduced materials. An aqueous solution is as a rule much easier to handle than a solution containing various reduction and condensation products of the solvent.

Several methods of obtaining good reduction speeds without the use of a solvent or stirring have been suggested, but their value is so uncertain that they need but be mentioned here.[39]

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[37] Tafel, Ber., **33**, 2215 (1900); Tafel and K. Naumann, Z. physik. Chem., **50**, 717 (1905).

[38] Löb and Moore, Z. physik. Chem., **47**, 432 (1904).

[39] D.R.P. 109051 (1898), Boehringer; D.R.P. 123544 (1899), R. Nithack; D.R.P. 297019 (1915), Gesell. f. Chem. Ind. in Basel.

CHAPTER IX

THE REDUCTION OF AROMATIC NITRO COMPOUNDS—PART I

GENERAL AND HISTORICAL

THE reduction of aromatic nitro compounds forms a series of reactions which are of great scientific and technical interest. Although much work has been carried out in this field, a large amount has still to be done. Kendall[1] in 1882 described, in the patent literature, a reaction in which nitrobenzene and nitrotoluene were cathodically reduced to the corresponding amino derivatives when electrolyzed in a catholyte containing dilute sulphuric acid or sodium chloride. In order to bring the cathode and the organic depolarizer into intimate contact the carbon cathode was used as a stirrer; it was also coated with a fibrous material which absorbed the nitro compound. This fibrous coating was used probably with the assumption that only contact with the electrode was necessary for the reduction of the nitro body. Kendall was also probably not aware of the fact that only the portion of the material in solution was reduced, and even that not completely.

The next nine years saw no developments in the field but at the end of this time K. Elbs carried out a very thorough study of the reduction of nitrophenols. He found that at plain platinum electrodes in acid solution, in all cases, the reduction goes completely to the amino derivative. The *p*-nitrophenol produces very smoothly *p*-aminophenol and dianilidoquinoneanil; *o*-nitrophenol besides the *o*-aminophenol produces small amounts of an unknown blue-colored compound. ? Partial reduction may be accomplished when more than one nitro group is present in the molecule. Accordingly 2, 4-dinitrophenol may yield either aminonitrophenol or diaminophenol, while picric acid yields picramic acid (dinitroaminophenol) and diaminonitrophenol, but no triaminophenol. The amount of reduction decreases with the number of nitro groups present in the molecule and also depends on the position of these groups with respect to the hydroxyl group.

The amount and rate of reduction is greater in alkaline than in acid solution. In the following table the amounts of hydrogen evolved are

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[1] D.R.P. 21131 (1882).

compared with the hydrogen evolved according to Faraday's law in the absence of the depolarizer with the same time and current:

TABLE XX

Depolarizer	Current	Temp. ° C.	Per Cent of Hydrogen Absorbed
.01 mol. of *o*-nitrophenol........	0.500	60.5	42.0
.01 mol. of *o*-nitrophenol........	1.348	60.1	21.9
.01 mol. of picric acid...........	0.416	49.9	43.1
.02 mol. of picric acid...........	0.419	49.9	51.6

The results for picric acid show that the portion of the current directed toward reduction increases with the concentration of the solution. Besides these compounds Elbs[2] was able to find in the cases of both *o*- and *p*-nitrophenol, the formation of dianilinoquinoneanil. In an alcoholic alkaline solution dinitrophenol yielded aminonitrophenol and diaminophenol.

In 1893 Häussermann and Elbs[3] electrolyzed a solution of 25 g. of nitrobenzene, 40 g. of sodium hydroxide, 50 cc. of water and 350 cc.of alcohol with a cathodic c. d. of 8.33 amperes between both platinum and iron electrodes at room temperature with the result that 60 per cent of the theoretical yield of hydrazobenzene was obtained, together with a strong evolution of hydrogen during the whole time the current was passing. Under similar conditions he reduced *o*-nitrotoluene, but obtained smaller yeilds of the corresponding hydrazotoluene. On the other hand in a sulphuric acid solution nitrobenzene yielded benzidine isolable as the sulphate, some azoxybenzene and a sensitive compound not studied, probably *p*-aminophenol and *p*-phenetidine when the current density was smaller than in the previous cases. If the nitrobenzene was added slowly from a dropping funnel into a stronger acid electrolyte at 60°, traces of aniline were obtained in the reduction products. *o*- and *p*-Nitrotoluene yielded the corresponding tolidine sulphates and some of the corresponding toluidine sulphates. Häussermann also studied the reduction of *m*-nitrobenzenesulphonic acid in a weak (6½ per cent) sulphuric acid solution with the result that the end product was the corresponding amino derivative metanilic acid. *o*-Nitroanisole was found to yield the corresponding azoxy and hydrazo compounds when

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[2] K. Elbs. J. prakt. Chem., [2], **43**, 39 (1891).

[3] C. Häussermann, Chem. Ztg., **17**, 129 and 209 (1893); Elbs, ibid., **17**, 209 (1893).

reduced in alkaline solution. The year 1893 saw the beginning of an intensive study of the reduction of aromatic nitro compounds and in this year the first unraveling of the reaction mechanism was started.[4] Elbs reported that in the reduction of a solution of 20 g. of nitrobenzene, 300 cc. of 10 per cent of sodium hydroxide, 100 cc. of alcohol, with a current of 1 to 2 amperes at 30° to 50° a lead or mercury electrode yielded azoxybenzene and azobenzene. Similarly nitrotoluene yielded the corresponding azo and azoxy compounds though the reduction was slower and the yields were poorer with nitrotoluene than with nitrobenzene. These reactions differed from those of Häussermann in that he electrolyzed for a shorter time. The reaction was entirely different in the acid solution.[5] A solution of 20 g. of nitrobenzene, 50 g. of sulphuric acid, 200 cc. of water, 200 cc. of alcohol with a c. d. of 10–15 amperes at a temperature of 40° to 60° at a zinc or lead cathode yielded mostly aniline.[6] This was the first reaction in which the influence of the cathode material was shown to have a large and important part in the directing of the final course of the reaction. "Without considering the other conditions of the experiment, the kind of metal employed as the cathode seems to exert an important influence."

The historical method of reviewing this work may very profitably be adhered to, in order to simplify the study of the reaction involved. The clarification of the mechanism by which any one of the seven products of reduction of nitrobenzene may be produced was necessarily rather a tedious and involved process. The variety of conditions that could be changed, to make new products possible, made the successful solution of the problem very difficult. There was so much confusion in the field, when Haber [7] announced the theory which considered the electrochemical reduction of these nitro compounds under certain conditions to be entirely parallel to the reactions by the purely chemical methods, that the theory was under severe fire for some time before it was finally accepted.

At the same time that Elbs and Häussermann were doing their work, Gattermann [8] also studied the reduction of nitrobenzene and related compounds, but he used an electrolyte of concentrated sulphuric acid

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[4] K. Elbs, Chem. Ztg., **17**, 209 (1893).

[5] Elbs, loc. cit.

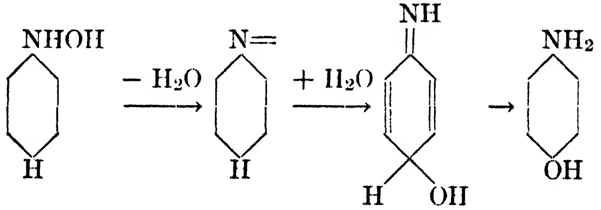
[6] Elbs and Silbermann, Z. Elektrochem., **7**, 589 (1901), used any cathode with a soluble Zn salt to get aniline.

[7] Haber, Z. Elektrochem., **4**, 506 and 577 (1898); Haber and Schmidt, Z. physik. Chem., **32**, 271 (1900); Z. angew. Chem., 433 (1900); see also Elbs, Z. Elektrochem., **7**, 133 (1900).

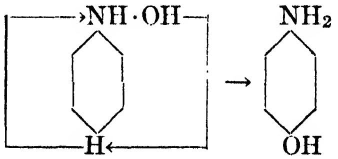
[8] L. Gattermann, Chem. Ztg., **17**, 210 (1893); Ber., **26**, 1844 (1893) and **27**, 1927 (1894); Koppert, Dissert., Heidelberg (1894).

instead of the dilute acid of the other investigators, with a c. d. of 12 to 24 amperes between smooth platinum electrodes. On account of the high resistance of this electrolyte the temperature of the bath rose to 80° without any deleterious results. A divided cell was used, the anolyte of which consisted of very strong sulphuric acid, even up to 100 per cent acid. The products obtained under these conditions were the sulphate salts of the *p*-aminophenols when the para-position was free. When the para-position was not free the corresponding *o*-aminophenol was produced. The sulphate salts were in some cases precipitated from the catholyte directly as they were formed, by cooling at the end of the reduction, or by diluting the electrolyte with water.

The *p*-aminophenols are formed by the rearrangement of the β-arylhydoxylamines in the presence of concentrated H_2SO_4. (The β-arylhydroxylamine is formed directly from the starting nitro compound.) In the case of β-phenylhydroxylamine Bamberger [9] conceives the rearrangement to be



That is, the formation of *p*-aminophenol is not due simply to an interchange of position between the hydroxyl group and the hydrogen atom in the para-position according to the scheme:



It is evident that large yields of *p*-aminophenol are formed by a rapid rearrangement accompanied by a slow speed of reduction of the intermediately formed β-phenylhydroxylamine. Gattermann was able to sustain this viewpoint by showing that under his described conditions only traces of aniline were formed.

Gattermann later was able also to prove that when a nitro group together with a keto group was present in compounds of certain types,

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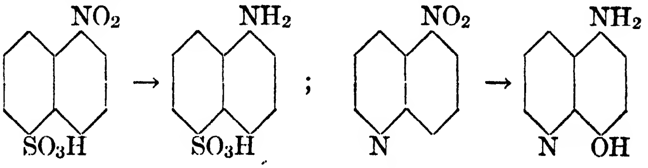
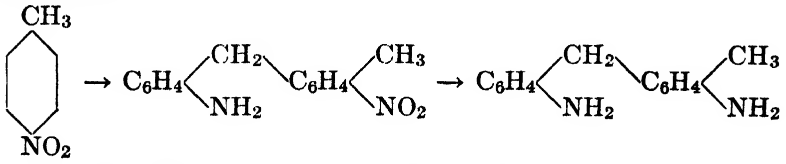
[9] Bamberger, Ber., **27**, 1349 and 1552 (1894); **28**, 246 (1895); **33**, 3600 and 3643 (1900); **34**, 61 (1901); **35**, 3886 (1902); **40**, 1893 (1907).

the nitro group was reduced while the keto group remained intact. In these cases he was able to obtain[10] from *m*-nitroacetophenone and *m*-nitrobenzophenone, respectively, the corresponding aminophenolic compounds. The use of these electrolytic reductions should be of service in the synthesis of derivatives of acridine which have particular germicidal values.

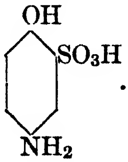
At this early stage the electrolytic reduction of bicyclic compounds was also studied to a small extent. Among which were investigated the nitro derivatives of the naphthalene and quinoline series, by Gattermann and Koppert,[11] who were able to reduce 1, 5-nitronaphthalenesulphonic acid to 1-amino-4-hydroxy-5-naphthalenesulphonic acid while a nitroquinoline yielded an aminohydroxyquinoline



Gattermann also discovered a very peculiar reaction at this time: a reaction in which a toluene derivative was reduced to a much more complex methane derivative. *p*-Nitrotoluene was reduced in two steps as follows, yielding first nitroaminophenyltolylmethane and on continued reduction this compound was reduced to the diaminophenyltolylmethane:



$$\rightarrow C_6H_4{<}\begin{matrix}CH_2\\NH_2\end{matrix}{>}C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CH_2\\NH_2\end{matrix}{>}C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix}$$

The year 1893 seemed to be a gala year for electrolytic reductions. Another group of men also reported work on the reduction of nitrobenzene. Noyes and Clement studied the reduction of nitrobenzene in 100 per cent sulphuric acid at a platinum cathode at 80 to 90°, obtaining the *o*-sulphonic acid instead of the expected *p*-aminophenol in 40 per cent yields  . This reaction did not take place to any

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[10] L. Gattermann, Ber., **29**, 3037 (1896); ibid., **36**, 23 (1903).

[11] L. Gattermann and Koppert, Ber., **26**, 2810 (1893); Gattermann, **29**, 3040 (1896).

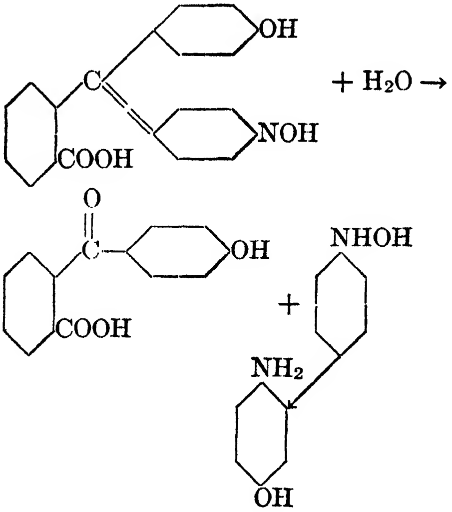
large extent when as little as 2.7 per cent of water was added to the electrolyte, but instead the regular reaction took place, that is, the *p*-aminophenol was formed as expected.[12]

When this work was being carried out the intermediate products in the reduction of aromatic nitro compounds to the amino compounds had not been discovered. One intermediate had been isolated in the aliphatic series, i.e., methylhydroxylamine, had been found as a product of the purely chemical reduction of nitromethane besides the usual methylamine:[13]

$$CH_3NO_2 + 2H_2 \rightarrow CH_3NHOH + H_2O$$

$$CH_3NO_2 + 3H_2 \rightarrow CH_3NH_2 + 2H_2O$$

The development of the theory by which these intermediates were formed is very interesting because there was a great amount of discussion as to the mechanism before any definite system was finally accepted. Friedländer [14] had about this time shown that the acid hydrolysis of the oxime of phenolphthalein yielded *p*-aminophenol (instead of the expected phenylhydroxylamine) according to the equation:



This study led to the assumption that the hydroxylamine derivative

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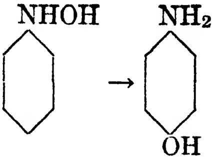
[12] A. A. Noyes and A. A. Clement, Ber., **26**, 990 (1893); Noyes and Dorrance, ibid., **28**, 2349 (1895).

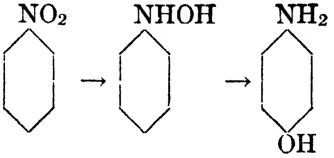
[13] V. Meyer and E. Hoffmann, Ber., **24**, 3528 (1891).

[14] P. Friedländer, Ber., **26**, 176 (1893).

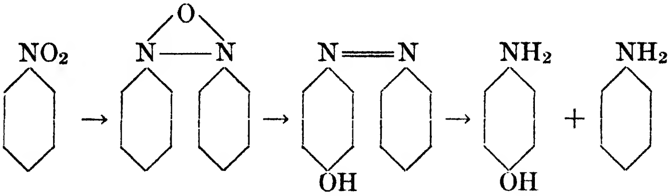
is very easily rearranged into the corresponding *p*-aminophenol according to the reaction:



Accordingly Gattermann came to the conclusion that this was a fundamental reaction:



Elbs [15] by a brilliant series of experiments in both sulphuric and acetic acid electrolytes was able to prove the formation of 40 per cent to 100 per cent of aniline in the electrolytic reduction of nitrobenzene, though in the case of the former electrolyte the amounts of *p*-aminophenol were smaller than in the case of the acetic acid electrolyte. Elbs also found that the use of a lead instead of a platinum cathode increased the yield of aniline. The mechanism developed by him was that in the reduction azoxybenzene was first formed and then rearranged into *p*-hydroxyazobenzene; this latter compound was then oxidized to *p*-aminophenol and aniline. (This also accounted for the formation of *p*-aminophenol.)



However this mechanism was not substantiated because when Elbs reduced azoxybenzene under the conditions for the reduction of nitrobenzene he obtained no *p*-aminophenol.

Gattermann [16] was able to sustain his assumption concerning this reaction, by electrolyzing a solution of 18 g. of nitrobenzene, 20 g. of

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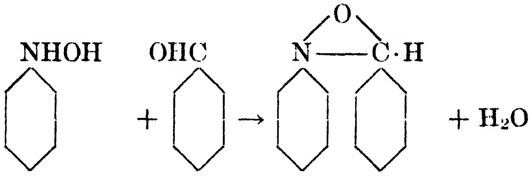
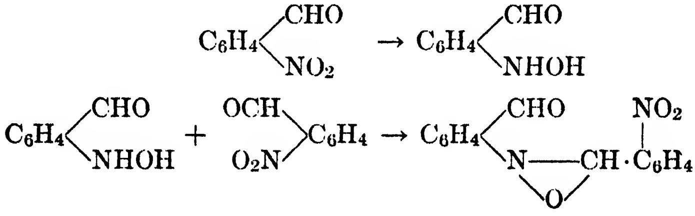
[15] K. Elbs, Z. Elektrochem., **2**, 472 (1896).

[16] L. Gattermann, Ber., **29**, 3040 (1896); see also D.R.P. 96564 (1896), Bayer.

benzaldehyde, 40 g. of acetic acid, 40 g. of sulphuric acid, between platinum electrodes. The products which he obtained could only be formed by the interaction of phenylhydroxylamine and benzaldehyde. Therefore the phenylhydroxylamine reacted before it could have time to rearrange into *p*-aminophenol; thus proving that the hydroxylamine derivative was an intermediate in the reduction of nitrobenzene:



This reaction was further proven by replacing the benzaldehyde by its nitro-derivative when the following reaction was found to take place:



$$C_6H_4\begin{cases}CHO\\NO_2\end{cases} \rightarrow C_6H_4\begin{cases}CHO\\NHOH\end{cases}$$

$$C_6H_4\begin{cases}CHO\\NHOH\end{cases} + \begin{matrix}OCH\\O_2N\end{matrix}\Big\rangle C_6H_4 \rightarrow C_6H_4\begin{cases}CHO\\N\text{——}CH\cdot C_6H_4NO_2\\\ \ \backslash O /\end{cases}$$

Both the *p*- and *o*-compounds behaved alike in this reduction. However continued reduction led to the formation of very complicated products in which even the nitro groups in the condensation product were reduced.

These assumptions of Gattermann were by no means entirely conclusive, because Elbs [17] showed that other reduction reactions might take place (i.e., those involving azoxybenzene and hydroxyazobenzene). He found that in concentrated sulphuric acid the reduction of the nitro derivatives led to the formation of products containing only one benzene ring while in an alcoholic alkaline solution the reduction led to compounds containing two benzene rings, namely, azoxybenzene, azobenzene, hydrazobenzene, and benzidine. These ideas were later very definitely cleared up.

In these early days another system was developed by W. Löb,[18] in which it was assumed that the molecule of nitrobenzene first took up two molecules of water to form an orthohydrate: $C_6H_5N(OH)_4$ and

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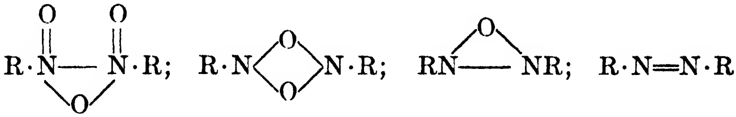
[17] K. Elbs, Z. Elektrochem., **3**, 48 (1897).

[18] W. Löb, Z. Elektrochem., **2**, 523 (1896).

this orthohydrate, under the influence of electrolytic reduction in the presence of alkalies, lost hydroxyl groups with the formation of the following system of radicals:

$$R(OH_3)N— ; \quad R(OH)_2N= ; \quad R(OH)N\equiv ; \quad RN\equiv$$

which were able to unite with each other to form condensation products as follows:



The reasons for this difference in reaction between alkaline and acid solutions Löb attributed to the fact that in acid solution the reduction was due to the evolution of hydrogen at the cathode while in alkaline solution the sodium discharged at the cathode had a certain catalytic action which changed the course of the reaction. He also assumed that during the reaction there was an ionization or dissociation of the nitro compound but offered no experimental data to prove it. Besides these theoretical contemplations he was able however to give assistance to the clearing up in general of the ideas that had been put forward by others. He reduced a 5 per cent solution of *o*-nitrobenzoic acid in 5 per cent sodium hydroxide at the platinum cathode of a divided cell at room temperature with a c. d. of 4 amperes for 8 to 10 hours when hydrogen began to be evolved from the catholyte. The yield was 50 per cent of the theoretical quantity of *o*-azoxybenzoic acid together with about 5 per cent to 10 per cent of *o*-hydrazobenzoic acid. The *m*- and *p*-nitrobenzoic acid yielded very easily the corresponding *m*- and *p*-azobenzoic acids in good yields. Under these same experimental conditions, i.e., a 5 per cent solution of *o*-nitrophenol in 5 per cent alkali [19] yielded 60 per cent of the theoretical quantity of aminophenol together with red and brown substances not studied which corresponded to the mechanism as deduced by Elbs.

An interesting substitution reaction was found to take place when, according to the method of Gattermann, 30 g. nitrobenzene in 150 cc. of fuming hydrochloric acid or a mixture of strong hydrochloric and acetic acids instead of the usual sulphuric acid was electrolyzed between platinum electrodes.[19] The product was a mixture of *o*- and *p*-chloraniline. Therefore the reaction went according to the Gattermann instead

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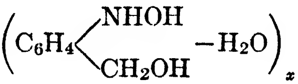
[19] W. Löb, Z. Elektrochem., **3**, 46 (1896); Ber., **29**, 1894 (1896).

of the Elbs mechanism, for in the latter case the expected aminophenol derivative was not detected:

$$C_6H_5NO_2 \rightarrow C_6H_5NHOH \xrightarrow{HCl} C_6H_5NHCl \rightarrow p\text{-}Cl \cdot C_6H_4 \cdot NH_2$$

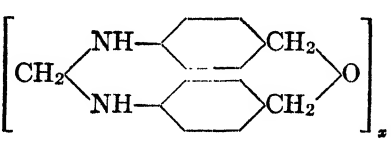
When the electrode was lead instead of platinum no chloranil could be detected, only aniline was present.

A new intermediate was discovered in the reduction process by W. Löb,[20] who electrolyzed a suspension of nitrobenzene in a mixture of alcohol and ammonium hydroxide, made a better conductor by the addition of ammonium chloride, with the result that azobenzene was formed at the cathode. He also obtained a product by the electrolytic reduction of nitrobenzene in the presence of concentrated hydrochloric acid and formaldehyde which is also formed by the purely chemical interaction of formaldehyde and β-phenylhydroxylamine, that is, the hydrochloride of the anhydride of p-hydroxylaminobenzyl alcohol which readily polymerizes into a molecule of unknown molecular weight:[21]

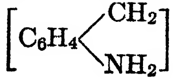


$$\left(C_6H_4{<}^{NHOH}_{CH_2OH} - H_2O\right)_x$$

With a lower current density under the same conditions Löb was able to isolate another condensation product, probably methylene-di-p-anhydroaminobenzyl alcohol which he considered as being formed by the removal of two molecules of water from two mols of aniline (the primary reduction product), and three mols of formaldehyde:



also some anhydro-p-amino benzyl alcohol



$$\left[C_6H_4{<}^{CH_2}_{NH_2}\right]$$

Löb showed also that the reduction of p-nitrotoluene in alcoholic alkaline solution did not lead to the results of Gattermann, who obtained with a concentrated sulphuric acid solution at a platinum cathode good yields of nitroaminophenyltolylmethane. Löb obtained large quantities of p-toluidine. On the other hand an alcoholic hydrochloric acid solution[22] in the presence of formaldehyde yielded a formaldehy decon-

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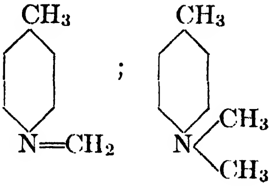
[20] W. Löb, Z. Elektrochem., 3, 471 (1896).

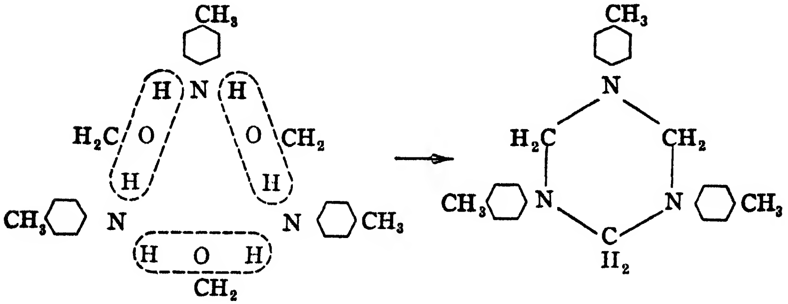
[21] W. Löb, Z. Elektrochem., 4, 428 (1897); D.R.P. 99312 and 100610 (1897).

[22] Löb, Z. Elektrochem., 4, 428 (1897); Goecke, ibid., 9, 470 (1903).

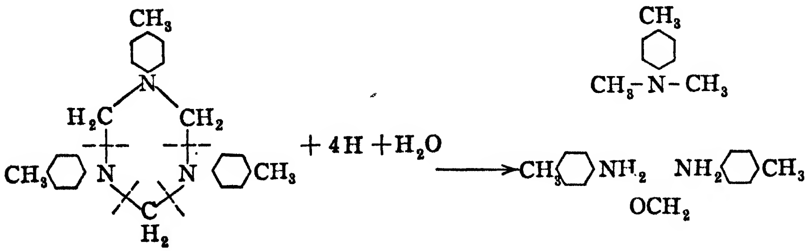
densation product of the *p*-toluidine besides some fairly large amounts of *p*-dimethyltoluidine and trimethylene-tri-*p*-toluidine:



The reaction which takes place probably is:



Under the influence of the acid and the cathodically evolved hydrogen the trimethylene-tri-*p*-toluidine hydrolyzes into dimethyl-*p*-toluidine, *p*-toluidine and formaldehyde:



During this time, the reduction of nitrobenzene by purely chemical methods was cleared up considerably by Bamberger. He was able by a difficult series of reactions to chemically reduce nitrosobenzene to phenylhydroxylamine[23] and to reverse this reaction on a large scale,

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[23] E. Bamberger, Ber., **27**, 1555 (1894).

that is oxidize β-phenylhydroxylamine to nitrosobenzene.[24] Two of the many reactions which he investigated in this connection are interesting in their application to this study of the mechanism of reduction, namely, the rearrangement of phenylhydroxylamine into *p*-aminophenol by the action of acids[25] which proved Gattermann's thesis, and a second reaction the coupling of phenylhydroxylamine with nitrosobenzene to form azoxybenzene by the removal of a molecule of water.[26]

The reduction of nitrobenzene to phenylhydroxylamine was found by Bamberger to lead also to the formation of nitrosobenzene (which could be detected only by its odor), aniline, azoxybenzene and azobenzene.

At this point Haber[27] took up the study of the problem. He looked over the previous work which was a maze of uncoordinated experimental data on the reduction of nitrobenzene, and from it, together with his own experimental work, developed a mechanism of reaction which applied to both the chemical and electrochemical reduction of nitrobenzene. The " Haber Scheme " rather than that of Löb is the basis for our present-day work.

According to Haber the reduction of nitrobenzene in an acid as well as in an alkaline solution was due to the action of the hydrogen ions discharged at the cathode. His first assumption was that " fundamentally oxidation and reduction processes are dependent on the potential of the electrode at which the reaction takes place; also the current density, duration of the electrolysis, electrode material are important only in so far as they influence the electrode potential in the course of the electrolysis."

A platinized-platinum cathode immersed in a solution of 50 g. of nitrobenzene, 40 g. of sodium hydroxide, 50 g. of water and 350 g. of alcohol assumed towards a decinormal calomel electrode a potential of -0.72 volt. Cathodic polarization with a c. d. of 3.5 amperes caused the potential first to sink and finally to assume a value of -1.29 volt on prolonged use; at this value hydrogen gas was evolved. With a low c. d. (1.25 amp.) the cathodic potential was -0.92 volt and gradually assumed the value for normal hydrogen evolution.

Haber hoped to prove that the reduction of nitrobenzene in an alcoholic alkaline solution proceeds according to the following scheme:[28]

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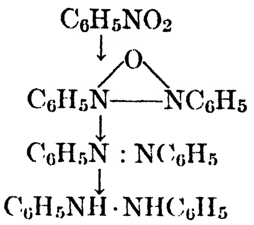
[24] Bamberger, Ber., **27**, 1348 and 1548 (1894).

[25] E. Bamberger, Ber., **28**, 1552 (1895).

[26] E. Bamberger, Ber., **30**, 2278 (1897).

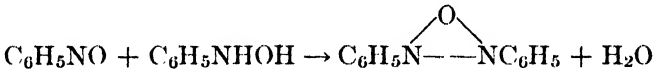
[27] Haber, Z. Elektrochem., **4**, 197 and 506 (1898); Haber and Schmidt, Z. physik. Chem., **32**, 271 (1900).

[28] Haber, Z. Elektrochem., **4**, 506 (1898).



and that the intermediate compounds could be isolated by a careful regulation of the cathodic potential. At a potential of −0.93 volt he obtained 76 per cent yields of azoxybenzene in an alcoholic alkaline solution. This potential was obtained with a c. d. of 0.5 ampere for only a short time and even then it tended to fall. As by-products he obtained azobenzene, hydrazobenzene, and aniline in small amounts with the aniline predominating over the hydrazobenzene. This led him to assume that hydrazobenzene was reduced to aniline. Then in an alkaline alcoholic solution he reduced hydrazobenzene with a cathodic potential of −1.4 to −1.3 volt, but obtained only traces of aniline. The replacement of the platinized-Pt cathode by one of zinc (Elbs methods, see later) at which the potential reached was −1.78 volt, did not increase the yield of aniline. This removed the hydrazobenzene as a possible source for the aniline and forced a search in another direction. As it happened β-phenylhydroxylamine was proven to be the source in question.

Bamberger [29] had shown that in the presence of sodium hydroxide a condensation of nitrosobenzene with β-phenylhydroxylamine took place:



Assuming this reaction to be a possible origin of the azoxybenzene it had to be proven that the first reduction of nitrobenzene led to the formation of nitrosobenzene:

$$C_6H_5NO_2 + 2H \rightarrow C_6H_5NO + H_2O$$

This was difficult to prove because nitrosobenzene is very fugitive under the conditions in which he worked. The chemical acumen of Haber asserted itself in the solving of this problem. He figured that if the nitrosobenzene could be made to react with another compound more rapidly than it could be further reduced electrolytically, the question was solved. To accomplish this he reduced an alcoholic alkaline solu-

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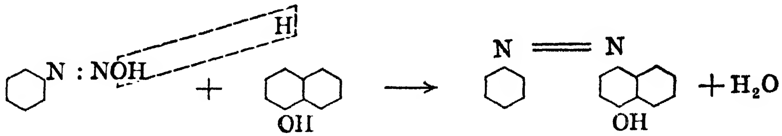
[29] Bamberger, Ber., **30**, 2278 (1897).

tion of nitrobenzene containing hydroxylamine hydrochloride and α-naphthol for two hours with a c. d. of 0.5–0.6 amp. with a reduction potential of −0.9 to −0.92 volt. The electrolytic solution turned red, due to the formation of benzene-azo-α-naphthol. The reactions which took place were:

1. $C_6H_5NO_2 \longrightarrow C_6H_5NO$

2. $C_6H_5NO + NH_2OH \longrightarrow C_6H_5N : NOH$

3.

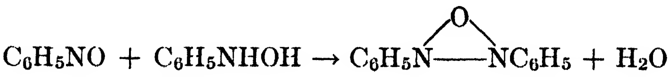


Haber further showed that nitrosobenzene is a better depolarizer than nitrobenzene; in fact the former is reduced at a potential of −0.48 volt while the latter is reduced at a value of −0.78 volt under similar conditions.

The next step was to prove the presence of β-phenylhydroxylamine, but this compound was also very fugitive and sensitive in the presence of a high concentration of hydroxyl ions, so that to overcome this difficulty Haber reduced nitrobenzene in an alcoholic ammonium hydroxide solution containing ammonium chloride to decrease the concentration of hydroxyl ions. By using a Pt coil cathode through which cold water was circulating Haber obtained a 38 per cent yield of β-phenylhydroxylamine and a 21 per cent yield of azoxybenzene. A Pb coil in place of the Pt coil decreased the yield of hydroxylamine compound. Therefore the second step in the reduction of an alcoholic alkaline solution of nitrobenzene is β-phenylhydroxylamine:

$$C_6H_5NO_2 + 4H \rightarrow C_6H_5NHOH + H_2O$$

In the presence of alkali there is an internal oxidation-reduction of two molecules of phenylhydroxylamine to form nitrosobenzene, aniline and a molecule of water; then the nitrosobenzene reacts with the unchanged hydroxylamine to form azoxybenzene:



$$C_6H_5NO + C_6H_5NHOH \rightarrow C_6H_5N\overset{O}{\text{——}}NC_6H_5 + H_2O$$

Bamberger was the first to observe that in the alkaline solution the hydroxylamine yielded half as much aniline as azoxybenzene. However the aniline obtained by Haber was only in traces, while the Bamberger scheme required the formation of more than traces of aniline. Haber explained this as being due to the fact that there is a direct condensation between the hydroxylamine and the electrolytically formed nitrosobenzene as well as that formed by the oxidation-reduction of two molecules of hydroxylamine. Then the hydroxylamine which does not so condense is further reduced to aniline:

$$C_6H_5NHOH + 2H \rightarrow C_6H_5NH_2 + H_2O$$

That is, the slower the condensation between nitrosobenzene and β-phenylhydroxylamine the more aniline will be formed; the aniline could not be formed from the hydrazobenzene by a further reduction because the latter is a very poor depolarizer.

At this same time Elbs and Kopp[30] had obtained with a high c. d. in alcoholic alkaline solution large amounts of azobenzene, and from this with a decreased c. d. hydrazobenzene. What was the source of the azobenzene? Alexjeff[31] had shown that chemically the reduction of azoxybenzene yielded hydrazobenzene, but not azobenzene. Similarly Haber had shown that the electrolytic reduction of azoxybenzene yielded hydrazobenzene and not azobenzene. The possibility therefore arose that like nitrosobenzene, the azobenzene was a better depolarizer than azoxybenzene, so never could get a chance to accumulate in the solution. However Elbs[32] showed azobenzene to be a very poor depolarizer and only very slowly reduced, which fact was substantiated by Haber and Schmidt,[33] who with a c. d. of 1.0 ampere found the potential of azoxy- and azobenzene to be -1.05 and -1.07 volt respectively, i.e., both are very poor depolarizers. This forced the conclusion that azobenzene was not an intermediate in the reduction of azoxybenzene to hydrazobenzene and correspondingly it also showed that the formation of hydrazobenzene took place through another intermediate which was probably of the nature of hydroxyhydrazobenzene:

$$C_6H_5\cdot\overset{\overset{OH}{|}}{N}\text{——}\overset{\overset{H}{|}}{N}\cdot C_6H_5$$

Haber and Schmidt did not consider that the Bamberger synthesis[34]

$$2C_6H_5NHOH \rightarrow C_6H_5N : NC_6H_5 + 2H_2O$$

was applicable because of the small yields; nor was the reaction

$$C_6H_5NO + C_6H_5NH_2 \rightarrow C_6H_5N : NC_6H_5 + H_2O$$

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[30] Elbs and Kopp, Z. Elektrochem., **5**, 108 (1898).

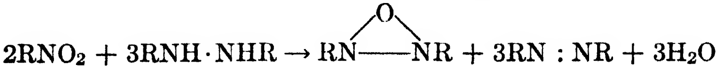
[31] Alexjeff, Krit. Zeit. f. Chem., 33 (1867).

[32] Elbs and Kopp, loc. cit.

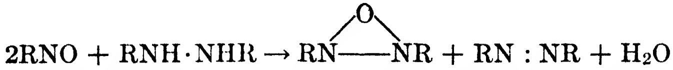
[33] Haber and Schmidt, loc. cit.

[34] Bamberger and Brady, Ber., **38**, 234 (1900).

applicable. On the basis of their own observations, not to include other evidence, it did not take place in alcoholic alkaline solution. The need for a new mechanism was important and that mechanism was supplied on the basis of well-known reactions as follows:



$$2RNO_2 + 3RNH\cdot NHR \rightarrow RN\overset{O}{\text{——}}NR + 3RN : NR + 3H_2O$$



$$2RNO + RNH\cdot NHR \rightarrow RN\overset{O}{\text{——}}NR + RN : NR + H_2O$$

Besides, oxygen from the air very rapidly oxidizes hydrazobenzene to azobenzene:

$$RNH\cdot NHR + O \rightarrow RN : NR + H_2O$$

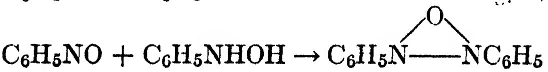
and air was not excluded from the apparatus used in these reductions. Haber accepted these facts as expressing the mechanism for the formation of azobenzene; that is:

(1) $C_6H_5NO_2 \rightarrow C_6H_5NO$

(2) $C_6H_5NO \rightarrow C_6H_5NHOH$

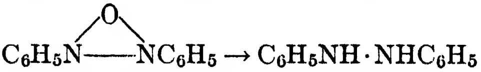
azoxy-

(3)



$$C_6H_5NO + C_6H_5NHOH \rightarrow C_6H_5N\overset{O}{\text{——}}NC_6H_5$$

(4)



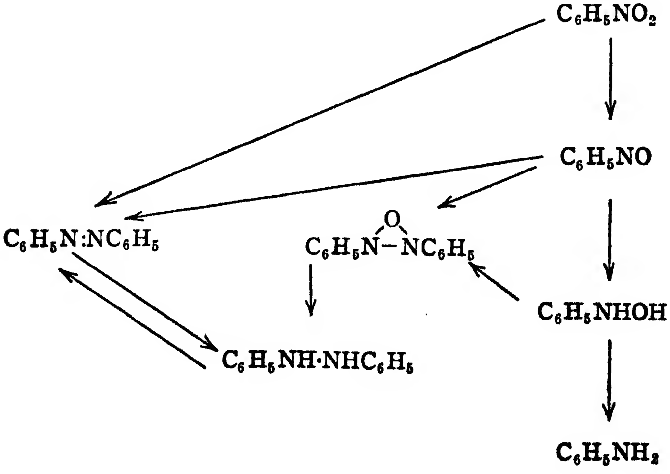
$$C_6H_5N\overset{O}{\text{——}}NC_6H_5 \rightarrow C_6H_5NH\cdot NHC_6H_5$$

hydrazo-

(5) $C_6H_5NH\cdot NHC_6H_5 + C_6H_5NO_2$
or C_6H_5NO or $O_2 \rightarrow C_6H_5N : NC_6H_5$

(6) $C_6H_5N : NC_6H_5 \rightarrow C_6H_5NH\cdot NHC_6H_5$

This makes the scheme for the alkaline reduction of nitrobenzene as follows:



We have now to clear up the reduction of nitrobenzene in an acid solution. Häussermann[35] in an alcoholic sulphuric acid solution at a platinum cathode obtained azoxybenzene, benzidine sulphate, some aniline sulphate, and possibly some *p*-aminophenol and *p*-phenetidine. On the other hand *o*-nitrotoluene yielded the corresponding toluidine and tolidine sulphates; but the *p*-compound gave only the toluidine sulphate. Elbs substituted cathodes of zinc or lead for the platinum and obtained only aniline.[36]

Haber showed that nitrobenzene was a poorer depolarizer in an acid solution than in an alkaline solution. In fact the cathodic reduction potential for nitrobenzene in an acid solution was +0.04 volt as against −0.72 volt in an alkaline solution. By polarization with a current density of 1 ampere the potential value sank to 0.32 volt below the normal, and at this potential Haber verified the formation of *p*-aminophenol according to the equations:

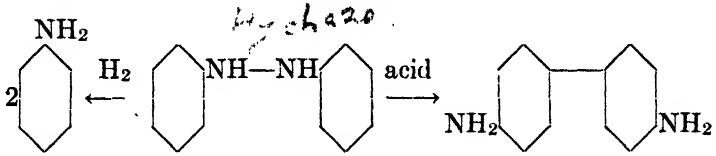
$$C_6H_5NHOH \rightarrow p\text{-}NH_2 \cdot C_6H_4OH;$$

$$C_6H_5NHOH + C_2H_5OH \rightarrow p\text{-}NH_2 \cdot C_6H_4 \cdot OC_2H_5 + H_2O$$

Haber was not entirely convinced that the benzidine was formed from the *β*-phenylhydroxylamine. He was of the opinion at that time that the reduction of the hydroxylamine derivative cause two molecules to condense:

$$2C_6H_5NHOH + 2H \rightarrow C_6H_5NH \cdot NHC_6H_5 + H_2O$$

and then the hydrazobenzene rearranged so slowly to benzidine that the molecule was attacked by more hydrogen to form aniline:



Experimentally Haber found that at a potential of − 0.3 volt *β*-phenylhydroxylamine in an alcoholic sulphuric acid solution yielded aniline but no benzidine, and as under the conditions the reaction

$$C_6H_5NH_2 + C_6H_5NHOH \rightarrow C_6H_5NH \cdot NHC_6H_5 + H_2O$$

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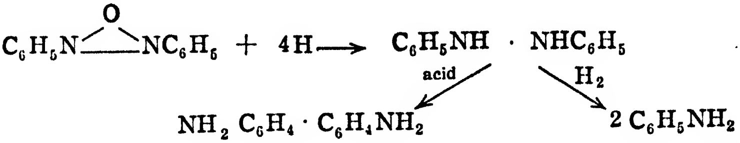
[35] Häussermann, Chem. Ztg., 17, 129 (1893).

[36] Elbs, ibid., 17, 209 (1893).

did not take place he was, for a while, unable to explain the acid reduction of nitrobenzene.

Though azoxybenzene in an acid solution is also a very poor depolarizer it does yield in an alcoholic sulphuric acid solution at a Pt cathode some benzidine and aniline:



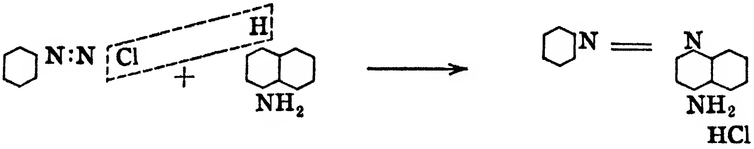
$$C_6H_5N\overset{O}{\frown}NC_6H_5 + 4H \longrightarrow C_6H_5NH \cdot NHC_6H_5 \xrightarrow{acid} NH_2C_6H_4 \cdot C_6H_4NH_2; \quad C_6H_5NH \cdot NHC_6H_5 \xrightarrow{H_2} 2\,C_6H_5NH_2$$

and so the azoxybenzene was an intermediate for the formation of benzidine in an acid solution as well as in an alkaline solution by the condensation of nitrosobenzene with β-phenylhydroxylamine, though the reaction was much slower in the acid than in the alkaline solution.

This scheme required that nitrosobenzene be shown to be an intermediate compound in the acid reduction of nitrobenzene. Haber accomplished this just as he did in the alkaline reduction, using in this case α-naphthylamine instead of α-naphthol as the coupling agent:

1. $C_6H_5NO + NH_2OH{\cdot}HCl \longrightarrow C_6H_5N{:}NCl + H_2O$

2.

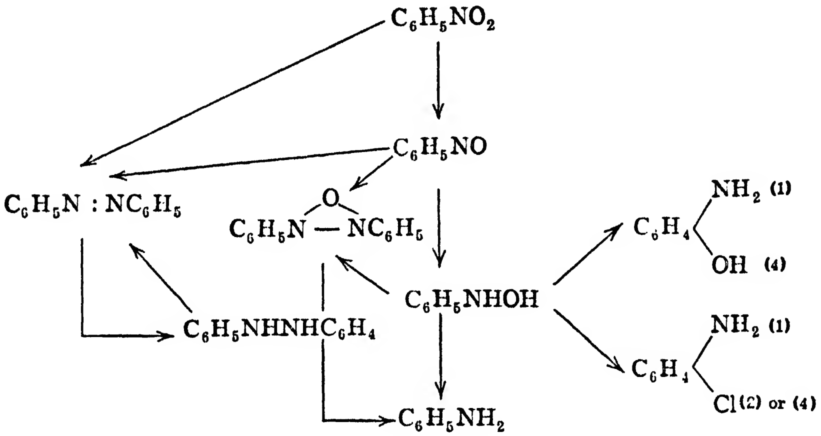


In an acid solution nitrosobenzene is fairly stable, but just as in an alkaline solution it is a better depolarizer than nitrobenzene, therefore it can never accumulate at the cathode, but is further reduced to the hydroxylamine derivative whenever it does not condense or act as an oxidizing agent.

At first Haber was only able to prove the formation of the hydroxylamine derivative by subsequent oxidation back to the nitroso compound, but later he prepared it in good yields by the reduction of nitrobenzene in a dilute acetic acid solution. Therefore the second step in the acid reduction of nitrobenzene was β-phenylhydroxylamine, which was further reduced to aniline.

The formation of azoxybenzene takes place by the condensation of a molecule of nitrosobenzene with a molecule of the hydroxylamine derivative whenever the hydroxylamine is not further reduced. Then the azo compound is reduced to hydrazobenzene, some of which arranges to benzidine, the rest being further reduced to aniline. That portion of the hydroxylamine not condensed or reduced rearranges to *p*-aminophenol.

Thus in an acid as well as in an alkaline solution the primary reduction products of nitrobenzene are nitrosobenzene, β-phenylhydroxylamine, and aniline. All other compounds isolated are formed from these three compounds by chemical changes, i.e., either rearrangements or interaction among themselves. The scheme sums up the results of Haber's efforts.[37]



Having reviewed briefly the development of the theory of electrolytic reduction of nitrobenzene, it will be of interest to note the changes in the course of reactions which variations in the predominating experimental conditions will cause. The theory of reduction as evolved by Haber gives not only a clear insight into the electrolytic and chemical processes at the cathode but also gives a generally clear correlation between the individual reaction conditions and the course of the electrolytic reduction. The keystone of this theory is the fact that the electrolytic, as well as the purely chemical reduction of nitrobenzene and its related compounds, yields directly the compounds expressed in the following scheme:

$$RNO_2—RNO \rightarrow RNHOH \rightarrow RNH_2$$

while the other intermediates not included in this scheme are formed by a series of secondary reactions between the various materials formed from time to time at the cathode. The products finally isolated as end

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[37] The vertical and horizontal lines mean electrochemical reductions, and the sloping lines chemical reactions.

products of the reduction therefore necessarily depend on the relative speeds with which concurrent reactions may take place.

Of all intermediates that may possibly be formed in the reduction of nitrobenzene the most versatile is phenylhydroxylamine. All intermediate or end products, except nitrosobenzene, that may be formed by the electrolytic reduction of nitrobenzene, owe their existence to some reaction involving β-phenylhydroxylamine as one of the reacting materials. It is interesting to study how a seemingly slight change in experimental conditions changes the end products when phenylhydroxylamine is the starting material.

At cathodes composed of zinc, lead, copper, or tin, or at any cathode in the presence of salts of these metals, phenylhydroxylamine is reduced just as well in acid as in alkaline solution to aniline and with such great speed that not even traces of other compounds are detectable. By using these cathodes, therefore, nitrobenzene may be easily and smoothly reduced to aniline. On the other hand with a platinum, nickel, or carbon cathode the reduction of phenylhydroxylamine is less rapid and so there is time for it to become involved in side reactions, the speed of which depends on the nature of the solution. The course of the reduction is not only varied by the use of different electrode materials but also by the concentration of the acid or alkali in the electrolyte.

The sum-total of the electrolytic reduction of nitrobenzene in alcoholic acid solution at cathodes of platinum, nickel or carbon is the formation of a mixture of benzidine salt, aniline and *p*-aminophenol. The speed of the formation of these three compounds is of the same order under certain conditions of the experimentation. But the amounts of each product formed is dependent on the acid concentration of the electrolyte. In a strongly acid solution the formation of *p*-aminophenol is enhanced at the expense of the other two products, but under no conditions can the formation of benzidine and aniline be completely prevented by increasing the acidity of the electrolyte.

On the other hand, in alkaline solution, the reaction is not the same as in acid solution, with the result that practically all of the β-phenylhydroxylamine is used to form azoxybenzene and on further passage of the current yields hydrazobenzene and to some extent azobenzene. Since hydrazobenzene cannot be further reduced by the electric current to aniline in alkaline solution it is one of the end products of the reaction. When a nickel cathode is used there are good yields of hydrazobenzene.

It must be recognized that the speed of electrolytic and chemical reactions is also a function of the individual materials used. That the reduction of nitrobenzene takes a certain course under certain conditions is no criterion for the assumption that the homologues and derivatives of nitrobenzene will behave similarly. However in the majority of cases the following generalization may be made concerning the reduction of mononitro compounds:

1. When the electrolyte is a dilute acid solution, an alcoholic acid solution, or merely a suspension in water at a zinc, lead, copper, tin, or mercury cathode or in the presence of salts of these metals the nitro derivative is readily and smoothly reduced in almost theoretical yields to the amino derivative, which may be isolated from the catholyte by steam distillation and recrystallization as the acid salt.[38]

2. Under similar conditions of an acid electrolyte in the presence of cathodes of nickel, carbon, or platinum the products formed are usually mixtures of the amine, the benzidine, and the hydroxyamino derivative.

3. With cathodes of nickel, carbon or platinum in alkaline solution depending on the current density used, the product may be either the azoxy, azo, or hydrazo derivative.[39]

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[38] C. F. Boehringer und Soehne, D.R.P. 116942 (1900); K. Elbs and F. Silbermann, Z. Elektrochem., 7, 589 (1901); see also W. Löb, ibid., 4, 436 (1898), etc.

[39] See F. Foerster, "Wässerige Lösungen," 619 et seq.

CHAPTER X

THE REDUCTION OF AROMATIC NITRO COMPOUNDS PART II—NEUTRAL AND ACID SOLUTIONS

REDUCTIONS IN NEUTRAL SOLUTION

By controlling the experimental conditions with care it is possible to prepare in good yields the various reduction products of the aromatic compounds containing one nitro group. The selective reduction is of sufficient importance to be considered somewhat in detail.

The Preparation of Nitroso Compounds.—Due to the fact that the nitroso compounds are most energetic cathodic depolarizers they cannot be prepared by the direct reduction of aromatic nitro derivatives.[1] However they are easily prepared by the oxidation of the phenylhydroxylamine derivatives. According to the method of Dieffenbach [2] the hydroxylamine derivative was prepared by electrolyzing the corresponding nitro derivative in the cathode compartment of a cell using a neutral electrolyte with a nickel or carbon cathode. Then with this hydroxylamine derivative in the anolyte of a second cell with a lead anode, the product was oxidized to the desired nitroso compound. The two processes can be coupled in the same cell by carrying out the oxidation in the anolyte while the corresponding reduction of the nitro derivative is being carried out in the catholyte. Both catholyte and anolyte must at all times during the reaction remain strictly neutral since the hydroxylamine derivative is stable only in neutral solution.

β-Arylhydroxylamine Compounds.—The purely chemical method of preparing these compounds in a neutral solution is not at all difficult.[3] β-Substituted hydroxylamines cannot be prepared by the electrolytic method in acid or alkaline solution because of their great sensitivity toward acid and alkali. They too easily undergo secondary reactions as fast as they are formed at the cathode. The speed of these secondary reactions is in direct proportion to the hydrogen ion and hydroxyl ion concentration; therefore their preparation must be carried out in an

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[1] See p. 197.

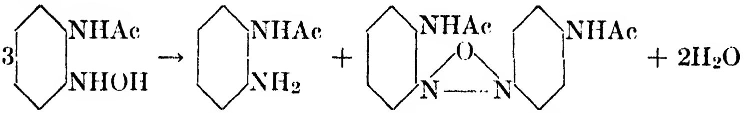
[2] D.R.P. 192519 (1908).

[3] Bamberger, Ber., **27**, 1347, 1548 (1894); Wohl, ibid., **31**, 2543 (1898); D.R.P. 84138 (1893).

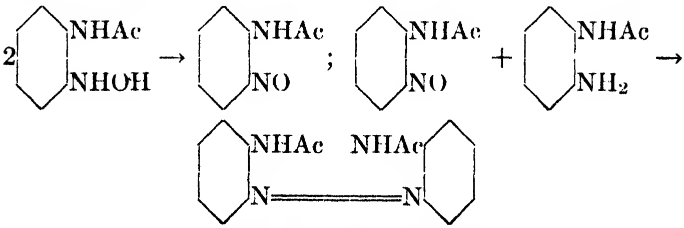
almost neutral solution.[4] Haber found that the best electrolyte for the preparation of these derivatives was a very dilute solution of acetic acid, or alcoholic NH_4OH containing sufficient NH_4Cl to insure neutrality. Brand [5] was able to get better conductivity in the electrolyte by using a solution of acetic acid and sodium acetate. He also tried an aqueous suspension and an aqueous alcoholic solution of nitrobenzene. In the neutral solution of acetic acid and sodium acetate there is no appreciable condensation of nitrosobenzene with the phenylhydroxylamine because of the negligible acidity. Hydroxylamine with only a drop of azoxybenzene and a trace of aniline were formed. Similarly *p*-chloronitrobenzene yielded *p*-chlorophenylhydroxylamine.

Another method has been worked out by F. M. Frederiksen,[6] in which the electrodes were of zinc and the electrolyte was a solution of ammonium chloride in alcohol. Yields of 21 to 29 per cent are claimed for this method. There is a question whether the use of a diaphragm would not raise the yields in this case, but then on the other hand the conductivity of the cell would be diminished. It is merely a question of current yield and power required as to whether the diaphragm should or should not be used.

In an almost neutral solution the reduction product of *o*-nitroacetanilide is *o*-hydroxylamine acetanilide. There were also traces of *o*-azo- and *o*-azoxy-derivatives formed.[7] These latter two compounds were shown to be formed by purely chemical reactions which take place on standing. According to Bamberger and Brady [8] the alkaline rearrangement goes as follows:



but according to the scheme of Haber and Schmidt it goes:



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[4] See Haber, Z. Elektrochem., **4**, 511 (1898); **5**, 77 (1898); Haber and Schmidt, Z. physik. Chem., **32**, 272 (1900); D.R.P. 10905 (1898), Boehringer. See p. 198.

[5] Ber., **38**, 3076 (1905); Elbs, "Übungsbeispiele," p. 94.

[6] J. Phys. Chem., **19**, 696 (1915); Trans. Am. Electrochem. Soc., **28**, 345 (1915).

[7] Brand and Stohr, Ber., **39**, 4058 (1906).

[8] Bamberger and Brady, Ber., **33**, 271 (1900).

That the former scheme is the correct explanation was shown by condensing *o*-nitroso- and *o*-hydroxylamineacetanilide in a neutral alcoholic solution to form the *o*-azoxy derivative. The rearrangement is practically entirely inhibited by the addition of acids and an excess of alkalies; the latter having more influence than the former.

p-Nitroacetanilide is reduced in an almost neutral solution to the hydroxylamine derivative.[9]

REDUCTION IN DILUTE ACID SOLUTION

The Preparation of Amines from Nitro Compounds.[10]—As stated above under the discussion of the Haber scheme, the reduction of aromatic mononitro compounds leads primarily to the successive formation of nitroso-, hydroxylamine-, and amino-compounds; and secondarily to the formation of azoxy-, azo-, and hydrazo-compounds, or aminophenols, and halogenated amines. The final reduction product, the amino compound, predominates only when the conditions of reduction are such that the secondary reactions are held in subordination to the electrolytic reduction, i.e., a very high reduction velocity combined with a very low rearrangement and condensation velocity (in order to decrease the formation of aminophenols and azoxy, etc., compounds, respectively), leads to the formation of the largest amounts of amines according to the equation:

$$C_6H_5NO_2 \rightarrow C_6H_5NO \rightarrow C_6H_5NHOH \rightarrow C_6H_5NH_2$$

The amines are prepared by the electrolytic reduction of the corresponding nitro compound in dilute sulphuric acid at a cathode of lead, tin, or zinc, as described above.[11] An excellent method for the prepara-

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[9] K. Brand and E. Stohr, Ber., **42**, 2478 (1909).

[10] Häussermann, Chem. Ztg., **17**, 129 (1893); Haber, Z. Elektrochem., **4**, 506 (1898); Elbs, ibid., **7**, 589 (1901); Chilesotti, ibid., **7**, 768 (1901); Elbs and Kreman, ibid., **9**, 416 (1903); Klappert, ibid., **8**, 791 (1902); Elbs and Wogrinz, ibid., **9**, 431 (1903); J. Möller, ibid., **7**, 741 (1901); **10**, 199 and 222 (1904); Voigt, Z. angew. Chem., 108 (1894); Weiss and Reiter, Ann., **355**, 175 (1907); Fichter and Sulzberger, Ber., **37**, 881 (1904); Hermann, Monatsch., **26**, 1021 (1905); Häussermann and Schmidt, Ber., **34**, 3770 (1901); Hostmann, Chem. Ztg., **17**, 1099 (1903); Weinerth, Dissert., Giessen (1906); Schudt, Dissert., Giessen (1902); Schumacher, Dissert., Giessen (1902); Brand, J. prakt. Chem., 2, **67**, 145 (1903); Meister, D.R.P. 168273 (1903); Schlemmer, Dissert., Giessen (1903); Boehringer, D.R.P. 116942 (1900); Weyprecht, Dissert., Giessen (1902).

[11] See also Elbs, Chem. Ztg., **17**, 209 (1893); Z. Elektrochem., **2**, 472 (1896); Elbs and Silbermann, ibid., **7**, 589 (1901); Löb, ibid., **4**, 430 (1895); J. Möller, ibid., **5**, 463 (1898). Löb used an alcoholic HCl solution. See also H. Inoue, J. Chem. Ind. Japan, **24**, 121 (1921); N. Otin, Z. Elektrochem., **16**, 674 (1910); Chilesotti, ibid., **7**, 768 (1901); D.R.P. 116942, 117007, 127815.

tion of aniline by the electrolytic reduction of nitrobenzene is given by Elbs or Müller.[12]

The addition of soluble salts of the heavy metals as copper, tin, lead, iron, chromium, mercury, or these metals in a finely powdered condition permits the reduction of nitrobenzene to aniline at any cathode without any particular trouble; but the absence of these salts with any cathode causes a variety of troubles. The use of these soluble salts of copper and tin is the basis of a patent assigned to Boehringer.[13]

The results of the Boehringer patents have been sustained by Chilesotti,[14] who also helped to develop the reasons for the use of these metals as described above. When these metals are not present, nitrobenzene at an unattackable cathode in an alcoholic sulphuric acid solution yields benzidine sulphate in large quantities, also diphenylene, *o*, *p*-diaminodiphenyl, azoxybenzene with only a very little aniline, some *p*-aminophenol and *p*-phenetidine.[15]

The activity of these hydrogen carriers is so great, according to the work of Chilesotti,[16] that an energetic reduction is possible even when an aqueous suspension of the nitro compound is used instead of the usual alcoholic solution. Table XXI, on page 210, taken from Chilesotti shows the variation of the results with the variation in the experimental conditions.

The acid content of the electrolyte should be so regulated that at the end of the reduction there is a free acidity in the catholyte to the extent of about 0.7–0.8 normal, and the solution should be perfectly clear. If the acid content is higher than this, there is a danger of the formation of *p*-aminohydroxy compounds as described by Gattermann, so lowering the yield of amine. On the other hand, if the acid concentration is too low, a clear solution is not obtained because of the formation of azoxy, etc., compounds.

Some of the results of Elbs and Silbermann are tabulated on page 211.[17] The table is self-explanatory though a few words of summation may not be amiss. It shows that the addition of zinc chloride to hydrochloric or sulphuric acids as the electrolyte, increases the yield of amine and at the same time decreases the yields of the secondary products, namely, benzi-

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[12] K. Elbs, "Übungsbeispiele," page 83. See also E. Müller, Elektrochemisches Praktikum, page 212.

[13] Boehringer, D.R.P. 116942 (1900). Also Elbs and Silbermann, Z. Elekrtochem., **7**, 589 (1901).

[14] Chilesotti, loc. cit.

[15] Häussermann, Chem. Ztg., **17**, 129 and 209 (1893).

[16] Chilesotti, loc. cit.

[17] Elbs and Silbermann, loc. cit.

dine, aminophenol, etc. Sulphuric acid does not give as large yields of amine as does HCl and it also increases the amounts of by-products.

TABLE XXI

Catholyte	Amp.-hours	Product	Yield	
			Material	Current
I. 20 g. $C_6H_5NO_2$ 30 cc. alc. 250 cc. H_2O 11 g. HCl 1 g. $SnCl_2 \cdot 2H_2O$	26.5	12.76 g. $C_6H_5NH_2$	84.4	83.5
II. 20 g. *o*-nitro-toluene 35 cc. alc. 300 cc. 5 per cent HCl 1 g. $SnCl_2 \cdot 2H_2O$	24	11.8 g. *o*-toluidine B. P. 197–199°	96.7	94.6
III. 12.6 g. *m*-nitro-aniline 250 cc. 6.5 per cent HCl 1 g. $SnCl_2 \cdot 2H_2O$	15	16.3 g. *m*-phenylene-diamine hydrochloride	98.7	95.9
IV. 20 g. $C_6H_5NO_2$ 30 cc. alc. 250 cc. H_2O 17.6 g. HCl 1 g. $CuCl_2 \cdot 2H_2O$	28.4	12.6 g. $C_6H_5NH_2$	83.1	75.1
V. 20 g. $C_6H_5NO_2$ 30 cc. alc. 250 cc. H_2O 23.6 g. H_2SO_4 1.5 g. $CuSO_4 \cdot 5H_2O$	28.2	11.8 g. $C_6H_5NH_2$	78.3	70.5

The Elbs method requires the reduction to take place at a zinc or lead rather than at a platinum cathode in an alcoholic-sulphuric acid solution. The Boehringer Patents do not require the solvent alcohol but use a suspension of the depolarizer in a dilute sulphuric acid solution in the presence of a tin salt,[18] or instead of a tin salt, a soluble salt of copper, iron, chromium, lead, mercury, or the finely divided metal itself,[19] or a titanium salt using an anode of lead, platinum, or carbon, with a platinum

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[18] D.R.P. 116942 (1899), Boehringer.

[19] D.R.P. 117007 (1900), Boehringer.

cathode in sulphuric acid solution if the diaphragm is to be eliminated.[20]

Table XXII

No.	Cathode	Catholyte	Products
1	Cu	15 g. $C_6H_5NO_2$; 25 g. $ZnCl_2$; 80 cc. conc. HCl; 120 cc. C_2H_5OH; 35 cc. H_2O	Aniline 66–75 per cent; benzidine 10 per cent; traces of *p*-aminophenol and *p*-chloro-aniline
2	Cu	Same as 1 without $ZnCl_2$	Same as 1, but *p*-chloro-aniline was 15 per cent
3	Cu	Same as 2, but HCl replaced by H_2SO_4	Same as 1, but *p*-amino-phenol 40–50 per cent
4	Cu	*o*-Nitrotoluene in alcoholic salt and acid solution with $ZnCl_2$	*o*-Toluidine 65–90 per cent, trace of *o*-tolidine, amino-cresol, chlorotoluidine
5	Cu	Same as 4 without $ZnCl_2$	Same as 4, but larger amount of 5-chloro-*o*-toluidine
6	Cu	Same as 5, but HCl replaced by H_2SO_4	*o*-Toluidine 50–60 per cent, 5-amino-*o*-cresol 20–40 per cent, traces of *o*-tolidine
7	Cu	*m*-Nitrotoluene in alcoholic salt and acid solution with $ZnCl_2$	*m*-Toluidine 70–80 per cent, trace of chlorotoluidine
8	Cu	Same as 7, but without $ZnCl_3$	Same as 7, but larger amounts of 6-chloro-*m*-toluidine
9	Cu	*p*-Nitrotoluene in alcoholic salt and acid solution with $ZnCl_2$	*p*-Toluidine 60–84 per cent, trace of by-products
10	Cu	Same as 9, without $ZnCl_2$	Same as 9, some 5-chloro-*p*-toluidine
11	Cu	Same as 10, but HCl replaced by H_2SO_4	*p*-Toluidine 75–85 per cent, evolution of H_2 easier than in case of *o*-compound
12	Pb	20 g. $C_6H_5NO_2$, 150 cc. C_2H_5OH, 125 cc. H_2SO_4 (sp. gr. 1.2)	Aniline as the sulphate 90 per cent
13	Pb	*o*-Nitrotoluene as in 12	*o*-Toluidine 90 per cent
14	Pb	*m*-Nitrotoluene as in 12	*m*-Toluidine 90 per cent
15	Pb	*p*-Nitrotoluene as in 12	*p*-Toluidine less than 90 per cent

Snowdon made a study of the formation of aniline by the reduction both chemically and electrochemically of nitrobenzene in the presence of ferrous chloride at the boiling temperature. Iron electrodes in

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[20] D.R.P. 168273 (1903), Meister.

hydrochloric acid containing ferrous chloride formed the best system. The current efficiency was found to increase with the current density.[21]

A purely chemical method[22] of reducing azo dyes to their corresponding amines calls for the use of the theoretical amount of tin and hydrochloric acid as reducing agent. The electrochemical aspect of this patent is the recovery of the tin from the solution of stannous chloride by electrolyzing with an unattackable cathode using a c. d. of about 18 amperes. It is always safest to have an excess of tin present. After the tin has been removed the amine is recovered as usual. Copper may replace the tin.[23]

A patent taken out by Boehringer[24] describes the preparation of amines by reduction of a suspension of the appropriate nitro derivative in an alkaline solution or in a solution of an alkali salt using for the reduction a freshly coppered cathode or any unattackable cathode provided there is in the solution a copper salt or finely divided copper.[25] Whenever the amine is unchanged chemically by the presence of the alkaline solution the yields of amine are almost 100 per cent. Other reductions described are:

o-nitrotoluene	to	*o*-toluidine
m-nitraniline	to	*m*-phenylenediamine
α-nitronaphthalene	to	α-naphthylamine.

A method for the production of aniline for technical uses was attempted on a laboratory scale by Farnau,[26] who obtained only aniline but 12 per cent of the starting material was unaccounted for at the end of the reaction.

Kendall claims the formation of dyes containing an amino group by the reduction of nitro compounds in an acetone-dilute-sulphuric acid solution, without the formation of the objectionable indulin blacks.[27]

An excellent method for the preparation of *p*-aminophenol by the reduction of nitrobenzene has been described recently.[28] The typical electrolyte is described. Catholyte: 540 cc. of nitrobenzene and 1800 cc.

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[21] Snowdon, J. Phys. Chem., **15**, 797 (1911).

[22] D.R.P. 123813 (Boehringer).

[23] D.R.P. 127815 (1901), Boehringer.

[24] D.R.P. 130742; F.P. 131404 (1902).

[25] The presence of copper powder is necessary according to Elbs and Brand, Z. Elektrochem., **8**, 789 (1902).

[26] E. F. Farnau, J. Phys. Chem., **16**, 249 (1912).

[27] E. D. Kendall, U.S.P. 132665 (1919). See also Otin, Z. Elektrochem., **16**, 674 (1910).

[28] McDaniel, Schneider and Bullard, Trans. Am. Electrochem. Soc., **39**, 441 (1921). See also H. Inoue, J. Chem. Ind. Japan, **24**, 121 (1921).

of 19 per cent sulphuric acid; The anolyte: Sulphuric acid of sp. gr. 1.75. The best electrodes are of platinum or gold, platinum plated gold or pure carbon; graphite does not work well. Only these cathodes may be used because the reaction does not take place in the presence of the heavy metals, though arsenic is an exception. Even care must be taken that the corroded materials of the connections to the cathode cannot fall into the bath. In the reduction some sulphonate is formed but this is settled out in time as a sludge together with the sulphates that are formed; they are worked up after the *p*-aminophenol has been removed from the solution. In this process the main item of cost is the sulphuric acid because the spent acid must be concentrated without contamination with heavy metals which is a difficult process on a large scale. In order to lower the electrical costs it was found possible to prepare at the same time good yields of ammonium persulphate in the anolyte.[29]

The Formation of By-products in the Preparation of Amines.—The groups other than nitro which are present on the ring of an aromatic nitro compound have something to do with the course of the reduction. The amine is not always formed in the quantities that would be expected when the Elbs or Boehringer methods are applied. Very often unexpectedly large quantities of azoxy, azo, and hydrazo compounds or benzidine, aminophenols, etc., are formed.

It was expected that the use of a dilute mineral acid as the electrolyte in the reduction of *o*-nitroacetanilide would lead, as in the case of the alkaline reduction (which see), to the formation of large amounts of μ-methylbenzimidazole. However these expectations were not fulfilled for the reason that the acetyl group was hydrolyzed out, making the main reduction the formation of *o*-phenylenediamine, though small amounts of the azo and azoxy compounds were also formed. The use of a hydrogen carrier as copper powder or zinc chloride made the phenylenediamine predominate. On the other hand the use of strong acetic acid gave 30 per cent yields of the benzimidazole when a nickel wire gauze cathode was used.[30]

These reactions support Haber's scheme and also tend to prove that when the hydrogen ion concentration in an acid solution is not as large

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[29] See also F.P. 483186 (1917), Soc. Anon. pour l'ind. chim. a Bale, in which the use of Pb or Bi carriers is described. T. Shoji, J. Chem. Ind. Japan, **21**, 117 (1918); U.S.P. 1239822 (1917), Piguet, Steinbuch, and Stocker, also use Bi as a carrier with a Pb cathode or cathodes of Bi, As, Sb, Cu, Ni, Sn, Hg, to decrease the formation of aniline and to promote the formation of the aminophenol. These cases seem to contradict the findings of McDaniel, etc., that the heavy metals inhibit the formation of the *p*-aminophenols.

[30] Brand and Stohr, Ber., **39**, 4058 (1906).

as the corresponding hydroxyl ion concentration of alkalies, the condensation between the *o*-nitroso- and the *o*-nitrohydroxylamine acetanilide to form azoxy derivatives is speeded up.[31]

In a mineral acid solution using the method of Boehringer an acetyl group is eliminated, forming *p*-phenylenediamine as the final product when *p*-nitroacetanilide is the starting material:

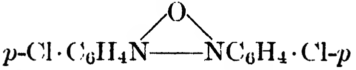
$$p\text{-}NO_2\cdot C_6H_4\cdot NHOCCH_3 \rightarrow p\text{-}NH_2\cdot C_6H_4\cdot NH_2 + CH_3COOH$$

but the use of acetic acid as the electrolyte prevents the hydrolysis of the acetyl group so that the product is *p*-aminoacetanilide:

$$p\text{-}NO_2\cdot C_6H_4\cdot NHOCCH_3 \rightarrow p\text{-}NH_2\cdot C_6H_4\cdot NHOCCH_3$$

In the preparation of *p*-chloroaniline by the Boehringer method from *p*-chloronitrobenzene the usual course is taken by the reduction, but notwithstanding the addition of zinc chloride the speed of the condensation between *p*-chloronitrosobenzene and *p*-chlorophenylhydroxylamine even in an acid solution is sufficiently rapid to permit the formation of considerable quantities of *p*-dichloro-azoxy-benzene:[32]

$$p\text{-}Cl\cdot C_6H_4\cdot NO + p\text{-}Cl\cdot C_6H_4\cdot NHOH \rightarrow$$



$$p\text{-}Cl\cdot C_6H_4N\overset{O}{\overline{\qquad\quad}}NC_6H_4\cdot Cl\text{-}p$$

though Bamberger and Rising showed[33] that a methyl group in the *o*- or *p*-position to the NO or NHOH groups decreased the speed of condensation. It seems that some substituents have the reverse effect. A systematic investigation of this problem is desirable.

In describing the Elbs method of reduction in alcoholic H_2SO_4 at a zinc cathode, mention was made of the formation of aminophenols and chlorinated amines; the same was true of the Boehringer method with the addition of heavy metal salts. Of course increasing the acid concentration will increase the formation of these compounds, as will also an increase in temperature. Pinnow was able to find[34] that the groups $—N(CH_3)_2$, $=NCH_3$, $—COCH_3$, $—OCH_3$, and $—CH_3$ when in the *o*-position to the NO_2 group caused an increased speed of formation of the aminophenols and halogenated amines, while the groups $—NH_2$ and $—NHCH_3$ were without any influence. He was of the opinion because of some purely chemical reactions that the same should be true when the Boehringer method was used, which fact was substantiated by Brand,[35]

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[31] See also Niementousky, Ber., **39**, 743 (1906).

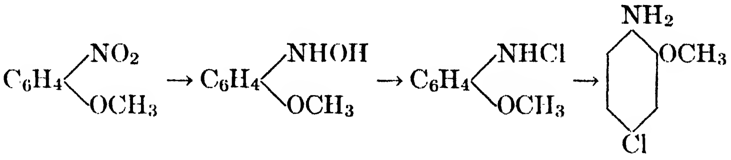
[32] Weinerth, Dissert., Giessen (1906); Elbs, "Übungsbeispiele," p. 86.

[33] Ann., **316**, 257 (1901).

[34] Pinnow, J. prakt. Chem., [2], **63** (1901); **65**, 579 (1902).

[35] K. Brand, J. prakt. Chem., [2], **67**, 145 (1903).

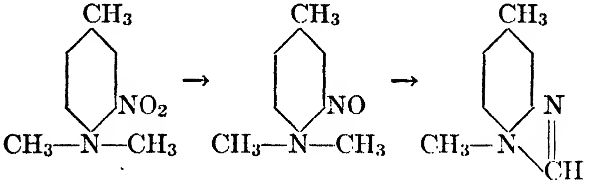
when in a hydrochloric acid solution at a Ni cathode in the presence of stannous chloride or at a copper cathode in the presence of copper powder rather large quantities of *p*-chloro-*o*-anisidine besides the *o*-anisidine were formed from *o*-nitroanisole:



When the hydrochloric acid is replaced by alcoholic sulphuric acid and a copper cathode in the presence of copper powder is used, instead of the *p*-chloro compound there is obtained besides *o*-anisidine some 3-methoxy-4-aminophenol.[36]

The possibilities of these methods are practically unlimited. By a change of conditions large yields should be possible, and some of these compounds are in great demand.

The Formation of Anomalous Compounds.—Certain groups in a position ortho to a nitro group cause an intra-molecular condensation with the formation of a heterocyclic compound instead of the expected reduction to the corresponding amine. The method of Löb[37] in the hands of Pinnow[38] when applied to the reduction of *m*-nitrodimethyl-*p*-toluidine formed dimethylbenzimidazole besides dimethyltoluylenediamine. What probably happened was that the nitro compound was first reduced to the nitroso derivative which then underwent a molecular rearrangement with the loss of a molecule of water to form benzimidazole:[39]



This reduction is not the same as the purely chemical reduction which leads only to the formation of the diamine.

Similar results were obtained by Brand and Stohr[40] in the reduction

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[36] Schudt, Dissert., Giessen (1902).

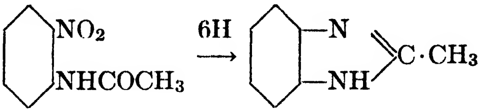
[37] Löb, Z. Elektrochem., **3**, 471 (1897).

[38] Pinnow, loc. cit.

[39] See page 250.

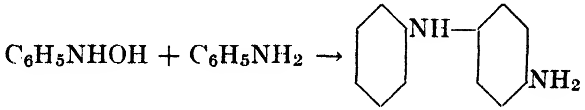
[40] Brand and Stohr, Ber., **39**, 4063 (1906).

of *o*-nitroacetanilide in 80 per cent acetic acid in the presence of stannous chloride at a nickel cathode when *μ*-methybenzimidazole was formed:

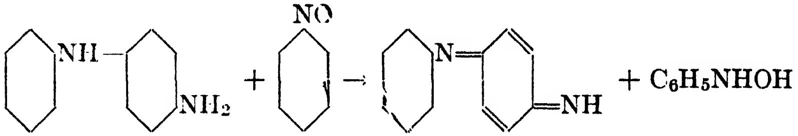


This reaction takes place only when the amino group is protected, otherwise the reaction leads to the formation of phenylenediamine.

Another step has been added to the Haber scheme by Nover.[41] In the course of the reduction he also found *β*-phenylhydroxylamine and *p*-aminodiphenylamine. The formation of this latter compound is supposed to be by the condensation of *β*-phenylhydroxylamine with aniline:



Then the semidine is oxidized by the nitrosobenzene to phenylquinonediimide,



the latter polymerizing into "Emeraldine." This same compound besides the *p*-aminodiphenylamine was also obtained by Frank[42] in the reduction of *p*-nitrosodiphenylamine. The normal course of the reduction evidently is the formation of the completely reduced compound.

Another very interesting intramolecular condensation was uncovered by Mette[43] in the reduction of 3-nitro-4-lactylaminophenetole by the Boehringer method. Instead of the expected amino compound two very complicated condensation products were found, the formation of which is expressed by the formulae given below. The compounds are considered as quinoxalines:

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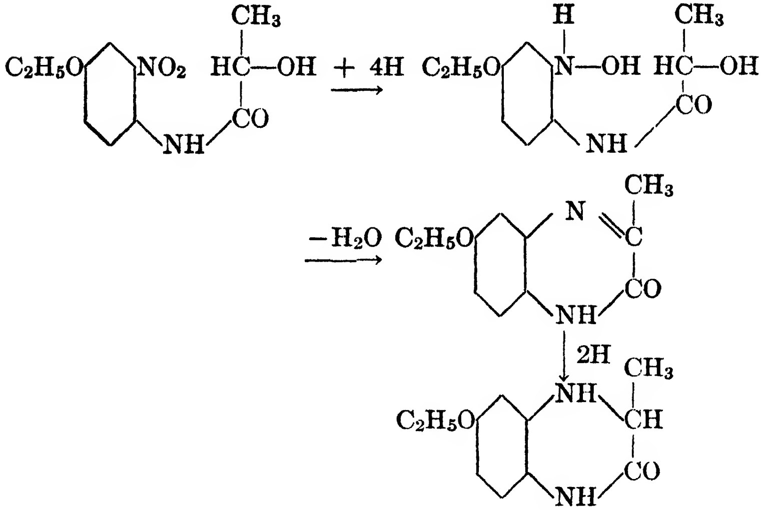
[41] Nover, Ber., **40**, 288 (1907).

[42] Dissert., Giessen (1903).

[43] Mette, Dissert., Giessen (1907).



The Reduction of Azoxy and Azo Compounds.—In the course of the historical development of the reduction of nitro compounds it was shown that the azoxy and azo compounds in a dilute acid solution were reduced to diphenyl or diphenylamine derivatives or to amines. The course of the reduction depends on the relative speed of electrolytic reduction and of rearrangement; since hydrazo compounds as a rule are sensitive to acids, the acidity of the solution assists greatly in the directing of the reaction to the formation of rearrangment products.

The Preparation of Hydrazo Compounds and their Rearrangement Products.—These compounds are next to azo compounds in the reduction of the nitro group. Häussermann[44] was the first to isolate a hydrazo compound at a platinum cathode in an alcoholic sulphuric acid solution; later Löb[45] applied the method in alcoholic hydrochloric acid. Löb was particularly interested in the benzidine formation and he found that formic, acetic, and oxalic acid solutions could be used with care though the benzidine produced was often very much discolored. On account of the Gattermann rearrangement of the β-phenylhydroxylamine to aminophenol it is very necessary when sulphuric acid is used to keep the acid concentration below a certain value to insure the best yields of benzidine.

As benzidine is of great importance in the dye industry, it is unfortunate that it cannot be prepared from nitrobenzene by a single elec-

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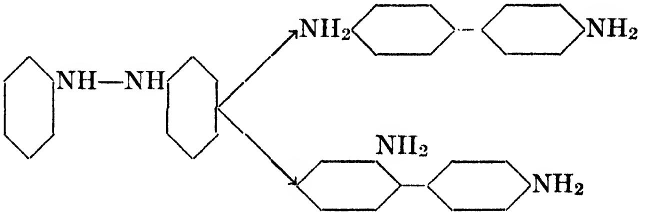
[44] Chem. Ztg., **17**, 129 and 209 (1893).

[45] Löb, Ber., **29**, 1894 (1896); **33**, 2329 (1900); Z. Elektrochem., **7**, 117; 300; 320; 333; 597 (1901); Z. physik. Chem., **34**, 641 (1900).

trolysis. It is readily formed in the reduction of azoxy or azobenzene in an acid solution. These two starting materials must, however, be prepared in an alkaline solution before being used for the acid reduction. If the starting material is nitrobenzene in an acid solution the product will not be benzidine but an aminophenol or a related compound.[46]

Benzidine and diphenylene are formed by the rearrangement in an acid solution of hydrazobenzene:



The diphenylene is found only in traces at a temperature of 20-30°.

The earliest method that was really of value was developed by Löb.[47] He used an alcoholic concentrated sulphuric acid electrolyte and so obtained benzidine sulphate from nitrobenzene, or toluidine sulphate from nitrotoluene.[48]

The method is hardly applicable on a technical scale because of the large quantities of solvent alcohol required. Löb was able to abandon the use of the alcohol by reducing the nitrobenzene first as a suspension in aqueous sodium hydroxide with very violent stirring at a temperature of 80–100° at a nickel, mercury, or platinum cathode to get good yields of the azoxybenzene.[49] This method is good because in an aqueous suspension the azoxy compound is a very poor depolarizer and therefore undergoes but a very slight reduction. When the catholyte is acidified and a carrier added the reduction may be carried beyond the azoxy stage. Such a carrier is found among the salts of titanium, vanadium, copper, lead, mercury or tin.[50] A better method is probably that found by Löb,[51] who recommends that with any electrode material after the azo stage has been reached there be added to the electrolyte a solution of hydrochloric acid containing 0.5 per cent to 1.5 per cent of stannous

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[46] See the discussion of these reactions above; also Häussermann, loc. cit., and Löb, loc. cit.

[47] Löb, Z. Elektrochem., 7, 337 (1901).

[48] See also D.R.P. 116871 (1899) Chem. Fab. vorm Weiler ter Meer.

[49] Löb, loc. cit., also D.R.P. 116467 (1900).

[50] D.R.P. 189312 (1906), Darmstädter; D.R.P. 141535 (1902) Meister. Haber used a Hg cathode with excellent results.

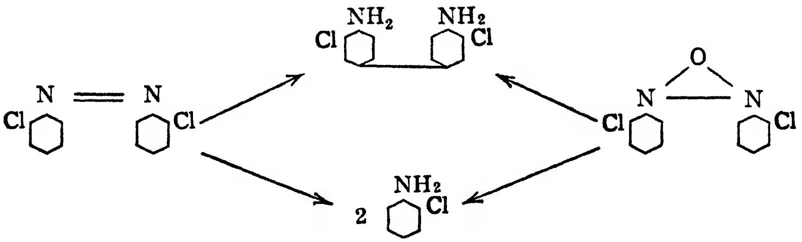
[51] D.R.P. 122046 (1900).

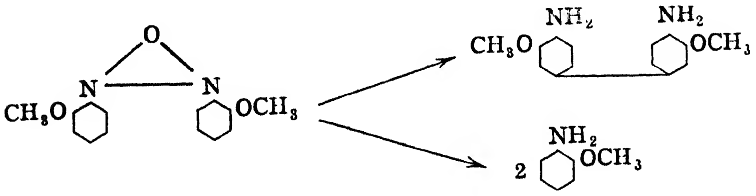
chloride and 25 per cent of hydrochloric acid and then continuing the reduction.

The use of a vanadium salt as a carrier has been made the basis of a patent.[52] A diaphragm is not necessary, if a titanium salt is used instead of the vanadic acid.[53] A titanium salt in a 10 per cent sulphuric acid solution at a nickel or lead cathode gives 57 per cent yields of benzidine sulphate.[54]

There are some cases on record in which substitution products of azoxy and azo compounds have been reduced to the corresponding hydrazo and benzidine derivatives, but not many compounds have been studied.

In a hydrochloric acid solution with the method of Boehringer *o*-dichlorazobenzene yields mostly *o*-dichlorobenzidine and some little *o*-chloraniline; similarly *o*-dichlorazoxybenzene is reduced to the same compound when stannous chloride is added but the two products formed are in equal amounts. The chlorazoxy compound at a copper cathode in the presence of copper powder forms mostly the chloraniline at the expense of the diphenyl derivative.[55] *o*-Azoxyanisole is similarly reduced.[56]





In an alkaline solution phenazone is stable toward electrolytically evolved hydrogen but in an acid solution to which zinc chloride has

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[52] D.R.P. 172654 (1903), Meister.

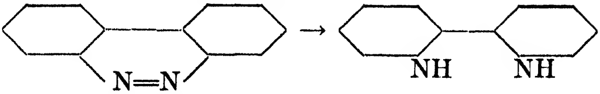
[53] D.R.P. 168273 (1903), Meister.

[54] H. Inoue, J. Chem. Ind. Japan, **24**, 121, (1921).

[55] Brand, J. prakt. Chem. [2], **67**, 146 (1903).

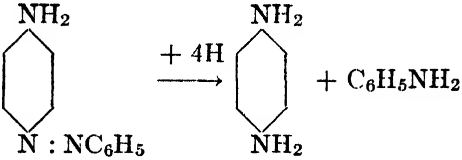
[56] Brand, loc. cit.

been added it yields hydrophenazone:[57]



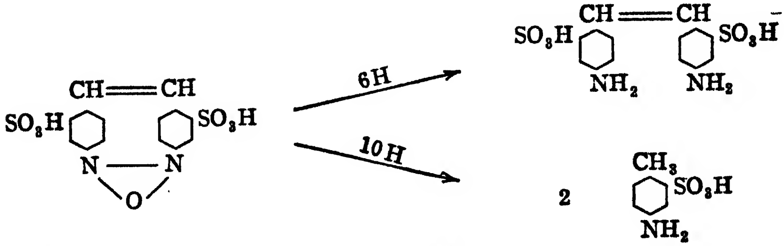
The Reduction of Azoxy and Azo Compounds to Amines.[58]—When hydrazobenzene has been prepared electrolytically in an acid solution if the rearrangement velocity (to form benzidine) is low, the compound will add more hydrogen to split the compound and form 2 molecules of aniline or aminophenol. This is especially true if there is an amino or a hydroxyl group in a position *o*- or *p*- to the azo group. This reaction is almost impossible or at least very difficult on the purely chemical scale.

The Boehringer Patents[59] describe the reduction of azo dyes in an hydrochloric acid solution at a tin cathode or at an unattackable cathode in the presence of stannous chloride. The advantage of this reduction lies in the fact that the resulting products are free from contamination by metallic salts, thus their recovery from the solution is greatly facilitated. By this method *p*-amino azobenzene is reduced to *p*-phenylenediamine and aniline:



Orange-2 to α-amino-β-naphthol and sulphanilic acid.

In studying " Sun Yellow," Elbs and Kremann[60] reduced *p*-azoxystilbenedisulphonic acid with a low c. d. and found that the azoxy linkage was broken to form the corresponding amine, i.e., *p*- *p*′-diaminostilbene-*o*-*o*′-disulphonic acid.



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[57] Wohlfahrt, J. prakt. Chem. [2], 65, 295 (1902).

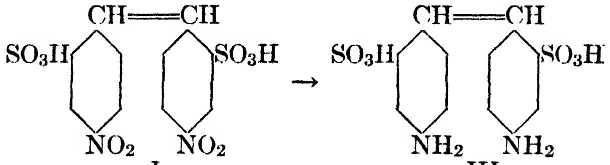
[58] Schneider, Dissert., Giessen (1906); Keiper, Dissert., Giessen (1903); Hesselmann, Dissert., Giessen (1905); Ahrens, Z. Elektrochem., 3, 100 (1896).

[59] D.R.P. 121835 and 116942 (1900).

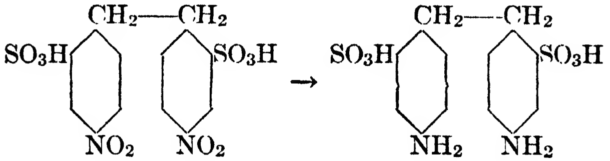
[60] Elbs and Kremann, Z. Elektrochem., 9, 416 (1903).

but with a higher c. d. both the azoxy and the ethylene linkages were broken to form *p*-toluidine-*o*-sulphonic acid.

It is very peculiar that neither *p*-dinitrostilbene-*o*-disulphonic acid (I) nor *p*-dinitrodibenzyl-*o*-disulphonic acid (II) under the influence of cathodic reduction suffer a scission of the C═C or the C—C union. These two compounds yield respectively *p*-diaminostilbene-*o*-disulphonic acid (III) and *p*-diaminodibenzyl-*o*-disulphonic acid (IV).



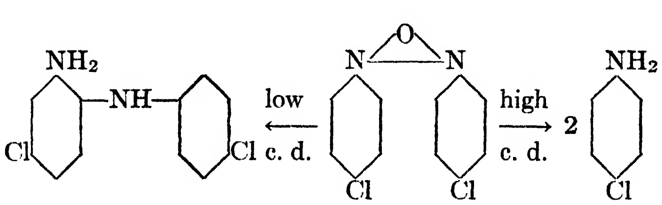
I III



II IV

At any rate the unsaturated C═C linkage is more difficult to saturate with electrolytic hydrogen than reducing an aromatic nitro compound.

With the Boehringer method *p*-dichlorazoxybenzene with a high c. d. gives quantitative yields of *p*-chloraniline but with a low c. d. forms a dichlorosemidine, i.e., 2-amino-5-4′-dichlorodiphenylamine:[61]



By the Boehringer method *m*-azoacetophenone and *m*-azobenzophenone on the other hand[62] are only very slowly and incompletely split to the corresponding amine.

When the benzene ring contains an acid group, as is the case in the nitroazo compounds, it is the azo rather than the nitro group which

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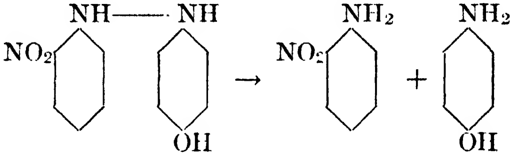
[61] Weinerth, Dissert., Giessen (1906).

[62] Elbs and Wogrinz, Z. Elektrochem., 9, 430 (1903).

undergoes the first reduction.[63] At a nickel cathode in alcoholic sulphuric acid *o*-nitrobenzeneazophenol yields *p*-aminophenol and *o*-nitraniline; the latter compound is further reduced to *o*-phenylenediamine. The *m*- and *p*- compounds are reduced to their corresponding amines.[64]

When the acid group is not a nitro group but an acetyl group the scission of the azo linkage is very difficult and slow. By the Boehringer method *m*-azoacetophenone and *m*-azobenzophenone have been successfully reduced respectively to *m*-aminoacetophenone and *m*-aminobenzophenone.[65]

Elbs and Keiper[66] showed that even though the hydrazo linkage is ordinarily very difficult to reduce it is more easily reduced than a nitro group which is present, i.e., nitrohydrazophenol yields *o*-nitraniline and aminophenol:



The reduction of hydroxyazo derivatives has been carefully studied by Puxeddu,[67] who found that the reaction went according to the equation:

$$HOR \cdot N : NR' + 2H_2 \rightarrow HORNH_2 + R'NH_2$$

and that in each case the double nitrogen bond was broken and the affinities of the nitrogen saturated by the electrolytic hydrogen. In all cases the reduction gave similar results, that is, two bases were always formed, one of which had the general structure of aniline and the other was the aminophenol corresponding to the phenol used in the coupling. The *p*- and *o*-hydroxyazo compounds behave on electrolytic reduction in the same manner that they behave toward other reduction processes. These compounds, and no others, could be found or identified in these reductions, when the given conditions were observed. If, however,

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[63] Elbs and Keiper, J. prakt. Chem., [2], **67**, 580 (1903); Keiper, Dissert., Giessen (1903); Hesselmann, Dissert., Giessen (1905).

[64] These electrolytic reductions are analogous to the purely chemical reductions of Staedel and Bauer, Ber., **19**, 1954 (1886) and Rassow and Rulke, J. prakt. Chem., [2], **65**, 105 (1902), also Werner and Stiasny, Ber., **32**, 3274 (1899).

[65] Elbs and Wogrinz, Z. Elektrochem., **9**, 430 (1903).

[66] Elbs and Keiper, loc. cit.

[67] E. Puxeddu, Gazz. chim. ital., **48**, ii, 25 (1918); **50**, ii, 149 (1920).

glacial acetic acid was used as the solvent the aminophenol could not be detected, and if the catholyte was a sodium hydroxide solution only the amine could be isolated.

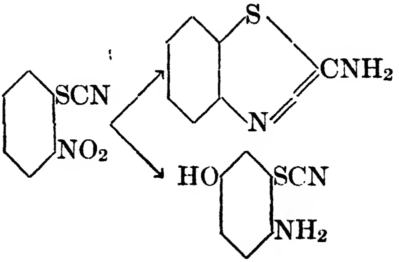
THE ELECTROCHEMICAL REDUCTION OF NITRATED BENZOTHIOCYANATES

The reduction of *o*-nitrophenyl, *p*-nitrophenyl, and 2, 4-dinitrophenyl thiocyanates by alcoholic ammonium sulphide causes the elimination of the thiocyanate grouping and the formation of nitrated diphenyl-disulphides.[68] On the other hand a reduction by means of stannous chloride causes a closing of a new ring to form a thiazole derivative.[69]

Electrochemical reduction takes place at both lead and copper cathodes. The former gives the more energetic reduction and is the only electrode at which the thiocyanate group is attacked. Phenylthiocyanate in 2 N-sulphuric acid using alcohol as the solvent yields 75.5 per cent of the expected quantity of the corresponding mercaptan according to the equation:

$$C_6H_5SCN + 2H + 2F \rightarrow C_6H_5SH + HCN$$

When a nitro group is present on the ring the reaction takes a different course. *o*-Nitrophenyl thiocyanate in a hydrochloric acid solution is reduced mostly to μ-aminobenzothioazole with some mercaptan in small amounts, at a rotating lead cathode. At a copper cathode the thiocyanate group is not attacked so that the product is 2-amino-5-hydroxyphenyl thiocyanate:



The *p*-nitrophenylthiocyanate is reduced in alcoholic hydrochloric acid solution at both lead and copper cathodes to the corresponding amino thiocyanate. However at a copper cathode an intermediate compound

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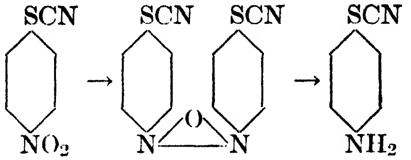
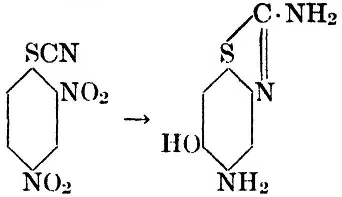
[68] Müller, Z. Farben Industrie, **5**, 357 (1906); Dissert., Basel (1905).

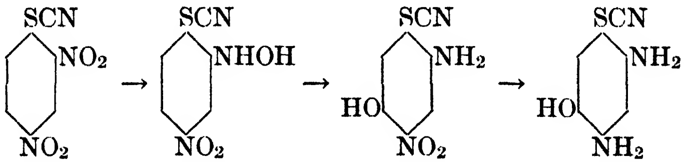
[69] Hoffmann, Ber., **12**, 1129 (1879).

p-thiocyanoazoxybenzene in the form of reddish yellow leaflets can be isolated:





2, 4-dinitrophenyl thiocyanate is reduced similarly at a lead cathode to *μ*-amino-4-amino-5-hydroxybenzothiazole-1, 2. That is the *o*-nitro group is first reduced to the amino group and then closes the thiazole ring forming the *μ*-aminobenzothiazole derivative. After this takes place the *p*-nitro group is reduced and according to the Gattermann method puts in an hydroxyl group ortho to itself. At a copper cathode the reaction takes a slightly different direction. The reduction in steps, determined by the isolation of the various compounds is as follows:



The compounds have all been isolated and their constitution proven.[70]

THE REDUCTION OF AROMATIC MONO NITRO COMPOUNDS IN A CONCENTRATED ACID SOLUTION

Reductions in Concentrated Sulphuric Acid.—*Normal reactions, i.e., the formation of p-aminohydroxy compounds.* Gattermann[71] in the year 1893 obtained *p*-aminophenol by reducing nitrobenzene at a platinum cathode in a warm concentrated solution of sulphuric acid. The

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[70] Fichter and Beck, Ber., **44**, 3636 (1911).

[71] Gattermann, Chem. Ztg., **17**, 210 (1893); Ber., **26**, 1844 (1893); **29**, 3034 and 3040 (1896). See also above, Elbs "Übungsbeispiele," p. 9; Gattermann, Ber., **27**, 1931 (1894); **26**, 1849 (1893); Darmstädter, D.R.P. 150800 (1901), 154086 (1903); Alway, Ber., **35**, 2434 (1902); **36**, 793 (1903); Friedländer, ibid., **38**, 2839 (1905).

method of Gattermann[72] requires the reduction to be carried out in a concentrated sulphuric acid solution at a smooth platinum cathode forming from 20–50 per cent of the theoretical yield of *p*-aminophenol. The low yields are due to the formation of *p*-aminophenolsulphonic acid,[73] aniline and benzidine.[74]

The Gattermann method permits of the easy preparation of a great many *p*-aminophenols that are otherwise very difficult to make, such as those of technical value as dye intermediates and also photographic developers.[75] The electrolytic preparation of *p*-aminophenols has had in the past some technical application.[76] *o*-Aminophenol, which is very difficult to prepare on a purely chemical method, is obtained as a by-product in the electrolytical method. The numerous ramifications of the field of aminophenols has only been touched in the electrolytic methods and much remains to be done in the future.

A series of patents in the name of Bayer and Co. have been taken out on the basis of the Gattermann reaction for the reduction of nitro compounds. At present these patents are public property, their terms having expired. The following list shows some of the possibilities in this field:

D.R.P. 75260, Aminophenols from aromatic nitro hydrocarbons (1893).

D.R.P. 77806, Aminohydroxycarboxylic acid from nitrocarboxylic acids (1893).

D.R.P. 78829, Aminophenols from nitroamines (1893).

D.R.P. 79865, Aminophenolcarboxylic acid esters from nitrocarboxylic acid esters (1894).

D.R.P. 80978, Aminophenols of the quinoline series (1894).

D.R.P. 81621, Aminophenolsulphonic acids from nitrobenzenesulphonic acids (1893).

D.R.P. 81625, Aklylated aminophenol derivatives from alkylated nitroamines (1894).

D.R.P. 82445, *o*-Amino-*m*-hydroxycinnamic acid from *o*-nitrocinnamic acid. Aminocoumarin from *m*-nitrocinnamic acid (1894).

[72] Gattermann, Ber., **26**, 1846 (1893); see also p. 244.

[73] Noyes and Clement, Ber., **26**, 990 (1893).

[74] Elbs, Z. Elektrochem., **2**, 472, (1896).

[75] Rodinal, Amidol, Glyzin, Metol, etc.

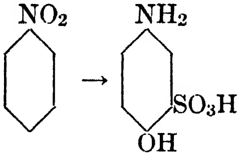
[76] Private communication from Dr. C. J. Thatcher.

In general the disadvantages of the Gattermann method are twofold: the use of the highly concentrated sulphuric acid causes the diaphragm to be seriously corroded while the conductivity of the cell is so very low that too much energy is lost. The initial cost of the large amounts of concentrated acid is a very serious problem to be solved.

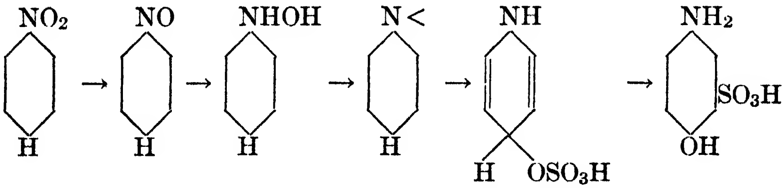
If the electrolytic method was to be of any value some changes had to be made. Darmstädter accomplished this in part by replacing the usual Pt cathode by a carbon stick. The patent claims the yields amount to 80 per cent at carbon, 40 per cent at copper, and 30 per cent at tin cathodes.[77] The method was further improved by making the catholyte a suspension of the nitro compound in 50 per cent sulphuric acid.[78]

p-Nitro- and *p*-nitrosodiethylaniline in concentrated sulphuric acid are reduced in good yields to the corresponding substituted aminophenols.[79]

Anomalous Reductions.[80]—When Gattermann's method is used but the concentrated sulphuric acid is replaced by fuming acid the nitrobenzene is reduced mostly to the *p*-aminophenolsulphonic acid:[81]



The mechanism for this reaction is probably



The *o*- and *m*-nitrotoluenes are similarly sulphonated.

When the *p*-position to the nitro group is open there is a reduction with the rearrangement to the *p*-aminophenol, but when the *p*-position is

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[77] D.R.P. 150800 (1901).

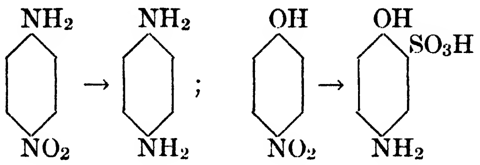
[78] D.R.P. 150800 (1901); 154086 (1903), Darmstädter.

[79] Rohde, Z. Elektrochem., **7**, 328 and 338 (1900).

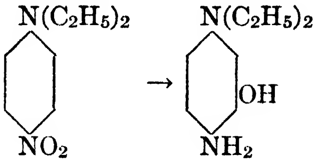
[80] Gattermann and Koppert, Ber., **26**, 1847 (1893); Gattermann and Abresch, ibid., **27**, 1929 (1894); Weiss and Reiter, Ann., **355**, 175 (1907); Darmstädter, D.R.P. 150800 (1901);. 154086 (1903); Bayer, 81621 (1893).

[81] A. A. Noyes and Clement, Ber., **26**, 990 (1893); Elbs, "Übungsbeispiele," p. 92.

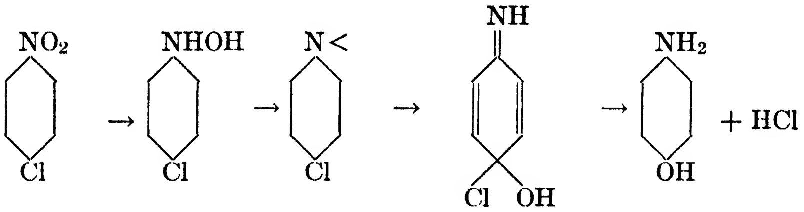
occupied something different must happen. Thus *p*-nitroaniline yields *p*-phenylenediamine and *p*-nitrophenol yields *p*-aminophenolsulphonic acid.[82]

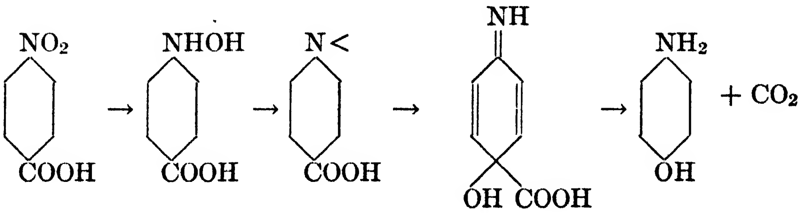


When the amino group is protected as in *p*-nitrodiethylaniline [83] the reaction is entirely different:



Another peculiar reaction is that in which *p*-chloronitrobenzene or *p*-nitrobenzoic acid is reduced.[84] In the one case the chlorine atom and in the other case the carboxyl group is removed from the molecule and replaced by an hydroxyl group. Expressed in terms of Bamberger's scheme these reductions take place:





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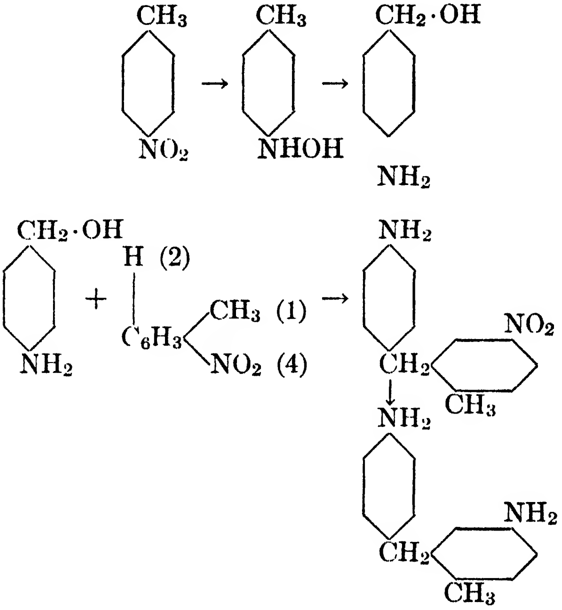
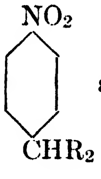
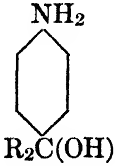
[82] Noyes and Dorrance, Ber., **28**, 2349 (1895).

[83] D.R.P. 81625 (1894), Bayer.

[84] Noyes and Dorrance, loc. cit.

In the reduction of *p*-nitrotoluene there is also a case of the anomalous introduction of an hydroxyl group to yield *p*-aminophenyl-*m*-nitro-*o*-tolylmethane.[85] What probably happens is as follows:



This shifting of hydroxyl groups from one position to another has a possible application in the triphenylmethane series of compounds which contain a nitro group in the *p*-position to the methane residue. That is compounds of the type  are transformed into carbinols of the type  in which R is an aromatic radical containing primary, secondary, or tertiary amino or hydroxyl groups. On this basis *p*-nitro-tetramethyl-diamino-triphenylmethane yields "*p*-Amino-bitter-almond

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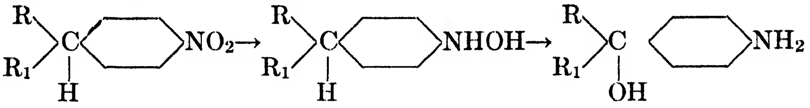
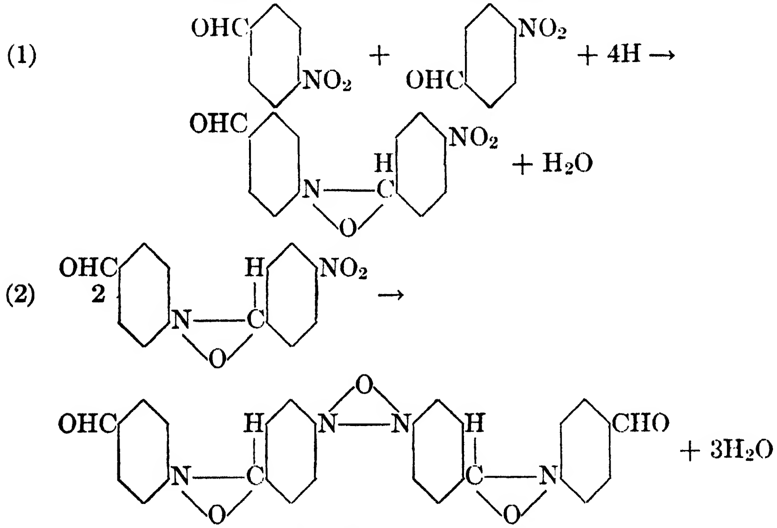
[85] Gattermann and Koppert, Ber., **26**, 1852 (1893); **26**, 2810 (1893); D.R.P. 75261 (1893), Bayer.

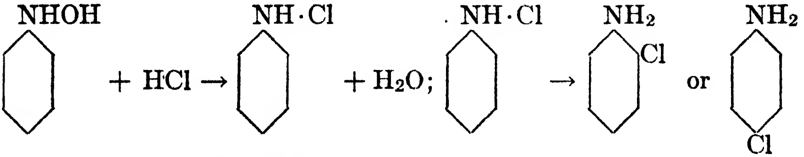
Oil Green." Also *p*-nitro-diamino-*o*-ditolylmethane and *p*-nitrotetraethyl-diamino-triphenylmethane were reduced:[86]



The reduction of *m*-nitrobenzaldehyde has been discussed above.[87] *p*-Nitrobenzaldehyde reacts similarly if not too much current is used, otherwise condensation products having a very high molecular weight are obtained. Alway obtained by a long continued electrolytic reduction the N-*p*-formylphenyl ether of *p*-azoxybenzaldoxime:[88]



Reductions in Fuming HCl.—Chlorinated amines are sometimes formed in the reduction of aromatic nitro compounds when the reaction takes place in strong HCl solution. Löb was able to bring this reaction into prominence; the chlorine atom going indifferently to the *o*- or *p*-position:[89]



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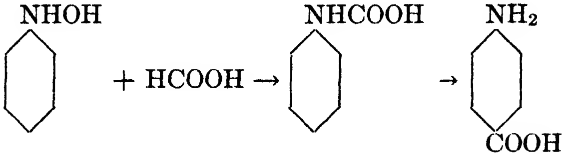
[86] D.R.P. 84607 (1895), Ges. f. Chem. Ind., Basel.

[87] See page 219.

[88] Alway, Ber., **36**, 23 (1903).

[89] Löb, Z. Elektrochem., **3**, 46 (1896); Ber., **29**, 1894 (1896).

Correspondingly, in fuming hydrobromic acid solution a bromination takes place. Analogously, Löb expected to obtain an amino carboxylic acid by using a strong solution of formic acid as the electrolyte according to the scheme: [90]

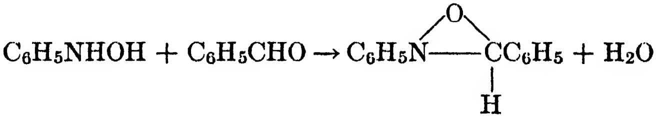


but unfortunately benzidine was the only product.

A unique method for the preparation of chloraniline has been developed. Nitrobenzene is put in a clay cell with strong hydrochloric acid,[91] and the whole put in a vessel containing dilute sulphuric acid and a zinc anode. A platinum cathode is immersed in the nitrobenzene solution and the two electrodes connected. Under these conditions a current circulates through the electrolyte at a low potential with the result that good yields of *o*- and *p*-chloraniline are formed. When sulphuric acid is used instead of the fuming hydrochloric acid the sulphate salt of the aminophenol is formed.

REDUCTIONS IN THE PRESENCE OF REACTIVE MATERIALS

It was Bamberger who first showed that *β*-phenylhydroxylamine and benzaldehyde condensed to form benzilidenephenylhydroxylamine,[92]



$$C_6H_5NHOH + C_6H_5CHO \rightarrow C_6H_5N\overset{O}{\text{——}}\underset{\substack{|\\ H}}{C}C_6H_5 + H_2O$$

and then Gattermann[93] formed this compound by the electrolytic reduction of nitrobenzene in the presence of benzaldehyde in concentrated sulphuric or acetic acids in his proof that *β*-phenylhydroxylamine was formed as an intermediate product in the electrolytic reduction of nitrobenzene.

When a keto acid and nitrobenzene are simultaneously reduced a substituted anilino acid is expected. On this basis levulinic acid and

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[90] Löb, Z. Elektrochem., **3**, 471 (1897).

[91] Löb, Ber., **29**, 1390 and 1894 (1896).

[92] Bamberger, Ber., **27**, 1557 (1894).

[93] Gattermann, Ber., **29**, 3040 (1896); D.R.P. 96564 (1896), Bayer. Elbs, "Übungsbeispiele," p. 93.

nitrobenzene on reduction should yield γ-anilinovaleric acid,[94] because generally a carboxyl group is not electrolytically attacked. But instead of this expected product Emmert isolated 40 per cent yields of 1-phenyl-5-methyl pyrrolidone which is the inner anhydride of the expected acid. These reactions may be explained (1) by the union of free radicals formed by the reduction, or (2) the condensation of the intermediately formed oxygenated bodies.

Gattermann reduced the following mixtures of nitro compounds in the presence of aldehydes, obtaining the corresponding condensation products:[95]

Nitrobenzene and benzaldehyde to form benzylidenephenylhydroxylamine;
o-Nitrotoluene and benzaldehyde to form benzylidene-*o*-tolylhydroxylamine;
m-Nitrotoluene and benzaldehyde to form benzylidene-*m*-tolyhydroxylamine;
p-Nitrotoluene and benzaldehyde to form benzylidene-*p*-tolylhydroxylamine;
Nitro-*p*-xylene and benzaldehyde to form benzylidene-*p*-xylylhydroxylamine;
m-Nitrobenzoic acid and benzaldehyde to form benzylidene-*m*-hydroxylaminobenzoic acid;
Nitrobenzene and vanillin to form vanillin-phenylhydroxylamine.

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[94] B. Emmert, Ber., **40**, 912 (1907).

[95] Gattermann, Ber., **29**, 3040–3042 (1896); Bayer, D.R.P. 96564 (1896).

CHAPTER XI

THE REDUCTION OF AROMATIC NITRO COMPOUNDS PART III—IN ALKALINE SOLUTION

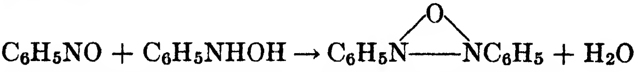
Azoxy, azo and hydrazo compounds are the normal products of the reduction of mononitro aromatic compounds in an alkaline solution. Under certain conditions amines may be formed as the principal product and in the case of some peculiar compounds heterocyclic derivatives may be formed.

The best method[1] for the reduction in alkaline solution is given by Elbs or Müller.

THE FORMATION OF AZOXY COMPOUNDS[2]

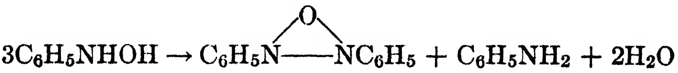
The position of azoxybenzene derivatives in the series of reduction products of nitrobenzene is such that the experimental conditions must be rather carefully regulated if there is not to be a further reduction. This reduction cannot be limited when the customary alcoholic alkali solution is the catholyte since under these conditions there is a reduction of the azoxy compound. This further reduction can be prevented by a regulation of the cathodic reduction potential within very narrow limits, which is, however, a very difficult task on a large scale.

Haber determined that in an alcoholic alkaline solution electrolytic reduction with a cathodic reduction potential of −0.93 volt gave 76 per cent of azoxybenzene when the c. d. was very low; the formation taking place by the condensation of nitrosobenzene with β-phenylhydroxylamine:

(1)


$$C_6H_5NO + C_6H_5NHOH \rightarrow C_6H_5\overset{O}{\overbrace{N\text{——}N}}C_6H_5 + H_2O$$

rather than by the condensation of the latter with itself:

(2)


$$3C_6H_5NHOH \rightarrow C_6H_5\overset{O}{\overbrace{N\text{——}N}}C_6H_5 + C_6H_5NH_2 + 2H_2O$$

because under normal conditions only traces of aniline are obtained. There are cases of constitutive properties in which equation (2) expresses

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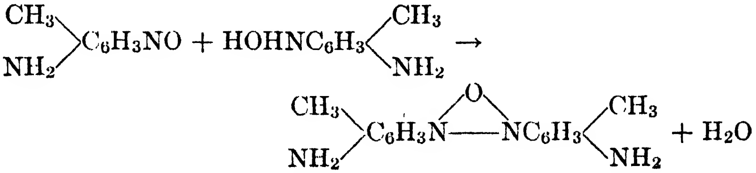
[1] Elbs, "Übungsbeispiele," page 95; Müller, "Praktikum," p. 231–33.

[2] For a complete list of references on the formation of these compounds see the Bibliography of Electro Organic Chemistry, National Research Council, Washington, D. C.

the course of the reaction. The reaction expressed by equation (2) will of course predominate under the conditions that the reduction of nitrobenzene to β-phenylhydroxylamine is very rapid or the condensation of nitrosobenzene with β-phenylhydroxylamine is very slow, in order that large quantities of the latter can accumulate at the cathode without undergoing too rapid a reduction.

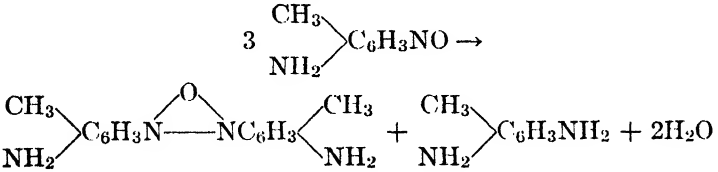
When a cathode with a strong reducing power is used the nitrobenzene is rapidly reduced to β-phenylhydroxylamine and equation (2) predominates. By this method *m*-nitro-*p*-toluidine in an alcoholic alkaline solution yields mostly azoxy- and azotoluidine together with a little diamine.[3] As the c. d. increases the diamine is increased at the expense of the two former compounds.[4] This means that as the c. d. gets high there is a deficiency of the nitroso compound for the condensation so that the hydroxylamine derivative condenses with itself or undergoes a further reduction to the diamine:

(3)



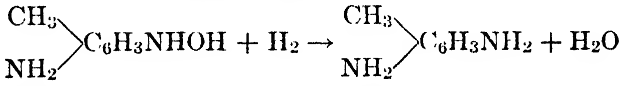
$$\substack{CH_3\\NH_2}\!>\!C_6H_3NO + HOHNC_6H_3\!<\!\substack{CH_3\\NH_2} \rightarrow \substack{CH_3\\NH_2}\!>\!C_6H_3N\overset{O}{\text{———}}NC_6H_3\!<\!\substack{CH_3\\NH_2} + H_2O$$

(4)



$$3\ \substack{CH_3\\NH_2}\!>\!C_6H_3NO \rightarrow \substack{CH_3\\NH_2}\!>\!C_6H_3N\overset{O}{\text{———}}NC_6H_3\!<\!\substack{CH_3\\NH_2} + \substack{CH_3\\NH_2}\!>\!C_6H_3NH_2 + 2H_2O$$

(5)



$$\substack{CH_3\\NH_2}\!>\!C_6H_3NHOH + H_2 \rightarrow \substack{CH_3\\NH_2}\!>\!C_6H_3NH_2 + H_2O$$

Some of the data from the work of Stohr is as follows:

TABLE XXIII

c. d. in Amp. dm. sq.	Azoxy and azo toluidine	*m*-toluylene diamine
1.5	82%	12%
4.0	63	17.7
6.0	50	25.0

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[3] Elbs and Schwartz, Z. Elektrochem., 5, 113 (1898).

[4] Stohr, Dissert., Giessen (1903).

A suspension of nitrobenzene in 2 per cent sodium hydroxide when reduced at a cathodic potential of −1.8 volt gives azoxybenzene and aniline with about half as much aniline as azoxybenzene.[5] It is very difficult if not impossible in most cases to prepare azoxybenzene free from azobenzene because of the reaction:

$$RN\overset{O}{—}NR \rightarrow RNH \cdot NHR \rightarrow RN : NR$$

Besides, there is a partial rearrangement:

$$2RNHOH \rightarrow RN : NR + 2H_2O$$

There are cases in which the azoxy derivative is more soluble in aqueous alcoholic solution and so may be removed from the sphere of further reduction. An example of this is the reduction of *p*-nitroanisole to *p*-azoxyanisole in almost quantitative amounts.

The best method[6] for the preparation of azoxy compounds is to use a non-alcoholic sodium hydroxide or a salt solution as the electrolyte and in this emulsify the nitro derivative to be reduced at a platinum, nickel or mercury cathode.

The data in the following table[7] have been recorded in the reduction of *m*- and *p*-nitrotoluene in an alkaline suspension, and refers in each case to 5 g. of the starting material.

TABLE XXIV

	m-Nitrotoluene				*p*-Nitrotoluene			
Cathode	Ni	Zn	Cu	Cu+Cu Powder	Ni	Zn	Cu	Cu+Cu Powder
Highest yield	62.5	94.5	100	100	100	100	100	100
Hours required to get 100 per cent current yields	...	...	3.2	4	2.75	3.5	4	4.75
Per cent of H_2 absorbed	36.	46.	54.	61	50	56	64	71
Azoxytoluene in g	2.4	2.4	1.8	1.3	2.6	2.5	2.1	1.7
Azotoluene in g	...	...	...	....	2.6	2.5	2.1	1.7
Tolidine or semidine in g	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.05
Toluidine in g	0.4	0.5	1.1	1.2	0.6	0.8	1.3	1.9

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[5] Löb and Moore, Z. Physik. Chem., **47**, 418 (1904); see page 197.

[6] Löb, Z. Elektrochem., **7**, 337 (1901); D.R.P. 127727 (1900), Meister.

[7] Löb and Schmidt, Z. Elektrochem., **10**, 756 (1904).

Clearly the cathode material influences the yields very much. The metals nickel, zinc, copper, and copper powder cause the toluidine to predominate. The para-compound is more easily reduced than the *m*-nitrotoluene and under the same conditions the para derivative gives a mixture of azo and azoxy derivatives while the meta gives almost pure azoxytoluidine. The yields of *p*-toluidine are always greater than the yields of *m*-toluidine.

An apparatus for the reduction of nitro compounds to their corresponding azoxy derivatives is shown in Fig. 7.

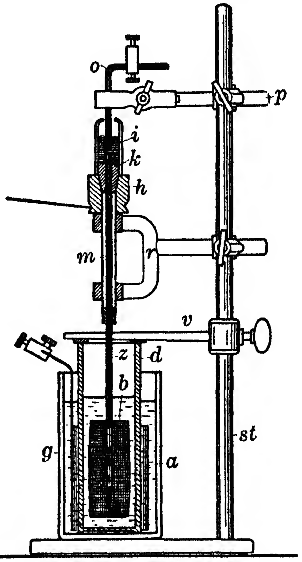
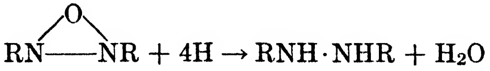


Fig. 8.—Apparatus for the Reduction of Nitro Compounds.—From Müller's "Elektrochemisches Praktikum."

THE FORMATION OF AZO DERIVATIVES[8]

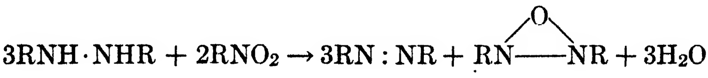
Haber showed that azobenzene was not a direct reduction product of azoxybenzene. The reduction went first to hydrazobenzene and then this compound was oxidized back to azobenzene; the oxidizing medium being nitro-, nitroso-, or azoxybenzene as well as oxygen of the air. Then too *β*-phenylhydroxylamine was converted to azobenzene. The equations expressing the formation of azobenzene are:

(1)



$$\mathrm{R}\overset{\mathrm{O}}{\widehat{\mathrm{N{-}{-}N}}}\mathrm{R} + 4\mathrm{H} \rightarrow \mathrm{RNH{\cdot}NHR} + \mathrm{H_2O}$$

(2) *a.*



$$\mathrm{3RNH{\cdot}NHR} + \mathrm{2RNO_2} \rightarrow \mathrm{3RN:NR} + \mathrm{R}\overset{\mathrm{O}}{\widehat{\mathrm{N{-}{-}N}}}\mathrm{R} + \mathrm{3H_2O}$$

b.

$$\mathrm{RNH{\cdot}NHR} + \mathrm{2RNO} \rightarrow \mathrm{RN:NR} + \mathrm{R}\overset{\mathrm{O}}{\widehat{\mathrm{N{-}{-}N}}}\mathrm{R} + \mathrm{H_2O}$$

c.

$$\mathrm{RNH{\cdot}NHR} + \mathrm{R}\overset{\mathrm{O}}{\widehat{\mathrm{N{-}{-}N}}}\mathrm{R} \rightarrow \mathrm{2RN:NR} + \mathrm{H_2O}$$

d. $\mathrm{RNH{\cdot}NHR} + \mathrm{O_2} \rightarrow \mathrm{RN:NR} + \mathrm{H_2O}$

(3) $\mathrm{2RNHOH} \rightarrow \mathrm{RN:NR} + \mathrm{2H_2O}$

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[8] See the Bibloigraphy of Electro-Organic Chemistry, National Research Council.

Compared with nitrobenzene, Haber found that azoxybenzene was a very poor depolarizer, therefore it is very possible that no azoxybenzene will be reduced as long as nitrobenzene is present. However as soon as all the nitrobenzene has been reduced the evolution of hydrogen starts showing that a poor depolarizer is present in place of a good one.

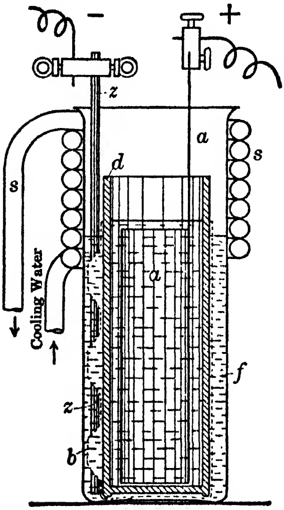


Fig. 9.—Apparatus for the Reduction of Nitro to Azo Compounds.—From Müller's "Elektrochemisches Praktikum."

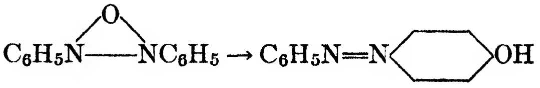
The formation of azo derivatives is easily accomplished by using an alcoholic alkaline or an alcoholic sodium acetate solution of the required nitro compound, carrying on the reduction at a Ni wire gauze cathode with a diaphragm to separate the catholyte from the anolyte.[9] Somewhat more than the theoretical amount of current must be passed before the reaction reaches the desired point according to the equation:

$$2RNO_2 + 8H \rightarrow RN : NR + 4H_2O$$

It would seem that the azoxy derivative first formed here could be isolated but this is at once reduced further to the hydrazo compound. The hydrazo compound cannot be isolated as long as there is any nitro derivative present because of the oxidizing action of the latter on the hydrazo compound.

In many cases an exceptionally pure compound can be prepared by reducing the nitro compound completely to the hydrazo derivative and then subsequently oxidizing this latter by air oxygen in an alkaline solution.

If the azoxy compound be treated with warm concentrated sulphuric acid there is a rearrangement to form a *p*-hydroxyazo derivative:



The hydroxy compounds are soluble in aqueous alkali while the azo derivatives are not; an easy separation is therefore possible.

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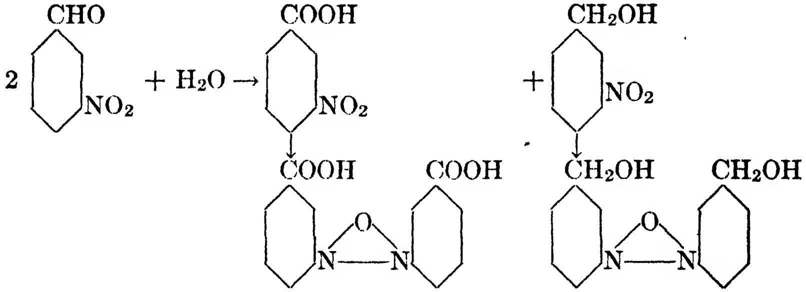
[9] Elbs and Kopp, Z. Elektrochem., **5**, 108 (1899); Elbs, Ibid., **7**, 133 and 141 (1901); Elbs, "Übungsbeispiele," p. 101; Swedish P. 41675 (1916), Ges. f. Chem. Ind.; U.S.P. 1225052 (1917) Piguet.

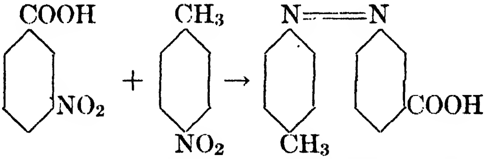
The Löb method for preparing azoxy derivatives goes on to azo derivatives when the temperature is over 90° or when attackable cathodes are used.[10]

m-Nitrobenzaldehyde in an alkaline solution yields traces of *m*-azobenzyl alcohol but larger amounts of *m*-azobenzoic acid [11] instead of the expected compounds. Probably there is an internal oxidation-reduction of the nitroaldehyde:



Löb,[12] however, could not confirm the formation of the azoxybenzoic acid, but did find *m*-benzylalcohol-azo-*m*-benzoic acid, *m*-azobenzyl alcohol, and *m*-azobenzoic acid.

Different radicals may be introduced into azo derivatives by electrolyzing at the same time a mixture of two nitro compounds. This mixed azo derivative is formed by the union of the hydroxylamine derivatives of the one with the nitroso of the other.[13] The mixture of equal parts of the two nitro compounds should be reduced in an alcoholic alkaline solution at a Pt cathode with a c. d. of 2.2 amperes using the theoretical amount of current. The yields of course vary with the starting materials. An example is:



m-nitrobenzoic acid and *p*-nitrotoluene

p-toluene-azo-*m*-benzoic acid 50 per cent

When mixed nitro derivatives are reduced, very often considerable amounts of the two symmetrical azo compounds are also formed.

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[10] D.R.P. 141535, Meister, (1902); 121899, 121900 (1899) Bayer.

[11] Kauffmann and Hof, Chem. Ztg., **20**, 542 (1896).

[12] Löb, loc. cit.

[13] Löb, Ber., **31**, 2201 (1898); Z. Elektrochem., **5**, 456 (1899).

THE FORMATION OF HYDRAZO DERIVATIVES[14]

These compounds are the next in order to the azo derivatives in the reduction of nitro aromatic compounds, and are more difficult to prepare than the azoxy compounds. With the appropriate nitro compound as the starting material the theoretical amount of current is passed to form the corresponding azo compound. When this reaction is complete the current is lowered to one-fifth of the original value to reduce the azo to the hydrazo stage with very good yields.[15] There is always danger that the hydrazobenzene will react with the unchanged nitro or nitroso compound if the current is stopped before the reduction has been completed. With a c. d. of 0.5 to 1.5 amperes, even at the boiling temperature, there is only a slight evolution of hydrogen; in other words practically all of the current is used in the actual reduction. But in order to make up for this loss of current about 10 per cent in excess of the theoretical amount must be used in order to bring the reduction to completion. If a nickel cathode is used the hydrazo compound is not further reduced and a very pure compound is the result.

The azo and hydrazo derivatives are of great commercial importance and naturally there are numerous patents covering their electrolytic preparation, several of which may profitably be described. In 1894 Straub took out a patent for the reduction of nitro derivatives to the corresponding hydrazo derivatives in an alcoholic alkaline solution.[16] In another series of patents part of the alkali is replaced by sodium acetate, the reduction to take place at the boiling temperature.[17] In these patents the preparation of *m*-diaminohydrazobenzene, a general method for the reduction of the halogenated nitrobenzenes, nitrobenzene sulphonic acids, and nitrobenzene carboxylic acids to their corresponding hydrazo derivatives are described, and also a general method for the reduction of aromatic nitro compounds to their respective azo and hydrazo compounds in alcoholic alkali acetate solutions.

Bayer and Co. developed a method to abolish the use of the solvent alcohol in the electrolyte but still permit the reaction to go smoothly from the nitro through the azo and then on to the hydrazo derivatives without any difficulties. The patent describes the use of a suspension of the required nitro compound in a solution of an alkali hydroxide with

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[14] For other compounds see the Bibliography of Electro-Organic Chemistry, National Research Council.

[15] Elbs and Kopp, Z. Elektrochem., 5, 108 (1898); Goldschmidt, ibid., 7, 263 (1901); Farup, Z. physik. Chem., 54, 231 (1906); Elbs, Übungsbeispiele," p. 105.

[16] Straub, D.R.P. 79731 (1894).

[17] D.R.P. 100233, 100234, 108427 (1898), A. Wulfing.

reduction at a cathode of lead, zinc, or tin. The suspension is maintained by energetic stirring which keeps a large amount of depolarizer always in contact with the cathode and so allows the cathodic current density to rise to 12 amperes per sq. dm. without the evolution of any large amounts of hydrogen. The presence in the electrolyte of the alkali salts of the heavy metals as lead, zinc, or tin permits the use of any metal which may be available as a cathode.[18]

A serious difficulty with this method is the fact that the reduction products stick in large quantities to the cathode and to the diaphragm which make the recovery of the hydrazo compound difficult and also greatly increase the resistance of the cell. This trouble was remedied in 1903 by Darmstädter,[19] who used in conjunction with the electrolyte a liquid immiscible with the water but which easily dissolved the reduction product. Such a liquid may be benzene, toluene, xylene, etc., with electrodes of lead, zinc, nickel or tin. There is evidently some disagreement here with the previous work done on the question of change of cathodic material. According to the work or Löb and others,[20] an alkaline solution of nitrobenzene is reduced at a nickel cathode only to azoxybenzene while these later patents describe azo and hydrazo derivatives as the sole products of the alkaline reduction at a nickel cathode. This matter should be cleared up.

The preparation of hydrazo derivatives has been greatly simplified in late years by the patent taken out by Brunner[21] which describes the production of hydrazobenzene, *o*-hydrazotoluene, *o*-hydrazoanisole and similar compounds from the corresponding nitro, azoxy, or azo compounds in the presence of alkalies. A reducing metal, the oxide of which is soluble in the alkaline solution, must be present. There will be formed on the cathode a deposit which is readily scraped off during the course of the reaction. The cathode may be of nickel, iron, lead, etc.; the best being nickel.

Though hydrazo compounds may be further reduced by electrolytic hydrogen to amines, this reaction need not necessarily take place in case the hydrazo compound fails to rearrange to benzidine.[22] Only those compounds are split which possess an amino or an hydroxyl group in the *o*- or *p*-position to the azo or hydrazo group. But such a possibility is seldom met in practice because *o*- or *p*-nitro amines and nitro phenols fail to form azoxy, azo and hydrazo compounds; instead they

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[18] D.R.P. 121899, 821900, Bayer and Co.

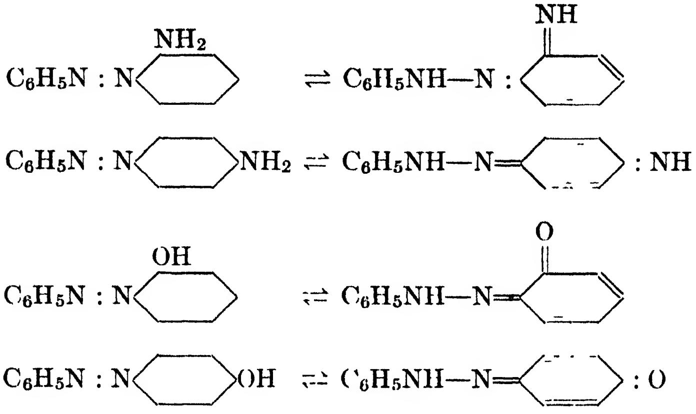
[19] D.R.P. 181116 (1903); Eng. P. 6924 (1906); D.R.P. 196979 (1906).

[20] Z. Elektrochem., 7, 336 (1901); D.R.P. 127727 (1900), Meister, see above.

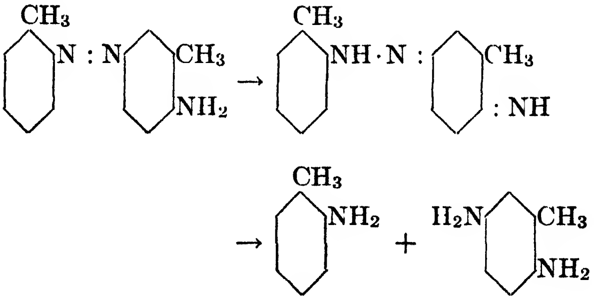
[21] Eng. P. 147541 (1920), E. Brunner.

[22] Stohr, Dissert., Giessen (1903).

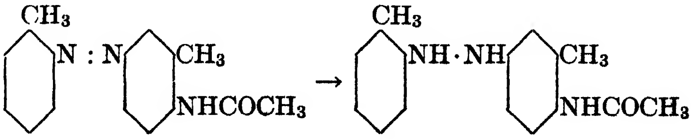
form the corresponding diamines. Stohr has further assumed that only those azo compounds which possess the ability to exist in tautomeric forms can be reduced and split into their respective diamines:



When this ability to form the tautomer is prevented, the compound does not so split. This fact is well shown by the reduction of *p*-aminoazotoluene in an alkaline solution to *p*-toluylenediamine and *o*-toluidine.[23]



But when one of the amino groups is protected as in acetyl-*p*-aminoazotoluene the reduction forms acetyl-*p*-amino-hydrazotoluene:



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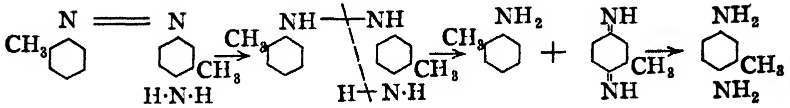
[23] Schneider, Dissert., Giessen (1906).

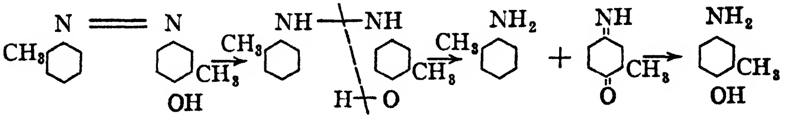
The same is true of the reduction of *p*-hydroxyazotoluene to *o*-toluidine and *p*-amino-*o*-cresol; but when the hydroxyl group is closed by alkylation as in *p*-methoxyazotoluene the product of the reduction is *p*-methoxyhydrazotoluene.

In view of the fact that this form of isomerism has not been definitely proven we are forced to assume that both forms are reducible to the same compound, i.e., to the hydrazo form and then this is further reduced in an alkaline solution with a scission of the molecule.

p-Amino-*o*-azotoluene (1) is reduced to *p*-amino-*o*-hydrazotoluene (2) and this, independently of the current is supposed to divide automatically to form *o*-toluidine (3) and *p*-toluenequinonediimide (4). The latter compound being an active depolarizer is further reduced to *p*-toluylenediamine:

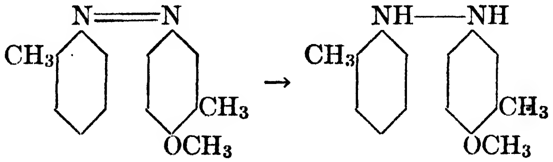


Correspondingly the reduction of *p*-hydroxy-*o*-azotoluene is:



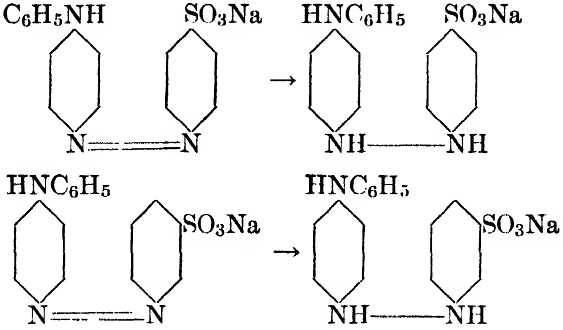
Since *m*-quinonoids are impossible the *m*-substituted azo and hydrazo compounds are not reduced to amines by a splitting of the molecule.

p-Methoxy-*o*-azotoluene contains no labile hydrogen (the methyl group is not labile), so it is reduced to the hydrazo compound:



and on further reduction there is no scission to form an amine. The protecting of an *o*- or *p*-amino group by acylation accomplishes the same purpose; i.e., *p*-acetylamino-*o*-azotoluene is reduced to the hydrazo derivative without a further reduction taking place. What holds for *p*-substituted compounds holds also for the *o*-compounds.

Diphenylamine Orange 1 is electrolytically reduced to the corresponding hydrazo compound and similarly Metanil Yellow 2 is reduced to its hydrazo compound:



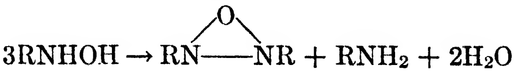
In this case electrolytic reduction in an alkaline solution is less violent than the purely chemical reduction using zinc and alkali which causes a splitting of the molecule of the hydrazo compounds to form the corresponding amines.

ABNORMAL REDUCTIONS[24]

Formation of Amines.—In the ordinary electrolytic reduction in an alkaline solution the normal reduction products are the azoxy, azo, and hydrazo derivative with sometimes a side reaction forming amines by the reduction and scission of the hydrazo compounds. There are, however, cases in which the formation of amines predominates and these amines cannot be traced to the further reduction of the previously formed hydrazo derivatives.

There are two other sources recognized from which these amines may spring:

(1) $$RNHOH \rightarrow RNH_2 + H_2O$$

(2)


$$3RNHOH \rightarrow RN\overset{O}{—}NR + RNH_2 + 2H_2O$$

Therefore it stands to reason that the more hydroxylamine derivative available for this further reduction by the electrolytic hydrogen, the more amine will be formed. To maintain large amounts of the hydroxylamine in the electrolyte the condensations of this compound must be prevented or at least decreased. Besides this, the speed of its reduction must be so increased that it cannot have time to condense. The third process for the formation of amines is due to the peculiarities of

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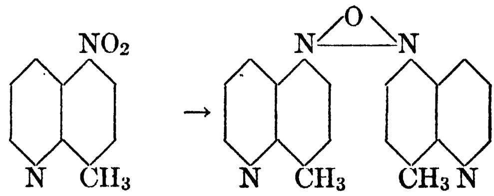
[24] See Bibliography of Electro-Organic Chemistry, National Research Council, for complete references.

individual compounds which by their constitution cannot be reduced to other compounds. These three processes will now be discussed in order.

The Formation of Amines Due to a Decrease in the Speed of Condensation of Nitroso with Hydroxylamine Derivatives.—The condensation of these two derivatives is influenced by steric hindrance according to Bamberger and Rising,[25] who used purely chemical methods; some compounds can condense and others can not; in some cases the yields are very much higher than in others. The same is true of the condensation of the electrolytically prepared nitroso and hydroxylamine derivatives. In an alcoholic alkaline solution nitrobenzene yields only traces of aniline; on the other hand *o*- and *p*-nitrotoluenes yield 7 per cent and 9 per cent respectively of their corresponding toluidines at a nickel cathode. The reason for this seems to be in the fact that the methyl group in the *o*- or *p*-position retards the formation of nitroso and therefore the hydroxylamine and azo derivatives, while the methyl group in the *m*-position does not have this effect, but permits a reduction to the azo compound, etc. The *o*- and *p*-toluylenehydroxylamines are fairly stable in alkaline solution and so may be reduced to amines; measurements show the greater the c. d. the greater the amount of amine formed.[26]

While Elbs and Schwartz[27] showed the formation of considerable quantities of toluylenediamine by the alkaline electrolytic reduction of *m*-nitro-*p*-toluidine, Stohr showed that an increase in the c. d. increased the yield of this compound; on the other hand *m*-nitro-*o*-toluidine,[28] yields very little of the diamine, which shows the effect of the methyl group in the various positions.

Steric hindrance is also in evidence in directing the course of the reduction of the nitrotoluoquinolines.[29] The reductions are as follows: (The first three are from Elbs and Zöckler)



ana-nitro-*o*-toluoquinoline

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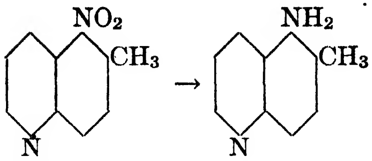
[25] Bamberger and Rising, Ann., **316**, 257 (1901).

[26] Stohr, Dissert., Giessen (1903).

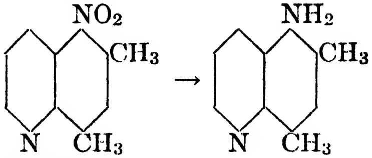
[27] Elbs and Schwartz, Z. Elektrochem., **5**, 113 (1897).

[28] Elbs and Schwartz, Z. Elektrochem., **7**, 144 (1900).

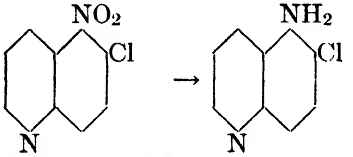
[29] Elbs, Z. Elektrochem., **10**, 579 (1904); Zöckler, Dissert., Giessen (1905). Elbs considered that the cathodic potential had nothing to do with the reduction.



ana-nitro-*p*-toluoquinoline



ana-nitro-*o*-*p*-xyloquinoline



ana-nitro-*p*-chloroquinoline[30]

Amine Formation by Increasing the Speed of Reduction of RNHOH.—This method requires the use of hydrogen carriers or reduction catalysts and has been discussed above in various places. Mention may however be made of the work of Chilesotti,[31] Brand and Elbs,[32] Löb and Moore,[33] and the various patents calling for the addition of the salts of the heavy metals or metallic powders to an alkaline solution, for example the Boehringer patents.[34]

The Formation of Amines Due to Constitutive Properties of Individual Compounds.—Of the three nitranilines when in alcoholic alkaline solution at a nickel cathode only the meta compound is reduced analogously to nitrobenzene with the formation of the corresponding *m*-diaminoazo derivatives according to the Haber scheme; under entirely similar conditions the *o*- and *p*-nitranilines are reduced to *o*- and *p*-phenylenediamine respectively through the nitroso and hydroxylamine stages.[35]

Elbs has assumed that this difference in reaction of the three nitranilines is due to the fact that the *o*- and *p*-nitranilines are first reduced

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[30] Weinerth, Dissert., Giessen (1906).

[31] Chilesotti, Z. Elektrochem., **7**, 768 (1901).

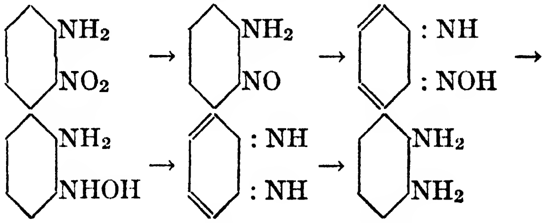
[32] Brand and Elbs, ibid., **9**, 480 (1903).

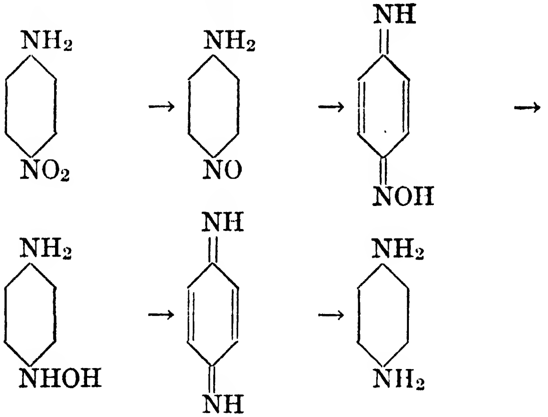
[33] Löb and Moore, Z. physik. Chem., **47**, 418 (1904).

[34] D.R.P. 130742 and 131044. See page 209, etc.

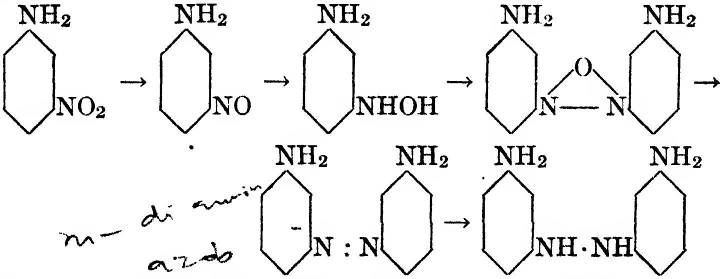
[35] Elbs and Kopp, Z. Elektrochem., **5**, 110 (1898); Rohde, ibid., **7**, 339 (1899); in the case of the *m*-nitraniline, Löb obtained also the corresponding azoxy and hydrazo compounds and some *m*-phenylenediamine.

to the corresponding aminophenylhydroxylamines which as soon as formed are transformed into compounds having a quinonoid structure by the removal of a molecule of water:[36]





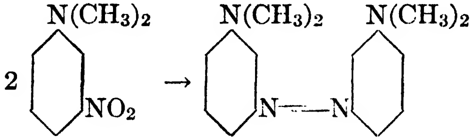
Therefore they are not able to form azoxy derivatives. The quinonimide on the other hand is very easily reduced to the diamine. As the *m*-nitraniline is unable to form a quinonimide, therefore it is reduced with the formation of the normal series of compounds; that is first the nitroso, then the hydroxylamine derivatives are formed; these two then react together to form the azoxy, etc., derivatives.



m- di amino azo

[36] Elbs, Berichte über einzelne Gebiete der angewandten physikalischen Chemie, Berlin (1904), page 34; also J. prakt. Chem., [2], **43**, 39 (1891); Elbs, Übungsbeispiele," p. 111.

Similarly *m*-nitrodimethylaniline yields tetramethyl-*m*-diamino-azobenzene or the hydrazo compound.[37]



The reasons for the reactions of the nitrophenols are the same as for the nitranilines. The nitrosophenols under the reducing influences are rearranged to a quinone monoxime with the hydroxylamine derivative being rearranged to a quinone monimide. The *o*- and *p*-nitrophenols at a platinum and nickel[38] or at Pb, Cu, Zn, and Zn amalgam cathodes[39] are smoothly reduced in over 90 per cent yields to the corresponding amino compounds through the intermediate formation of the quinonimide; the *m*-nitrophenol which forms no quinonoid compounds can yield no amino phenol but goes through a series of azo compounds.[40] *o*-Nitrophenol is readily reduced to the *o*-aminophenol;[41] but it is only recently that a really good method has been developed.[42]

Elbs assumed that all the hydrogen that was absorbed by the solution was utilized in reducing the nitrophenol to aminophenol, but gave very little data concerning the experimental conditions. Löb calculated the yields on the amounts actually obtained by reductions in both acid and alkaline solutions. The yields were in no case over 60 per cent and as a rule were very much below this figure. Brown and Warner then took up the problem and studied the effect on the reduction of (1) the cathodic current density, (2) the concentration of the sodium hydroxide, (3) temperature, (4) concentration of the *o*-nitrophenol, (5) the addition of new amounts of starting material during the course of the reduction. As optimum conditions they describe the following procedure: Reduction is carried out at a copper wire gauze cathode in a divided cell, the catholyte containing 3–5 g. of *o*-nitrophenol per 100 cc. of 15 per cent sodium hydroxide. The temperature is kept slightly below the boiling point. During the early part of the reduction a c. d. of

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[37] Rohde, Z. Elektrochem., **7**, 328 and 338 (1900).

[38] E. Klappert, Z. Elektrochem., **6**, 509 (1899); Löb, ibid., **2**, 533 (1896); Elbs, J. prakt. Chem., [2], **43**, 39 (1891); Elbs, "Übungsbeispiele," p. 111.

[39] O. W. Brown and J. C. Warner, J. Phys. Chem., **27**, 455 (1923).

[40] Klappert, loc. cit.

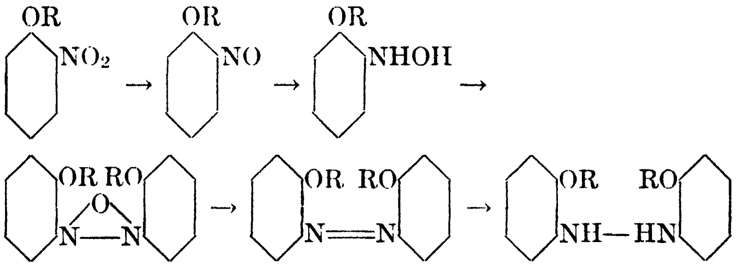
[41] See Elbs, Jour. prakt. Chem., [2], **43**, 39 (1891); Löb, Z. Elektrochem., **2**, 533 (1896).

[42] O. W. Brown and J. C. Warner, Trans. Am. Electrochem. Soc., **41**, 225 (1922).

10 amperes is used. When one-half of the starting material is reduced, one-half of the original amount of starting material is added. After another such period a similar amount is added. The reduction is continued with a c. d. of 10 amperes until the concentration of *o*-nitrophenol drops to 1.5 g. per 100 cc. of catholyte, and then the c. d. is lowered to 4 or 5 amperes and the temperature to 60° or 70°, electrolysis being continued till the concentration of the starting material is 0.8 g. per 100 cc. By finishing electrolysis with a c. d. of 1–2 amperes, it is possible to detain a yield of 97–99 per cent.

Yields of 99.0–99.5 per cent are obtained when *p*-nitrophenol is reduced in 8 per cent sodium hydroxide solution at a lead cathode. The sodium hydroxide solution permits higher yields than a solution of sodium carbonate, or bicarbonate, or sulphuric acid, and the lead cathode is better than any other readily available metal because it permits a higher current density to be used.[43]

When the phenol group of *o*- or *p*-nitrophenol is changed by replacing the hydrogen of the hydroxyl group by methyl, ethyl, or benzyl, radicals to form the corresponding ether, the dehydration of the aminohydroxylamine is prevented with the result that the reduction goes smoothly in alkaline solution through all the intermediate steps to the azo and hydrazo derivatives, exactly as do the *m*-nitro derivatives:[44]



In an alkaline solution *o*- and *p*-nitrophenol ethers, *p*-nitrophenol *p*-tolyl ether and hydroquinone *p*-nitrodiphenyl ether, have also been reduced.[45]

The closing of the amino group of a nitro amine as in *o*-nitro or *p*-nitro acetanilide leads to the formation of normal reduction products:[46]

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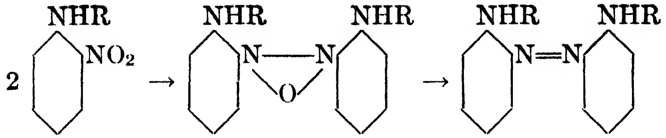
[43] J. C. Warner and O. W. Brown, J. Phys. Chem., **27**, 652 (1923).

[44] Sonneborn, Z. Elektrochem., **6**, 509 (1900); Elbs, ibid., **7**, 145 (1900); Häussermann, Chem. Ztg., **17**, 209 (1893); Brand, J. prakt. Chem., [2], **67**, 145 (1903); Gaumer, Dissert., Giessen (1901).

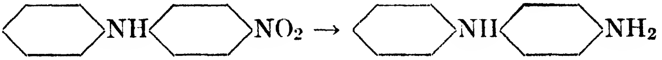
[45] Häussermann and Schmidt, Ber., **34**, 3769 (1901).

[46] Brand and Stohr, Ber., **39**, 4058 (1906); Weinerth, Dissert., Giessen (1906); Sonneborn, Z. Elektrochem., **6**, 509 (1900).

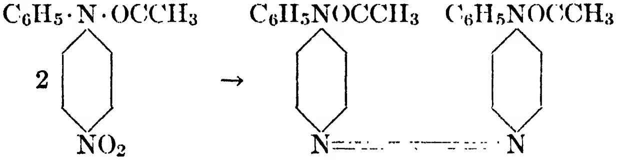


But in an acetic acid solution the reductions go to the diamine.

p-Nitrodiphenyalmine in an alkaline solution yields *p*-aminodiphenylamine:[47]



but a tertiary amine goes differently; i.e., acetyl-*p*-nitrodiphenylamine[48] yields the azo compound, i.e., acetyl-*p*-azodiphenylamine:

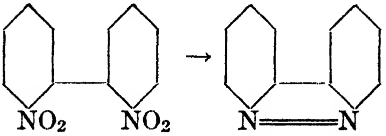


and benzoyl-*p*-nitrodiphenylamine[49] yields the azo and azoxy derivatives. *p*-Nitrodimethylaniline yields *p*-azodimethylaniline[50] though Rohde[51] obtained *p*-aminodimethylaniline. Why *p*-nitrodimethylaniline and *p*-nitrodiphenylamine do not yield analogous products is not known.

THE FORMATION OF HETEROCYCLIC COMPOUNDS

Constitutive properties can often cause the alkaline reduction of aromatic nitro compounds to yield heterocyclic compounds.

A very interesting reduction is that in which *o*- *o*′-dinitro-diphenyl is reduced at a nickel wire gauze cathode in an alkaline solution to diphenazon:[52]



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[47] Rohde, Z. Elektrochem., 7, 339 (1900).

[48] Elbs, Z. Elektrochem., 7, 145 (1900).

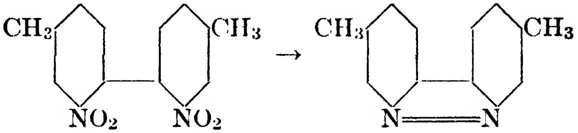
[49] Rohde, loc. cit.

[50] Löb, Z. Elektrochem., 5, 459 (1898).

[51] Rohde Z. Elektrochem., 7, 145 and 328 and 338 (1900).

[52] Wohlfahrt, J. prakt. Chem., [2], 65, 295, (1902).

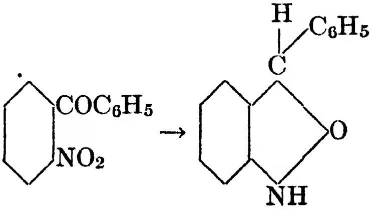
This interesting method was slightly revised by Ullmann and Dieterle [53] who obtained much larger yields of the diphenazon when the dinitro derivative was dissolved in alcohol. For their work Ullmann and Dieterle used 2-2′-dinitro-4-4′-ditolyl in an hot alcoholic solution containing sodium acetate to obtain dimethyldiphenazon:



Under entirely similar conditions *o*-*o*′-dinitrobenzidine yielded 80 per cent of the theoretical quantity of diaminodiphenazon. Dinitro-tetramethyldiaminodiphenyl yielded 56 per cent theoretical quantities of tetramethyldiaminodiphenazon. This same product was obtained in 60 per cent yields by the electrolytic reduction of tetramethyldiamino diphenazonoxide. In the same apparatus 3,8-tetraethyldiaminodiphenazon was obtained from dinitrotetraethyl-diamino-diphenyl; and also 3,8-diamino-2,9-dimethoxydiphenazon, from dinitrodianisidine, i.e., 4-4′-diamino-3-3′-dimethoxy-6-6′-dinitrodiphenyl. The position of the NO_2 groups in 6-6′ is possible but they may also assume positions 2-2.′

These phenazine derivatives contain chromophoric and auxochrome groups and therefore there is every evidence that they themselves should be dyes, the value of which cannot be predicted. By tetrazotizing and coupling with naphthionic acid, a dye somewhat similar to Congo red should be obtained, i.e., a direct cotton or substantive dye.

o-Nitrobenzophenone in an alkaline solution at a lead cathode is reduced to anhydro-*o*-hydroxylaminodiphenylcarbinol: [54]



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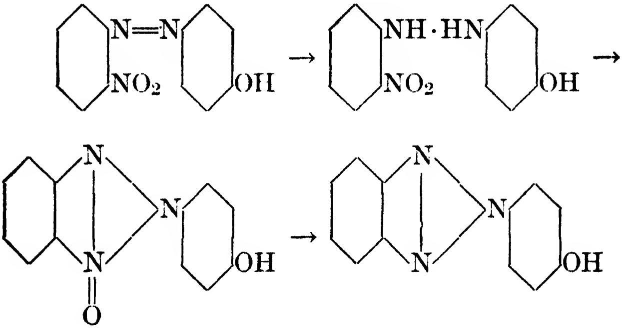
[53] Ber., **37**, 23 (1904).

[54] C. Bäzner and Gardiol, Ber., **39**, 2514 (1906).

This reduction is different from the reduction of *m*-nitroacetophenone and *m*-nitrobenzophenone which yield only the corresponding amines.[55]

The reduction of nitro-azo compounds has also received attention;[56] *m*- or *p*-nitroazo compounds being reduced in an alkaline solution to the corresponding trisazo derivatives,[57] but the *o*-nitroazo derivatives are reduced to probably first a hydrazo compound without reducing the nitro group; this hydrazo derivative then loses a molecule of water to form a phentriazole oxide and finally a phentriazole. On this basis *o*-nitroazophenol yields first *o*-nitrohydrazophenol which loses water to form phenolphentriazole oxide and then phenolphentriazole:



Hesselmann determined that a very low c. d. and only the calculated amount of current may be passed to insure the best results.

Above in the reduction in acid solution it was noted that Mette[58] reduced 3-nitro-4-lactylaminophenetole to a quinoxaline derivative by the Boehringer method. This same compound is obtained in an alkaline solution. Another reaction that has a parallel in acid solution is the formation of μ-methylbenzimidazole according to Brand and Stohr.[59] In an alkaline solution *p*-nitro-*o*-toluidine and *o*-nitro-*p*-toluidine are reduced to the corresponding toluylenediamines; the *m*-nitro-*p*- and *m*-nitro-*o*-toluidines to the azo derivatives.[60]

But the reaction which we are particularly interested in here is the reduction of the substituted toluidines, which is different.[61]

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[55] Which see.

[56] Elbs and Keiper, J. prakt. Chem., [2], **67**, 580 (1903); Keiper, Dissert., Giessen (1903); Hesselmann, Dissert., Giessen (1905).

[57] See Keiper and Hesselmann, op. cit.

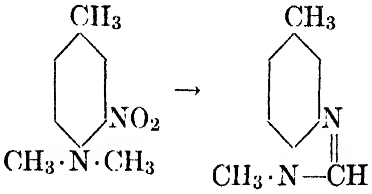
[58] Mette, Dissert., Giessen (1906).

[59] Brand and Stohr, Ber., **39**, 4058 (1906). See page 215.

[60] Elbs, Z. Elektrochem., **7**, 145 (1900).

[61] Pinnow, J. prakt. Chem., [2], **63**, 352 (1901); **65**, 579 (1902).

m-Nitro-dimethyl-*p*-toluidine yields with graphite powder as a carrier dimethylbenzimidazole and dimethyltoluylenediamine:



On the other hand *m*-nitro-dimethyl-*o*-toluidine goes normally in alkaline solution to the tetramethyl-*m*-diamino-*p*-azotoluene, and the hydrazo derivative.

CHAPTER XII

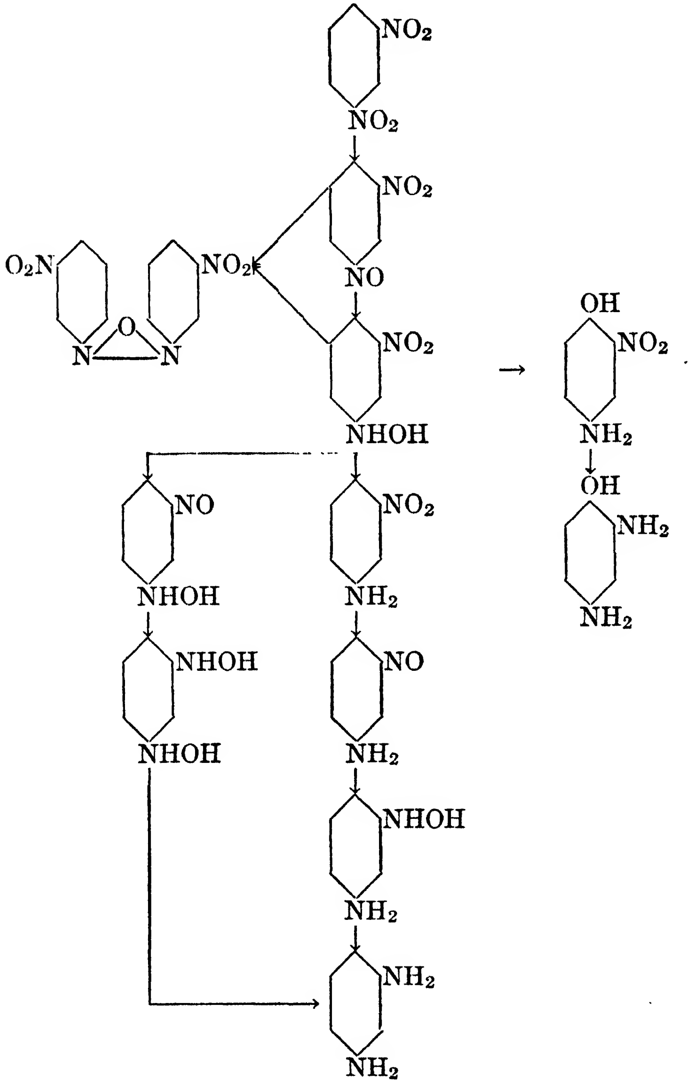
THE REDUCTION OF AROMATIC NITRO COMPOUNDS PART IV.—POLYNITRO COMPOUNDS

GENERAL

According to the experimental conditions used, either one or both nitro groups of a dinitro compound may be reduced with the formation of compounds which correspond to Haber's scheme for reduction of the mononitro derivatives.

While the study of polynitro compounds is not so complete as the study of the mononitro compounds, sufficient work has been reported to show that even though the electrolytic reduction proceeds readily in most cases, the products of the reduction are very difficult to separate. The reductions are not as clear-cut as in the mononitro series. In many cases the usual hydroxylamine, azo, azoxy, hydrazo, or amino groups are obtained by reducing only one nitro group at a time; the reactions being for the most part not at all complete or satisfactory. The chemical separation of these more or less complex reduction products makes a determination of the course of the reduction a very complicated problem. However, sufficient has been reported on the reduction of *m*-dinitrobenzene to indicate that the Haber scheme as shown on opposite page applies:

The first formed *m*-nitro-nitrosobenzene may be isolated in an almost neutral solution, but in an alkaline solution this compound condenses with *m*-nitro-phenylhydroxylamine to form dinitroazoxybenzene, which is very slightly soluble in an aqueous alkaline solution, therefore is removed from the sphere of further reduction as rapidly as it is formed; it is on this account obtainable in good yields. The rearrangement by the Gattermann method takes place when the hydroxylamine derivative is formed by reduction in a concentrated sulphuric acid solution to form *o*-nitro-*p*-aminophenol, which is then further reduced to the diaminophenol. Reduction in a very dilute acid solution leads to the formation of nitrosophenylhydroxylamine, then *m*-phenylenedihydroxylamine, which, however, has not been isolated but detected by the color it imparts to a ferric chloride solution, and its final reduction to *m*-phenylenediamine. When copper chloride or zinc chloride is added to a hydrochloric acid solution the first product formed is *m*-nitraniline which is further reduced to *m*-phenylenediamine. The reduction products of polynitro compounds will now be examined more completely.



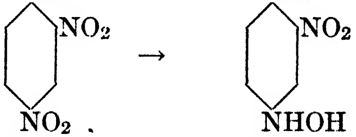
REDUCTIONS IN ALMOST NEUTRAL SOLUTION

The use of strongly alkaline solutions as described by Elbs for the reduction of nitro groups does not apply in the reduction of *m*-dinitrobenzene because of the solid condensation products which are formed on the cathode in such large amounts as finally to stop the passage of the current. The electrolysis may be carried out successfully if during the course of the reduction acetic acid is added drop-wise in quantities sufficient to maintain a neutral reaction in the catholyte, so preventing the formation of this skin on the surface of the cathode. Using this method Brand was able to isolate *m*-nitrophenylhydroxylamine from the reduction products of *m*-dinitrobenzene.[1] The formation of the azoxy compound was accompanied by very few difficulties, but the hydroxylamine derivative required a very careful regulation of the acidity of the solution. By using as a catholyte a neutral solution of acetic acid and sodium acetate and as the anolyte a sulphuric acid solution, the hydroxylamine compound could be readily prepared. The use of a sodium carbonate solution as the anolyte caused a condensation of the *m*-nitrophenylhydroxylamine inside the diaphragm to take place, so raising the resistance of the system enormously. A nickel cathode does not work nearly so well as a pure silver or a silvered nickel cathode.

The formation of the undesirable skin on the surface of the cathode may be eliminated by using a mercury cathode with violent stirring. Under these conditions the mercury remains bright during the entire reduction.

By using a neutral solution with the theoretical amount of current required for the formation of *m*-nitraniline a small amount of this substance was formed together with a larger quantity of *m*-phenylenediamine. The addition of tin or copper salts did not change matters as the copper and tin were quickly deposited on the cathode and so rendered inactive as catalysts. When a little acid was added according to the method of Boehringer [2] both nitro groups were still reduced. It seems that the hydroxylamine group of the *m*-nitrophenylhydroxylamine is so slowly reduced that the second nitro group is attacked.

The toluene derivatives undergo a similar reduction:[3]



2-4-dinitrotoluene → 2-nitro-4-hydroxylaminotoluene

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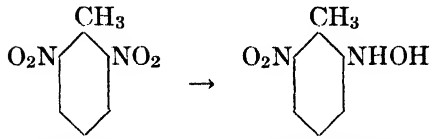
[1] Brand, Ber., **38**, 4006 (1905).

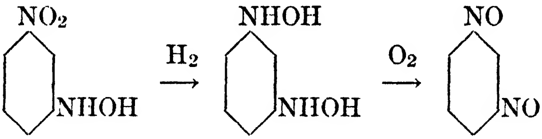
[2] Boehringer, loc. cit.

[3] Brand and Zöller, Ber., **40**, 3324 (1907).


2-6-dinitrotoluene 2-nitro-6-hydroxylaminotoluene

The two nitrotoluene hydroxylamines are readily removed from the solution by dilution with water in which they are insoluble.

After the hydroxylamine derivative has been formed, the passage of more current reduces the second nitro group, and though the dihydroxylamine is extremely fugitive its presence has been proven by its color reaction with ferric chloride and also its oxidation by air oxygen to the dinitroso compound:



In a neutral solution 2,4-dinitroanisole yields 4-nitro-2-anisyl-hydroxylamine with some 5-5′-dinitro-*o*-azoxyanisole.[4]

REDUCTIONS IN AN ACID SOLUTION

Complete Reduction.—Elbs' method, i.e., a lead cathode in an alcoholic sulphuric acid solution or the Boehringer method by the addition of zinc or copper chloride in hydrochloric acid, leads to the formation of polyamine compounds in good yields.[5] The partial reduction of a compound is very difficult to accomplish for the reason that the —NHOH group is not a very good depolarizer, consequently, before it is completely reduced to the amine derivative, the second nitro group is attacked by the electrolytic hydrogen. By the two methods[6] mentioned above good yields of particularly pure polyamino compounds are obtained which is not always the case, from the standpoint of purity, in the chemical reductions. Hydrogen cannot be added to the ring nor can a carboxyl group on the ring be reduced.[7]

The following polynitro compounds have been reduced: *m*-dinitrobenzene[8] to *m*-phenylenediamine (85–95 per cent yields); 2-4-dinitro-

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[4] Brand and Eisenmenger, J. prakt. Chem., [2], **87**, 487 (1913).

[5] D.R.P. 116942 and 117009 (1900), Boehringer.

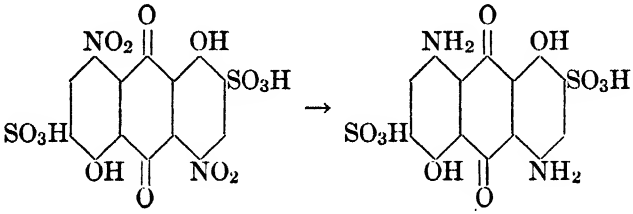
[6] i.e. the Elbs' or Boehringer method.

[7] J. Möller, Z. Elektrochem., 10, 199 and 222 (1904).

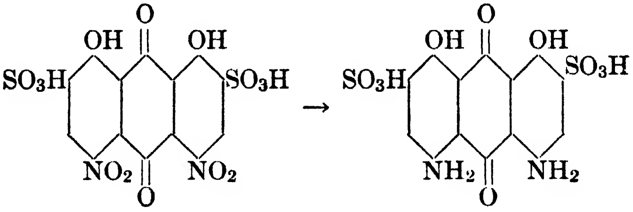
[8] D.R.P. 116942 (1900), Boehringer; Hofer and Jakob, Ber. **41**, 3187 (1908).

toluene[9] to 2-4-toluylendiamine and 2-2′-azoxy-4-4′-dinitrotoluene; 2-6-dinitrotoluene yielded the corresponding diamine and 2-2′-azoxy-6-6′-dinitrotoluene[10]; 2-4-dinitrophenol to 2-amino-4-nitrophenol[11] and 2-4-diaminophenol by the Boehringer method. Picric acid to picramic acid, diaminonitrophenol, and other unidentified products;[12] 1-5-dinitronaphthalene[13] to 1-5-naphthylenediamine; 1-8-dinitronaphthalene[14] to 1-8-naphthylenediamine; 1-5-dinitroanthraquinone[15] to 1-5-diaminoanthraquinone; α-dinitroanthraquinone[16] (1-8-dinitro-) to α-diaminoanthraquinone (1-8-diamino-). The following have been reduced according to the method of Bayer:[17]

Dinitroanthrarufindisulphonic acid to diaminoanthrarufindisulphonic acid



Dinitrochrysazinedisulphonic acid to diaminochrysazinedisulphonic acid



2-7-dinitrophenanthraquinone to 2-7-diaminophenanthraquinone.

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[9] Weyprecht, Dissert., Giessen (1902). The former compound is formed in 7 per cent yields by the Boehringer method and the latter by the Elbs' method in alcoholic H_2SO_4; Hofer and Jakob, loc. cit.

[10] Hofer and Jakob, loc. cit.

[11] Elbs, J. prakt. Chem., [2], **43**, 38 (1891); Weyprecht, loc. cit.

[12] Elbs, loc. cit. and Weyprecht, loc. cit.

[13] J. Möller, Elektrochem. Z., **10**, 199 and 222 (1903).

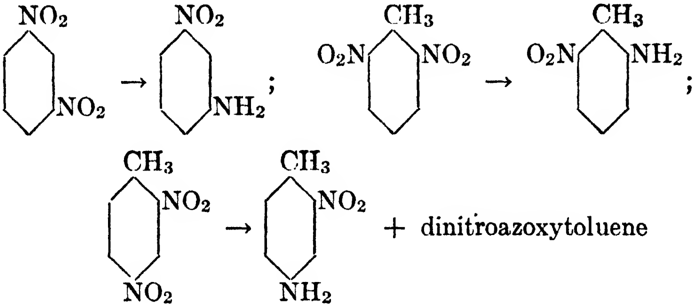
[14] J. Möller, loc. cit.

[15] J. Möller, Z. Elektrochem., **7**, 741 and 797 (1901) and loc. cit.

[16] J. Möller, loc. cit.

[17] D.R.P. 105501 (1900), at a Pb cathode in H_2SO_4 solution.

Partial Reductions.—In at least a 10 per cent solution of HCl with the Boehringer method, *m*-dinitrobenzene at a Cu cathode with the addition of copper chloride and a small c. d. at 80–90° yields *m*-nitraniline, and some dinitroazoxybenzene.[18] The toluene derivatives are also reduced in this manner.[19]



The reduction of the 2-4-dinitrotoluene by the purely chemical method zinc chloride and hydrochloric acid leads to the formation of the opposite compound using, namely, 2-amino-4-nitrotoluene.[20]

The use of oxide of vanadium as a carrier in the reduction of polynitro derivatives leads to various amounts of partially reduced compounds when different cathodes are used. Starting with 20 g. of 2-4-dinitrotoluene the following table [21] is self-explanatory.

Table XXV

Product	Electrode			
	Pt	Pb	Sn	C
p-Nitrotoluidine	14.5 g.	3.5	4.	12.5
Dinitro-azoxytoluene	5.5	9.0	7.0	

p-Amino-nitrophenol is formed from 1, 2, 4-dinitrophenol; 4-amino-2, 6-dinitrotoluene from 1, 2, 4, 6-trinitrotoluene; picramic acid from picric acid.[22]

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[18] Brand, Ber., **38**, 4006 (1905); see also Hofer and Jakob, Ber., **41**, 3187 (1908).

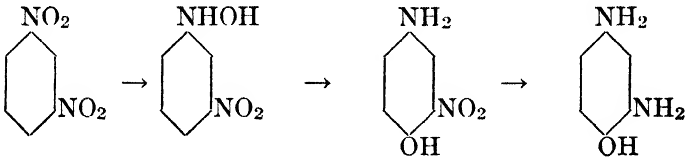
[19] Brand and Zöller, Ber., **40**, 3324 (1907); Zöller, Dissert., Giessen (1907). Hofer and Jakob, loc. cit.

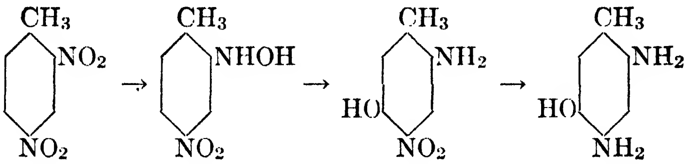
[20] Anschütz and Heusler, Ber., **19**, 2161 (1896).

[21] Hofer and Jakob, Ber., **41**, 3187 (1908).

[22] Hofer and Jakob, loc. cit.

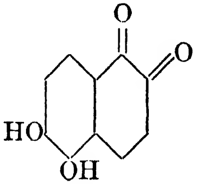
Reductions in a Concentrated Acid Solution.—As stated above, Gattermann's reduction method holds for polynitro compounds of the benzene series.[23] The course of the reaction is considered as being:





Condensation products of these compounds with formaldehyde may all be formed [24] if the reduction is carried out in the presence of formaldehyde.

α_1-α_4-dinitronaphthalene or a mixture of α_1-α_3- or α_1-α_4-dinitronaphthalene, concentrated sulphuric acid at 130° are electrolytically reduced to a compound which on dilution of the catholyte with water yields naphthazarin.[25] Dinitroanthraquinone has also been reduced.[26]



Boehringer's method has been applied to the reduction of alkylated polynitrophenols by Brand.[27] At a copper cathode in the presence of copper chlorite in sulphuric acid, 2-4-dinitroanisole yields 4-nitro-*o*-anisidine.

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[23] Gattermann and Abresch, Ber., **26**, 1848 (1893); D.R.P. 75260 (1893).

[24] Löb, D.R.P. 99312 (1897).

[25] D.R.P. 79406 (1894), Badische.

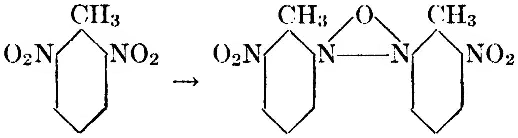
[26] D.R.P. 92800 and 92998 (1896).

[27] Brand and Eisenmenger, J. prakt. Chem., [2], **87**, 487 (1913).

REDUCTIONS IN AN ALKALINE SOLUTION

The reduction of polynitro compounds in an alkaline solution is very difficult because the starting materials are either decomposed or else resins and incrustations cover the cathode which ultimately stop the passage of the current, especially in the case of nickel cathodes.[28]

The deleterious effects of this skin are not so great when a mercury cathode is used,[29] because violent stirring may be resorted to to keep the mercury in agitation and so continually break the skin of non-conducting material, keeping the surface of the cathode always bright and active. The apparatus of Orbig[30] is excellent for these reductions. With this method Brand[31] reduced *m*-dinitrobenzene to *m*-dinitroazoxybenzene in almost quantitative yields and 2, 6-dinitrotoluene to 2, 2′-dinitro-6, 6-azoxytoluene:



2, 4-Dinitrotoluene is less smoothly reduced than the 2, 6-compound. The products are 2, 2′-dinitro-4, 4′-azoxytoluene[32] or 4, 4′-dinitro-2, 2′-azoxytoluene.[33]

When the phenol group is closed by alkylation as in 2-4-dinitroanisole, reduction at a mercury cathode in an alkaline solution forms 5, 5′-dinitro-*o*-azoxyanisole.[34] However the azoxy compound is not formed in an acid solution. The reduction of 2, 4, 6-trinitrotoluene in an alkaline solution yields products which have so far defied separation and identification.

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[28] Weyprecht, Dissert., Giessen (1902).

[29] Brand, Ber., **38**, 4012 (1905).

[30] Orbig, Dissert., Giessen (1906).

[31] Brand, loc. cit.

[32] Brand and Zöller, Ber., **40**, 3329 (1907).

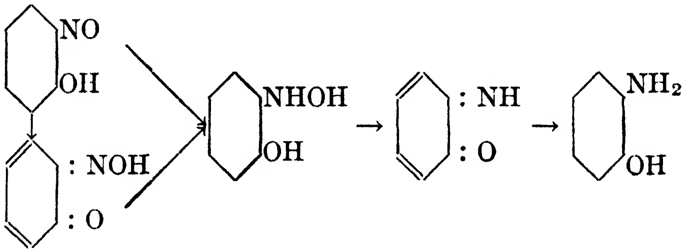
[33] Weyprecht, Dissert., Giessen (1902).

[34] Brand and Eisenmenger, J. prakt. Chem., [2], **87**, 487 (1913).

CHAPTER XIII

THE REDUCTION OF NITROSO COMPOUNDS, ETC.

As stated above these derivatives in most cases are very fugitive and are only intermediate in the course of the reduction of nitro derivatives, therefore are seldom used as starting materials. The reduction of the nitroso compounds using *o*-nitrosophenol as the example, has been shown to be



The reduction products always are amines. *p*-Nitrosodiphenylamine in acid and alkaline solutions yields *p*-aminodiphenylamine in more than 70 per cent yields,[1] or " Emeraldine." [2]

At room temperature *p*-nitrosodimethylaniline in an alcoholic alkaline solution on a nickel cathode yields dimethyl-*p*-phenylenediamine but at a slightly higher temperature yields *p*-aminophenol.[3] *p*-Nitrosophenol forms *p*-aminophenol,[4] *p*-nitrosoresorcinol yields *p*-aminoresorcinol,[4] while α-nitroso-β-naphthol yields α-amino-β-naphthol.[4]

THE REDUCTION OF ALIPHATIC NITRO COMPOUNDS

Very little is found in the literature concerning the electrochemical reduction of aliphatic nitro compounds. Nitromethane yields β-methylhydroxylamine:

$$CH_3NO_2 + 4H \rightarrow CH_3NHOH + H_2O$$

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[1] Frank, Dissert., Giessen (1903).

[2] Nover, Ber., 40, 288 (1907).

[3] Frank, loc. cit.; D.R.P. 168273 (1903).

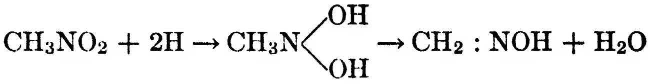
[4] Frank, loc. cit.

at room temperature in an alcoholic sulphuric acid solution; as the temperature rises the reduction continues:

$$CH_3NHOH + 2H \rightarrow CH_3NH_2 + H_2O$$

till at about 75° the complete reduction is almost quantitative. Nitroethane and nitropropane are similarly reduced to the corresponding β-hydroxylamine or the normal amine.[5]

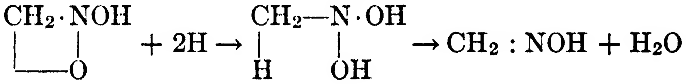
On the other hand in concentrated hydrochloric acid or 90 per cent sulphuric acid the reduction takes a very different course. There seems to be an intermediate formation of the oxime of the corresponding aldehyde which is hydrolyzed by the concentrated acid to form the aldehyde and hydroxylamine: [6]

(1)


$$CH_3NO_2 + 2H \rightarrow CH_3N\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \rightarrow CH_2 : NOH + H_2O$$

(2) $$CH_2 : NOH + H_2O \rightarrow CH_2O + NH_2OH$$

On the basis of the Knoevenagel and Flürscheim conception of the aliphatic nitro compounds [7] three transformations may be expressed:



The results are practically the same even when chlorinated nitro compounds are electrolytically reduced. Frank [8] reduced chloropicrin in a dilute acid solution at a platinum cathode and obtained good yields of β-methylhydroxylamine, though at a lead cathode the reduction went completely to the amine:

$$CCl_3NO_2 + 10H \rightarrow CH_3NHOH + 3HCl + H_2O$$

$$CCl_3NO_2 + 12H \rightarrow CH_3NH_2 + 3HCl + 2H_2O$$

This differential action of platinum as opposed to lead as a cathode was observed in the case of the reduction of aromatic nitro compounds.

Phenyl nitromethane in an aqueous suspension or an alcoholic solution in the presence of hydrochloric acid on a tin cathode or on any cathode in the presence of a tin salt yields benzylamine: [9]

$$C_6H_5CH_2NO_2 + 6H \rightarrow C_6H_5CH_2NH_2 + 2H_2O$$

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[5] Pierron, Bull. soc. chim., [3], **31**, 780 (1899).

[6] Pierron, loc. cit.

[7] Knoevenagel and Flürscheim, J. prakt. Chem., [2], **66**, 16 (1902).

[8] M. Frank, Dissert., Giessen (1903).

[9] D.R.P. 116942 (1900), Boehringer.

Several nitramines of the aliphatic series have been reduced at tin-plated copper or lead cathodes to their corresponding hydrazines[10] using a catholyte which varies with the stability of the starting material. The catholyte may be either dilute sulphuric acid or a mixture of sulphuric and acetic acids if an acid solution is needed. Neutral solutions are best made from acetic acid neutralized by the addition of sodium acetate. An alkaline medium is obtained by the use of sodium carbonate. By this method methyl nitrourethane in a neutral solution yielded methylhydrazine carboxylate in 88 per cent yields:

$$O_2N \cdot HNCO \cdot OCH_3 \rightarrow H_2N \cdot HN \cdot COOCH_3$$

Ethyl nitrourethane gave 70 per cent yields of the corresponding ethyl hydrazine carboxylate,

$$O_2N \cdot HNCOOC_2H_5 \rightarrow H_2N \cdot HN \cdot COOC_2H_5$$

and nitrourea in the acetic-sulphuric acid solution on a tin cathode covered with black tin gave 74 per cent of semicarbazide.[11] Nitroguanidine[12] and also nitrobiuret[13] have similarly been reduced.

The electrochemical reduction of secondary nitroamines gives much better yields than the purely chemical reduction by means of metallic zinc and acetic acid. The best results are obtained by using a dilute sulphuric acid solution as the catholyte with a copper cathode coated with tin. In some cases the addition of acetic acid increases the yields. The following list gives the nitramines reduced and the yields of the corresponding hydrazines:[14]

Dimethyl nitramine to 69 per cent of the corresponding hydrazine derivative.

N-nitro piperidine to 52 per cent of the corresponding hydrazine derivative.

Dinitro piperazine to 24 per cent of the corresponding hydrazine derivative.

Ethylene-bis-methylnitroamine to 67 per cent of the corresponding hydrazine derivative.

Methyl methylnitroaminoformate to 51 per cent of the corresponding hydrazine derivative.

Phenyl methylnitroamine to 54 per cent of the corresponding hydrazine derivative.

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[10] Boehringer, D.R.P. 167637 (1902).

[11] H. J. Backer, Rec. trav. chim., **31**, 1 (1912); Holroyd, J. Chem. Soc., **79**, 1326 (1901); H. Ochi, Japanese Pat. 39219 (1921).

[12] D.R.P. 167637, Boehringer; Frank, Dissert., Giessen (1903).

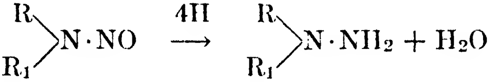
[13] Elbs, In Brand " Elektrochemische Reduktion," p. 266.

[14] H. J. Backer, Rec. trav. chim., **36**, 142 (1912).

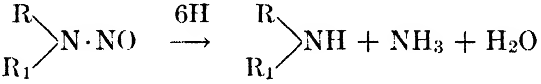
The nitrosamines of the aliphatic series do not yield the expected hydrazines by purely chemical methods of reduction. An electrolytic reduction in a slightly acid solution at a copper cathode yielded the corresponding hydrazides. The method has been applied to only two compounds namely oxalyl-bis-methyl nitrosamide, and succinyl-bis-methyl nitrosamide; in both cases the yields were around 10 per cent of the theoretical value.[15]

THE REDUCTION OF NITROSAMINES

The reduction of nitrosamines may take two courses:

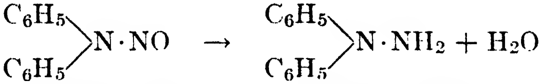
(1)


$$\begin{matrix}R\\R_1\end{matrix}\!>\!N\cdot NO \xrightarrow{4H} \begin{matrix}R\\R_1\end{matrix}\!>\!N\cdot NH_2 + H_2O$$

(2)


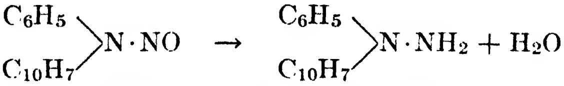
$$\begin{matrix}R\\R_1\end{matrix}\!>\!N\cdot NO \xrightarrow{6H} \begin{matrix}R\\R_1\end{matrix}\!>\!NH + NH_3 + H_2O$$

Reaction 1 is accomplished by a chemical reduction using zinc and acetic acid or by an electrochemical reduction in the same acid with a nickel cathode.



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!N\cdot NO \rightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!N\cdot NH_2 + H_2O$$

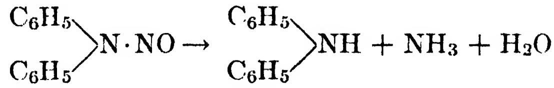
diphenylnitrosamine — *as*-diphenyl hydrazine



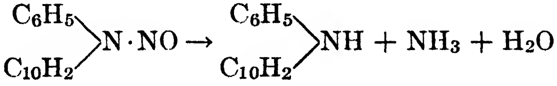
$$\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!N\cdot NO \rightarrow \begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!N\cdot NH_2 + H_2O$$

phenyl-α-naphthyl nitrosamine — *as*-phenyl-α-naphthyl hydrazine

The second type of reduction takes place with zinc chloride in hydrochloric acid solution or by electrolytic reduction in a mineral acid solution.[16]



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!N\cdot NO \rightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!NH + NH_3 + H_2O$$



$$\begin{matrix}C_6H_5\\C_{10}H_2\end{matrix}\!>\!N\cdot NO \rightarrow \begin{matrix}C_6H_5\\C_{10}H_2\end{matrix}\!>\!NH + NH_3 + H_2O$$

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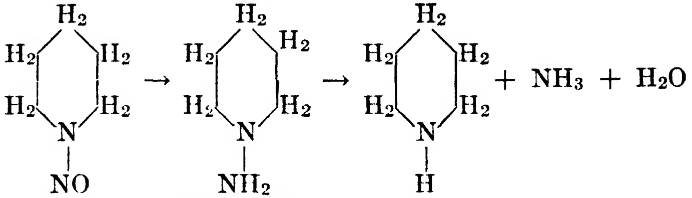
[15] H. J. Backer, J. Chem. Soc., **101**, 592 (1912).

[16] Elbs in Brand, " Elektrochemische Reduktion," page 266–7.

Several members of the pyridine and quinoline series have also been reduced.[17] In a sulphuric acid solution on a lead cathode with an elevated temperature the following reductions have been accomplished:



nitrosopiperidine piperyl hydrazine main product piperidine by-product

This is a typical reduction in this series. The following reductions have also been accomplished:[18]

Nitroso-α-pipecoline to α-pipecoline hydrazine.

Nitroso-β-pipecoline to β-pipecoline hydrazine.

Nitroso-γ-pipecoline to γ-pipecoline hydrazine.

Nitroso-α-α-lupetidine to α-α-dimethylpiperyl hydrazine.

Nitroso aldehyde copellidine to aldehyde copellidine hydrazine.

Nitroso-*sym*-trimethylpiperidine to *sym*-trimethylpiperyl hydrazine.

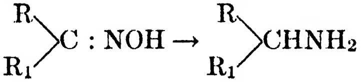
Similarly on a lead cathode in a dilute sulphuric acid solution the following have been reduced:[19]

4-amino-5-isonitroso-2-6-dihydroxypyrimidine to 4-5-diamino-2-6-dihydroxypyrimidine.

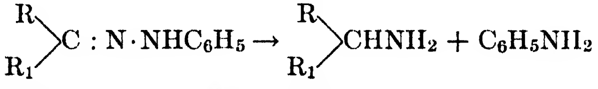
3-methyl-4-amino-5-isonitroso-2-6-dihydroxypyrimidine to 3-methyl-4-5-diamino-2-6-dihydroxypyrimidine.

THE REDUCTION OF OXIMES AND SIMILAR COMPOUNDS

Oximes and hydrazones in 50 per cent sulphuric acid are easily reduced to the corresponding amines at a lead cathode with excellent material and current yields.[20] According to the equation:



$$\begin{matrix}R\\R_1\end{matrix}\!\!>C : NOH \rightarrow \begin{matrix}R\\R_1\end{matrix}\!\!>CHNH_2$$



$$\begin{matrix}R\\R_1\end{matrix}\!\!>C : N \cdot NHC_6H_5 \rightarrow \begin{matrix}R\\R_1\end{matrix}\!\!>CHNH_2 + C_6H_5NH_2$$

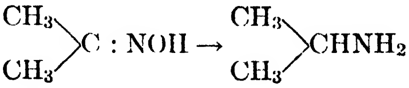
[17] Ahrens, Z. Elektrochem., **2**, 578 (1896); Ber., **30**, 533 (1897); **31**, 2272 (1898); Ahrens and Sollmann, Chem. Zeitsch., **2**, 414 (1903); Z. Elektrochem., **10**, **391** (1904).

[18] Ahrens, loc. cit.

[19] D.R.P. 166267, Merck.

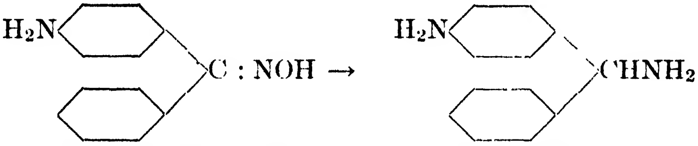
[20] J. Tafel and E. Pfeffermann, Ber., **35**, 1510 (1902); D.R.P. 141246 (1903), Boehringer; C. Marie, Compt. rend., **140**, 1248 (1905).

Since most oximes are very sensitive to strong acids, it is safest to work at a temperature well below 20°. By the use of electrolytic reduction some very unusual amines may be formed without very much difficulty. When 100 g. of acetoxime in 500 cc. of 50 per cent sulphuric acid are reduced at a lead cathode by a c. d. of 16 amperes, 66 per cent of the theoretical amount of isopropylamine is obtained:



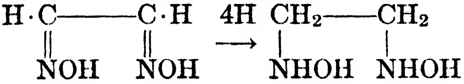
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C:NOH \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHNH_2$$

Under similar conditions benzaldoxime yields benzylamine, acetoxime yields phenylethylamine, camphoroxime yields bornylamine; benzophenoneoxime in 60 per cent sulphuric acid on a lead, but especially on a mercury cathode yields benzhydrylamine, $(C_6H_5)_2CHNH_2$.[21] The technical preparation of bornylenediamine from the oxime of aminocamphor, isonitrosocamphor, and isonitrocamphor has been described by P. Duden.[22] The preparation of amino and the substituted amino derivatives of benzophenonoxime have been described in a patent assigned to Merck.[23]



p-aminobenzophenoneoxime p-aminobenzhydrylamine

Once in a while the reaction does not go as described above. In the case of glyoxime the expected ethylenediamine is not formed at a lead cathode,[24] in sulphuric acid, but in its place a compound is formed in 60 per cent yields having the composition $C_2H_8O_2N_2$ which is supposed to have the structural formula of β-ethylenedihydroxylamine, together with some glyoxal and glyoxalic acid and ammonia:



$$\begin{matrix} H\cdot C & \text{——} & C\cdot H \\ \| & & \| \\ NOH & & NOH \end{matrix} \xrightarrow{4H} \begin{matrix} CH_2 & \text{——} & CH_2 \\ | & & | \\ NHOH & & NHOH \end{matrix}$$

The dioximes of β-diketones are reduced in part to the corresponding diamines, but the main reaction is the formation of pyrazolidine derivatives. These latter compounds are difficult to prepare by purely chemical methods. The dioxime of acetyl acetone yields some 2-4-diamino-

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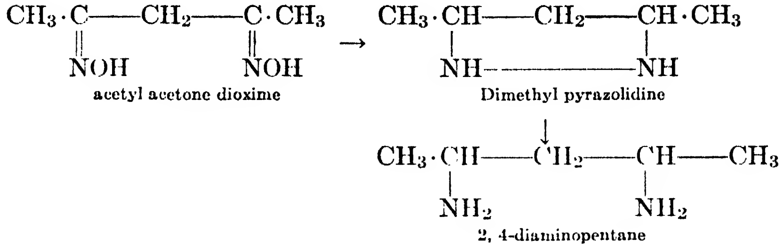
[21] Tafel and Pfeffermann, loc. cit.

[22] D.R.P. 160103 (1903), P. Duden.

[23] D.R.P. 167053 (1904), E. Merck.

[24] J. Tafel and E. Pfeffermann, Ber., **35**, 1510 (1901).

pentane but mostly dimethyl pyrazolidine in 30 per cent sulphuric acid.[25]



$$\begin{array}{ccc}CH_3\cdot C & —CH_2— & C\cdot CH_3\\ \| & & \|\\ NOH & & NOH\end{array} \longrightarrow \begin{array}{ccc}CH_3\cdot CH & —CH_2— & CH\cdot CH_3\\ | & & |\\ NH & ——— & NH\end{array}$$

acetyl acetone dioxime

Dimethyl pyrazolidine

$$\downarrow$$

$$\begin{array}{cccc}CH_3\cdot CH & —CH_2— & CH & —CH_3\\ | & & | & \\ NH_2 & & NH_2 & \end{array}$$

2, 4-diaminopentane

Acid oximes are rather easily hydrolyzed in an acid solution so that it is difficult to reduce them to the corresponding amine by purely chemical methods. The electrolytic method permits a better control of temperature and acidity, thereby decreasing the hydrolysis to a minimum. At temperatures below 10° γ-isonitrosovaleric acid and α-isonitrosopropionic acid have been successfully reduced in acid solutions containing less than 8 per cent sulphuric acid. The current yields were 61 per cent and 93 per cent and the material yields were 84 per cent and 95 per cent respectively.[26]

By the reduction of isonitrosoacetone in dilute sulphuric acid the compound expected was aminoacetone but in reality the product was dimethylpyrazine, $C_6H_8N_2$.[27]

THE REDUCTION OF ALDEHYDE-AMMONIA CONDENSATION PRODUCTS

Hydrogen may be added by the electrolytic method to the condensation product of aldehydes with ammonia and substituted ammonias to form amines. Since the substituted ammonias are very sensitive to the presence of strong sulphuric acid the yields are always low; the starting material being decomposed to variable extents depending on the experimental conditions.

When hexamethylenetetramine is dissolved in a 50 per cent sulphuric acid solution as an electrolyte and reduced at a lead cathode, the product is a mixture containing almost equal amounts of mono-, di-, and trimethylamine in about 50 per cent yields when the temperature of the electrolyte is around 12–18°.

Methylamine and formaldehyde are reduced to di- and trimethylamine. Acetaldehyde ammonia yields ethylamine and diethylamine, but no trace of triethylamine has been detected. Hydrobenzamide yields

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[25] J. Tafel and E. Pfeffermann, Ber., **36**, 219 (1903).

[26] Masayoshi Ishibashi, Trans. Am. Electrochem. Soc., **45**, 160 (1924).

[27] Ahrens and Meissner, Ber., **30**, 532 (1897).

50 per cent of the theoretical amounts of benzylamine. Benzylidene methylamine forms 60 per cent yields of benzylmethylamine. Ethylideneimine yields mono- and diethylamine.

The probable mechanism for these reactions is that the hexamethylenetetramine is hydrolyzed by the sulphuric acid to pentamethylenetetramine and then to trimethylenetriamine: [28]

$$C_6H_{12}N_4 + H_2O \rightarrow C_5H_{12}N_4 + CH_2O$$

$$C_5H_{12}N_4 + 2H_2O \rightarrow C_3H_9N_3 + 2CH_2O + NH_3$$

Then the triamine or a further decomposition product of it, as CH_2NH, is reduced to a methylamine. This theory is supported by the fact that hexamethylenetetramine is completely hydrolyzed by sulphuric acid in one hour at 18°, while three hours are required at 12°; and also by the work of Cambier and Brochet,[29] Duden and Scharff,[30] who found that in an acid solution hexamethylenetetramine is hydrolyzed to formaldehyde and pentamethylenetetramine. The sulphuric acid used as the electrolyte in this method may be replaced by hydrochloric acid.[31]

There must be some explanation other than that of hydrolysis for the course of the reduction in an acid solution, because a neutral or even an alkaline solution works almost as well as an acid solution. By the use of an alkaline or a neutral solution the difficultly obtainable condensation products of aldehyde and ammonias are not required. A mixture of the aldehyde with ammonia or the ammonium salt suffices.[32] Hexamethylenetetramine in a sodium sulphate solution free from chloride as the catholyte when reduced with a c. d. of 3 amperes at 40° yields methyl- and trimethylamine. The alkali formed at the cathode during the electrolysis must be neutralized by dilute sulphuric acid at the end of the electrolysis, and the amine distilled.

The use of a salt solution as the electrolyte has been applied with success to the formation of secondary amines from the condensation products of aldehydes with primary amines by Brand:[33]

$$RCH : NR_1 + 2H \rightarrow RCH_2NHR_1$$

The catholyte consisted of 18 g. of benzylideneaniline, 15 g. of sodium acetate, 200 cc. of alcohol and 30 cc. of water. A lead cylinder was the cathode. Electrolysis at a temperature of 80° with a c. d. of 1.5–2.0

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[28] P. Knudsen, Ber., **42**, 3994 (1909); D.R.P. 143197 (1903).
[29] Cambier and Brochet, Bull. soc. chim., [3], **13**, 392 (1895).
[30] Ann., **288**, 218 (1895).
[31] D.R.P. 175071 (1906), Boehringer.
[32] D.R.P. 148045 (1902), Meister.
[33] K. Brand, Ber., **42**, 3460 (1909).

amperes at a potential of 6–8 volts produced good yields of benzylaniline:[34]

$$C_6H_5CH : NC_6H_5 + 2H \rightarrow C_6H_5CH_2NHC_6H_5$$

Similarly p-methoxybenzylideneaniline yielded p-methoxybenzylaniline:

$$p\text{-}CH_3O \cdot C_6H_4 \cdot CH : NC_6H_5 + 2H \rightarrow p\text{-}CH_3O \cdot C_6H_4 \cdot CH_2 \cdot NHC_6H_5$$

Numerous benzylidine bases have been reduced[35] in a neutral solution and the products identified as being analogous to those formed in the reduction of aldehydes. One product was always a resin. Two other compounds having formulae $RCH_2 \cdot XH$ and $RCH(XH)CH(XH)R$ respectively were always identified, being similar to the alcohols and hydrobenzoins formed in the reduction of aldehydes, but no compound analogous to the stilbene, i.e., a compound without an X group, was ever isolated in weighable amounts. The course of the reduction is probably:

$$\text{(I)} \quad R \cdot CH : X + 2H = RCH_2XH$$

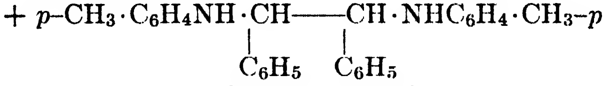
$$\text{(II)} \quad 2R \cdot CH : X + 2H = RCH(XH) \cdot CH(XH) \cdot R$$

The following reductions were accomplished:

$$C_6H_5CH : NC_6H_5 \rightarrow C_6H_5CH_2 \cdot NHC_6H_5 + C_6H_5 \cdot CHO + C_6H_5NH_2 + \text{resin}$$

The aniline and benzaldehyde were probably formed by the hydrolysis of the starting material. No dianilinodibenzyl was formed according to equation (II) above.

$$\underset{\text{benzylidene-}p\text{-toluidine}}{C_6H_5CH : NC_6H_4 \cdot CH_3\text{-}p} \rightarrow \underset{\text{benzyl-}p\text{-toluidine}}{C_6H_5CH_2 \cdot NHC_6H_4 \cdot CH_3\text{-}p}$$



$$+\ p\text{-}CH_3 \cdot C_6H_4NH \cdot \underset{C_6H_5}{\underset{|}{CH}} — \underset{C_6H_5}{\underset{|}{CH}} \cdot NHC_6H_4 \cdot CH_3\text{-}p$$

di-p-toluidino-dibenzyl

Two isomeric forms of di-p-toluidinodibenzyl were found.

Benzylidene-m-toluidine → benzyl-m-toluidine + resin.

Benzylidene-o-toluidine → benzyl-o-toluidine.

The o-, m-, and p-toluidine anilines yielded their respective methyl benzyl anilines.

o-, m-, p-Chlorobenzylidene anilines yielded the corresponding chlorobenzyl anilines plus a resin. The amount of resin formed diminished

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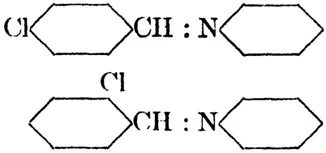
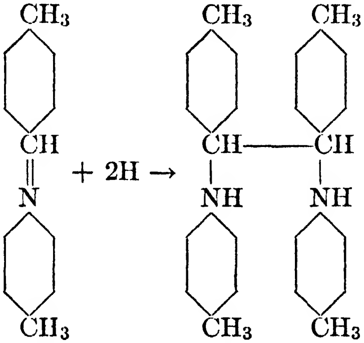
[34] Elbs, "Übungsbeispiele," p. 130.

[35] H. D. Law, J. Chem. Soc., **101**, 154 (1912).

as the substituent group moves toward the center of the molecule; that is produces more resin than



The *p*-tolylidine-toluidines are reduced to the corresponding *p*-tolyltoluidines and resin; some di-*p*-toluidine-di-*p*-methyldibenzyl is also formed.



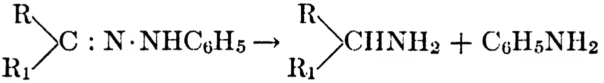
m-tolylidine-*m*-toluidine yields only *m*-tolyl-*m*-toluidine but *m*-tolylidine-*p*-toluidine yields, it is thought, di-*m*-toluidino-di-*p*-methyldibenzyl besides the *m*-tolyl-*p*-toluidine. Considering the amounts of resin formed in these cases it seems that the least resin is formed when the substituting groups are evenly distributed in the two nuclei. Finally the *p*-chlorobenzylidine derivatives of *o*-, *m*-, and *p*-toluidine yield the corresponding *p*-chlorobenzyl-toluidines. Only in the case of the latter compound (i.e., the *p*-*p*′-compound) are complex molecules produced.

Several conclusions may be drawn from the results of this work. Resinification is troublesome in most cases, but the structure of the molecule seems to effect the amount of resin formed: (1) the amount of resin decreases as the substituent groups move in toward the center of the molecule; (2) the amount of resin also decreases as the substituent groups are evenly distributed in the two nuclei; (3) the influence of the substituents in the two nuclei is different.

The presence of the *p*-toluidine group in the molecule causes an unexpected tendency to polymerize so that two molecules of the original compound on reduction behave as do aldehydes when hydrobenzoins are formed.

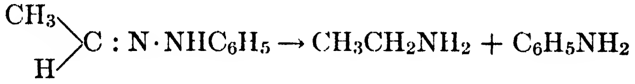
The use of alkaline solutions for the reduction of this type of compound is not always possible. Ethylideneamine is not reduced by the electrolytic method either in alkaline or neutral solution. Instead of the expected ethylamine there is another reaction, probably a hydrolysis, which leads to the formation of aldehyde ammonia. The consumption of hydrogen at the cathode in this case is probably due to the reduction of the aldehyde group in the aldehyde ammonia.[36] The use of an alkaline solution is sometimes of value in making a reaction go in a different direction from that which takes place in an acid solution. An example of this is the reduction of hydrobenzamide in an alkaline solution at a lead cathode to benzylamine and dibenzylamine. Knudsen[37] was able to reduce hydrobenzylamine in a sulphuric acid solution to benzylamine alone, the only product which was obtained also by reduction using sodium amalgam.[38]

Hydrazones in 50 per cent sulphuric acid solution are readily reduced at a lead cathode to the corresponding amines according to the equation:

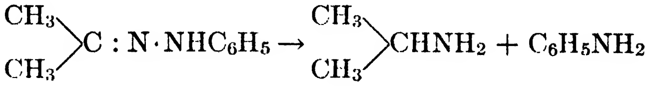


$$\begin{matrix}R\\R_1\end{matrix}\!\!>C:N\cdot NHC_6H_5 \rightarrow \begin{matrix}R\\R_1\end{matrix}\!\!>CHNH_2 + C_6H_5NH_2$$

the yields being around 60 per cent. Three hydrazones have been reduced: ethylidenephenylhydrazone yielded ethylamine, and acetone phenylhydrazone yielded isopropylamine, and benzylidenephenylhydrazone yielded benzylamine and aniline:[39]



$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C:N\cdot NHC_6H_5 \rightarrow CH_3CH_2NH_2 + C_6H_5NH_2$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C:N\cdot NHC_6H_5 \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHNH_2 + C_6H_5NH_2$$

THE REDUCTION OF QUATENARY AMMONIUM SALTS AND RELATED COMPOUNDS

Various results have been obtained in the electrolysis of ammonium salts using different cathodes. When ammonium salts are electrolyzed with a mercury cathode an ammonium amalgam is formed[40]

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[36] K. Brand and A. Hoing, Z. Elektrochem., **18**, 745 (1912).

[37] Knudsen, loc. cit.

[38] O. Fischer, Ber., **19**, 748 (1886) and Ann., **241**, 328 (1887).

[39] J. Tafel and E. Pfeffermann, Ber., **35**, 1510 (1902).

[40] Seebeck, Ann., **66**, 191 (1808); Le Blanc, Z. Physik. Chem., **5**, 467 (1890); Coehn, Z. anorg. Chem., **25**, 430 (1900). See also Mellor, Inorganic and Theoretical Chemistry, vol. 4, page 1005, Longmans, 1923.

In studying the evidence in favor of the theory of free electro-positive radicals having metallic properties, Le Blanc[41] electrolyzed a solution of an ammonium salt with a mercury cathode in such an apparatus that polarization potential measurements could be made. The potential rose in a few minutes to a maximum value which was nearly as great as that given by a sodium salt. The really important result was obtained after the polarizing current was shut off. Then the mercury cathode showed an inflation characteristic of an ammonium amalgam. That this material was an ammonium amalgam was shown by the fact that it precipitated cadmium and zinc from their solutions in the cold and that with a solution of barium chloride it formed a barium amalagm.[42] Similarly the sodium and potassium amalgams have been formed.[43]

Substituted ammonium amalgams have been prepared by the electrolytic method.[44] The electrolysis of aqueous solutions of the chloride at a mercury cathode leads only to the formation of colloidal mercury at the cathode. An alcoholic solution of the chloride, however, works very differently. Tetramethyl ammonium chloride was dissolved in absolute alcohol to form a saturated solution and then electrolyzed at −10° at a mercury cathode for 30 minutes. The amalgam so prepared was in the form of shining crystals silvery-white in color, slightly soluble in mercury and decomposing slowly at 0° but rapidly at 25° into trimethylamine, methane and ethylene.[45] When brought into contact with water the amalgam reacted very violently, evolving hydrogen, and the whole mixture becoming black, rapidly turning gray and forming a gray colloidal solution. A very convenient apparatus built up from a Gooch crucible is described.

Monomethyl ammonium chloride was similarly electrolyzed and formed an amalgam. Eighteen additional salts were studied without the formation of an amalgam.[45]

When tetramethyl ammonium salts are electrolyzed in liquid ammonia, blue streaks appear on the cathode surface. The constitution of the streaks has not been determined.[46]

Schlubach [47] studied the electrolysis of tetraethyl ammonium salts in liquid ammonia using a divided cell. The materials and apparatus

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[41] Le Blanc, loc. cit.; see also Smith, J. Am. Chem. Soc., **29**, 844 (1907), for references concerning the theories concerning these amalgams, also McCoy and Moore, ibid., **33**, 273 (1911).

[42] Coehn, loc. cit. (1900).

[43] G. M. Smith, J. Am. Chem. Soc., **29**, 844 (1907).

[44] H. N. McCoy and W. C. Moore, J. Am. Chem. Soc., **33**, 273 (1911).

[45] See H. N. McCoy and F. L. West, J. Phys. Chem., **16**, 261 (1912).

[46] W. Palmaer, Z. Elektrochem., **8**, 729 (1902).

[47] H. H. Schlubach, Ber., **53**, 1689 (1920).

were thoroughly dried and maintained free from moisture and oxygen during the work. The ammonia was distilled from sodium and the ammonium salts were free from alkalies. At the instant the circuit was closed there at once appeared on the cathode dark blue striations, which in a few minutes spread over the whole catholyte to form a deep blue solution; the intensity of the color increased as the electrolysis proceeded. If after passing 1.5 times the calculated amount of current the deep blue solution was allowed to stand at −78°, the color persisted for some hours and then slowly faded out. The solution showed strong absorption in the violet and red portions of the spectrum. On evaporation at 15 mm. only a little unchanged ammonium salt was recovered from a fresh sample of the electrolyte. When evaporated at ordinary pressure some triethylamine remained besides some of the original ammonium salt. When the solution was poured on somewhat less than the calculated amount of iodine, there was an immediate decolorization accompanied by an evolution of ammonia. When the residue from this process was recrystallized from water, about 80 per cent yield of tetraethyl ammonium iodide was obtained.

If during the electrolysis some dry oxygen was introduced into the cathode area the streaks on the cathode at once decolorized and on evaporating the solution there remained a faintly yellowish residue which by analogy with potassium might have been expected to be a peroxide, but on examination it proved to be 8 per cent of unchanged chloride together with about 70 per cent tetraethyl ammonium hydroxide.

When KI is electrolyzed in the same apparatus while dry acetylene is introduced at the cathode, some monopotassium acetylide is formed (CH : CK) similar to that obtained by Moissan.[48] If the acetylene is similarly introduced during the electrolysis of the tetraethyl ammonium chloride decolorization occurs, but when the product is treated with water no product analogous to CH : CH is formed. All these reactions except the last show a similarity between the ammonium radical and the alkali metals. Tetramethyl ammonium iodide and tetrapropyl ammonium iodide behave like the above chloride while triethylphenyl ammonium iodide yields diethylanilide at the cathode.

From this work it is seen that there is a discharge at the cathode of ammonium ions. On this basis there should be the formation of unsaturated or unstable complex ions of the type $-NRR^1R^2R^3$ which analogous to the action of the alkali metal ions should react with water to liberate hydrogen and form the compound $NRR^1R^2R^3OH$.[49] However

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[48] Moissan, Compt. rend., **127**, 911 (1898).

[49] B. Emmert, Ber., **42**, 1507 (1909).

this reaction does not take place; in its place is another as follows:

$$-NRR^1R^2R^3 + H = NR^1R^2R^3 + HR$$

that is removing one of the alkyl groups as a hydrocarbon leaving as a residue a substituted ammonia. At lead cathodes the following results were obtained: The percentages being the theoretical yields of the compound mentioned:

trimethylphenyl ammonium iodide
= 77 per cent trimethylamine + 75 per cent benzene.

dimethylethylphenyl ammonium iodide
= 69 per cent dimethylethylamine and benzene.

methyldiethylphenyl ammonium iodide
= 68 per cent diethylmethylamine and benzene.

methylethylpropylphenyl ammonium iodide
= 45 per cent methylethylpropylamine and benzene.

The derivatives are not obtained when platinum cathodes are used, probably because the cathodic potential required is not obtained, or because the proper intermediate compounds can not be formed with platinum electrodes.

When dimethyloxyethylphenyl ammonium iodide is electrolyzed in the apparatus of Tafel,[50] using platinum electrodes, some dialkyl aniline and dimethylaminoethyl alcohol are formed. Similarly methylethyloxyethylphenyl ammonium iodide yields methylethylaminoethyl alcohol.[51]

On the other hand the pyridinium salts do not react like the quaternary ammonium salts. They react according to one example of the Kolbe hydrocarbon synthesis, in that two residues unite to form a dipyridyl.[52] Benzyl pyridinium chloride yields dibenzyl-dihydrodipyridyl similar to the compound prepared by Hoffmann,[53] and ethyl pyridinium chloride forms diethyldihydrodipyridyl. The quinoline compounds yield corresponding diquinolyl compounds and of the latter group, methyl and ethyl quinolinium iodides have been studied. The assumption is that possibly some unsaturated residues are formed which react later with the solvent water to form benzyl pyridinium hydroxide, or probably the nitrogen tends to become tri-valent and in so doing frees

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[50] Tafel, Ber., **33**, 2223 (1900).
[51] B. Emmert, Ber., **45**, 430 (1912).
[52] B. Emmert, Ber., **42**, 1507 (1909).
[53] Hoffmann, Ber., **14**, 1503 (1881).

a carbon valence in the pyridine nucleus with the result that two such residues unite to form the complex:

$$C_6H_5CH_2\cdot N\left\langle\begin{matrix}CH\cdot CH\\ CH\cdot CH\end{matrix}\right\rangle CH\cdot CH\left\langle\begin{matrix}CH\cdot CH\\ CH\cdot CH\end{matrix}\right\rangle N\cdot CH_2C_6H_5$$

The position of the free carbon linkage may be either in the orthometa- or para-position, but the definite settling of the position has not yet been accomplished.

CHAPTER XIV

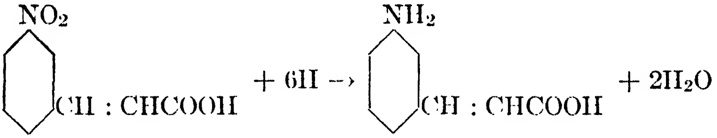
THE ADDITION OF HYDROGEN TO UNSATURATED COMPOUNDS

GENERAL

The addition of hydrogen to double-bond (unsaturated) carbon atoms may often be accomplished electrolytically as well as by purely chemical methods:

$$—CH : CH— + 2H \rightarrow —CH_2 \cdot CH_2—$$

The cathodic potential at which the hydrogen is evolved must be high if an ethylene linkage is to be saturated. The saturation of such a linkage is much more difficult than the reduction of a nitro group. In the reduction of *m*- or *p*-nitrocinnamic acid at a smooth platinum or nickel cathode only the nitro group is reduced leaving the ethylene bond untouched:[1]



A very high cathodic potential at a smooth unattackable electrode is necessary to accomplish the addition of hydrogen at a double bond, but on a cathode coated with a very finely divided metallic black, such as nickel- or platinum-black, the reduction proceeds quickly. Any cathode at all may be used if the electrolyte contains in solution some soluble nickel salt or a suspension of palladium-black, in which case practically 100 per cent of the hydrogen discharged at the cathode is absorbed by the depolarizer.

UNSATURATED HYDROCARBONS

Very little has been reported on the reduction of the aliphatic hydrocarbons. Billitzer investigated the reduction of acetylene at a platinized paltinum cathode in both alkaline and acid solution obtaining ethylene

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[1] Marie, Compt. rend., **136**, 1331 (1903). See Marie, ibid., **140**, 1248 (1905).

and ethane. He found [2] that by regulating the cathodic potential at 0.75 to 0.15 volt below the voltage of a normal hydrogen electrode only ethylene was formed; when the voltage was lower than this a mixture of ethylene, ethane and hydrogen was evolved. With a smooth platinum electrode there was no sign of a reduction. An interesting reaction [3] for the preparation of ethyl ether occurs when acetylene is passed through the catholyte containing 65 per cent sulphuric acid as close to the cathode as possible. The acetylene is reduced to ethylene which then reacts with the sulphuric acid at 100° to form an addition product, ethylsulphuric acid. The addition of water to the system liberates ethyl ether from the ethyl-sulphuric acid. Though interesting, the method is entirely without value under the conditions specified.

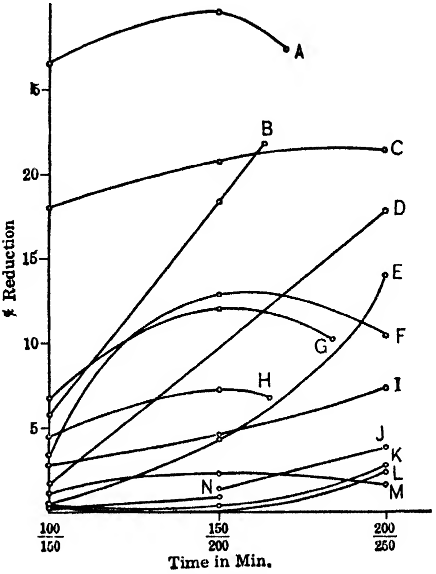

Fig. 10.—The Curves Show the Rate of Reduction in 0.1 Normal H_2SO_4-alcoholic. Taken from Pomilio, loc. cit.

A—Maleic acid	*H*—Crotonic acid
B—Fumaric acid	*I*—Oleic acid
C—Linoleic acid	*J*—Linolenic acid
D—Itaconic acid	*K*—Allylmalonic acid
E—Aconitic acid	*L*—Allylacetic acid
F—Mesaconic acid	*M*—Erucic acid
G—Citraconic acid	*N*—Undecylenic acid

UNSATURATED ACIDS

The possibilities in the reduction of unsaturated acids are enormous because of the great commercial importance which saturated acids possess.

There is practically no addition of hydrogen to an unsaturated acid on a smooth platinum, and slightly less reaction at a smooth copper or lead cathode. Most of the current passed is lost in the form of gaseous hydrogen.[4] A platinized-platinum or a freshly nickeled cathode in an

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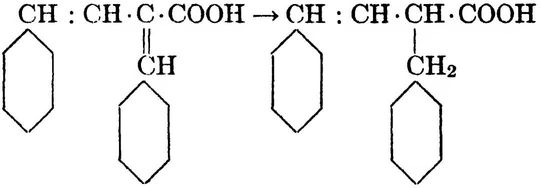
[2] Billitzer, Z. Elektrochem., 7, 683 and 959 (1901); Monatsheft, 23, 302 (1902).

[3] U.S.P. 711565 (1902), Harris.

[4] Kekule, Ann., **131**, 85 (1864); Marie, Compt. rend., **136**, 1331 (1903); Z. Elektrochem., **9**, 643 (1903); Fokin, ibid., **12**, 749 (1906); Boehringer, D.R.P., 189332 (1908); Petersen, Z. Elektrochem., **11**, 549 (1905); Elbs, "Übungsbeispiele," p. 129.

acid solution or a mercury cathode in an alkaline solution yields very much better results. A hot slightly alkaline solution of cinnamic acid at a mercury cathode is reduced to phenylpropionic acid. Similarly fumaric and maleic acids yield succinic acid[5] while mesaconic and itaconic acids are readily reduced to methylsuccinic acid.[6] Dibenzal propionic acid is reduced at a lead cathode in mineral acid solution to α-benzylphenylisocrotonic acid:[7]



An aqueous solution of aconitic acid of which one-half is in the form of the sodium salt,[8] is reduced at a mercury cathode, after the passage of twice the theoretical amount of current, to about 60 per cent of the theoretical current yield of tricarballylic acid. Linoleic, linolenic, allylmalonic, allylacetic, undecylenic, and citraconic acids have been reduced.[9] Of greatest technical interest is the hydrogenation of oleic acid.

$$CH_3(CH_2)_7CH : CH(CH_2)_7COOH \rightarrow CH_3(CH_2)_7CH_2 \cdot CH_2(CH_2)_7COOH$$

This reaction has been studied to some extent but not with sufficient intensity to make the process commercial.[10]

All investigators have used a solution of oleic acid in an aqueous-alcoholic mixture made slightly acid with sulphuric or hydrochloric acid, using "blacked" electrodes of platinum, palladium, nickel or copper.

Fokin,[11] using a freshly nickeled electrode, claims 80 per cent yields, but the analytical method of determining the amount of stearic acid formed must be questioned. Mettler has been able to get very good results using a platinized-platinum cathode.[12] Another attempt to get a

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[5] Pomilio, Z. Elektrochem., **21**, 444 (1915).

[6] S. Fokin, J. Russ., phys. Chem. Soc., **39**, 607 (1907). Pomilio, loc. cit.

[7] C. Mettler, Ber., **39**, 294 (1906).

[8] Marie, loc. cit.; Pomilio, loc. cit.

[9] Pomilio, loc. cit.

[10] Petersen, Z. Elektrochem., **11**, 549 (1905); Fokin, ibid., **12**, 749 (1906); Boehringer D.R.P. 187788 and 189332 (1906); Lewkowitsch, J. Soc. Chem. Ind., **27**, 489 (1908).

[11] Fokin, loc. cit.

[12] Mettler, Ber., **39**, 2943 (1906).

method that would be applicable on a commercial scale was tried,[13] but the complications are too numerous for the advantages that are claimed for the method.

The work that has been done on the question of the solidification of the liquid fats and oils indicates that there is a large amount of work to be done before definite results will be available. The use of alcohol as the solvent leads to the formation of the ethyl ester of oleic acid which, of course, causes losses and is generally undesirable. The low conductivity of the various electrolytes prevents the general application of the method on a large scale as a substitute for the purely chemical method of hydrogenation that is in vogue at present.

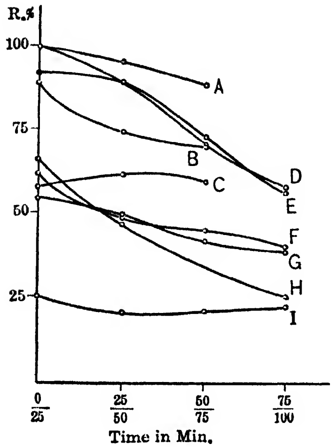

FIG. 11.—Rate of Reduction of acids. Taken from Pomilio, loc. cit.

A—Maleic acid
B—Itaconic acid
C—Fumaric acid
D—Allylacetic acid
F—Aconitic acid
G—Mesaconic acid
H—Allylmalonic acid
I—Citraconic acid

AROMATIC COMPOUNDS

Heterocyclic compounds have been investigated more than the homocyclic compounds. Several general characteristics of the aromatic compounds stand out as being the opposite of similar reactions of the aliphatic series. For the reduction of aromatic compounds a high cathodic overvoltage is required; probably the best electrode for the electrolytic reductions is prepared from lead, though the presence in the solution of the salts of other metals lowers the final yield.

REDUCTIONS IN THE NUCLEUS

The reduction of carboxyl group, etc., will be taken up later in a separate section. At this point we are only interested in the effects of electrolytic reduction in the nucleus. It suffices therefore merely to mention that under certain conditions the carboxyl group may be attacked while under other conditions the nucleus only will be attacked. At a mercury cathode in an alkaline solution benzoic acid is reduced to tetrahydrobenzoic acid[14] which reaction is entirely analogous to the

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[13] D.R.P. 126446 (1899), Magnier, Brangier and Tissier.

[14] Mettler, Ber., **39**, 2933 (1906).

reduction of benzoic acid on the purely chemical process in alkaline solution.

The dicarboxylic acids in acid solution are reduced in the nucleus and not in the carboxyl group.[15] Phthalic acid yields a single reduction product namely, Δ-3-5-dihydrophthalic acid from a hot 15 per cent solution of sulphuric acid. Strong cooling at the end of the reaction causes the dihydrophthalic acid to crystallize. Terephthalic acid in 200 cc. of alcoholic sulphuric acid is reduced to the corresponding dyhydro compound Δ-2-5-dihydroterephthalic acid. The dimethyl ester of terephthalic acid yielded the dimethyl ester of Δ-2-5-dihydroterephthalic acid similar to that described by Bayer.[16] Isophthalic acid does not behave like the other two acids, but forms an oil from which *m*-xylylene dialcohol crystallizes, though small amounts of hydrogenated isophthalic acid are also formed.

The *m*-acid forms xylylene dialcohol. *o*-Diphenyldicarboxylic acid yields phenanthrene hydroquinone which is oxidized by the air to phenanthrene quinone, the same as Graebe [17] obtained from *o*-diphenoldicarboxylic acid chloride by reduction with Zn and HCl.

With the present development in the commercial applications, much more work should be done on the electrolytic hydrogenation of the aromatic hydrocarbons. Hexahydrobenzene and the hydronaphthalenes, both have great value as fuel and as dye intermediates. Electrochemistry should place these compounds on the market some day.

REDUCTION OF HETEROCYCLIC COMPOUNDS

Pyridine. — More work has been reported on the hydrogenation of pyridine and quinoline and their related compounds than has been reported on the homocyclic compounds. On a lead cathode in a solution of 1 part of pyridine in 10 parts of 10 per cent sulphuric acid, there is a smooth and almost quantitative reduction of the pyridine to piperidine.[18] One of the first and foremost requirements of the process is not only the purity of the pyridine and the acid but also a freshly prepared lead cathode. In order to avoid complications, the acid content of the electrolyte must be limited to 4 equivalents of acid to one of pyridine. The

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[15] Mettler, Ber., **39**, 2933 (1906).

[16] Ann., **251**, 296 (1889).

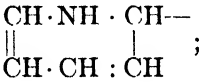
[17] Ann., **247**, 268 (1888).

[18] F. Ahrens, Z. Elektrochem., **2**, 577, (1895); Ber., **30**, 533 (1897); **31**, 2272 (1898); Pimkusohn, Z. anorg. Chem., **14**, 397 (1897); E. Merck, D.R.P. 90308 (1896), 104664 (1898); Tafel, Z. physik. Chem., **34**, 220 (1900); Doan, Thesis, Cambridge, Mass. (1920).

use of a diaphragm permits the product to be worked up directly from the electrolyte without any difficulty.[19]

An excellent method for the preparation of piperidine has been worked out by E. v. Zappi. The requirements are that the catholyte be a solution of 60 g. of pyridine, 53 cc. of 66° Bé. sulphuric acid and 200 cc. of water enclosed in a porous cup over a pure mercury cathode. The yields are good and the reaction goes smoothly, but the method of recovery is somewhat complicated. The addition of carriers which are active in other reductions does not seem to work in the case of pyridine reductions. It is found that colloidal palladium prepared by the Bredig method absolutely prevents the absorption of any hydrogen, while the addition of a few drops of lead chloride solution reduces the absorption of hydrogen from 40 per cent to 8 per cent.[20]

Emmert [21] expected from pyridine, using Ahrens' method, to get several types of unsaturated radicals., i.e., unsaturated in positions 1, 2, 3, or 4, as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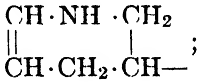
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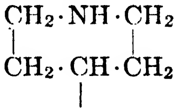

These radicals could add oxygen and form piperidine or they could unite among themselves to form piperidyls. Pyridine in 40 per cent H_2SO_4 at a Pb cathode yielded mostly piperidine together with γ-γ'-dipiperidyl, α-α'-dipiperidyl and a substance that could not be identified without decomposition but which was probably a poly-piperidyl. During the reduction the lead cathode was visibly attacked and a substance, which was probably an intermediately formed lead-pyridinium alloy, seemed to coat the metallic surface. This compound undoubtedly had something to do with the course of the reduction.

Quinoline.—The quinoline molecule when reduced in sulphuric acid solution may absorb either two or four atoms of hydrogen yielding both dihydroquinoline and tetrahydroquinoline.[22] Continued electrolysis favors the tetrahydro compound:

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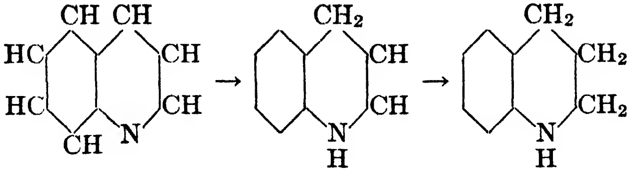
[19] In a strong H_2SO_4 solution at a Pt cathode, a compound containing both nitrogen and sulphur is formed.

[20] E. v. Zappi, Anal. soc. quim. Argentina, **3**, 433 (1915).

[21] Emmert, Ber., **46**, 1716 (1913); Ahrens, Z. Elektrochem., **2**, 577 (1895); D.R.P. 90308 (1896), Merck.

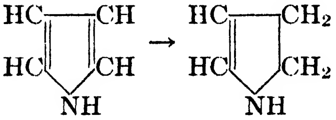
[22] Ahrens, Z. Elektrochem., **2**, 580 (1895); Merck, D.R.P. 90308 and 104664 (1898). With a Pb cathode and a Pt anode Ahrens obtained the following compounds: $(C_9H_9N)_3$; $(C_9H_9N)_2$ and $C_9H_{11}N_2$ (?).



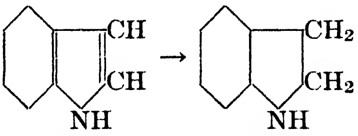
The dihydro compound which is very difficult to prepare otherwise is separated from the tetrahydro compound by steam distillation, the latter being very volatile.

Acetyltetrahydroquinoline[23] and quinaldine[24] yield ethyl tetrahydroquinolene and dihydroquinaldine respectively.

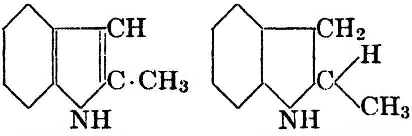
Miscellaneous.—The chemical reduction of pyrrole by zinc and acetic acid is very incomplete, but the method of Dennstedt [25] in which dilute sulphuric acid is used as the electrolyte for the suspended pyrrole is claimed to yield almost quantitative amounts of dihydropyrrole:



Indole derivatives are reduced only in alcoholic acid solution; there being no addition of hydrogen in an alkaline solution.[26] The following reductions have been reported in excellent yields:



indole indoline



α-methyl indole α-methyl indoline

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[23] Baillie and Tafel, Ber., **32**, 74 (1899). This is like the reduction of benzoyl piperidine, which see.

[24] Ahrens, loc. cit.

[25] D.R.P. 127086 (1901).

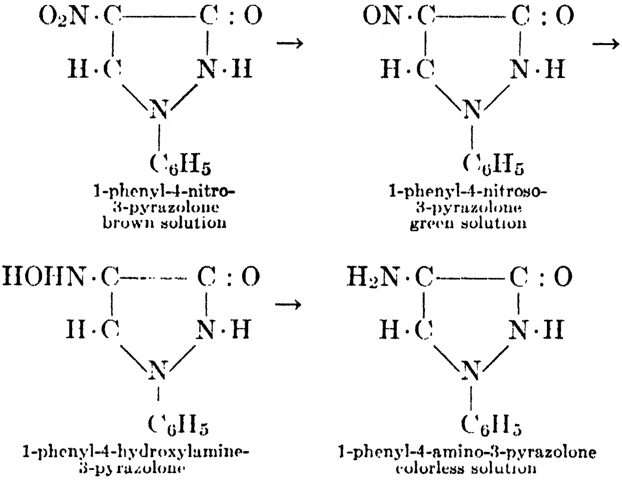
[26] Carasco, Gazz. chim. ital., **38**, ii, 301 (1908).

α-β-dimethylindole → α-β-dimethylindoline.

N-methylindole → N-methylindoline.

Tetrahydrocarbazol → Carbazoline.

By the method of Elbs and Silbermann,[27] Kummel and Remy have reduced heterocyclic 5-ring compounds containing a nitro group to obtain compounds similar to those obtained by the reduction of the nitro compounds of the benzene series:[28]



1-phenyl-4-nitro-3-pyrazolone brown solution

1-phenyl-4-nitroso-3-pyrazolone green solution

1-phenyl-4-hydroxylamine-3-pyrazolone

1-phenyl-4-amino-3-pyrazolone colorless solution

The electrolytic reduction of indigo to indigo white should find a large application in technical work, but so far this has not been the case.[29]

The very slight solubility of indigo in water of course makes a suspension of indigo a very poor depolarizer. At room temperatures when the electrodes are copper, carbon, plain or platinized-platinum only a very small amount of hydrogen is absorbed. At the boiling temperature or in the presence of zinc salts at ordinary temperatures the reduction goes too far so that appreciable losses occur due to a further reduction of the leuco compound.

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[27] Z. Elektrochem., **7**, 591 (1900).

[28] G. Kummel and E. Remy, Z. Elektrochem., **16**, 254 (1909).

[29] Goppelsröder, Dissert., Reichenberg (1885); Ding. Polyt. J., **251**, 465 (1881); Chem. Ztg., **8**, 361 (1884); Wartha, ibid., **8**, 431 (1884); Mullerus, ibid., **17**, 1454 (1893); Grotthus, Ann. Chim. et phys., [1], **63**, 18 (1811).

In a divided cell[30] a suspension of indigotin in sodium hydroxide (sp. gr. 1.1186) yields on a copper wire gauze cathode only very small amounts of the leuco compound. When a solution containing 3.88 per cent of zinc is electrolyzed with about 11 times the theoretical quantity of current, all the indigo is reduced, though only about 36 per cent material yields are obtained; the rest is probably lost by a further reduction.

A much more satisfactory method is that described in a patent assigned to Meister.[31] This method takes advantage of the fact that the electrolytic reduction of a sulphite yields a so-called hydrosulphite, and the reducing action of a hydrosulphite solution on indigo is well known. So besides the depolarizing action of the indigo the secondary action of the hydrosulphite is utilized. A suspension of indigo in a warm sulphite solution electrolyzed at almost any electrode using almost any current density without a diaphragm gives excellent yields of indigo white. The electrolyte must remain neutral or become only very slightly alkaline during the course of the reduction. The anodic oxygen is often absorbed by the sulphite before it can oxidize the leuco compound. A typical example is: 300 g. of 20 per cent indigo paste are suspended in 415 cc. of 30 per cent sodium sulphate and 415 cc. of sodium sulphate solution (containing 10 per cent SO_2) and 55 cc. of 40 per cent sodium bisulphite with stirring and electrolyzed at 80° at a lead cathode after 24 ampere hours of current have passed the reduction is complete and the leuco compound can be filtered and washed clean with hot water. The bromo leuco derivatives of bromoindigo can also be prepared but with great difficulty in an acid electrolyte.[32] A method has been described by Chaumat in which the solid indigo is incorporated with a conducting material as graphite to form a cathode and electrolyzed using a sodium carbonate solution.[33] The sulphuric acid of indigo has also been reduced.[34]

A dye derived from callocyanine has been prepared by the electrolytic reduction of the condensation product of gallocyanine and *p*-phenylenediamine, according to the scheme:

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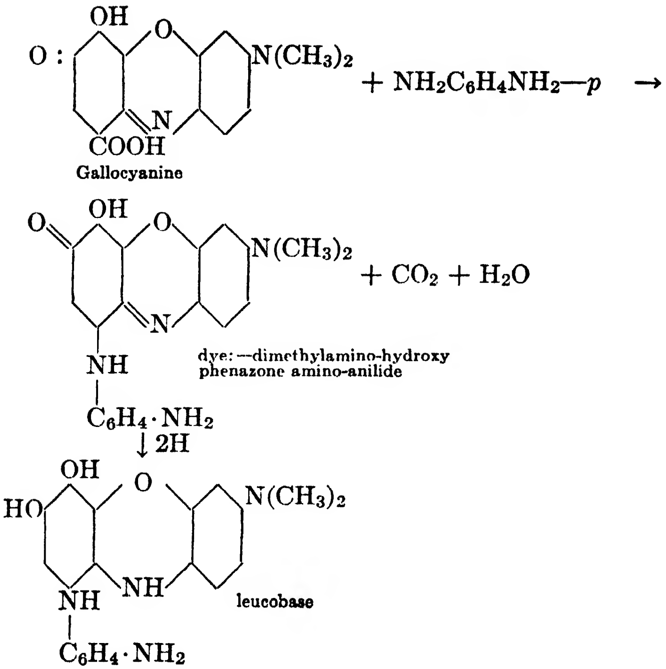
[30] A. Binz, Z. Elektrochem., **5**, 103 (1898); **9**, 599 (1903); Binz and Hagenbuch, ibid., **6**, 261 (1899).

[31] D.R.P. 139567 (1902).

[32] D.R.P. 145602 (1902), Meister.

[33] Chaumat, Compt. rend., **145**, 1419 (1907); Bull. de la Soc. internal des Electrochem., **8**, 13 (1908); E. P. 379041 (1907).

[34] Mullerus, Chem. Ztg., **17**, 1454 (1893).



The reduction is completed when the leuco compound is entirely soluble to give a green colored solution in the catholyte.[35]

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[35] D.R.P. 189941 (1906), Hoguenin and Co.; see D.R.P. 164320 (1905).

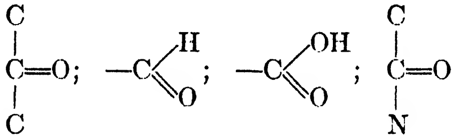
CHAPTER XV

THE REDUCTION OF THE CARBONYL GROUP

GENERAL

NEXT to the nitro compounds the most work has been done on the reduction of the carbonyl group. Many of the results of electrolytic reduction have not as yet been obtained by purely chemical reductions. Electrolytically, aromatic acids may be smoothly reduced to the corresponding primary alcohols, ketones to hydrocarbons, uric acid and its derivatives to their corresponding purones.

The carbonyl group means the $=C=O$ group situated in compounds as follows: between two carbon atoms (ketones); between a carbon and a hydrogen atom (aldehydes); between a carbon and an oxygen atom (acids or the carboxyl group); between a carbon and a nitrogen atom (acid amides, imides, and uric acid derivatives), i.e.,



With the exception of the aldehydes, the carbonyl group as a rule is very difficult to reduce. That the group is much more difficult to reduce than the nitro group in aromatic compounds is evidenced by the reduction of nitrobenzophenone to the corresponding *p*-aminophenol, the carbonyl group being left intact by the electrolytically evolved hydrogen.

The cathode material used is of great importance. There is some uncertainty about the use of the different metals as cathode material. But it is well known that a high cathodic overvoltage is always necessary. Therefore, the best cathodes are those made from lead, mercury and cadmium,[1] and to these thallium has lately been added.[2] Only in isolated instances which will be discussed later may those metals be used which have a low cathodic overvoltage such as platinum, nickel, and copper. The individuality of the metals even of high overvoltages often directs the reductions into unexpected channels. Sometimes metals of the same overvoltage do not have the same reducing ability

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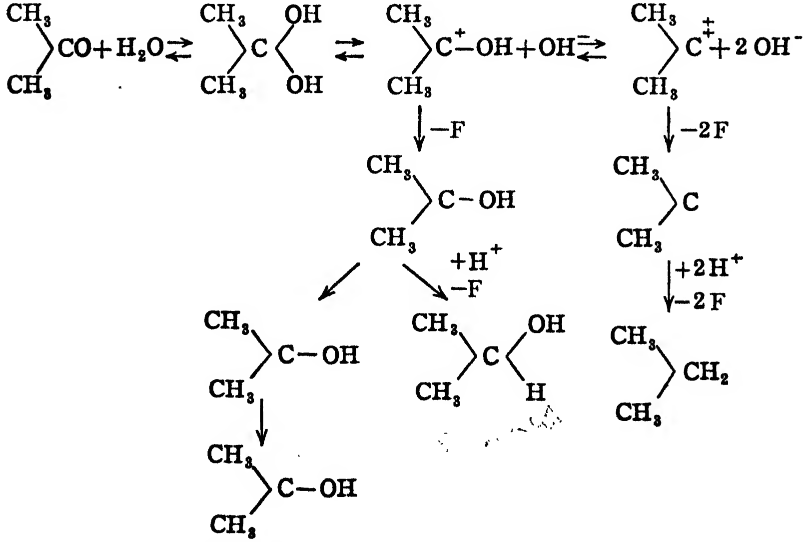
[1] Tafel, Ber., **33**, 2215 (1900); Tafel and Naumann, Z. physik. Chem., **50**, 717 (1905).

[2] G. Zerbes, Z. Elektrochem., **18**, 619 (1912).

and a certain reduction can be accomplished by the use of only one particular metal. When several reduction products are possible, the use of one metal causes the reaction to take one direction and the use of another metal causes the reaction to go in an entirely different direction. For the reduction of the carbonyl groups in general, a lead cathode prepared according to the method of Tafel[3] is the most desirable.

The formation of any one desired product is in many cases complicated by purely chemical changes, such as condensations and other reactions which lead to a variety of products. Examples of this are numerous. Acetone in the presence of alkali is changed to mesityl oxide and phorone; in an acid solution pinacol is changed to pinacolin; under certain conditions of current strengths benzophenone is reduced to benzpinacolin, there being in the acid solution a rearrangement of the intermediately formed benzpinacol. In order to reduce the possibility, conditions being favorable for the purely chemical changes to take place, it is best to work at rather low temperatures, or at least to prevent a local or even general overheating of the electrolyte by means of cathodic cooling.

Aldehydes and ketones form hydrocyanides and metallic hydrogensulphites which has led Erich Müller[4] to postulate the intermediate formation of a hydrate in the case of the electrolytic reduction of these compounds.



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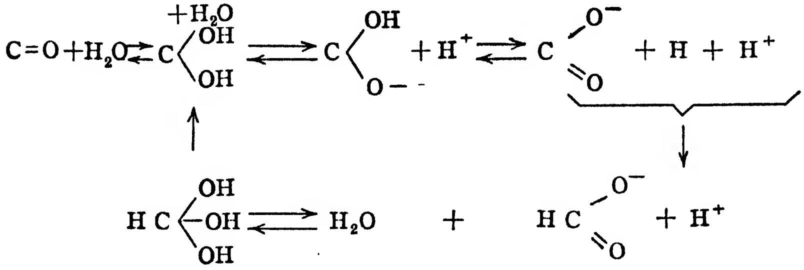
[3] Tafel, Ber., 33, 2224 (1900).

[4] E. Müller, Z. angew. Chem., 35, 698 (1923).

So the formation of the three compounds, pinacol, isopropyl alcohol and propane is explained and each compound is not an intermediate in the formation of the others.

The " hydroxidation " of carbon monoxide may also be schematized:



ALIPHATIC ALDEHYDES

Formaldehyde and acetaldehyde, the simplest of the aliphatic aldehydes, under certain circumstances are almost quantitatively reduced in alkaline solution at a copper or silver cathode. On the other hand in an acid solution they are not so easily reduced. Platinum and silver cathodes are without action, but copper or mercury cathodes lead to the formation of small quantities of methane when formaldehyde is the starting material, or to ethane when the acetaldehyde is used. This formation of a hydrocarbon is enhanced by the use of a cadmium cathode and so pure propane may be prepared in good quantities from the propionaldehyde, but not in such large quantities as are obtained by the reduction of acetone.[5] In the reduction of aliphatic aldehydes mercury and lead electrodes as a rule give excellent results but the yields are always lower than those obtained with a cadmium electrode. In the use of lead and mercury cathodes with aldehydes no metal alkyl compounds are formed as in the reduction of acetone at these electrodes.[6]

The industrial production of acetaldehyde and paraldehyde from acetylene has led to the development of several interesting methods for their reduction to a variety of products that are of immense value, especially alcohol and ethyl acetate.[7] According to these patents the electrolyte is 5–10 per cent sulphuric acid or sodium sulphate or orthophosphoric acid. The presence of a mercury salt in solution permits the passage of the acetylene directly into the electrolyte without being converted into acetaldehyde by a previous and separate process. The for-

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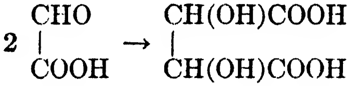
[5] F. Müller, Dissertation, Dresden, (1921).

[6] See later.

[7] Brit. P. 140115 (1918); 140527 (1919); Pascal, Swiss P. 88188 (1921).

mation of alcohol requires the use of a diaphragm to prevent anodic oxidation, but ethyl acetate is so stable that no diaphragm is needed when it is the end product. The cathode should be of lead, either pure, antimoniated, amalgamated or electroplated. Instead of the lead cathode a mercury cathode may be substituted. For non-solvent purposes the alcohol prepared at carbon or graphite cathodes is desirable as it has a very agreeable " bouquet." The temperature, the acidity, the concentration of the unreduced aldehyde, the current density and the duration of the reaction must be held as low as possible, as otherwise there will be too large a formation of undesired by-products such as 1-3-butandiol, crotonyl alcohol, butyl alcohol, and ethyl ether. The second patent above requires the raising of the temperature slowly as the electrolysis proceeds in order to insure the formation of reduction and polymerization products of crotonaldehyde in large yields; other conditions remaining the same as in the principal patent.[8]

Several patents have been granted for the electrolytic reduction of glyoxylates to tartrates in either neutral or alkaline solutions.[9] The acid or its salts or esters are reduced with excellent yields in an alkaline or neutral solution at cathodes of Cu, Au, Pt, Ag, Ni, Fe, or C, using a c. d. of 1–4 amperes, at a potential of 5 volts. The exact mechanism of this reaction is at present unknown. At least it combines a reduction with a condensation:



$$2\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{COOH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH(OH)COOH}\\ |\\ \mathrm{CH(OH)COOH}\end{array}$$

Of the hydroxy aldehydes only one compound has been studied. A solution of 20 per cent of glucose in 5 per cent sulphuric acid was reduced at Pb and graphite electrodes with an absorption of hydrogen to form a pentose and formic acid but not a hexahydric alcohol. There was some reaction between the hydrogen and the glucose because there was a loss of glucose as the reduction proceeded.[10] Mannitol [11] is claimed to be formed in a more dilute solution, but more recent work by Hibbert and Read [12] sustains the results of Findlay and Williams, at the same time discrediting the O'Brien Gunn patent claims.

Hibbert and Read [13] have attempted to measure the " reactivity of

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[8] See also B. P. 124195 (1918); Aciers, D.R.P. 328342.

[9] Can. P. 178644 (1917), M. Vaygouny; U.S.P. 1190845 (1916), L. H. Baekeland and A. H. Peters; Brit. P. 12467 (1912), Janson, Cobb, Pearson & Co.

[10] A. Findlay and V. H. Williams, Trans. Faraday Soc., **17**, 453 (1922).

[11] D.R.P. 140318 (1900), O'Brien Gunn.

[12] Hibbert and Read, J. Am. Chem. Soc., **46**, 983 (1924).

[13] Hibbert and Read, J. Am. Chem. Soc., **46**, 983 (1924).

the carboxyl group " or its " residual valency," which they consider as connected with the " tendency toward polymerization " by determining the lowering of the cathodic potential and the current efficiency obtained during the reduction of various aliphatic aldehydes. A pure, highly polished lead cathode was used for the reductions in twice normal sulphuric acid. The curves show the results of the reduction of the aldehydes. Unfortunately the results do not yield the information which was desired.

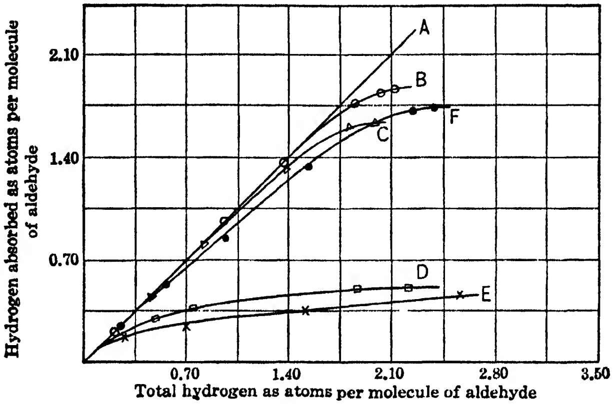


Fig. 12.

A—Curve of 100% efficiency
B—Acetaldehyde
C—Propionaldehyde
D—Isobutyraldehyde
E—Butyraldehyde
F—Acetaldol

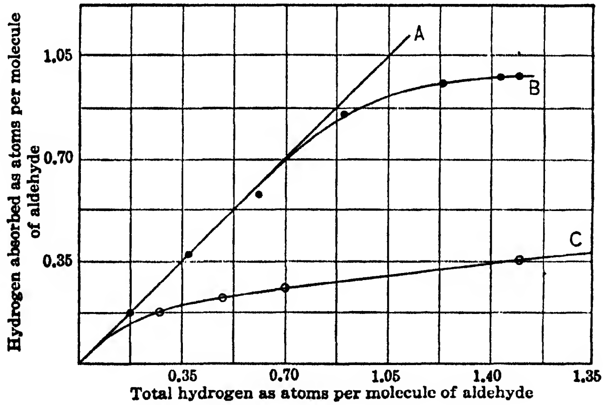


Fig. 13.

A—Curve of 100% efficiency *B*—Crotonaldehyde *C*—Butyraldehyde

The products of the reduction were not particularly studied except in the case of crotonaldehyde when dimethylcyclopentene aldehyde was formed by way of the dialdehyde.

In the following table regarding the lowering of the cathodic potential by the various aldehydes, the values given were those obtained immediately following the addition of the aldehyde and therefore represent the maximum lowering:[13]

TABLE XXVI

THE LOWERING OF THE CATHODIC POTENTIAL BY ALDEHYDES

The lowering of the cathodic potential at a lead cathode with c. d. 0.016 amp.; temp. 12°; concentration of the aldehyde 0.83 mol. per liter

Aldehyde	Potential Drop in Volts	Catholyte
Acetaldehyde	0.30	$2N \cdot H_2SO_4$
Propionaldehyde	0.30	$2N \cdot H_2SO_4$
Iso-butyraldehyde	0.17	$2N \cdot H_2SO_4$
Butyraldehyde	0.12	$2N \cdot H_2SO_4$
Acetaldol	0.25	$2N \cdot H_2SO_4$
Furfuraldehyde	0.58	$2N \cdot H_2SO_4$
Crotonaldehyde	0.58	$2N \cdot H_2SO_4$

Normal and iso-butyraldehyde and heptaldehyde were also reduced in twice normal sulphuric acid containing ethyl alcohol.

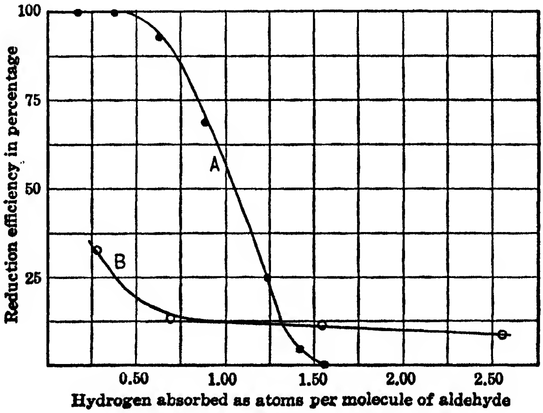


FIG. 14.

A—Crotonaldehyde *B*—Butyraldehyde

AROMATIC ALDEHYDES

The reduction of aromatic aldehydes is the parallel of the formation of pinacol; that is, the aldehyde is reduced to the corresponding hydro- and isohydrobenzoin:

$$2RCHO + 2H \rightarrow RCH(OH)\cdot CH(OH)R$$

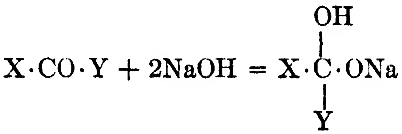
The reduction of benzaldehyde according to the method of Kauffmann[14] proceeds easily in a solution containing sodium bisulphite but better in alcoholic alkali:

$$2C_6H_5CHO + 2H \rightarrow C_6H_5CH(OH)\cdot CH(OH)C_6H_5$$

Benzoin, benzil, and acetophenone all give similar products to the above general formulae.

The scheme suggested by Law[15] for this reduction is:

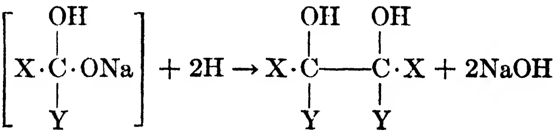
1.



$$X\cdot CO\cdot Y + 2NaOH = X\cdot\overset{OH}{\underset{Y}{C}}\cdot ONa$$

Probably the sodium hydroxide reacts with the aldehyde (possibly a hydrolysis reaction). This idea is supported by the easy solubility of benzaldehyde in sodium hydroxide solution containing a little alcohol. Then the compound so formed is readily reduced because two hydroxyl groups are present on one carbon atom which condition as a rule is unstable. The reaction then proceeding:

2.



$$\left[X\cdot\overset{OH}{\underset{Y}{C}}\cdot ONa\right] + 2H \rightarrow X\cdot\overset{OH}{\underset{Y}{C}}\text{——}\overset{OH}{\underset{Y}{C}}\cdot X + 2NaOH$$

The reduction proceeded in an alcoholic acid solution every bit as well as in alcoholic alkali, at cathodes either of nickel, copper, lead or platinum. It is advisable to work with a large c. d. in order to overcome the undesirable resinification of the aldehyde in the presence of the alkali. Some aldehydes as furfural and cinnamaldehyde yield only resins due to the side reactions of a purely chemical nature.

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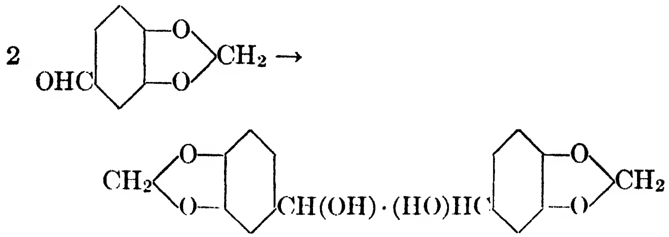
[14] Kauffmann, Z. Elektrochem., **2**, 365 (1895); **4**, 461 (1898).

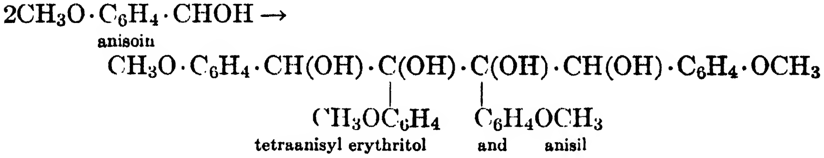
[15] H. D. Law, J. Chem. Soc., **89**, 1512 (1906).

The following hydrobenzoins were obtained in 70–90 per cent yields:



Piperonaldehyde → hydro- and isohydropiperonyloin.
Benzaldehyde → hydro- and isohydrobenzoin.
Cuminaldehyde → hydro- and isohydrocuminoin.
Anisaldehyde → hydro- and isohydroanisoin.
Vanillin [16] → hydrovanilloin.
Salicylaldehyde → hydrosalicyloin.

Furfural and cinnamaldehyde yielded only tarry products which could not be purified sufficiently to isolate a definite compound. In several other cases the benzoin was further reduced and condensed with itself to form an erythritol derivative:



$$\underset{\text{anisoin}}{2CH_3O \cdot C_6H_4 \cdot CHOH} \rightarrow \underset{\text{tetraanisyl erythritol}}{CH_3O \cdot C_6H_4 \cdot CH(OH) \cdot \underset{CH_3OC_6H_4}{\overset{|}{C}}(OH) \cdot \underset{C_6H_4OCH_3}{\overset{|}{C}}(OH) \cdot CH(OH) \cdot C_6H_4 \cdot OCH_3} \text{ and anisil}$$

Cuminoin → tetracuminyl erythritol.
Piperonyloin → tetrapiperonyl erythritol + piperonil.

Law [17] has assumed that the presence of such groups as the —OH, —OCH_3 and $=O_2CH_2$ groups on the benzene nucleus change the direction of the predominating reaction to some extent. He has come to the conclusion that several things may change the course of the reaction. The aldehydes which most easily resinify under the action of an electrical strain contain an unsaturated carbon-carbon linkage and from this point of view the aromatic compounds must be regarded as a class intermediate between the saturated and the unsaturated substances. Benzaldehyde partially resinifies at an electrode with a high cathodic potential such as lead. So with *p*-tolualdehyde and anisalde-

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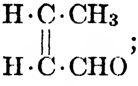
[16] See also work of Schepps, page 297.

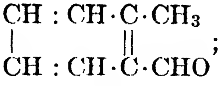
[17] Law, loc. cit.

hyde, but especially with *o*-tolualdehyde (II) and *m*-tolualdehyde (III), complete resinification takes place even with platinum and nickel cathodes. The latter substances behave like true unsaturated compounds and are comparable to crotonaldehyde (I) which they resemble closely in structure:



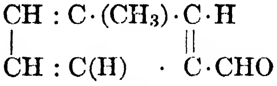
$$\begin{array}{c} H\cdot C\cdot CH_3 \\ \| \\ H\cdot C\cdot CHO \end{array};$$

I



$$\begin{array}{ll} CH : CH\cdot C\cdot CH_3 \\ | \quad\quad\quad\ \ \| \\ CH : CH\cdot C\cdot CHO \end{array};$$

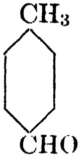
II



$$\begin{array}{ll} CH : C\cdot (CH_3)\cdot C\cdot H \\ | \quad\quad\quad\quad\quad\quad\ \ \| \\ CH : C(H) \quad \cdot\ C\cdot CHO \end{array}$$

III

The combined influence of the aldehyde and the methyl groups tend to make the benzene nucleus an unsaturated aggregate, but this action will be felt only in an unsymmetrical configuration. *o*-Tolualdehyde (VI) is the least symmetrial, therefore, mostly easily resinified; the *p*-tolualdehyde (IV) behaves like an ordinary ring compound. If we take (V) and (VI) and introduce a counter influence by means of another meta substituent, a symmetrical arrangement results with the almost complete loss of the tendency to resinify, thus from (VII) a well-crystallized substance is obtained on reduction, but (VIII) yields 40 per cent resin due to only a partial neutralization (it being an almost symmetrical compound). The groups —OH, —OCH$_3$, :O$_2$CH$_2$ also have a marked effect on the character of the benzene nucleus:



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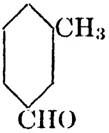

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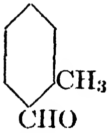

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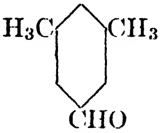
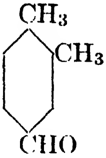
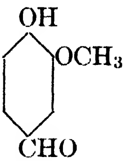


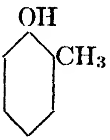
VII



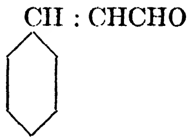
VIII



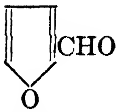
X



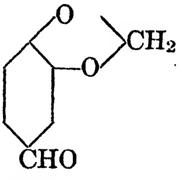
IX



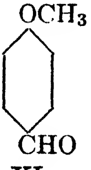
XIV



XIII



XII



XI

(IX) gives non-crystalline substances unless the hydroxyl group is removed during the reaction. (X) is nearly symmetrical and gives 5 per cent crystalline product in alkaline solution. (XI) yields only crystalline substances. (XII) resinfies in an acid solution. (XIII) is symmetrical and unsaturated and (XIV) is unsaturated, so both easily resinify. Thus it seems quite clear that such groups which can bring about resinification when substituted in the benzene nucleus do so most readily when arranged so as to distort the whole molecule, a condition fulfilled with an asymmetrical grouping.[18]

The following reductions were accomplished in an alcoholic 5 per cent KOH solution:

p-tolualdehyde → hydrotoluoin + *p*-dimethylstilbene + isohydrotoluoin.
m-tolualdehyde → resinified in methanol and ethyl alcohol, sodium hydroxide and a solution of potassium carbonate and acetate.
o-tolualdehyde → resinified as did *m*-tolualdehyde
3,5-dimethylbenzaldehyde → hydroxyloin + isohydroxyloin + 5 per cent resin.
2,4-dimethylbenzaldehyde → hydro and isohydroxyloin + 50 per cent resin.

In an acid solution the reaction is entirely different, the products being primary alcohols, saturated and also unsaturated hydrocarbons. The reduction is sensitive to a change in temperature which is not the case when the electrolyte is alkaline. At ordinary temperature benzaldehyde yields benzyl alcohol but as the temperature rises hydrobenzoins are formed.

From the results of the electrolysis it seems that acids do not act on the aldehyde group as do alkalies. When reduction takes place the double link is broken forming a substance of the general formula: —RCHO— which immediately unites with two atoms of hydrogen to form RCH_2OH. At the same time the union of two radicals —RCH(OH)— is prevented by the close proximity of the carbon and oxygen. It is possible however to break both links and completely remove the oxygen, so destroying its influence. In this latter case we have:

$$RCH : = RCH : CHR$$
$$RCH : + H = RCH_2CH_2R$$
$$RCH_2 - + H = RCH_3$$

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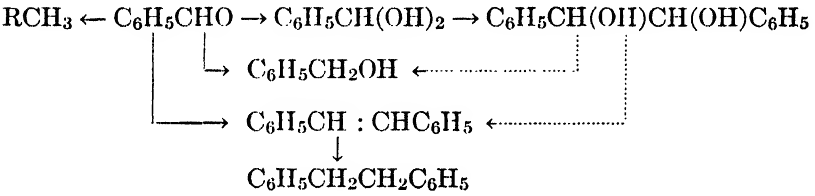
[18] Law, J. Chem. Soc., **91**, 748 (1907).

that is, from benzaldehyde we may obtain stilbene, toluene, or dibenzyl. The two former have been identified in the reaction products and the latter, probably, also was present. As the temperature of the acid mixture rises the reaction of the benzaldehyde with the sulphuric acid makes itself more and more apparent and derivatives of dihydric alcohols are probably formed:

$$RCHO + H_2O = RCH(OH)_2$$

Thus as in the case of the alkaline solutions the close proximity of the carbon and oxygen atoms has been destroyed, and readily reducible compounds have been formed. The reduction then proceeds:

$$RCH(OH)_2 + H \rightarrow RCHOH \rightarrow RCH(OH) \cdot CH(OH)R$$



(The dotted lines represent a very slow reaction.) . This is analogous in every way to the reduction of nitro compounds, and takes place with almost all aldehydes except salicylaldehyde, vanillin, and piperonaldehyde which resinify.

Using 250 cc. of 5 per cent alcoholic sulphuric acid as the electrolyte and a c. d. of 5 amperes passing 22 ampere hours of electricity at a copper cathode the following results were obtained: [19]

TABLE XXVII

With Benzaldehyde

Subst.	Temp.° C.	Benzene	Benzyl Alcohol	Hydrobenzoin	Stilbene
26 g.	5	1 g.	9 g.	6 g.	3–4 g.
26	17	1	5–7	8–9	3–4
26	34	1	3–4	15	3–4

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[19] Law, loc. cit.

TABLE XXVIII

With *p*-tolualdehyde

Subst.	Temp. ° C.	Toluene	Xylyl Alcohol	Hydro-toluoin	*p*-Dimethyl-stilbene
24 g.	14	1 g.	10 g.	6 g.	4 g.
24	35	1	4	13	4

Hydrobenzoins were reduced to benzyl alcohol and stilbene:

m-tolualdehyde = *m*-xylene + *m*-xylyl alcohol + $\left\{\begin{matrix} m\text{-dimethyl-} \\ \text{stilbene} \end{matrix}\right\}$ + resin.

o-tolualdehyde = *o*-xylene + *o*-xylyl alcohol + isomeric hydrotoluoins + *o*-dimethyl stilbene + resin.

2,4-dimethylbenzaldehyde = ψ-cumene + ψ-cumyl alcohol + tetramethyl-stilbene.

3,5-dimethylbenzaldehyde = mesitylene + mesityl alcohol + isohydroxyloin.

anisaldehyde = dimethoxystilbene + anisic alcohol + anisole.

cuminaldehyde = cymene + cuminyl alcohol + diisopropylstilbene.

Trouble is caused in many cases by the formation of resins during the electrolysis, probably due to the action of the free alkali on the aldehyde. The formation of resins is a complication that hindered the successful reduction of nitro derivatives for a long time. It was from the work of Elbs[20] that a method was finally developed for the easy reduction of nitro derivatives without the formation of these resins. He used ethyl acetate as the solvent. This same method is used in the reduction of aromatic aldehydes according to the method of Law.[21] The configuration of the aldehydes in question is not the only factor influencing the course of these reductions. The nature of the electrolyte also has a great influence. The reduction product varies according to the acidity or alkalinity of the electrolyte. An effective neutral solvent has not been found, but a compromise has been developed which is composed of water, ethyl acetate and alcohol with the addition

[20] Elbs, Ber., **38**, 4012 (1905). See page 254.

[21] H. D. Law, J. Chem. Soc., **99**, 113 (1911).

of potassium acetate as the conducting medium. The free alkali generated during the course of the electrolysis at the cathode in a divided cell cannot under these conditions accumulate, but is utilized in hydrolyzing the ethyl acetate. The amount of resin formed decreases and crystalline substances may be obtained which cannot be identified under other circumstances. *p*-Chlorobenzaldehyde yields *p*-chlorotoluene, *p*-chlorobenzyl alcohol, *p,p'*-dichlorohydrobenzoin, and *p, p'*-dichlorostilbene. *m*-Chlorobenzaldehyde resinifies in both acid and alkaline solution but in neutral solution yields *m*-chlorobenzyl alcohol with *m, m'*-dichlorohydrobenzoin. *o*-Chlorobenzaldehyde resinifies both in an acid and alkaline solution but in a neutral solution yields *o*-chlorobenzyl alcohol and resin. Similarly in a neutral solution *o*-tolualdehyde forms isohydrotoluoin, but *m*-tolualdehyde yields *m*-xylene and *m*-methyl benzyl alcohol. This work supports the assumption that the more unsymmetrical the molecule the greater the resinification.

Tafel and Schepps,[22] with the method and apparatus which the former used for the reduction of ketones,[23] studied in particular the reduction of anisaldehyde in an aqueous alcoholic solution using sulphuric acid as the electrolyte with a cadmium cathode. They expected this method to work as well, if not better, with aldehydes than it did with ketones. The products isolated were: anisic alcohol, *p*-methyl anisole, hydroanisoin, dimethoxystilbene, dimethoxydibenzyl. The complete reduction of the aldehyde group to the methyl group takes place to a much greater extent with a cadmium cathode than with other metals. Under the conditions employed by Law,[24] a 37 per cent yield of *p*-tolyl methyl ether was obtained and the yield could be further increased to 50 per cent by increasing the c. d. while the temperature remained below 25°. Only a little anisic alcohol is formed, which is contrary to the results obtained by Law with a copper cathode.[25] The total quantity of bimolecular compounds increases very rapidly with a rise in temperature. At 35° the amount formed is independent of the strength of the current within fairly wide limits. Only 0.5–7.0 per cent of resin is formed but this value increases as the electrolyte becomes acid.

A more complete study [26] of reductions at a cadmium or mercury cathode has been reported. As the number of carbon atoms in the aldehyde increases a higher current density is required for the reduction.

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[22] Tafel and Schepps, Ber., **44**, 2148 (1911); **46**, 2564 (1913).

[23] Tafel, Ber., **42**, 3146 (1909); **33**, 2215 (1900).

[24] Law, J. Chem. Soc., **89**, 1512 (1906); **91**, 748 (1907); **99**, 1113 (1911).

[25] Law, loc. cit.

[26] W. Schepps, Ber., **46**, 2564 (1913); much valuable experimental data is given in this paper.

Propylaldehyde is less easily reduced than acetone but forms no alkyl metal compounds as does acetone. The following reductions were studied: Propylaldehyde, heptaldehyde, benzaldehyde, salicylaldehyde, protocatechuic aldehyde piperonal, *p*-dimethylaminobenzaldehyde. In many cases the results of Schepps and Law do not agree, even under seemingly similar conditions.

THE REDUCTION OF KETONES

The reduction of ketones may proceed in any one or more of three directions, namely:

(1) Formation of a pinacol;
(2) Formation of a secondary alcohol;
(3) Formation of a hydrocarbon.

Of these three reactions the third is not a continuation of the second because as a rule the secondary alcohols are not very easily reduced by electrolytic methods,[27] though there are exceptions. Each reaction has as its starting material the carbonyl compound itself, and the reaction which takes place is dependent on the kind of electrode, the condition of the electrolyte (that is whether acid, alkaline, or neutral) and the environment of the $=CO$ group.[28]

Usually the pinacol and the alcohol are the main products of the reaction and are formed in quantities depending on the conditions of the electrolysis and on the constitution of the ketone. According to the investigations of Brand and Elbs,[29] in an alkaline solution with a lead cathode the aliphatic and pure aromatic ketones are reduced to the corresponding alcohol,[30] while in an acid solution a mixture of the pinacol and the alcohol are the result (aromatic ketones usually produce only the pinacol). The cathode material also has a great influence on the results of the reduction. In a sulphuric acid solution acetone yields mostly the saturated hydrocarbon at a cadmium cathode, while at a lead or mercury cathode the products are isopropyl alcohol, pinacol and hydrocarbon and metallic alkyl compounds.[31]

At a copper cathode Michler's ketone yields a pinacol, and at a lead cathode under exactly similar conditions yields a secondary alcohol,

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[27] Tafel and Schepps, Z. Elektrochem., **17**, 972 (1911).

[28] Tafel and Emmert, ibid., **17**, 569 (1911).

[29] Brand and Elbs, ibid., **8**, 783 (1902).

[30] This is like the reduction with sodium or zinc plus alkali in the purely chemical method.

[31] J. Tafel and W. Schepps, Z. Elektrochem., **17**, 972 (1911).

while at a nickel cathode both alcohol and pinacol are formed in almost equal amounts.[32]

Only a little work has been done on the change of products as the experimental conditions change. Practically nothing has been reported on the effects of current density, duration of the reaction, and temperature on the products of the reduction. It seems, however, that raising the temperature and the current density in general has the effect of increasing the percentage of pinacol formed at the expense of the secondary alcohol.

Aliphatic Ketones.—In general, aliphatic ketones as acetone do not lend themselves to reduction in an alkaline solution because of the ease with which they form condensation products such as phorone and mesityl oxide. However, in a sulphuric acid solution they respond to electrolytic reduction though they withstand the reducing action of zinc and acetic acid. At a lead cathode acetone is reduced to isopropyl alcohol and pinacol with mesityl oxide and phorone as by-products.[33]

Tafel and Schmitz [34] were able to prevent the formation of the pinacol and so increase the amount of isopropyl alcohol formed by using a mercury cathode. The yields were almost 100 per cent material and about 50 per cent current yields. By electrolyzing a 10 per cent solution of acetone in 30 per cent sulphuric acid at a cadmium cathode at room temperature, a current yield of 90 per cent of propane contaminated with only traces of hydrogen was obtained.[35] According to this method methyl ethyl ketone is similarly reduced to the hydrocarbon. The higher ketones as methyl isoamyl ketone require a very much greater current density before good yields of the hydrocarbon are obtained. At a lead cathode [36] methyl ethyl ketone is reduced to a mixture of secondary butyl alcohol and methyl ethyl pinacol in small yields.[37] At a cadmium cathode, isoamyl methyl ketone yields isoheptane when the temperature is 60° and the current density is high.[38] In general the reduction of ketones, especially the higher ketones, is one of the best methods for the preparation of many of the saturated hydrocarbons which are very difficult to prepare by any other method.

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[32] Escherich and Moest, ibid., **8**, 843 (1902).

[33] Elbs and Brand, ibid., **8**, 783, 1902; E. Merck, D.R.P. 113719 (1899). See also Elbs, ibid., **7**, 644 (1901); Elbs and Schmitz, J. prakt. Chem., [2], 51, 591 (1895); Elb, "Übungsbeispiele," p. 124; D.R.P. 324919, 324920, 306304 (1917–1918), Bayer.

[34] Tafel and Schmitz, Z. Elektrochem., **8**, 288 (1902).

[35] Tafel and W. Schepps, Z. Elektrochem., **17**, 972 (1911).

[36] Brand and Elbs, ibid., **8**, 783 (1902); Merck D.R.P. 113719 (1899).

[37] A Pb cathode in an alkaline solution does not work; however a sulphuric acid solution is somewhat better.

[38] Tafel, Ber., **42**, 3146 (1909).

The method of Hibbert and Read [39] was also applied to the reduction of ketones with results similar to those obtained in the reduction of aldehydes; that is no conclusions concerning the reactivity of the carbonyl group in ketones could be drawn from cathodic potential lowering and current efficiency.

The following table is self-explanatory.

TABLE XXIX

THE LOWERING OF THE CATHODIC POTENTIAL BY KETONES

The lowering of the cathodic potential at a Pb cathode with c. d. 0.016 amp.; temp. 12°; conc. of ketone 0.83 mol, per liter.

Ketone	Lowering in Volts	Catholyte
Dimethyl ketone	0.06	$2N \cdot H_2SO_4$
Methylethyl ketone	0.06	$2N \cdot H_2SO_4$
Methylpropyl ketone	0.04	$2N \cdot H_2SO_4$ + 50 per cent alcohol
Diacetone alcohol	0.15	$2N \cdot H_2SO_4$ + 50 per cent alcohol

The curves show the results of this work.

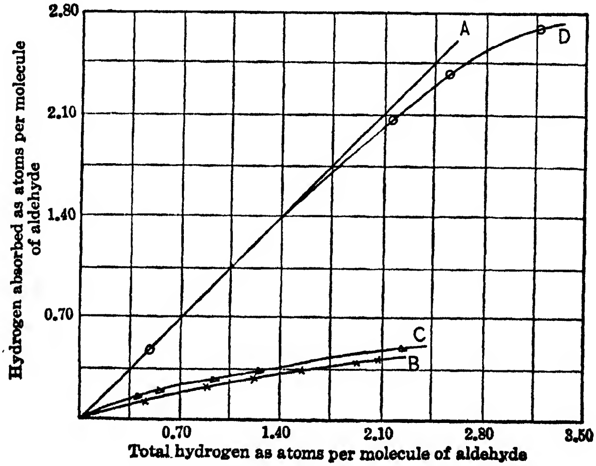

FIG. 15.

A—Curve of 100% efficiency
C—Dimethyl ketone
B—Methyl ethyl ketone
D—Diacetone alcohol

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[39] See page 289 of this book.

The Formation of Metallic Alkyl Compounds During the Reduction of Aldehydes and Ketones.—In many cases the reduction products of aldehydes and ketones in an acid solution are contaminated by organic compounds containing metallic atoms, especially lead. Law found that the members of the citral series of aldehydes were particularly capable of forming lead complexes,[40] which are red oils containing considerable quantities of the combined metal. It also seems that these complexes are peculiar to the aliphatic series alone; the aromatic compounds invariably leaving the cathode unattacked.

In the electrolytic reduction of methyl ethyl ketone in sulphuric acid solution at 40–60° with a cathodic c. d. of 25 amperes large quantities of a red oil insoluble in water are formed.[41] Methyl isoamyl ketone at a lead cathode yields mostly isoheptane but also a red oil which is supposed to be a lead complex.[42] Acetone similarly yields a red oil which was shown to be composed of a yellow oil, lead tetra-isopropyl, and a red colored fraction containing about 20 per cent of lead di-isopropyl to which the color of the original oil was due. Both of these compounds were characterized by the products which they yielded on being brominated and chlorinated.[43] Lead tetra-secondary butyl and lead tetra-di-gamma-amyl have also been prepared as red oils.[44]

The formation of these metallic complexes so far has only been found in the case of the reduction of aliphatic aldehydes and ketones when the cathodes were of lead or mercury; the noble metals and even cadmium fail to give analogous compounds. Mercury di-secondary butyl has been found by Tafel during the reduction of methyl ethyl ketone in a sulphuric acid solution. The equation suggested by him[45] is:

$$2C_4H_8O + Hg + 6H \rightarrow (C_4H_9)_2Hg + 2H_2O$$

From the standpoint of the ionic theory this reaction is rather anomalous. The mercury going to the anode against the direction of the current. However the explanation may be lacking, the experimental evidence holds.

The preparation of these metallic alkyls is accompanied by some inconvenience due to the poisonous nature and very unpleasant odor of their vapors. The yields of these compounds seem to be enhanced by the use of a cathode made from a lead-copper alloy rich in lead. The

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[40] Law, J. Chem. Soc., **101**, 1016 and 1544 (1912).

[41] J. Tafel, Ber., 39, 3626 (1906); ibid., 45, 3321 (1912).

[42] J. Tafel, Ber., **42**, 3146 (1909).

[43] Tafel, Ber., **44**, 323 (1911); Tafel and Schepps, Z. Elektrochem., **17**, 972 (1911).

[44] Renger, Ber., **44**, 337 (1911).

[45] Tafel, Ber., **39**, 3626 (1906); Taicl and Schepps, loc. cit.

electrode should be so suspended in the catholyte that the oil as rapidly as it is formed may fall to the bottom of the vessel, leaving the surface of the metal always clean.[46]

Aromatic Ketones.—Aromatic ketones upon reduction do not form condensation products as do the aliphatic ketones. As a rule in an alcoholic solution of sodium acetate the only product is a secondary alcohol of the benzohydrol series.

When a solution of benzophenone in alcoholic sodium acetate is electrolyzed at the boiling point on a lead cathode a 90 per cent material yield of benzhydrol is obtained.[47]

The hydrol is formed according to the equation:

$$C_6H_5 \cdot CO \cdot C_6H_5 + 2H \rightarrow C_6H_5CH(OH)C_6H_5$$

Quantitive yields are also obtained with the following ketones in an alkaline solution:

phenyl-*p*-tolyl ketone = phenyl-*p*-tolylcarbinol;
phenyl-*m*-xylyl ketone = phenyl-*m*-xylylcarbinol;
phenyl-α-naphthyl ketone = phenyl-α-naphthylcarbinol;
tetramethyldiaminobenzophenone = tetramethyldiaminobenzohydrol.[48]

At room temperature the reduction of the ketone in an alcoholic acid solution yields similar results. At the boiling temperature the reaction yields the pinacol, but if the pinacol is sensitive to the presence of an acid the pinacoline is the final product. So it has been found that benzophenone in a warm alcoholic sulphuric acid solution yields mostly β-benzpinacolin while in an acetone-phosphoric acid solution it yields the α-benzpinacolin though a higher current density is required in the case of the phosphoric acid than with the sulphuric acid electrolyte:

$$\begin{aligned} 2C_6H_5 \cdot CO \cdot C_6H_5 + 2H &\rightarrow (C_6H_5)_2C(OH) \cdot C(OH)(C_6H)_2 \\ &\rightarrow (C_6H_5)_3C \cdot CO \cdot C_6H_5 + H_2O \end{aligned}$$

p-Hydroxybenzophenone is not reduced in alkaline solution but is reduced in alcoholic sulphuric acid to *p*-hydroxybenzpinacol. Similarly, phthalyl-*p*-aminobenzophenone yields very little of the pinacol.[49] A solution in acetic acid at moderate temperatures yields only the pinacol. Sometimes the pinacol is not rearranged to the pinacolin. Thus

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[46] D.R.P. 303303 (1917), Bayer.

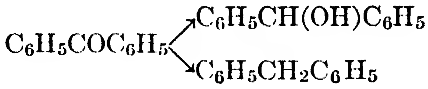
[47] Elbs and K. Brand, Z. Elektrochem., **8**, 783 (1902); Elbs, "Übungsbeispiele," p. 123.

[48] Dibenzyl ketone was also present.

[49] Elbs. and Brand, loc. cit.

in a warm sulphuric acid solution phenyl *p*-tolyl ketone gives 80 per cent material yields of phenyl *p*-tolyl pinacol [50] because this latter product is not sensitive to the presence of the acid.

When the reduction is carried out at low temperatures and with a small current density in an acid solution, the formation of the pinacol is always subordinated in favor of the benzohydrol. At 0° with a small current density benzophenone yields no pinacol, the product being benzohydrol and diphenylmethane: [51]



$$C_6H_5COC_6H_5 \begin{cases} \rightarrow C_6H_5CH(OH)C_6H_5 \\ \rightarrow C_6H_5CH_2C_6H_5 \end{cases}$$

By this same method *p*-hydroxybenzophenonebenzoate in sodium acetate solution yields only the carbinol.

This latter work of Elbs and Brand has been repeated by Cohen,[52] who also worked at low temperatures and low current densities, but was unable to detect the formation of the benzohydrol, obtaining only pinacol and some β-pinacolin.

The reduction of tetramethyl-*p*-diaminobenzophenone (Michler's ketone) is of interest because the cathode material enters into the reaction. At a platinum or copper cathode there is a great deal of pinacol formed but at a lead or mercury cathode only the hydrol is formed; a nickel cathode yields about equal amounts of the hydrol and pinacol.[53] The hydrol is not attacked by the anodic oxygen and there is a chance that the reduction may form some tetramethyldiaminodiphenylmethane. Therefore if the electrolyte contains at the start both Michler's ketone and the diphenylmethane derivative a diaphragm need not be used and the reduction will form the hydrol while the anodic oxygen oxidized the diphenylmethane derivative to the hydrol.[54] The method is to electrolyze in a sulphuric acid solution between lead electrodes so that the two reactions take place simultaneously.

Tetramethyl-*m*-diaminoditolyl ketone has been similarly reduced to the corresponding carbinol by Reitzenstein and Runge.[55] Anthraquinone in H_2SO_4 is reduced to a mixture of anthrols and hydroanthrols.[56]

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[50] Elbs, Übungsbeispiele, p. 122.

[51] Elbs and Brand, loc. cit. See also Kauffler, Z. Elektrochem., **13**, 633 (1907); Müller, ibid., **16**, 236 (1910).

[52] W. D. Cohen, Rec. trav. chim., **38**, 72 and 113 (1919).

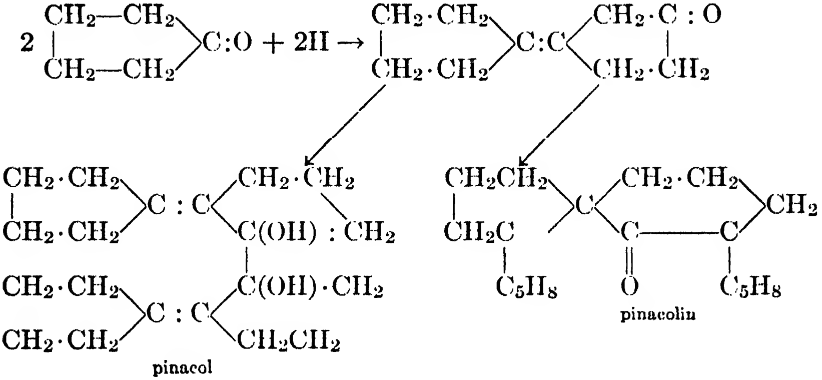
[53] Escherich and Moest, Z. Elektrochem., **8**, 849 (1902); D.R.P. 133896 (1901); Elbs, " Übungsbeispiele," p. 125.

[54] Reitzenstein and O. Runge, J. prakt. Chem., [2], **71**, 113 (1905).

[55] Reitzenstein and Runge, loc. cit, p. 103.

[56] Perlin, Dissert., Berlin (1899).

The cycloparaffin derivatives behave very much like the aromatic compounds: Cyclopentanone has been reduced in an alkaline solution to cyclopentylidene-cyclopentanone together with some complex compounds which are supposed to be tetracyclopentane derivatives. It is very probable that in the course of the reduction the first reaction is the condensation of two molecules of the pentanone and then this new compound further condenses to give the pinacol and the pinacolin. At any rate the two unknown compounds are supposed to be a pinacol and a pinacolin respectively. That is the reactions may be expressed as being:[57]



The ease with which quinone is reduced at a cathode to quinol has been discussed on page 103, et seq., in connection with the oxidation of benzene, etc. Excellent yields of quinol may be obtained by the reduction of quinone suspended in an acid solution using titanous chloride as the carrier. A platinum or any other indifferent cathode in the presence of the carrier yields only the quinol but without the carrier the reduction stops at the quinhydrone stage.[58]

In an attempt to stimulate the industrial applications of electrolytic methods Lowy and Ebberts started an investigation of the reduction of some soluble anthraquinone derivatives with the view to extending the work to vat dyes of this series. They started with β-anthraquinone sulphonic acid and reduced it in an acid solution at a platinum cathode; in a second case they started with the sodium salt and reduced it at an iron cathode. In each case there were changes in color that indicated the course of the reduction but no definite compounds were isolated

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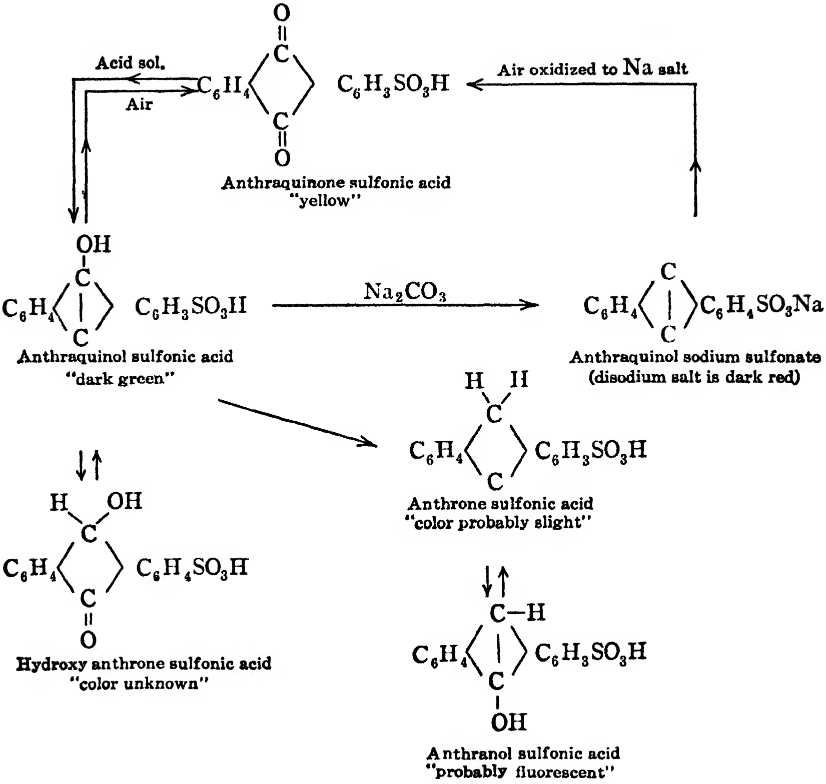
[57] M. Godechot and F. Tarboury, Bull. soc. chim., [4], **13**, 12 (1913).

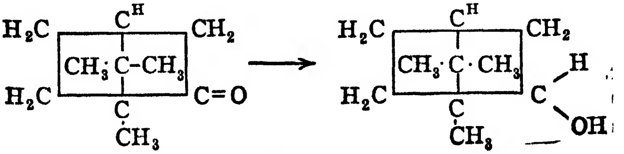
[58] D.R.P. 168273 (1903); F.P. 338934 (1903), Meister. See also Kempf, D.R.P. 117251 (1899), page 103; Cross, Bevan and Heidelberger, Ber., **33**, 2015 (1900) and Martinon, Bull. soc. chim. [2], **43**, 156 (1885).

from the reduced solutions. The scheme of reduction is indicated tentatively as follows:[59]



The continuation of this work into the field of anthraquinone vat dyes will be awaited with interest.

Hydroaromatic Ketones.—The methods of electrolytic reduction have been applied with good results to the hydroaromatic ketones, especially to the congeners of the camphors. Camphor is not easily reduced at a lead cathode, but at a mercury cathode when the electrolysis is carried on with an alcoholic solution of camphor in 75 per cent HCl and at 22° a yield of 45 per cent of borneol is obtained.[60]



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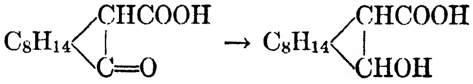
[59] Trans. Am. Electrochem., Soc., 45, 173 (1924).

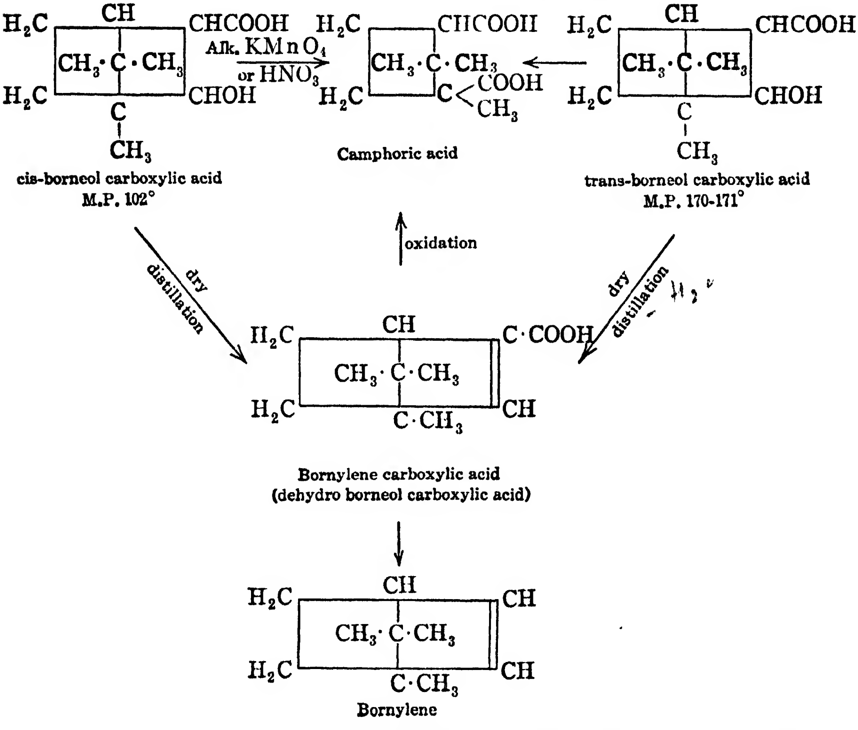
[60] Tafel and Schmitz, Z. Elektrochem., 8, 288 (1902).

In nearly all cases the secondary alcohol is obtained. This is not always possible by purely chemical reductions.

By reduction in potassium carbonate solution with a potassium amalgam cathode, camphor carboxylic acid yields a mixture of borneol carboxylic acid and an isomer which crystallized in needles melting at about 101°. These two isomerides bear the relation *cis* and *trans* to each other. The course of their reactions is as follows: [61]



$$C_8H_{14}\left\langle \begin{array}{l} CHCOOH \\ | \\ C{=}O \end{array}\right. \rightarrow C_8H_{14}\left\langle \begin{array}{l} CHCOOH \\ | \\ CHOH \end{array}\right.$$



The electrochemical reduction of camphonic acid yields a mixture of the two isomers of camphonolic acid.[62]

Other cyclic ketones respond very nicely to electrolytic reduction. Triacetone amine, a condensation product of acetone and ammonia, when reduced in a 10 per cent ammonium sulphate solution yields the corresponding secondary alcohol.[63]

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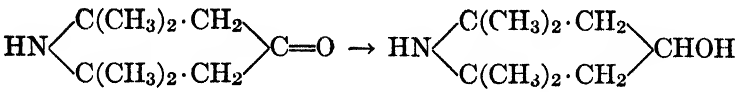
[61] Bredt, Ann., **348**, 200 (1906); ibid., **366**, 1-70 (1909).

[62] Bredt, J. prakt. Chem., [2], 84, 786 (1911).

[63] D.R.P. 95623, E. Schering.



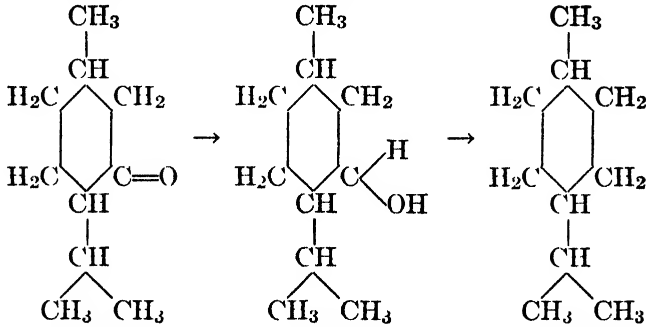
$$HN\begin{cases}C(CH_3)_2\cdot CH_2\\C(CH_3)_2\cdot CH_2\end{cases}C{=}O \rightarrow HN\begin{cases}C(CH_3)_2\cdot CH_2\\C(CH_3)_2\cdot CH_2\end{cases}CHOH$$

The reduction of tropinon at a lead cathode leads to the formation of tropin and pseudotropin. In an alkaline solution the main product is the former while in an acid solution the latter predominates. These two isomeric alcohols are easily separated by making use of their differential solubility in ether.[64] Besides these two products tropane has also been identified as a by-product.[65]

It is not often that the reduction of a ketone leads to the formation of the oxygen-free compound. However, it sometimes occurs as when methyl granatonine is reduced to methyl granatanine.[66]

In an entirely analogous manner it has been demonstrated that under suitable conditions pseudopelletierine may be reduced to the corresponding hydrocarbon in 68.7 per cent yields; a by-product being the corresponding secondary alcohol.

It seems that the hydroaromatic ketones undergo a more complete reduction than the other types of ketones. Menthone is reduced to menthol and menthane in current yields of not more than 25 per cent, when alcoholic sulphuric, or hydrochloric acid is used as the electrolyte. The reduction is found to take place best at cathodes of lead or tin amalgams. Pure mercury is the best cathode, but then the amounts of menthane formed are very large. If menthane is formed during the reaction it rises as an oil to the surface of the electrolyte while the menthol remains dissolved in the electrolyte: [67]



menthone menthol menthane

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[64] D.R.P. 96362 (1897); E. Schering, Friedländer 6, 1149; D.R.P. 115517 (1900); Merck, Friedlander 7, 1149; D.R.P. 128855 (1901).

[65] R. Willstatter and H. Veraguth, Ber., 38, 1985 (1905).

[66] A. Piccinini, Gazz. chim. ital., **32**, i, 260 (1902).

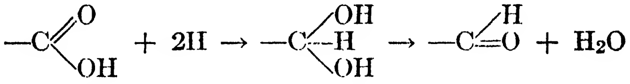
[67] Schall and Krist, Z. Elektrochem., **29**, 537 (1923); H. D. Law, J. Chem. Soc., **101**, 1016 (1912); M. Matsui and S. Shimisu, Mem. Coll. Sci. Kyoto Imp. Univ., **4**, 245 (1920).

Santonine has been reduced in an acetic acid solution on a platinum cathode.[68]

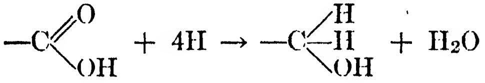
Mixed Aliphatic-aromatic Ketones.—Acetophenone may be reduced either in acid or neutral solutions to the corresponding pinacol or carbinol with varying yields.[69]

CARBOXYLIC ACIDS AND THEIR ESTERS

Aliphatic Acids.—*General.*—The carbonyl portion of the carboxyl group,—COOH, responds to electrolytic reduction with the possibility of two reactions taking place; the reduction may stop at the aldehyde or it may continue to the saturated primary alcohol:



$$-\mathrm{C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + 2\mathrm{H} \rightarrow -\mathrm{C}\begin{smallmatrix}\nearrow \mathrm{OH}\\ -\mathrm{H}\\ \searrow \mathrm{OH}\end{smallmatrix} \rightarrow -\mathrm{C}\begin{smallmatrix}\nearrow \mathrm{H}\\ =\mathrm{O}\end{smallmatrix} + \mathrm{H_2O}$$



$$-\mathrm{C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix} + 4\mathrm{H} \rightarrow -\mathrm{C}\begin{smallmatrix}\nearrow \mathrm{H}\\ -\mathrm{H}\\ \searrow \mathrm{OH}\end{smallmatrix} + \mathrm{H_2O}$$

Carbonic Acid.—Carbonic acid may be reduced under a variety of conditions. A pure aqueous solution of carbonic acid yields traces of formic acid. A strongly acid solution also yields traces of formic acid though this is not the case in a neutral solution. There is no reduction at iron, platinum, copper, or nickel cathodes; there is, however, a good reduction when the electrodes are of mercury, amalgamated zinc, zinc, or amalgamated copper. It seems that the reduction takes place only when the hydrogen is produced at an electrode with a large overvoltage. The fact that a bicarbonate solution yields the best results is an indication that it is not the undissociated acid that is reduced nor is it the carbonate ion, $CO_3^{=}$, but rather the bicarbonate ion, HCO_3^-, which acts as the depolarizer at the cathode.[70] Lead cathodes have been shown to work well under certain conditions. Electrolytic zinc, amal-

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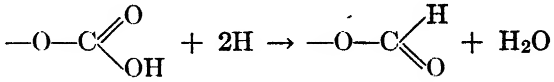
[68] Pannain, Atti. R. Accad. d. Lincei., **17**, ii, 499 (1908).

[69] Elbs and Brand, Z. Elektrochem., **8**, 783 (1902); Kauffler, ibid., **13**, 633 (1907); Müller, ibid., **16**, 236 (1910).

[70] Royer, Compt. rend., **70**, 731 (1870); A. V. Lieben, Monatsch., **16**, 211 (1895). Both Royer and Lieben claim to have obtained HCOOH from H_2CO_3 at cathodes of Zn or Zn—Hg. This was substantiated by Jahn, who used K_2SO_4 solutions with Zn—Hg cathode. It is doubtful whether or not Bach found any HCHO; Lieben, Monatsch., **18**, 582 (1897); Bach, Compt. rend., **126**, 479 (1898); Coehn and St. Jahn, Ber., **37**, 2836 (1904); Ehrenfeld, ibid., **38**, 4135 (1905). A confirmation of this work has been accomplished with a maximum current efficiency of 50 per cent.—Private communication from Dr. Max Knobel.

gamated copper and specially prepared lead cathodes also give good results.[71]

If the carbon dioxide is led through the solution at high pressures the reaction goes much more completely. At 50 atmospheres pressure the current yield of formic acid is 49 per cent. Under certain conditions a slight trace of methanol was detected in the reaction products, but no methane could be found. The best electrolytes are solutions of potassium, sodium, or lithium sulphates:



$$-O-C\genfrac{}{}{0pt}{}{\diagup O}{\diagdown OH} + 2H \rightarrow -O-C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown O} + H_2O$$

The possibility of the industrial manufacture of CH_3OH or HCHO from CO_2 is an interesting problem.

Carbon monoxide has not yet been reduced electrolytically.[72]

Only the very lowest members of the aliphatic series of acids yield to electrolytic reduction, namely formic, oxalic, glyoxylic and phenyl acetic acid. Nearly all of the aromatic acids are readily reduced to the corresponding alcohol. Malonic, succinic, tartaric acids are not reduced;[73] nor are triphenylacetic, and hexahydrobenzoic acids.[74] Pyroracemic acid is reduced but not in the carboxyl group. Both aliphatic and aromatic esters yield a variety of products which will be discussed later.

Formic Acid.—Formic acid is reduced at room temperature to formaldehyde and methanol[75] in a divided cell, the catholyte of which contains 10 per cent mineral acid, with a cathode of lead, nickel, or platinized-platinum. A hydrogen carrier such as a cerium salt is very desirable. The addition of 10 per cent of a strong mineral acid prevents loss due to the depression of the ionization of the formic acid. Naturally there is danger of a reaction between the formic acid and the mineral acid but this may be prevented to a large extent by cooling the cell during the electrolysis. The reaction may be made to take place in steps. With low current densities the product is mostly formaldehyde but with

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[71] $K_2C_2O_6$ was isolated from a saturated solution of K_2CO_3 containing CO_2. Constam and Hansen, Z. Elektrochem., **3**, 137 and 445 (1896). See also Salzer, ibid., **8**, 901 (1902).

[72] F. Fischer and O. Prziza, Ber., **47**, 256 (1914). For the pressure work the especially constructed electrolytic bomb described by F. Fischer and O. Prziza, Ber., **46**, 698 (1913) should be used.

[73] Tafel and Friedrichs, Ber., **37**, 3187 (1904).

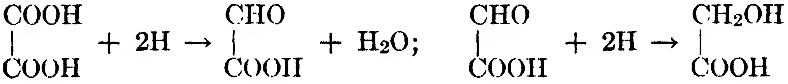
[74] Mettler, Ber., **39**, 2923 (1906).

[75] U.S.P. 867575, (1907), Ellis and McElroy.

higher densities the reduction goes on to the formation of methanol:[76]

$$HCOOH + 2H \rightarrow HCHO + H_2O$$
$$HCHO + 2H \rightarrow CH_3OH$$

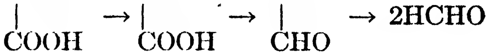
Oxalic Acid.—Two products may be obtained from the reduction of oxalic acid; glyoxylic acid is obtained at temperatures below 10° while at much higher temperatures at lead or mercury cathodes in sulphuric acid the product is glycollic acid. Royer[77] claims to have detected formic acid, but E. Baur[78] could not verify this claim. The early investigators in this field allowed the temperature of the bath to rise too high and so were able to identify only glycollic acid in the products.[79]



$$\begin{array}{l}COOH\\|\\COOH\end{array} + 2H \rightarrow \begin{array}{l}CHO\\|\\COOH\end{array} + H_2O; \quad \begin{array}{l}CHO\\|\\COOH\end{array} + 2H \rightarrow \begin{array}{l}CH_2OH\\|\\COOH\end{array}$$

Several methods are described for the formation of glyoxylic acid.[80] Only very small amounts of glycollic acid are formed by the further reduction of glyoxylic acid. A temperature of 40 or 50° causes the reduction to go so rapidly and completely that glycollic acid is obtained in practically a pure state.[81] The use of the sulphuric acid electrolyte to a great extent simplifies the recovery of the glycollic acid.

In later years the presence of some formaldehyde in the reduction products of oxalic acid has been proven,[82] while the cathode gas contained only hydrogen; carbon dioxide, carbon monoxide and oxygen were proven absent. The only source for this formaldehyde would be that some glyoxylic acid was reduced to glyoxal and then this in turn was reduced to formaldehyde,



$$\begin{array}{l}COOH\\|\\COOH\end{array} \rightarrow \begin{array}{l}CHO\\|\\COOH\end{array} \rightarrow \begin{array}{l}CHO\\|\\CHO\end{array} \rightarrow 2HCHO$$

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[76] See Baur, Z. Elektrochem., **25**, 102 (1919), who does not agree with this statement.

[77] Royer, Compt. rend., **69**, 1374 (1869); Balbiano and Alessi, Gazz. chim. ital., **12**, 190 (1882); Tafel and Friedrichs, Ber., **37**, 3189 (1904). Esters of oxalic acid are easily reduced.

[78] Z. Elektrochem., **25**, 102 (1919).

[79] Balbiano and Alessi, loc. cit.; Avery and Dales, Ber., **32**, 2237 (1899).

[80] Tafel and G. Friedrichs, Ber., **37**, 3189 (1904); U.S.P. 1227706 (1917), Vaygouny; D.R.P. 163842 (1903), 210693 (1909), Kinzelberger.

[81] D.R.P. 194038 and 204787 (1907), Deutsch. Gold-u. Silberscheideanstalt; O. Liebknecht, U.S.P. 837038 (1907).

[82] E. Baur, Z. Elektrochem., **25**, 102 (1919).

or as Baur[83] states the equation:

$$\begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{COOH}\end{array} + 2\mathrm{F} \rightarrow 2\mathrm{H}^+ + \mathrm{CO_2} + \mathrm{HCHO}$$

This work led Baur to the conclusion that a carbon-carbon linkage may be broken by electrolytic reduction, but that the reverse reaction is impossible. Which means that the reaction:

$$\mathrm{C_2O_4}^{=} + 2\mathrm{F} = 2\mathrm{CO_2} \text{ is irreversible}$$

While the reduction of one of the carboxyl groups of oxalic acid has been accomplished by electrolytic means, the reduction of the second by the same method has up to the present time been impossible so that glycol has never been prepared on this basis. Foerster[84] has made a general law as follows: In the simple aliphatic acids and their substitution products (glycollic acid being considered as hydroxyacetic acid) the carboxyl group resists electrolytic reduction. If the work of Baur has completely refuted, the results obtained by Ellis and McElroy,[85] and if it has also shown that formic acid is not reduced to formaldehyde and methanol, then there remains only one exception to the rule of Foerster, and that is the case of phenylacetic acid, which, under certain conditions of electrolysis at a lead or lead dioxide cathode, yields β-phenylethyl alcohol.[86]

Other Acids.—Of course in the case of phenylacetic acid there may be a certain directive influence of the benzene ring which takes this compound out of the field of pure aliphatic acids into the field of substituted aromatic acids, making Foerster's rule hold in all cases. More work needs to be done before a definite statement can be justifiably made.

In an alkaline solution at a prepared lead cathode at 20° levulinic and dimethyllevulinic acids were reduced to corresponding hydroxyacids or lactones. In acid solution some alkali had to be added to prevent the formation of a non-conducting film of valeric acid on the surface of the cathode, or else replace the Pb cathode by one of Hg which is not cooled. Levulic acid formed valeric acid; α-dimethyllevulinic acid gave a lactone and a little dimethylvaleric acid; hydroxyvaleric acid,

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[83] E. Baur, loc. cit.

[84] Foerster, "Wässerige Lösungen," p. 636.

[85] Ellis and McElroy, U.S.P. 867575 (1907).

[86] C. Marie, R. Marquis, and Birkenstock, Bull. soc. chim., **25**, 512 (1919); H. J. Inoue, J. Chem. Ind. Japan, **24**, 906 (1921); Heuser, Dissert., Munich (1901). This is contrary to the previously reported work of Mettler, Ber., **39**, 2934 (1906), who showed that phenylacetic acid is not reduced at a Pb cathode.

valerolactone and α-dimethylvalerolactone are not reduced at all under these conditions.[87]

Aromatic Acids.—Monocarboxylic acids of the aromatic series at lead and mercury cathodes in an acid solution are easily reduced to their corresponding aromatic alcohols of the benzyl series. This reaction is the opposite to that which occurs in an alkaline solution, namely that the nucleus is hydrogenated. In an acid solution only the carboxyl group is attacked though in some cases only a trace of the hydrogenated ring product is obtained.[88]

The advent of the Grignard reaction with its sundry ramifications and variations made it very desirable to have a good and easy method of preparing aromatic esters and alcohols. The usual method was to reduce the corresponding acid with alcohol and sodium, but so many undesirable products were formed that the method has not been very successful. The purely chemical methods are not very easily applied to the preparation of substituted aromatic alcohols because the nascent hydrogen either hydrogenates the ring or attacks the substituent on the ring besides reducing the carboxyl group. An electrolytic method has been developed which is eminently successful.[89]

In order to get around the low solubility of benzoic acid in an aqueous solution of sulphuric acid it has been found advisable to use an alcoholic sulphuric acid solution, to get 85 per cent yields of benzyl alcohol:[90]

$$C_6H_5COOH + 4H \longrightarrow C_6H_5CH_2OH + H_2O$$

Mettler[91] has been able to apply his method to the reduction of substituted benzoic acids, encountering but very few exceptions. There are always good yields of the corresponding alcohols. The nature of the substituent in the nucleus regulates the course of the reaction. It is well known that halogens in the position ortho to the carboxyl group are particularly active. But even in the cases of the various chloro and bromo acids the electrolytic reduction only attacks the carboxyl group. The case of the iodobenzoic acids is somewhat different. The *o*-iodobenzoic acid is almost completely, and the meta compounds are partially, reduced to the halogen-free benzyl alcohol. This also shows that of the three halogens the iodine atom has the least affinity for the benzene nucleus.

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[87] Tafel and Emmert, Z. Elektrochem., **17**, 569 (1911).

[88] C. Mettler, Ber., **38**, 1747 (1905); **37**, 3692 (1904); **39**, 2933 (1906); C. Mettler, D.R.P. 166181 (1905).

[89] Tafel and Friedrichs, Ber., **37**, 3187 (1904); Mettler, loc. cit.

[90] C. Mettler, loc. cit. See also H. Inoue, J. Chem. Ind. Japan, **24**, 806 (1921); Elbs. "Übungsbeispiele," p. 126.

[91] Mettler, Ber., **39**, 2933 (1906).

In many cases the substituted benzyl alcohols are very difficult to obtain by purely chemical methods, though the corresponding benzoic acids are very easy to prepare. The electrolytic method of reduction offers a very desirable method for the preparation of these otherwise inaccessible compounds. The ortho- and para-phenolic acids do not respond very readily to this kind of reduction,[92] but the ethers of these phenolic acids are readily reduced. The methoxybenzoic acids are much more easily reduced than the corresponding hydroxybenzoic acids, the phenol group being untouched.

The best method is that given by Mettler [93] in which the catholyte is a 20–30 per cent alcoholic sulphuric acid solution of the acid to be reduced. The electrodes should be lead sheets especially prepared according to the method of Tafel.[94] In order to prevent the formation of any ester during the reduction the temperature of the bath must be held below 30°. The following reductions have been accomplished: [95]

m-bromobenzylalcohol from *m*-bromobenzoic acid,
o-, *m*-, and *p*-, chlorobenzyl alcohol from *o*-, *m*-, and *p*-, chlorobenzoic acid,
o-, and *m*-, aminobenzylalcohol from *o*-, and *m*-, nitrobenzoic acid,
3, 5-dichlorosaligenin from 3, 5-dichlorosalicylic acid,
3, 5-dibromosaligenin from 3, 5-dibromosalicylic acid,
5-chlorosaligenin from 5-chlorosalicylic acid,
5-bromosaligenin from 5-bromosalicylic acid,
3, 5-dichloro-*p*-hydroxybenzyl alcohol from 3, 5-dichloro-*p*-hydroxybenzoic acid,
o-, and *p*-, tolyl alcohol from *o*-, and *p*-, toluic acid,
m-hydroxybenzylalcohol from *m*-hydroxybenzoic acid,
3, 5-dichloro-*p*-hydroxybenzyl alcohol from 3, 5-dichloro-*p*-hydroxybenzoic acid,
o-, and *m*-, methoxybenzyl alcohol from *o*-, and *m*-, methoxybenzoic acid,
α-, and *β*-, naphthobenzyl alcohol from *α*-, and *β*-, naphthoic acid,
o-, *m*,- and *p*-tolylethyl alcohol from *o*-, *m*-, *p*-tolylacetic acid.[96]

The presence of free boric acid stops the reduction of the benzoic acid at benzaldehyde in the electrolytic method when a mercury cathode

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[92] *m*-Hydroxybenzoic acid is readily reduced.

[93] Mettler, loc. cit.

[94] J. Tafel, Ber., **33**, 2209 (1900).

[95] Mettler, loc. cit.

[96] Kling, Anzeig. Akad. Wiss., Krakow, 448 (1907); 632 (1908).

is used,[97] and also in the purely chemical method when sodium amalgam is used.[98]

It is claimed that the method is also good for substituted benzoic acids such as the halogen benzoic acids; the hydroxynaphthoic acids are less suitable, and the acids of the type of phenylacetic acid or saturated aliphatic acids not at all. What probably happens in this case is that the mercury cathode absorbs the sodium discharged at the cathode to form a sodium amalgam which then acts as a chemical agent in the presence of the boric acid as described by Weil.

This mechanism is borne out by the extensive researches of Tesh and Lowy [99] on the electrolytic reduction of salicylic acid to the aldehyde. They were able to obtain the aldehyde only when the cathode was mercury. Copper amalgam and lead cathodes formed only traces of the desired product. They draw the following conclusions from their work: "lower temperatures (15° to 18°) favor the yield of salicylaldehyde. At higher temperatures less salicylaldehyde is produced and more of the resinous product. Up to a current density of 8 amp./sq. dm. the yield of salicylaldehyde is increased. Intermittent electrolysis or stirring after electrolysis is necessary for good current efficiency since a sodium amalgam is built up during the electrolysis. Increasing the time of electrolysis seems to increase the quantity of the resin formed. Increasing the concentration of salicylic acid (sodium salt) has little or no effect."

Salicylaldehyde is very easily reduced to salicyl alcohol. This means that in order to obtain any aldehyde at all it must be fixed, as soon as it is formed, in such a manner as to preclude any further reduction. Lowy and Tesh tried a continuous steam distillation, continuous extraction with benzene, combination with *p*-toluidine, β-naphthylamine, or sodium bisulphite. The latter method worked the best.

The carboxyl group of cinnamic acid has finally yielded to electrolytic reduction. At a lead dioxide, PbO_2, cathode in an alcoholic sulphuric acid solution, cinnamic acid has been reduced to γ-propyl alcohol and racemic γ-δ-dihydroxy-α-ζ-diphenyl hexane. The former in 38 per cent yields.[100]

Ellagic acid in a sodium hydroxide solution yields a variety of products at different temperatures.[101]

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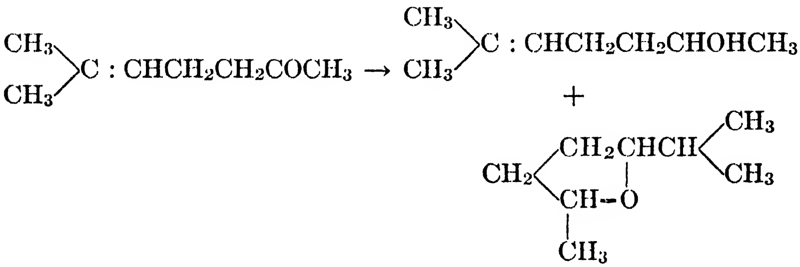
[97] Mettler, Ber., **41**, 4148 (1908); D.R.P. 196239 (1908), Weil.
[98] H. Weil, Ber., **41**, 4147 (1908).
[99] K. S. Tesh and A. Lowy, Trans. Am. Electrochem. Soc., **45**, 37 (1924).
[100] H. Inoue, J. Chem. Ind. Japan, **24**, 906 (1921).
[101] Nierenstein and Rixon, Ann., **394**, 249 (1912).

UNSATURATED ALDEHYDES AND KETONES AND ACIDS

These compounds respond to electrolytic reduction in several ways: The double bond may be saturated by the addition of hydrogen followed by a reduction of the carbonyl group,[102] as when crotonaldehyde is reduced at a lead cathode in either acid or alkaline solution to normal butyl alcohol:

$$CH_3CH : CHCHO \rightarrow CH_3CH_2CH_2CH_2OH$$

Similarly methyl heptenone in a sulphuric acid solution yields the corresponding methyl heptenol and an inner ether:



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C : CHCH_2CH_2COCH_3 \rightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C : CHCH_2CH_2CHOHCH_3$$

Evidently the double bond in some cases is less easily attacked than the carbonyl group.

When these unsaturated compounds are reduced in an alkaline solution on a lead cathode the course of the reaction very closely resembles the reduction by means of sodium or sodium amalgam. On the other hand the electrolytic reduction in an acid solution takes a slightly different course, due to the more vigorous reaction and also due to the fact that a lead electrode is attacked by the materials in solution with the formation of organic lead compounds. Cathodes of copper, tin, zinc, or lead amalgam are not so attacked.

The position of the reducible group in a compound has something to do with the course of the reduction. If two reducible groups are conjugate to one another the complete reduction is carried on easier than if there is only one such group, or two groups widely separated. Each double bond preserves its individuality, and reduction may take place at either one or at both simultaneously. It may be safely assumed that the reduction takes place in stages, commencing at the most reactive point in the molecule. However, the most susceptible point depends on the individuality of the compound. A doubly linked pair of carbon atoms toward the center of a molecule is saturated by the addition of

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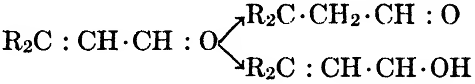
[102] H. D. Law, J. Chem. Soc., **101**, 1016 (1912).

hydrogen. The carbonyl group does not always behave this way. Such a reduction may take two directions:



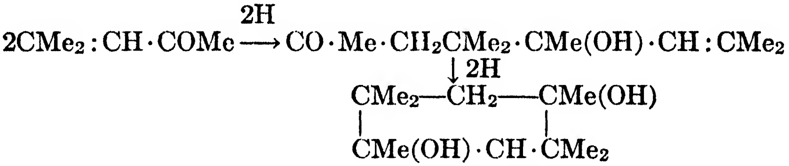
$$\mathrm{R_2C:CH\cdot CH:O} \begin{array}{l} \nearrow \mathrm{R_2C\cdot CH_2\cdot CH:O} \\ \searrow \mathrm{R_2C:CH\cdot CH\cdot OH} \end{array}$$

The fact that two directions are possible is shown by the result obtained by a slight change in the conditions. Three things may happen, i.e., (1) the compound may be further reduced, (2) a condensation of two molecules may occur, or (3) the electrode may be attacked. Metallic catalysts speed up the addition of the second molecule of hydrogen. Polymerization takes place as usual most easily in an alkaline solution with a moderate cathodic potential. Metallic organic compounds are formed only in an acid solution when base metals, like lead, are used, but not with the noble metals.

α-β-unsaturated compounds are more easily reduced in the presence of finely divided copper than at a sheet lead cathode. At a lead cathode a heavy red oil forms. This oil is probably a compound of lead with the partly reduced compound.[103] Mesityl oxide yields a variety of compounds as follows:

(1) $\mathrm{2CMe_2:CH\cdot COMe \xrightarrow{2H} COMe\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2COMe}$

(2) $\mathrm{2CMe_2:CH\cdot COMe \xrightarrow{2H} CMe_2:CHCMe(OH)\cdot CMe(OH)\cdot CH:CMe_2}$

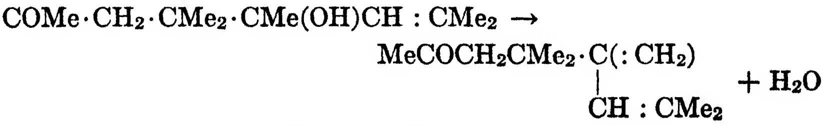
(3) 

$$\begin{array}{l} \mathrm{2CMe_2:CH\cdot COMe \xrightarrow{2H} CO\cdot Me\cdot CH_2CMe_2\cdot CMe(OH)\cdot CH:CMe_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \mathrm{2H} \\ \qquad\qquad\qquad\qquad\qquad \begin{array}{l} \mathrm{CMe_2—CH_2—CMe(OH)} \\ | \qquad\qquad\quad\ | \\ \mathrm{CMe(OH)\cdot CH\cdot CMe_2} \end{array} \end{array}$$

Probably mesityl oxide is first attacked at the carbonyl group according to the equation (2) and then a subsequent loss of a water molecule forms a ketone (pinacol-pinacolin transformation):

$$\mathrm{CMe_2:CH\cdot CMe(OH)\cdot CMe(OH)CH:CMe_2 \rightarrow H_2O + CMe_2:CH\cdot CMe_2\cdot CO\cdot CH:CMe_2}$$

or possibly equation (3) is the start followed by a loss of water on distillation:



$$\mathrm{COMe\cdot CH_2\cdot CMe_2\cdot CMe(OH)CH:CMe_2 \rightarrow} \begin{array}{l} \mathrm{MeCOCH_2CMe_2\cdot C(:CH_2)} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad \mathrm{CH:CMe_2} \end{array} + \mathrm{H_2O}$$

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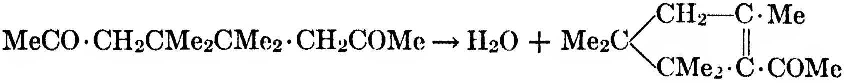
[103] H. D. Law, J. Chem. Soc., 101, 1544 (1912).

Desoxymesityl oxide, another product,[104] may be formed by the elimination of a molecule of water from the product formed according to (1):



$$MeCO\cdot CH_2CMe_2CMe_2\cdot CH_2COMe \rightarrow H_2O + Me_2C\left\langle\begin{array}{l} CH_2\text{—}C\cdot Me \\ \qquad\quad \| \\ CMe_2\cdot C\cdot COMe \end{array}\right.$$

The electrolytic reduction of dimethylmesityl oxide in alkaline solution is similar to that of mesityl oxide but the products have not yet been entirely identified.

Other reductions [105] have been attempted but not entirely cleared up:

Citronellaldehyde does not respond to methods used;
Citral in dilute H_2SO_4 yields anhydrogeraniol + geraniol + $C_{20}H_{34}O_2$;
Menthone forms menthol + α-menthopinacol (M.P. 94°), in an acid solution;
Carvone in alkaline solution forms an oil + carvelone (M.P. 149–150°) + α-carvelone (M.P. 150°);
Pulegone yields menthone + $C_{20}H_{34}O_2$ (M.P. 119°) + crystals melting at 148°;
Pulegone in sulphuric acid yields menthone + menthol + other products as in alkaline reduction;

Cinnamaldehyde resinified in acid and alkaline solution, but in a neutral solution yielded β-phenyl propyl alcohol and an unidentified product. In a neutral solution:

Styryl methyl ketone yields benzyl acetone + dibenzyl diacetone and resin.
p-Methoxystyryl methyl ketone yields anisylacetone + diamisyl acetone.

The following reductions were carried out in a sulphuric acid solution (5 per cent) with the addition of a little copper sulphate when a copper cathode was used. Finely divided copper was slowly deposited as the reduction proceeded.[106]

Mesityl oxide → isohexylene, hexane, isobutyl ketone, desoxymesityl oxide and acetone.
citral → same as in dilute H_2SO_4.
pulegone → 95–100 per cent menthone with copper cathode; 50–60 per cent menthone with lead cathode.
carvone → dihydrocarvone at a copper cathode.
p-benzoquinone → hydroxy compounds similar to those formed in reduction of pulegone and carvone at both copper and lead cathodes. Quinhydrone was precipitated but was further reduced.

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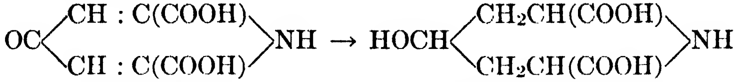
[104] See work of Hibbert and Read, page 300.
[105] H. D. Law, J. Chem. Soc., **101**, 1016 (1912).
[106] H. D. Law, J. Chem. Soc., **101**, 1544 (1912).

An alkaline solution of chelidamic acid I yields the compound II, isolated finally as the hydrochloride salt.[107]



$$OC\left\langle\begin{matrix}CH : C(COOH)\\ CH : C(COOH)\end{matrix}\right\rangle NH \rightarrow HOCH\left\langle\begin{matrix}CH_2CH(COOH)\\ CH_2CH(COOH)\end{matrix}\right\rangle NH$$

chelidamic acid (I) 4-hydroxypiperidine, 2-6-dicarboxylic acid (II)

THE REDUCTION OF THE CARBONYL GROUP IN ESTERS

The esters of aliphatic acids also respond to electrolytic reduction in certain cases. However, there is some evidence that the nature of the acid residue which is esterified has a great influence on the course of the reduction. For instance the ethyl esters of acetic, cyanoacetic, and phenylacetic acids are not reduced, while the esters of formic, succinic, and tartaric acids are slowly reduced. The most easily reduced are the esters of oxalic, malonic, acetoacetic, oxalacetic, benzoic, phthalic, and benzoylacetic acids. Cinnamic and maleic esters are reduced only at the double bond carbon atoms.

Phthalic and acetoacetic ester must be reduced in the carboxyl group because each molecule absorbs 6 atoms of hydrogen.[108] Benzoylacetic ester and oxalacetic ester require only two atoms of hydrogen so that apparently only the keto group is reduced. This leads to the conclusion that the presence of a second carboxyethyl or an acetyl group increases the reducibility of the carboxyethyl group, when the groups are separated by only one or two carbon atoms; the reducibility of the groups decreases as the distance between them increases. From the reduction products of benzoylacetic ester and oxalacetic ester it must be concluded that the ketone group is more easily reduced when attached directly to the carboxyl group. The presence of the cyanogen group seems to have no action on the reducibility of the carboxyethyl group. Cyanoacetic ester is not attacked by electrolytic hydrogen. Cyanoformic ester, however, is attacked, but the only reduction that can be detected is that the cyanogen group is split off with the formation of hydrocyanic acid and formic ester. The carboxyl group remaining intact.

The products of reduction have been isolated only in a few instances. Ethers and alcohols are obtained from most of the esters of the aromatic acids, that is the ethyl and methyl ester of benzoic acid yield the corresponding ether of benzyl alcohol:

$$C_6H_5COOC_2H_5 + 4H \rightarrow C_6H_5CH_2OC_2H_5 + H_2O$$

or

$$C_6H_5CH_2OH + C_2H_5OH$$

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[107] Emmert and Herterich, Ber., **45**, 661 (1912).

[108] See Tafel, Ber., **33**, 2216 (1900); Tafel and Friedrichs, Ber., **37**, 3187 (1904).

In the case of the phthalic ester a compound having the property of an aldehyde is obtained which is probably a dialcoholate of phthalaldehyde. In the other cases only the number of hydrogen atoms absorbed has been measured, and there is a difference in the amount absorbed depending on whether the reduction is carried out in a dilute alcoholic sulphuric acid solution or in a dilute aqueous H_2SO_4 solution. In the former case oxalic ester absorbs two atoms of hydrogen and in the latter case four atoms of hydrogen. Malonic ester absorbs between two and four while succinic ester is not reduced in the former but absorbs between two and three atoms of hydrogen in a pure aqueous solution of sulphuric acid.[109] The reduction of substituted benzoic acid esters has led to a convenient method of preparing substituted esters, and the corresponding substituted aromatic alcohols. In an alcoholic sulphuric acid solution at a lead cathode the following reactions have been accomplished:[110]

Ethyl ester of *o*-chlorobenzoic acid to *o*-chlorbenzyl ethyl ether and *o*-chlorobenzyl alcohol.
Ethyl ester of *m*-bromobenzoic acid to *m*-bromobenzyl ethyl ether and *m*-bromobenzyl alcohol.
Ethyl ester of *m*-chlorobenzoic acid to *m*-chlorobenzyl ethyl ether and *m*-chlorobenzyl alcohol.
Ethyl ester benzoic acid to benzyl ethyl ether and benzyl alcohol.
Methyl ester of benzoic acid to benzyl methyl ether and benzyl alcohol.

The ease with which these substituted benzyl alcohols are prepared may be of interest at some future date because these alcohols are very readily oxidized to the corresponding aldehydes, some of which are of great importance in the dye industry.[110]

Phenyl benzoate yields phenyl benzyl ether and benzyl benzoate yields dibenzyl ether so that now both aliphatic and aromatic esters of aromatic acids have been included in the study of the problem.[111]

In some cases the free acid is obtained by the reduction of the ester, if there is a reducible carbonyl group present in the molecule. The ethyl ester of oxanilic acid on reduction at a mercury cathode in a strong sulphuric acid solution yields phenyl glycine:[112]

$$C_6H_5NHCO \cdot COOC_2H_5 \rightarrow C_6H_5NHCH_2COOH$$

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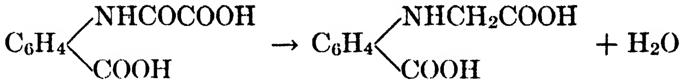
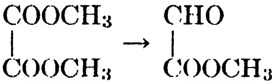
[109] J. Tafel, and G. Friedrichs, Ber. **37**, 3187 (1904).
[110] C. Mettler, **37**, 3692 (1904).
[111] C. Mettler, Ber., **38**, 1745 (1905).
[112] D.R.P. 210693 (1909), Kinzelberger & Co.

And similarly oxalylanthranilic acid yields phenylglycine-*o*-carboxylic acid:[113]



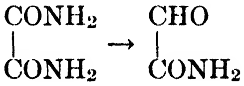
$$C_6H_4\begin{matrix}\diagup NHCOCOOH\\ \diagdown COOH\end{matrix} \rightarrow C_6H_4\begin{matrix}\diagup NHCH_2COOH\\ \diagdown COOH\end{matrix} + H_2O$$

The dimethyl ester of oxalic acid yields the methyl ester of glyoxylic acid:



$$\begin{matrix}COOCH_3\\ |\\ COOCH_3\end{matrix} \rightarrow \begin{matrix}CHO\\ |\\ COOCH_3\end{matrix}$$

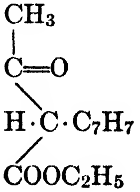
and oxamide yields the amide of glyoxylic acid:[114]



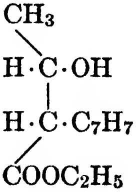
$$\begin{matrix}CONH_2\\ |\\ CONH_2\end{matrix} \rightarrow \begin{matrix}CHO\\ |\\ CONH_2\end{matrix}$$

A large variety of compounds are obtained when the more complicated esters containing keto groups are reduced by the electrolytic method. In benzoylacetic ester and oxalylacetic ester the ketone groups are more readily reduced than the carboxyl groups.[115]

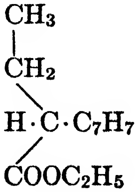
In the reduction of benzylacetoacetic ethyl ester (I) there is a possibility of 14 different compounds being formed either by the union of two molecules, i.e., pinacol formation, or direct reduction. The following were identified:[116] ethyl ester of α-benzyl-β-hydroxy-butyric acid (II); ethyl ester of α-benzyl butyric acid (III), α-benzyl-β-keto-butyraldehyde (IV), benzyl-butyl ethyl ether, (V); 2-benzyl butane (VI).



(I)



(II)



(III)

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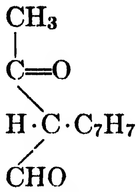
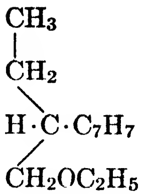
[113] D.R.P. 163842 (1905), Kinzelberger & Co.

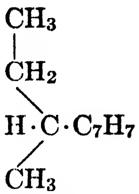
[114] D.R.P. 163842.

[115] J. Tafel and G. Friedrichs, Ber., **37**, 3188 (1904).

[116] Tafel and Hahl, Ber., **40**, 3312 (1907).


(IV)


(V)


(VI)

The experimental conditions were that 7.5 g. of benzylacetoacetate were dissolved in 22.5 g. of 30 per cent sulphuric acid and 70 cc. of 90 per cent alcohol and reduced at a lead cathode by a c. d. of 12 amperes.

The results obtained by the reduction of acetoacetic ester and its derivatives in alcoholic sulphuric acid solution at lead cathode by means of a high current density has led to different results at the hands of the same investigators, namely the formation of 60° saturated hydrocarbons in at least 50 per cent yields, but the difficulty in identifying the hydrocarbons so formed has caused trouble. Tafel and Jurgens,[117] first obtained the following compounds:

butane	from	acetoacetic ester.
3-methylhexane	from	propylacetoacetic ester.
3-methylheptane	from	butylacetoacetic ester.
2, 4-dimethylhexane	from	isobutylacetoacetic ester
3-methyl-3-ethylpentane	from	diethylacetoacetic ester
2-benzylbutane	from	benzylacetoacetic ester
2-methyl-2-benzylbutane	from	methylbenzylacetoacetic ester.

On repeating this work Tafel[118] came to the conclusion that the range of boiling points of the products points to their uniformity, but the values do not agree in all cases with those recorded and accepted for the compounds obtained in each case. It seems that the methyl group formed in the complete reduction of derivatives of acetoacetic ester is transposed or transferred, and is replaced not as a side chain but as a part of the main chain. Of course the electrolysis gave the same results as were obtained in the previous work but materials formed have been identified as being different. That is instead of the one product being identified as 2-4-dimethyl hexane it was β-methylheptane or γ-methylheptane from isobutylacetoacetic ester. The other results were:

Propylacetoacetic ethyl ester to *n*-heptane not 3-methylhexane.
Butylacetoacetic ethyl ester to *n*-octane not 3-methylheptane.

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[117] J. Tafel and W. Jurgens, Ber., **42**, 2548 (1909).

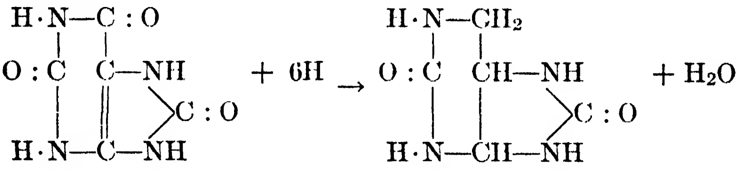
[118] Tafel, Ber., **45**, 437 (1912).

Isobutylacetoacetic ethyl ester to octane not 2-4-dimethylhexane.
Diethylacetoacetic ethyl ester to 3-ethylhexane not 3-methyl-3-ethylpentane.
Benzylacetoacetic ethyl ester to $C_{11}H_{16}$ not 2-benzylbutane.
Methylbenzylacetoacetic ethyl ester to $C_{12}H_{18}$ not 2-methyl-2-benzylbutane.
Sec. butylacetoacetic ethyl ester to γ-methylheptane or a mixture of *d*-methylheptane or γ-ethylhexane.
Isopropylacetoacetic ethyl ester to impure β- or γ-methylhexane.
Ethylacetoacetic ethyl ester to γ-methylheptane (?).
Methylisopropylacetoacetic methyl ester to octane (B.P. 756 mm., 110–118°), i.e., mixed hydrocarbons.
Methylpropylacetoacetic methyl ester to *d*-methylheptane or γ-methylheptane, or ethylhexane or a mixture of the latter and *d*-methylheptane.

REDUCTIONS IN THE URIC ACID SERIES

The application of hydrogen produced at a cathode with a high overvoltage to the reduction of the carbonyl group received its first stimulus at the hands of Tafel and his collaborators when uric acid with many of its derivatives were subjected to electrolytic reduction. The materials to be reduced were usually dissolved in sulphuric acid of sufficient strength to increase the solubility of the depolarizer but yet not sufficiently strong to decompose it.

By purely chemical methods uric acid has not yielded to a reduction but at a Pb cathode [119] in 75 per cent sulphuric acid below 12° it is readily reduced to purone according to the equation.[120]



That is the reduction takes place at the double bond and at the carbonyl group in position 6 while the two urea carbonyl groups remain intact.

If the concentration of the sulphuric acid is too high (i.e., around

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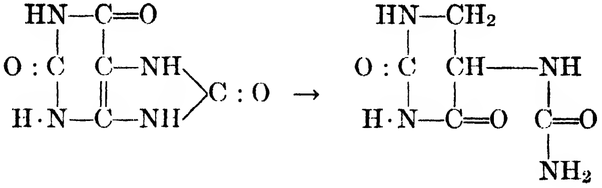
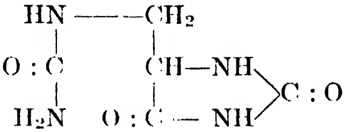
[119] Tafel, Ber., **33**, 2223 (1900).

[120] Tafel, Ber., **34**, 258 (1901); Tafel and Houseman, ibid., **40**, 3745 (1907); see also Tafel and Ach, ibid., **34**, 1165 (1901).

80%) the reduction of uric acid leads to the formation of tetrahydrouric acid:



or



The cooling to below 12° is also necessary to prevent the rearrangement of purone to isopurone, $C_6H_8O_2N_4$.[121] Tetrahydrouric acid is not reduced to purone by a change of experimental conditions so that it cannot be considered as an intermediate in the reduction of uric acid to purone.

The methylated uric acids are reduced in a manner entirely analogous to uric acid, yielding the corresponding methylated purones. Compounds corresponding to the tetrahydrouric acid are not formed in any case. Six hydrogen atoms are absorbed by each molecule of starting material.[122]

The following substituted uric acids have been reduced:

3-methyluric acid to isomeric methyl purones.

1, 3-dimethyl uric acid to 1, 3-dimethyl purone slowly in 75 per cent sulphuric acid.

3, 9-dimethyl uric acid to 3, 9-dimethyl purone.

7, 9-dimethyl uric acid to 7, 9-dimethyl purone.

1, 3, 7-trimethyluric acid to 1, 3, 7-trimethylpurone in 60 per cent sulphuric acid.

Tetramethyl uric acid to tetramethyl purone in 50 per cent sulphuric acid.

The reduction of xanthine and the methylated xanthine bases takes place very easily when carried out in a 50 per cent sulphuric acid solution

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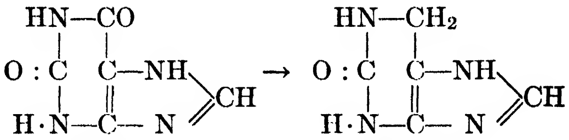
[121] Tafel, Ber., **40**, 3743 (1907).

[122] J. Tafel, Ber., **34**, 279 (1901).

at 18° using 20 per cent excess of the theoretical required current. The desoxy derivatives are obtained in 70 per cent material yields.[123]



xanthine → desoxyxanthine

3-Methylxanthine [124] → Desoxy-3-methylxanthine.

7-Methylxanthine [125] → Desoxyheteroxanthine.
(Heteroxanthine)

Theophylline [126] → Desoxytheophylline.

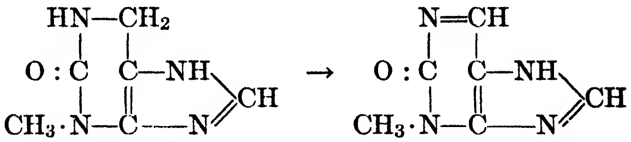
Paraxanthine [127] → Desoxyparaxanthine.

Theobromine [128] → Desoxytheobromine.

Caffeine [129] → Desoxycaffeine.

The course of the reduction of the xanthine bases is slightly different from that of the reduction of the uric acid. The double bonds are not attacked; the urea carbonyl group also remains untouched. A patent [130] covers their electrolytic preparation.[131]

If these desoxy compounds are suitably oxidized chemically they lose 2 atoms of hydrogen and pass into the corresponding oxypurines. For example 3-methylxanthine gives 3-methyl-2-oxypurine. These oxidations prove the constitution of the respective desoxy compounds:



3-methylxanthine → 3-methyl-2-oxypurine

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[123] J. Tafel and B. Ach, Ber., **34**, 1165 (1901).

[124] J. Tafel, and A. Weinschenk, Ber., **33**, 3369 (1900).

[125] Tafel and Weinschenk, loc. cit.

[126] J. Tafel and J. Dodt, Ber., **46**, 3752 (1907).

[127] Tafel and Dodt, loc. cit.

[128] J. Tafel, Ber., **32**, 3194 (1899).

[129] J. Tafel and T. B. Baillie, Ber., **32**, 68 and 3206 (1899); Elbs, "Übungsbeispiele," p. 127.

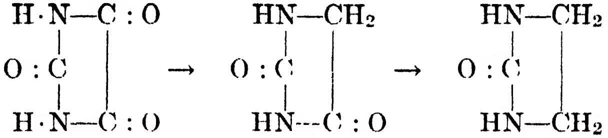
[130] D.R.P. 108577 (1898), Boehringer.

[131] Adenine and hypoxanthine or sarcine have also been reduced.

Guanine is reduced electrolytically as if it were a xanthine derivative, yielding by the above method an oxygen free base, desoxyguanine.[132]

The oxidation products of uric acid, such as parabanic acid, alloxan, barbituric acid, and other cyclic ureides, are easily reduced when they are dissolved in 60–70 per cent sulphuric acid. These compounds contain two adjacent carbonyl groups or two carbonyl groups separated by another carbon atom. On reduction one or both carbonyl groups are attacked. Both reduction products are in many cases formed and are very difficult to separate. The urea carbonyl group is unattacked in all cases.

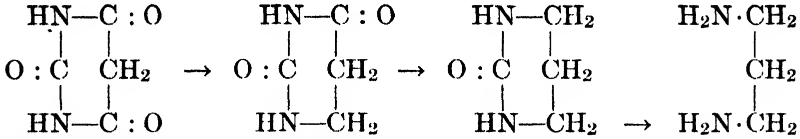
Parabanic acid[133] yields both reduction products in almost equal amounts:



$$\begin{array}{l} \mathrm{H{\cdot}N{-}C:O} \\ \mathrm{O:C} \\ \mathrm{H{\cdot}N{-}C:O} \end{array} \rightarrow \begin{array}{l} \mathrm{HN{-}CH_2} \\ \mathrm{O:C} \\ \mathrm{HN{-}C:O} \end{array} \rightarrow \begin{array}{l} \mathrm{HN{-}CH_2} \\ \mathrm{O:C} \\ \mathrm{HN{-}CH_2} \end{array}$$

parabanic acid hydantoine ethylene urea

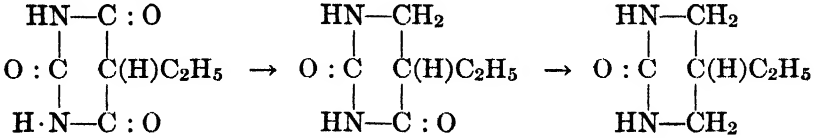
Barbituric acid yields at room temperature equal amounts of both products. Lower temperatures favor the formation of hydrouracil and higher temperatures favor the formation of trimethyleneurea:[134] The trimethylene ureas are very easily decomposed by water into the diamine and carbon dioxide, CO_2, therefore an excellent method is at hand for the preparation of these diamines. Trimethylene urea therefore yields 1, 3-diaminopropane and methyluracil yields 1, 3-diaminobutane:



$$\begin{array}{lll} \mathrm{HN{-}} & \mathrm{C:O} \\ \mathrm{O:C} & \mathrm{CH_2} \\ \mathrm{HN{-}} & \mathrm{C:O} \end{array} \rightarrow \begin{array}{ll} \mathrm{HN{-}} & \mathrm{C:O} \\ \mathrm{O:C} & \mathrm{CH_2} \\ \mathrm{HN{-}} & \mathrm{CH_2} \end{array} \rightarrow \begin{array}{ll} \mathrm{HN{-}} & \mathrm{CH_2} \\ \mathrm{O:C} & \mathrm{CH_2} \\ \mathrm{HN{-}} & \mathrm{CH_2} \end{array} \rightarrow \begin{array}{l} \mathrm{H_2N{\cdot}CH_2} \\ \mathrm{CH_2} \\ \mathrm{H_2N{\cdot}CH_2} \end{array}$$

barbituric acid hydrouracil trimethylene urea

Analogously 5-ethylbarbituric acid yields the corresponding reduction products:[135]



$$\begin{array}{ll} \mathrm{HN{-}} & \mathrm{C:O} \\ \mathrm{O:C} & \mathrm{C(H)C_2H_5} \\ \mathrm{H{\cdot}N{-}} & \mathrm{C:O} \end{array} \rightarrow \begin{array}{ll} \mathrm{HN{-}} & \mathrm{CH_2} \\ \mathrm{O:C} & \mathrm{C(H)C_2H_5} \\ \mathrm{HN{-}} & \mathrm{C:O} \end{array} \rightarrow \begin{array}{ll} \mathrm{HN{-}} & \mathrm{CH_2} \\ \mathrm{O:C} & \mathrm{C(H)C_2H_5} \\ \mathrm{HN{-}} & \mathrm{CH_2} \end{array}$$

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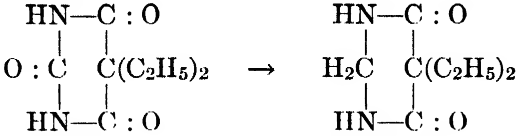
[132] Tafel and Ach, Ber., **34**, 1170 (1901).

[133] J. Tafel and L. Reindl, Ber., **34**, 3287 (1901).

[134] J. Tafel and A. Weinschenk, Ber., **33**, 3383 (1900).

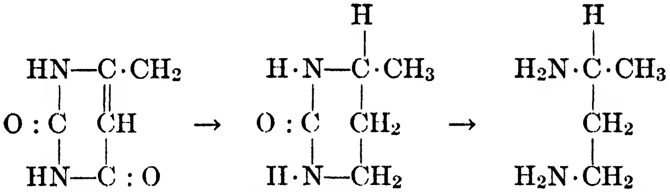
[135] J. Tafel, and H. B. Thompson, Ber., **40**, 4489 (1907).

On the other hand in diethylbarbituric acid (veronal) the presence of the two ethyl groups in the malonic acid residue makes the two carbonyl groups of this residue so stable that the carbonyl group of the urea residue is more easily attacked. The product of this reduction is therefore mostly desoxyveronal:[136]



veronal desoxyveronal

In a 50 per cent sulphuric acid solution at a lead cathode methyluracil yields both methyltrimethyleneurea and 1,3-diaminobutane. These diamines are very difficult to prepare by purely chemical methods:[137]



methyl uracil methyl-trimethylene urea 1, 3-diaminobutane

Dialuric acid, uramil and alloxan readily respond to electrolytic reduction with the formation of many unexpected compounds.[138] Dialuric acid is reduced to hydrouracil, trimethyleneurea and hydroxytrimethyleneurea; violuric acid to uramil and hydrouracil, while alloxan is reduced to hydrouramil, alloxantine and non-crystallizable gums.

ACID AMIDES AND IMIDES

According to the researches of Tafel and Baillie[139] acid amides are reduced in sulphuric acid solution at a lead cathode to the corresponding amine:

$$RCONH_2 + 4H \rightarrow RCH_2NH_2 + H_2O$$

In general the material yields are rather poor. Acetamide is not reduced at all, though acetanilide, after the passage of a very great

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[136] J. Tafel and H. B. Thompson, loc. cit.

[137] J. Tafel and A. Weinschenk, Ber., **33**, 3378 (1900).

[138] J. Tafel and Weinschenk, Ber., **33**, 3383 (1900); Tafel and Reindl, ibid., **34**, 3290 (1901).

[139] J. Tafel and T. B. Baillie, Ber., **32**, 68 (1899).

excess of current, is slightly attacked with only small amounts of ethylaniline being formed. On the other hand 67.5 per cent yields of dimethylbenzylamine are obtained from dimethylbenzamide, and 76 per cent yields of ethyl tetrahydroquinoline from acetyl tetrahydroquinoline,

$$(CH_3)_2C_6H_3CONH_2 \rightarrow (CH_3)_2C_6H_3CH_2NH_2$$

$$CH_3COC_9H_{10}N \rightarrow CH_3CH_2C_9H_{10}N$$

and acetyl *o*-toluidine is reduced to ethyl *o*-toluidine. That is, the carbonyl group is reduced to a methylene group.

Kindler has found that with compounds such as benzamide and thiobenzamide, the electrochemical reduction is more rapid the more methyl groups present in combination with the nitrogen atom; there is also a correspondingly slower reduction by amalgams in the purely chemical method. The following compounds have been reduced in which reductions the corresponding amino alcohols and thio alcohols are not intermediate products:[140]

$$C_6H_5CH_2CONH_2$$

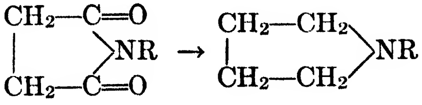
$$C_6H_5CH_2CONHCH_3$$

$$C_6H_5CH_2CON(CH_3)_2$$

$$C_6H_5CH_2CSNHCH_3$$

$$C_6H_5CH_2CSN(CH_3)_2$$

When acid imides are dissolved in sulphuric acid and reduced at a lead cathode only one carbonyl group is reduced to a methylene group. Succinimide[141] in 50 per cent sulphuric acid yields pyrrolidone in fair amounts with only a trace of pyrrolidine; and compounds of a higher B.P.



Pyrrolidones as a rule are rather difficult to prepare by other methods. Succinimide dissolved in 50 per cent sulphuric acid after the passage of

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[140] Kindler, Ber., **57**, 773, (1924).

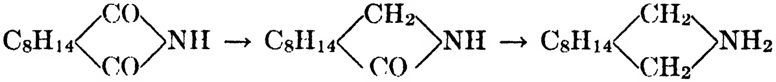
[141] J. Tafel and M. Stern, Ber., **33**, 2224 (1900); Tafel and Emmert, Z. physik. Chem., **54**, 433 (1905).

378 ampere hours yielded 60 per cent of the theoretical amount of pyrrolidone. Other pyrrolidones produced by this method are:

Isopropylpyrrolidone [142] from isopropylsuccinimide in 80 per cent yields.

Phenylpyrrolidone from succinanil; *p*-tolylpyrrolidone from *p*-tolylsuccinimide.[143]

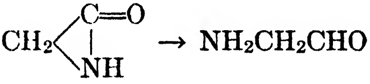
The acid imides of camphoric acid also undergoes a similar reduction,[144] the products being an oxygen-free compound, camphidine, and two isomeric camphidones:



$$C_8H_{14}\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH \rightarrow C_8H_{14}\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle NH \rightarrow C_8H_{14}\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle NH_2$$

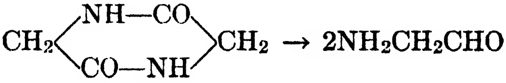
imide of camphoric acid camphidone camphidine

The electrolytic reduction of diketopiperazine and related compounds forms compounds that are new, i.e., α-aminoaldehydes, having never been prepared by the purely chemical method. The material was dissolved in normal sulphuric or normal hydrocholoric acid and reduced at a mercury cathode. Cathodes of platinum, platinized-platinum, copper, silver, gold, cadmium, lead, and impure mercury had no reducing power. Under these conditions of electrolysis glycine [145] yielded aminoacetaldehyde, identified as the osazone,



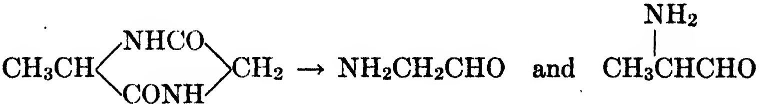
$$CH_2\left\langle\begin{matrix}C{=}O\\|\\NH\end{matrix}\right. \rightarrow NH_2CH_2CHO$$

or



$$CH_2\left\langle\begin{matrix}NH{-}CO\\CO{-}NH\end{matrix}\right\rangle CH_2 \rightarrow 2NH_2CH_2CHO$$

Glycine alanine anhydride yielded α-aminoacetaldehyde and also α-α-aminomethylacetaldehyde; both identified as the osazone:



$$CH_3CH\left\langle\begin{matrix}NHCO\\CONH\end{matrix}\right\rangle CH_2 \rightarrow NH_2CH_2CHO \text{ and } CH_3\overset{\overset{NH_2}{|}}{C}HCHO$$

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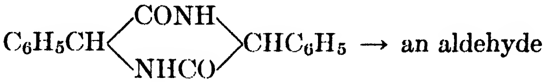
[142] Tafel and Friedrichs, Ber., **33**, 2224 (1900).

[143] Baillie and Thomas, Ber., **32**, 68 (1899).

[144] J. Tafel and K. Eckstein, Ber., **34**, 3274 (1901); J. Tafel and H. Bublitz, Ber., **38**, 3806 (1905); D.R.P. 126196 (1901), Boehringer

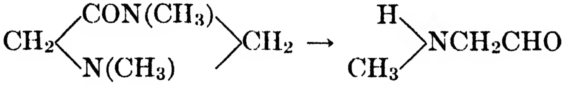
[145] G. W. Heimrod, Ber., **47**, 338 (1908).

C-phenylglycine anhydride on very prolonged reduction, because of its very slight solubility, finally yielded a product that reduced Fehling's solution, indicating the presence of an aldehyde:



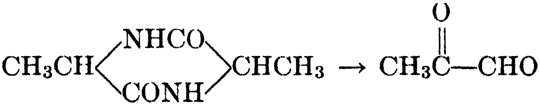
$$C_6H_5CH\begin{matrix}\diagup CONH \diagdown\\ \diagdown NHCO \diagup\end{matrix}CHC_6H_5 \rightarrow \text{an aldehyde}$$

Sarcosine anhydride yielded methylaminoacetaldehyde: (osazone M.P. 169–175°).



$$CH_2\begin{matrix}\diagup CON(CH_3) \diagdown\\ \diagdown N(CH_3) \quad \diagup\end{matrix}CH_2 \rightarrow \begin{matrix}H \diagdown\\ CH_3 \diagup\end{matrix}NCH_2CHO$$

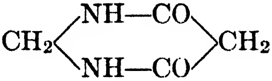
Alanine anhydride yielded a compound which gave an osazone of methylglyoxal, melting at 154.8°:



$$CH_3CH\begin{matrix}\diagup NHCO \diagdown\\ \diagdown CONH \diagup\end{matrix}CHCH_3 \rightarrow CH_3\overset{\overset{O}{\|}}{C}—CHO$$

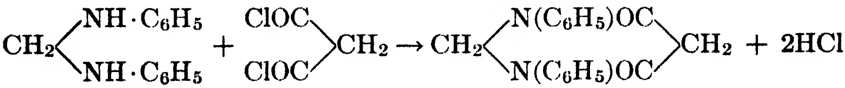
Sodium amalgam or aluminium amalgam reduction methods never form these compounds. In fact such a cleavage of a CO-NH group has only occurred in the case of benzamide which yielded benzaldehyde and ammonia besides some benzylamine.[146] As a rule the reduction leads to the formation of the amines by the reduction of the carbonyl group.

It would be interesting to determine the course of the reduction in the case of the isomeric but unsymmetrical compounds of which the simplest member is:



$$CH_2\begin{matrix}\diagup NH—CO \diagdown\\ \diagdown NH—CO \diagup\end{matrix}CH_2$$

Homologues such as the condensation product of dianilinomethane with malonyl chloride should yield most conclusive results:



$$CH_2\begin{matrix}\diagup NH\cdot C_6H_5\\ \diagdown NH\cdot C_6H_5\end{matrix} + \begin{matrix}ClOC \diagdown\\ ClOC \diagup\end{matrix}CH_2 \rightarrow CH_2\begin{matrix}\diagup N(C_6H_5)OC \diagdown\\ \diagdown N(C_6H_5)OC \diagup\end{matrix}CH_2 + 2HCl$$

ALKALOIDS

Electrochemical reduction methods have been used for the unraveling of the complex structure of some of the alkaloids. A solution of narcotine in sulphuric acid was reduced at a prepared lead cathode to a

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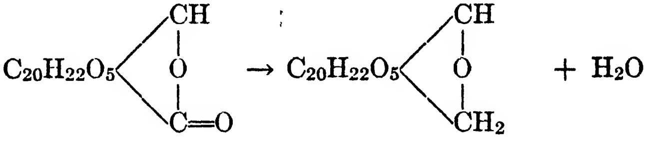
[146] J. Tafel and T. B. Baillie, Ber., **32**, 68 (1899); J. Tafel and Stern, ibid., **33**, 2224 (1900).

complex mixture of several compounds from which only one compound could be isolated and identified with any degree of success. This compound had the formula $C_{22}H_{25}O_6N$, and melted at 126°. It was found to contain no hydroxyl groups, and to be very stable toward alkalies. The compound was probably a hydrodesoxynarcotine formed according to the equation:[147]



A less energetic reduction led to the formation of a tetrahydronarcotine of the formula $C_{22}H_{22}O_7N$. Further study[148] of this problem led to the preparation of a compound of the formula: $C_{22}H_{27}O_7N$, probably also a tetrahydronarcotine.

It is interesting to see how several unsaturated groupings in a complex compound behave under the influence of electrolytic reduction. A current density of 2.0 amperes per sq. dm. according to the method of Tafel[149] reduced cinchonine to dihydrodesoxycinchonine while under practically similar conditions a large current density, 25 amperes per sq. dm., cinchotine was reduced to dihydrodesoxycinchotine. It seems a general rule that in a sulphuric acid solution most alkaloids take up two atoms of hydrogen per molecule of alkaloid.[150]

By the method of Tafel at 40° it has been found possible to reduce strychnine first to tetrahydrostrychnine which immediately loses water to form strychnidine; and similarly brucine yields first tetrahydrobrucine which loses water at 200° to form brucidine.[151] In the same manner quinine, cinchonine and cinchonidine yield their corresponding tetrahydro derivatives;[152] cotarnine and hydrastine yield respectively hydrocotarnine and hydrohydrastine.[153]

Lees and Shedden[154] investigated some of the morpholones.

[147] Freund and Hammel, Dissert., Erlangen (1910).

[148] C. Finzi and M. Freund, Ber., **45**, 2322 (1912).

[149] See page 286.

[150] Freund and Bredenberg, Ann., **407**, 43 (1914).

[151] Tafel, Ann., **301**, 291 (1898); ibid., **304**, 24, (1898); Tafel and Naumann, Ber., **34**, 3291 (1901); Bourgoin, Bull. Soc. Chim., **12**, 400 (1869).

[152] Tafel and Naumann, loc. cit.

[153] Brandon and Wolffenstein, Ber., **31**, 1577 (1898); D.R.P. 94949 (1897).

[154] Lees and Shedden, Proc. Chem. Soc., **19**, 132 (1903); J. Chem. Soc., **83**, 750 (1903). A sulphuric acid solution was used.

CHAPTER XVI

THE REDUCTION OF COMPOUNDS CONTAINING ARSENIC, CHLORINE, SULPHUR, MERCURY, ETC.

THE REDUCTION OF ORGANIC ARSENIC COMPOUNDS

THE application of the methods of electrolytic reduction to organic compounds containing arsenic should lead to results of value from the standpoint of the purity required for the use of such compounds in Chemotherapy. Very little has been reported in this field. However sufficient work has been done to show that there is much of value in the methods which may be used.

Historically, the first arsenic compound to be reduced was cacodylchloride.[1] Two products were formed, namely cacodyl and dimethylarsine as follows:

$$2(CH_3)_2AsCl \rightarrow (CH_3)_2As{-}As(CH_3)_2$$

$$2(CH_3)_2AsCl \rightarrow 2(CH_3)_2AsH$$

The cell used was designed to exclude the air. Platinum electrodes separated by a porous clay diaphragm gave the best results. The catholyte was 5 gm. cacodyl chloride, 90 gm. formic acid, 8 gm. alcohol (the mixture had a sp. gr. of 1.08). The anolyte was sulphuric acid of sp. gr. 1.008.

Though cacodylic acid is readily reduced to dimethyl arsine by zinc and hydrochloric acid, a corresponding electrolytic reduction does not take place; there is only a decomposition of water:[2]

$$(CH_3)_2AsO_2H \rightarrow (CH_3)_2AsO_2^- + H^+$$

$$2(CH_3)_2AsO_2^- + H_2O \rightarrow (CH_3)_2AsO_2H + \tfrac{1}{2}O_2$$

Cacodylic acid in twice normal H_2SO_4 quickly absorbs the electrolytic hydrogen evolved at a Pb or Hg-Zn cathode forming cacodyl and dimethyl arsine. But with an alkaline solution in an undivided cell it is oxidized at the anode to arsenic acid. (For some reason Dehn did not obtain similar results.) Cacodylic acid is stable toward the chemical

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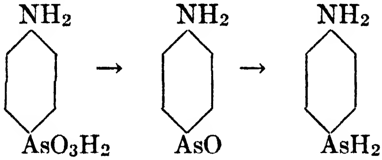
[1] W. H. Dehn, J. Am. Chem., **33**, 119 (1905); **40**, 97 (1908).

[2] Dehn, loc. cit.

oxidizing media as nitrous acid, aqua regia, chromic oxide, and potassium permanganate.

From 1908 until 1916 nothing of any value was reported. A German patent [3] had been issued covering electrochemical methods for the reduction of aromatic arsenicals (mostly phenolic) but the descriptions are entirely too meager to be workable. Klason [4] merely mentions that ethyl cacodylic acid was reduced to ethyl cacodylic oxide.

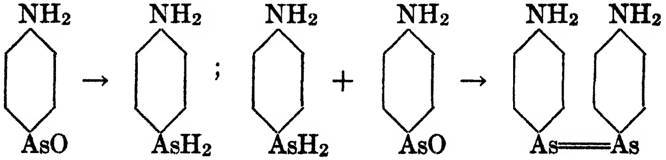
The reduction of pentavalent arsenic by the electrolytic method is possible only in an acid solution.[5] Arsenic acid and arsenites are, however, reduced also in alkaline solution. On this basis *p*-aminophenylarsonic acid in twice normal hydrochloric acid at a lead cathode is reduced according to the scheme.[6]



In the order of increasing efficiency, cathodes of copper, lead, mercury, lead amalgam and zinc were used, of which, with a c. d. of 8 amperes the last-named electrode gave by far the best current yields. Alcoholic hydrochloric acid is preferable to aqueous HCl because with the more slowly acting electrode there is sometimes a deficiency of hydrochloric acid at the cathode so permitting the *p*-aminophenylarsine to float as an oil on the surface of the liquid.

In all these reductions strong cooling is required, otherwise aniline and arsenic are formed, the latter being finally reduced to arsine. Air must be excluded from the apparatus because the great majority of the end products are sensitive to the oxygen of the air.

In hydrochloric acid and even more readily in an alkaline solution, *p*-aminophenylarsenoxide is reduced mostly to the arseno compound, $(NH_2—C_6H_4As=)_2$, though this is to some extent further reduced to the arsine. The reaction probably is as follows:



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[3] D.R.P. 270569 (1911), H. Bart.

[4] Ber., **47**, 2634 (1914).

[5] See Covelli, Chem. Ztg., **33**, 1209 (1909).

[6] F. Fichter and E. Elkind, Ber., **49**, 239 (1916).

In an alkaline solution the condensation according to the second equation above takes place very rapidly. When a lead cathode is used, the *p*-aminoarsenobenzene is obtained in quantitative amounts with very little more than the calculated consumption of hydrogen.[7]

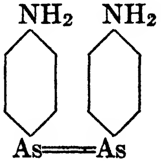
Ehrlich and Bertheim [8] did not entirely clear up this reaction by the purely chemical method. However it is claimed by Bart [9] that there is no fundamental difference in the reactions of the arsonic acids and the arsenoxides. In the electrochemical reduction of *p*-amino phenylarsonic acid, *p*-$NH_2C_6H_4AsO_3H_2$, the intermediate compound *p*-aminophenylarsenoxide, *p*-NHC_6H_4AsO, has not been isolated, nor is *p*-arsenoaniline the end product.

From the purely chemical standpoint *p*-aminophenylarsenoxide is more easily reduced than the corresponding arsonic acid, but the reason why the former cannot be isolated in the electro-chemical method is because the cathodic potential required to start the reduction of the arsonic acid is more than sufficient to reduce the oxide.

Phenylarsonic in an aqueous alcoholic solution of hydrochloric acid is smoothly reduced at all electrodes to phenylarsine, $C_6H_5AsH_2$.

The presence of a nitro group in the benzene ring of an arsonic acid adds complications. Not only are there formed the usual products to be expected when nitro benzene derivatives are reduced but the arsonic acid group is also attacked.

o-Nitrophenylarsonic acid, *o*-$NO_2C_6H_4AsO_3H_2$, in 2N acetic acid at a lead cathode yielded $H_2O_3AsC_6H_4NH \cdot NHC_6H_4AsO_3H_2$ (hydrazobenzol- *o*-*o*′-arsonic acid), and also a little $H_2NC_6H_4AsO_3H_2$ (*o*-aminophenylarsonic acid). In a hydrochloric acid solution at a lead cathode there was formed a clear yellow solution which gave an 82.5 per cent yield of the hydrochloride of *o*-arsenoaniline:



A partial reduction of the *p*-nitro acid in an ammoniacal ammonium carbonate solution yielded the hydrazo compound which the presence of air oxidized to the azo acid: azobenzene-*p*-*p*′-diarsonic acid.[10]

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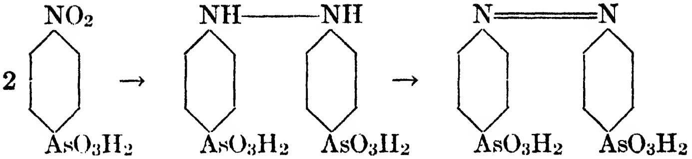
[7] Fichter and Elkind, loc. cit.

[8] Ehrlich and Bertheim, Ber., **44**, 1260 (1911).

[9] Bart., loc. cit.

[10] See Karrer, Ber., **45**, 2357 (1912).



LEAD AND MERCURY COMPOUNDS

Triethyl-lead hydroxide has been reduced in alcoholic solution at a lead cathode to form an oil which was probably mostly lead hexaethyl.[11]

Methylmercuric acetate is reduced to mercury-dimethyl in a pyridine solution.[12]

THE REDUCTION OF ORGANIC COMPOUNDS CONTAINING CHLORINE

The rapid advances that are being made at present in the chlorination of petroleum and the separation of the chlorinated products will probably lead to an entirely new group of intermediate compounds. With the development of new methods of preparation, commercial production may be in a position to accept the electrochemical methods of treating some of these compounds. Besides being valuable as solvents these chlorinated compounds are also of some use as intermediates in several industries.

For solvent purposes in general and especially for spot removers or " dry cleaning " dichloracetylene is of value. This compound is made with some difficulty by purely chemical methods, but a method has been worked out on the basis of the electrochemical reduction of a higher chlorine derivative. Tetrachloroethane, in a catholyte containing 10 per cent zinc chloride separated by means of a clay cell from the anolyte which is also a zinc chloride solution, and is reduced at a copper cathode with a c. d. of 20 amperes at a temperature of 100°. The anode should be of sheet platinum.[13] At 100° the dichloroacetylene is entirely volatile and by using a reflux condenser the tetrachloroethane boiling at 147° is retained in the electrolyte, while the dichloroacetylene distils over in 80 per cent yields. It is estimated that between 3.7 and 4 K.W.H. are required for the preparation of 1 kg. of dichloroacetylene. As no zinc is used up because the zinc that is corroded off the electrode falls to the bottom as zinc-black in the process, the costs should be much lower than by the purely chemical method. The free chlorine which

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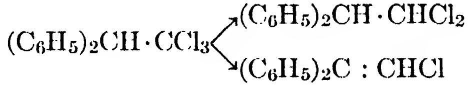
[11] Midgley, Hochwalt and Calingaert, J. Am. Chem. Soc., **45**, 1821 (1923).

[12] Maynard and Howard, J. Chem. Soc., **123**, 960 (1923).

[13] P. Askenasy and C. Vogelsohn, Z. Elektrochem., **15**, 773 (1909); see also D.R.P. 154687 and 168186, Askenasy and Mugdan.

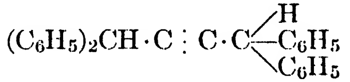
is evolved during the reaction may be utilized and further decrease the cost of the product.

Chemical reductions of chlorinated compounds by means of metallic zinc usually cause the removal of all of the chlorine from the molecule. An electrochemical reduction does not, as a rule, cause so complete a reduction. From the purely chemical standpoint *assym*-diphenyltrichloroethane was expected to yield stilbene when reduced by an electric current. But this was not the case. On a lead cathode a solution of this compound in an alcoholic sodium acetate solution yielded mostly diphenyldichloroethane together with a little diphenylmonochloroethylene. This later compound was probably formed by the action of sodium hydroxide on the first reduction product:



$$(C_6H_5)_2CH\cdot CCl_3 \begin{cases} \nearrow (C_6H_5)_2CH\cdot CHCl_2 \\ \searrow (C_6H_5)_2C : CHCl \end{cases}$$

The use of an acid catholyte yielded the same results but about four times the theoretical amount of current had to be passed. When an alcoholic hydrochloric acid solution was reduced the products were the same as both reductions above but a new compound was formed at 100°, namely *symm*-tetraphenyldimethylacetylene (tetraphenylcrotonylene):



$$(C_6H_5)_2CH\cdot C \vdots C\cdot C \begin{matrix} \diagup H \\ -C_6H_5 \\ \diagdown C_6H_5 \end{matrix}$$

Similarly ditolyltrichlorethane yields p, p'-dimethylstilbene and a hydrocarbon of rather complex nature.[14]

At a copper cathode in alcoholic hydrochloric acid solution the diaryltrichloro compounds are reduced to the corresponding diaryldichloro compounds sometimes with the formation of other products as indicated.[15]

Assym-diphenyltrichloroethane to *assym*-diphenyldichloroethane.

Assym-di-*p*-tolyltrichlorethane to *assym*-di-*p*-tolyldichloroethane.

Assym-di-*p*-methoxyphenyltrichloroethane to *assym*-di-*p*-methoxyphenyldichloroethane.

The diethoxy compound yielded the corresponding dichloroethane together with some diethoxystilbene. The use of a copper cathode gave a purer compound than a lead cathode because, except in the last case mentioned above, the stilbenes were not formed; they however were formed at lead cathodes. The dichloro compounds as a rule are insoluble in the catholyte, therefore separate during the course of the reduc-

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[14] K. Brand, Z. Elektrochem., **16**, 669 (1910).

tion. This fact proves that they are not formed after the electrolysis during the working up of the reduction products. However, the fact that diarylmonochloroethanes on distillation lose hydrochloric acid forming the stilbene derivatives seems to indicate that these monochloro derivatives are intermediates in the electrochemical formation of stilbene compounds. Zinc electrodes yield hydrocarbons:

$$R_2CHCCl_3 \rightarrow R_2CHCH_3 \qquad R = C_6H_5 \text{ or } CH_3C_6H_4$$

and the cathodes are visibly attacked by the reaction. But zinc amalgam electrodes behave like the copper cathodes yielding the dichloroderivatives:[15]

$$R_2CHCCl_3 \rightarrow R_2CHCHCl_2$$

Lead cathodes at the boiling point of the catholyte reduce these trichloro compounds to hydrocarbons of a rather uncertain constitution, and a stilbene derivative. The reduction removes the three chlorine atoms from each of two molecules and the residues then unite:

$$2(CH_3 \cdot C_6H_4)_2CHCl_3 \rightarrow (CH_3C_6H_4)_2CH \cdot C \vdots C \cdot CH(C_6H_4CH_3)_2$$

The formulae for the hydrocarbons produced from the ditolyltrichloro compound have either of the two following formulae; just which formula is correct has not yet been proven:

$$(CH_3C_6H_4)_2CH \cdot C \vdots C \cdot CH(C_6H_4CH_3)_2$$

or

$$(CH_3C_6H_4)_2C : C : CHCH(C_6H_4CH_3)_2$$

Assym-diphenyltrichloroethane, *p*, *p'*-ditolyltrichloroethane and the dianisyl compounds have been reduced according to this method.[16]

The halogen attached to a ring carbon in compounds of the benzene series is not removed in the process of electrolytic reduction. No haloogen derivatives of benzene have as yet been reduced. But halogen nitro derivatives have been reduced with the above results. Under the conditions which Brand[17] stipulated for the preparation of phenylhydroxylamine from nitro benzene, i.e., in a neutral solution of acetic acid and sodium acetate containing alcohol as the solvent, *p*-chloronitrobenzene is reduced to *p*-chlorophenylhydroxylamine which compound was identical with the compound of Bamberger and Knecht.[18]

The reaction may go on a little farther than the hydroxylamine stage as is the case in the reduction of *m*-chloronitrobenzene in an alcoholic

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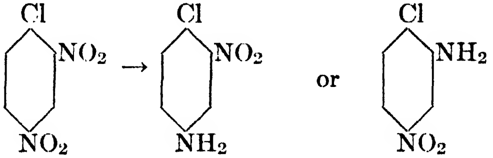
[15] K. Brand, Ber., **46**, 2935 (1913).

[16] Brand and Matsui, Ber., **46**, 2942 (1913).

[17] K. Brand, Ber., **38**, 3076 (1905), see page 207.

[18] Bamberger and Knecht, Ber., **29**, 264 (1896).

alkaline solution at a nickel wire gauze cathode when an 80 per cent yield of *m*-dichloroazoxybenzene is formed.[19] When more than one nitro group is present on the benzene ring it is not recorded that more than one of them is reduced. Electrolytic reduction seems to be indifferent in its choice as to which nitro group is reduced; sometimes one and sometimes the other is reduced but never both on the same ring. 2, 4-dinitrochlorobenzene yields both nitro chloroanilines in both alkaline and neutral solutions at different cathodes:[20]

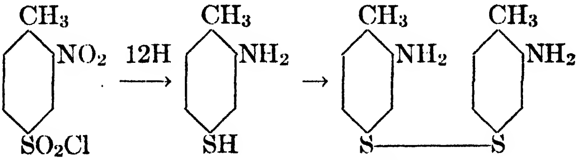


Chloro derivatives of the aromatic aldehydes are reduced as if no chlorine were present in the molecule.[21, 22]

Aromatic sulphonyl chlorides, being typical acid chlorides, are reduced first to the corresponding sulphinic acid, and then finally to the mercaptan. With *p*-toluenesulphonyl chloride the reactions are:[23]

$$CH_3C_6H_4SO_2Cl \rightarrow CH_3C_6H_4SO_2H \rightarrow CH_3 \cdot C_6H_4SH$$

When a nitro group is present on the ring it is first reduced to the amino group. The aminoarylsulphonyl chloride is soluble as a rule in the acid catholyte and the reduction goes very smoothly yielding the corresponding aminomercaptan. On standing in a closed vessel in the form of the sulphate, this amino mercaptan forms a disulphide. In the case of the sodium salt of 2-nitro-4-toluenesulphonic acid the equations are:[24]



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[19] Elbs and Kreman, Z. Elektrochem., **9**, 416 (1903).

[20] K. Brand and T. Eisenmenger, J. prakt. Chem., [2], **87**, 487 (1913).

[21] See page 297.

[22] The reduction of many other chloro compounds is referred to at various places in this text.

[23] Fichter, Verhandl. d. Naturf. Ges., Basel, **19**, 37 (1906); Fichter and Bernoulli, Z. Elektrochem., **13**, 310 (1907).

[24] Fichter and Bernoulli, Ber., **42**, 4308 (1909). Methods for the preparation of the starting material are given in detail.

The following sulphonyl chlorides have been reduced by this method:[25]

α-Naphthalenesulphonyl chloride, β-naphthalenesulphonyl chloride, benzene-1, 3-disulphonyl chloride, *p*-anisole sulphonyl chloride, *m*-nitrobenzene sulphonyl chloride, dimethylaniline-*p*-sulphonyl chloride.

In the electrolysis of organic sulphur compounds it was first thought that the reaction really took place at the anode, but later work with a divided cell showed that the process was not an oxidation but a reduction. Price and Twiss[26] have shown that the electrolysis of a solution of benzyl thiosulphates yields dibenzyldisulphide. When the electrolysis is carried out in an undivided cell the results are the same as in the case of the electrolysis of an alkali acetate:

$$2\mathrm{CH_3COO^-} \rightarrow \mathrm{C_2H_6} + 2\mathrm{CO_2}$$

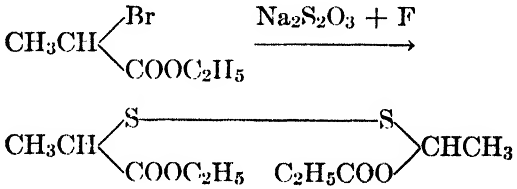
$$2\mathrm{C_6H_5CH_2S{\cdot}SO_3^-} \rightarrow \mathrm{C_6H_5CH_2S{\cdot}SCH_2C_6H_5} + 2\mathrm{SO_3}$$

When a pure aqueous solution of sodium benzyl thiosulphate is electrolyzed the solid dibenzyldisulphide is contaminated by a pungent oil, known to be benzyl mercaptan. However, if the electrolyte is kept neutral by the addition of sodium carbonate or bicarbonate no mercaptan is formed. The formation of the disulphide is due to the reduction of the thiosulphate with the simultaneous formation of hydrogen-sulphite ions:

$$2\mathrm{C_6H_5CH_2S{\cdot}SO_3} \xrightarrow{2\mathrm{H}} \mathrm{C_6H_5CH_2S{\cdot}SCH_2C_6H_5} + 2\mathrm{HSO_3^-}$$

Bernthsen[27] had previously shown that the aromatic thiosulphates were smoothly reduced to mercaptans while the aliphatic thiosulphates were reduced to the dithioacids. He had succeeded in reducing the following compounds in the presence of sodium thiosulphate:

α-Bromopropionic ethyl ester to diethyl ester of α-dithio-dilactic acid:



$$\mathrm{CH_3CH}\left\langle\begin{matrix}\mathrm{Br}\\ \mathrm{COOC_2H_5}\end{matrix}\right. \xrightarrow{\mathrm{Na_2S_2O_3} + \mathrm{F}}$$

$$\mathrm{CH_3CH}\left\langle\begin{matrix}\mathrm{S}\text{————————}\mathrm{S}\\ \mathrm{COOC_2H_5}\quad\mathrm{C_2H_5COO}\end{matrix}\right\rangle\mathrm{CHCH_3}$$

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[25] Fichter and Tamm, Ber., **43**, 3032 (1910).

[26] Price and Twiss, Proc. Chem. Soc., **22**, 260 (1906).

[27] Bernthsen, Ann., **251**, 1 (1889).

β-iodopropionic acid ethyl ester to the diethyl ester of β-dithio-di-lactic acid.
α-bromobutyric acid ethyl ester to the diethyl ester of α-dithio-dibutyric acid.
α-bromoisobutyric acid ethyl ester to the diethyl ester of α-dithio-diisobutyric acid.
α-bromoisovaleric acid ethyl ester to the diethyl ester of α-dithio-diisovaleric acid.

These esters are colorless mobile liquids without definite odor but in time decomposing in the air to form evil-smelling compounds of mercaptan nature. They are easily decomposed by hydrochloric acid.

Price and Twiss [28] on the basis of this work expected to get a mercaptan by a strenuous reduction with electrolytic methods but they found only the formation of disulphides. In a solution which is kept neutral or alkaline with sodium carbonate no mercaptan is found, in the case of the aliphatic series. Fichter and Bernoulli had in the case of the aromatic compounds obtained the mercaptans,[29] with a Pb cathode and a low c. d.; however nickel or platinum cathodes did not work this way.

The following compounds have been reduced: Diethyl disulphide,[30] dibenzyl disulphide,[30] *p*-nitrobenzyl disulphide,[31] *m*-nitrobenzyl disulphide,[31] *o*-nitrobenzyl disulphide,[31] dimethyl dithio-diglycollic acid,[32] diethyl-dithio-diglycollic acid,[32] diethyl-α-dithio-dilactylic acid,[32] diethyl-β-dithio-dilactylic acid.[32]

Diselenides [33] have also been formed by these methods.

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[28] Price and Twiss, J. Chem. Soc., **91**, 2021 (1907).

[29] Fichter and Bernoulli, Z. Elektrochem., **13**, 310 (1907).

[30] Price and Twiss, loc. cit.

[31] Price and Twiss, J. Chem. Soc., 93, 1401 (1908).

[32] Price and Twiss, ibid., **93**, 1645 (1908). See also Price and Twiss, ibid., **95**, 1050 and 1489 (1909).

[33] Price and Jones, Proc. Chem. Soc., **24**, 234 (1908).

INDEX OF AUTHORS

(In cases where the number of references is too large for convenience, the more important references are indicated by bold-face type.)

INDEX OF PATENTS

INDEX OF SUBJECTS