

Chapter 4

Correlation between Equilibrium Constant and Stabilization Energy

4.1. Introduction:

In the last chapter, formalism to take care of the solvent effect on the DFRT based stabilization energy in the adduct formation process was developed by introducing some thermochemical equations [i.e., equations (3.1) - (3.4)]. Using these equations, the 'net desolvation energy' (ΔE_{desolv}^{net}) was computed through a conventional approach [equation (3.1)] which, when added to DFRT based stabilization energy in gas phase [$\Delta E_{SE(AB)}^{gas}$] generates the stabilization energy in solvent [i.e., $\Delta E_{SE(AB)}^{solvent}$] [equation (3.7)]. Further, these stabilization energy values [i.e., $\Delta E_{SE(AB)}^{solvent}$] were correlated with the experimental formation constants for the methyltrioxorhenium (MTO)-pyridine adduct formation process in different solvents.

It was concluded in chapter 3 that the experimental formation constant values decrease with the decrease of stabilization energies of the adduct formation processes. However, no direct relation between formation constant and stabilization energy was developed in the previous chapter. In the present chapter, a relation is derived between formation constant (K) and $\Delta E_{SE(AB)}$ for adduct formation process with the help of chemical and statistical thermodynamics which is of analytical importance. Further, DFRT based $\Delta E_{SE(AB)}$ [equation (1.48)] is tested on three different adduct forming processes in both the gas phase as well as in solvent and compared with experimentally reported K values.

Parr and Pearson's expression¹ of stabilization energy, based on density functional reactivity theory (DFRT),²⁻⁴ provides a mathematical explanation of a well-known principle in chemistry i.e., Hard-Soft Acid-Base (HSAB) principle.⁵ Roy and collaborators⁶ carried out a study on Parr and Pearson's expression of stabilization energy and formulated a scheme known as Comprehensive Decomposition Analysis of Stabilization Energy (CDASE). In this scheme overall stabilization energy equation, proposed by Parr and Pearson, is fragmented in the two energy components: the kinetic component and the thermodynamic component. The kinetic component represents the energy raising component while the thermodynamic component represents the energy lowering component.

Further, Roy and co-workers employed CDASE scheme on various interacting chemical and biological systems⁷⁻¹² to explain the kinetics, thermodynamics and overall stabilization involved in those interactions.

Hamid *et al.*¹³ extended the CDASE scheme after including the perturbation on external potential of the two interacting species (discussed thoroughly in chapter 2). With the extended formalism they could explain the charge transfer limit when an adduct is formed between an electron donor and an electron acceptor. The extended formalism also conjectured the effect of solvent polarity on stabilization energy. The numerical support in favor of the conjecture was provided after introducing a new parameter termed as ‘net desolvation energy’, which happens to be the negative of ‘net free energy of solvation’.¹⁴

It is well known that the extent of interaction between the electron acceptor (A) and the electron donor (B) is measured by equilibrium constant (K) of the equilibrium $A + B \rightleftharpoons AB$. So, in principle, the K values of the interaction (or reaction) between A and B in the process of adduct (or Lewis adduct)¹⁵ formation can be correlated to the stabilization energy values generated by the CDASE scheme. This is because more is the stabilization of the adduct AB, more the equilibrium is shifted towards right, increasing the value of K.

Keeping in view of the above conceptual analogy the present chapter tries to investigate the reliability of the DFRT based (CDASE scheme-based, to be more specific) stabilization energy [$\Delta E_{SE(AB)}$] in producing the trend of equilibrium constant (K). Also, as K is thermodynamically related to standard Gibbs free energy of reaction (i.e., $\Delta_r G^\ominus$), trend of $\Delta E_{SE(AB)}$ and $\Delta_r G^\ominus$ has also some conceptual analogy [to be discussed in details in section 4.2 (b)]. Finally, as K is a thermodynamic parameter and $\Delta E_{SE(AB)}$ is obtained quantum mechanically, statistical mechanical concept needs to be invoked to explain the correlation between K and $\Delta E_{SE(AB)}$ for the adduct formation process of the type $A + B \rightleftharpoons AB$.

The chapter is structured in the following sections: Section 4.2 (a) discusses about the theoretical background related to DFRT based reactivity descriptors. Thermodynamic relation between $\Delta_r G^\ominus$ and K, for the adduct formation process $A + B \rightleftharpoons AB$ is discussed in section 4.2 (b). This is further extended to correlate K with $\Delta E_{SE(AB)}$. Computational details are elaborated in section 4.3, which also reports the systems chosen as electron acceptor (A), electron donor (B) and the corresponding adduct, AB. Section 4.4 demonstrates the correlation between experimental values of equilibrium constant (K) and calculated values of $\Delta E_{SE(AB)}$ in gas phase [section 4.4 (a)] as well as in solvents [sections 4.4 (b) and 4.4 (c)] (used in experimental study to generate K values). Correlation of K with global electrophilicity (w)

values of the acceptors are shown for reactions between substituted benzaldehydes and semicarbazide. Finally, in the concluding section (section 4.5) the whole study is summarized and the ways of extending the study are discussed.

4.2. Theoretical background:

(a) Density functional reactivity theory based descriptors:

The formation of adduct as a result of electron transfer from the electron donor to the electron acceptor species results in the change of their energies. The adduct formed as a result of electron transfer gets stabilized. The stabilization energy in the process of adduct formation was first given by Parr and Pearson¹ in terms of DFRT based global reactivity descriptors [chemical potential, $(\mu)^{1,15,16}$ and chemical hardness $(\eta)^1$]. They derived the expression of total energy after electron is transferred from the donor to the acceptor [equation (1.46)].

Further, Roy and collaborators⁶ re-denoted the expression of stabilization energy by arguing that when the donor and acceptor are of comparable sizes, the mutual effect of each other cannot be neglected. This re-denoted stabilization energy was fragmented into two energy components, one representing the kinetic component (i.e., energy raising component, $\Delta E_{B(A)}$) and another representing the thermodynamic component (i.e., energy lowering component, $\Delta E_{A(B)}$). Mathematically, these two components were represented by equations (1.49) and (1.50). The amount of charge transfer from the electron donor (B) to the electron acceptor (A) is given by equation (1.48).

Thus, calculation of two global reactivity descriptors e.g., chemical potential $(\mu)^{1,15,16}$ and chemical hardness $(\eta)^1$, of both the donor (B) and the acceptor (A) species, are required to explain chemical interaction through CDASE scheme. The analytical expressions of chemical potential and chemical hardness are as: $\mu = \left(\frac{\partial E}{\partial N}\right)_v$ and $\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v$ (here, v is external potential, i.e., potential due to positions of nuclei), whereas the operational equations for μ and η are given by equations (1.15) and (1.20a). Chemical potential and chemical hardness parameters of the donor (B) and the acceptor (A) require the calculation of their ionization potential (IP) and electron affinity (EA).

In 1999, Parr, Szentpaly and Liu proposed another important global reactivity descriptor for any chemical species, which they defined as ‘global electrophilicity (w)’.^{17,18} The analytical expression of w is given by equation (1.23).

Thus, when there is an interaction between an electron donor (B) and an electron acceptor (A), the w values of A (i.e., w_A) will indicate extent of interaction between A and B. Higher the value of w_A stronger will be the interaction.

(b) Relation between equilibrium constant (K) and stabilization energy [$\Delta E_{SE(AB)}$] for the process $A + B \rightleftharpoons AB$:

From chemical thermodynamics it is well known that the equilibrium constant (K) for any gas phase reaction (in the present case it is adduct formation) is related to standard reaction Gibbs energy ($\Delta_r G^\ominus$) through the following equation (assuming the reactants and products behave ideally),

$$\Delta_r G^\ominus = -RT \ln K \quad (\text{Here } R \text{ is ideal gas constant and } T \text{ is absolute temperature})$$

$$\Rightarrow K = e^{-\left(\frac{\Delta_r G^\ominus}{RT}\right)} \quad (4.1)$$

In case of adduct formation of the type, $A + B \rightleftharpoons AB$, $\Delta_r G^\ominus$ can be written as,

$$\Delta_r G^\ominus = (\varepsilon_0 + G_{corr})_{AB} - [(\varepsilon_0 + G_{corr})_A + (\varepsilon_0 + G_{corr})_B] \quad (4.2)$$

Here, ε_0 denotes ground state electronic energy and G_{corr} denotes thermal correction to Gibbs free energies.

Again G_{corr} term of each species can be elaborated as,

$$G_{corr} = H_{corr} - TS_{tot}$$

(H_{corr} denotes thermal correction to enthalpy)

or,

$$G_{corr} = E_{tot} + k_B T - TS_{tot}$$

(E_{tot} = thermal correction to energy, k_B = Boltzmann constant)

or,

$$G_{corr} = E_t + E_r + E_v + E_e + k_B T - TS_{tot} \quad (4.3)$$

Here, E_t , E_r , E_v and E_e denote, respectively, the thermal correction to translational, rotational, vibrational and electronic energy components (each including zero point energy also) and k_B is Boltzmann constant. $S_{tot} = S_t + S_r + S_v + S_e$ (i.e., total entropy contribution). Thus, the value of K can be calculated using equation (4.1) after inserting the values of different thermodynamic

parameters as elaborated in equations (4.2) and (4.3). It is obvious from equation (4.1) that as $\Delta_r G^\ominus$ become more negative, K value also increases.

Now, from equations (4.1) and (4.2) we can write,

$$K = e^{-\left(\frac{\Delta_r G^\ominus}{RT}\right)} = e^{-\left[\frac{\varepsilon_{0(AB)} - \varepsilon_{0(A)} - \varepsilon_{0(B)}}{RT}\right]} \times e^{-\left[\frac{G_{corr(AB)} - G_{corr(A)} - G_{corr(B)}}{RT}\right]} \quad (4.4)$$

From equation (4.4) we can argue that, in a series of reactions where any one between the donor, B or the acceptor, A is fixed and the other one is variable, the first exponential term in R.H.S will make major contribution in the value of K. This is because the change of the value of $[\varepsilon_{0(AB)} - \varepsilon_{0(A)} - \varepsilon_{0(B)}]$ will be more significant than the value of $[G_{corr(AB)} - G_{corr(A)} - G_{corr(B)}]$. Analyzing the terms in equation (4.3) the argument can be made more obvious. Here, $E_e = 0$ (normally), the values of E_t and E_r are same for all the variable reactants at same temperature (equal to $\frac{3}{2}RT$). Only difference of $E_v - TS_{tot}$ between the product (i.e., the adduct AB) and the reactant which is varying (i.e., either A or B) will make some difference in E_{tot} (i.e., thermal correction to energy). This difference in E_{tot} is not expected to be that much as that of the difference in ε_0 values. However, in a series of reactions if some of the reactants (the one which is being varied) have low lying electronic states then, $E_e \neq 0$. Also, if strengths and types of bonds in the variable reactants change significantly, difference in contribution in $E_v - TS_{tot}$ will no longer be negligible as one goes from one reaction in a series to another. In such a scenario the trend of K obtained just from the first exponential term in equation (4.4) might differ from the one obtained when both the exponential terms are considered.

Now, the DFRT based stabilization energy $[\Delta E_{SE(AB)}]$ of the adduct formation process is derived from the ground state electronic energies of the neutral, cationic and anionic systems of A (i.e., electron acceptor) and B (i.e., electron donor) in isolation [equations (1.48 – 1.50)]. Thus, while evaluating $\Delta E_{SE(AB)}$, DFRT does neither consider the difference of ground state electronic energies between the adduct and the reactants [the first exponential term in equation (4.4)] nor different thermal corrections [as is done conventionally while calculating $\Delta_r G^\ominus$, the second exponential term in equation (4.4)]. This is because conceptual origin of $\Delta E_{SE(AB)}$ in DFRT^{1,6} is different from that of the conventional $\Delta_r G^\ominus$ parameter. However, the expression of $\Delta E_{SE(AB)}$ [equation (1.48)] represents net stabilization of the adduct formation process and obtained after

addition of energy changes of the electron donor (B) and the electron acceptor (A) when chemical potentials of both are equalized. In that sense $\Delta E_{SE(AB)}$ and $\Delta_r G^\ominus$ are conceptually analogous to each other and it is quite logical to conclude that in a series of reaction the trend of $\Delta E_{SE(AB)}$ values and $\Delta_r G^\ominus$ values will be similar.

An alternative approach to show how K is intuitively related to $\Delta E_{SE(AB)}$, at least for gas phase reactions, is as follows:

For a gas phase reaction (or an adduct formation) of the type $A + B \rightleftharpoons AB$, where A and B are assumed to be gas of independent molecules (i.e., perfect gas, in spite of the fact that this limitation will introduce some error depending on the extent of non-ideality of any system being studied). The equilibrium constant (K) can be expressed in terms of corresponding molar partition function ($q_{X,m}^\ominus$, where X = A, B and AB) and difference of ground state energies ($\Delta_r E_0$) between the adduct and the reactants as,

$$K = \frac{\left(\frac{q_{AB,m}^\ominus}{N_A}\right)}{\left(\frac{q_{A,m}^\ominus}{N_A}\right)\left(\frac{q_{B,m}^\ominus}{N_A}\right)} e\left(\frac{-\Delta_r E_0}{RT}\right)$$

[N_A = Avogadro's number]

$$= \frac{q_{AB,m}^\ominus \times N_A}{q_{A,m}^\ominus \times q_{B,m}^\ominus} e\left(\frac{-\Delta_r E_0}{RT}\right) \quad (4.5)$$

Now, the standard molar partition function of the individual species can be written as,

$$\begin{aligned} q_{AB,m}^\ominus &= q_{AB}^e \times q_{AB}^t \times q_{AB}^R \times q_{AB}^v \\ &= g_{AB} \times \left(\frac{RT}{P^\ominus \Lambda_{AB}^3}\right) \times q_{AB}^R \times q_{AB}^v \\ &= \frac{g_{AB} \cdot RT \cdot q_{AB}^R \cdot q_{AB}^v}{P^\ominus \Lambda_{AB}^3} \end{aligned} \quad (4.6)$$

Here, q_{AB}^e , q_{AB}^t , q_{AB}^R and q_{AB}^v are, respectively, electronic, translational, rotational and vibrational contribution to partition function, g_{AB} is the degeneracy of the ground electronic state of AB (assuming first and higher electronic states are entirely inaccessible i.e., the system does not have any low lying excited state), P^\ominus is the standard pressure and Λ_{AB} is the thermal wavelength of the species AB.

Similarly,

$$q_{A,m}^{\theta} = \frac{g_A \cdot RT \cdot q_A^R \cdot q_A^v}{P^{\theta} \Lambda_A^3} \quad (4.7)$$

$$q_{B,m}^{\theta} = \frac{g_B \cdot RT \cdot q_B^R \cdot q_B^v}{P^{\theta} \Lambda_B^3} \quad (4.8)$$

Substituting (4.6), (4.7) and (4.8) in (4.5), we get,

$$K = \left(\frac{g_{AB}}{g_A \times g_B} \right) \times \frac{(RT)}{(RT) \times (RT)} \times \frac{(P^{\theta} \times P^{\theta})}{P^{\theta}} \times \frac{(q_{AB}^R \times q_{AB}^v)}{(q_A^R \times q_B^R)(q_A^v \times q_B^v)} \times \frac{(\Lambda_A^3 \times \Lambda_B^3)}{\Lambda_{AB}^3} \times N_A e^{\left(\frac{\Delta_r E_0}{RT} \right)} \quad (4.9)$$

Now, we can assume $g_{AB} = g_A = g_B = 1$ (i.e., ground electronic states of all the three species are non-degenerate). Also, assuming the first vibrational level to be the zero of energy and the anharmonicities are so small that the normal modes are independent, equation (4.9) can be modified to,

$$K = \left(\frac{N_A P^{\theta}}{RT} \right) \left(\frac{\Lambda_A^3 \times \Lambda_B^3}{\Lambda_{AB}^3} \right) \left(\frac{q_{AB}^R}{q_A^R \times q_B^R} \right) \times \left[\frac{\left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_{AB}}{\left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_A \left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_B} \right] \times e^{\left(-\frac{\Delta_r E_0}{RT} \right)}$$

(Here, $\theta_{V,K}$ indicates the vibrational temperature of the mode K)

$$\begin{aligned} &= \left(\frac{P^{\theta}}{k_B T} \right) \times \frac{h^3}{(2\pi m_A k_B T)^{\frac{3}{2}}} \times \frac{h^3}{(2\pi m_B k_B T)^{\frac{3}{2}}} \times \frac{(2\pi m_{AB} k_B T)^{\frac{3}{2}}}{h^3} \\ &\quad \times \left(\frac{q_{AB}^R}{q_A^R \times q_B^R} \right) \times \left[\frac{\left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_{AB}}{\left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_A \left(\prod_K \frac{1}{1 - e^{\left(\frac{\theta_{V,K}}{T} \right)}} \right)_B} \right] \times e^{\left(-\frac{\Delta_r E_0}{RT} \right)} \end{aligned}$$

$$\begin{aligned}
 K &= \left(\frac{P^\ominus}{k_B T} \right) \times \frac{h^3}{(2\pi k_B T)^{\frac{3}{2}}} \times \left(\frac{m_{AB}}{m_A m_B} \right) \\
 &\quad \times \left[\frac{\frac{1}{\sigma_{AB}} \times \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \times \left(\frac{\Pi}{\tilde{A}\tilde{B}\tilde{C}} \right)_{AB}^{\frac{1}{2}}}{\frac{1}{\sigma_A} \times \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \times \left(\frac{\Pi}{\tilde{A}\tilde{B}\tilde{C}} \right)_A^{\frac{1}{2}} \times \frac{1}{\sigma_B} \times \left(\frac{k_B T}{hc} \right)^{\frac{3}{2}} \times \left(\frac{\Pi}{\tilde{A}\tilde{B}\tilde{C}} \right)_B^{\frac{1}{2}}} \right] \\
 &\quad \times \left[\frac{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_{AB}}{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_A \left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_B} \right] \times e^{\left(\frac{-\Delta_r E_0}{RT} \right)}
 \end{aligned}$$

(here, σ_{AB} , σ_A and σ_B are the symmetry numbers of the corresponding species,

$$\begin{aligned}
 &= \left(\frac{P^\ominus}{k_B T} \right) \times \frac{h^3}{(2\pi k_B T)^{\frac{3}{2}}} \times \left(\frac{hc}{k_B T} \right)^{\frac{3}{2}} \times \left(\frac{m_{AB}}{m_A m_B} \right) \times \frac{1}{(\Pi)^{\frac{1}{2}}} \\
 &\quad \times \frac{\sigma_A \times \sigma_B}{\sigma_{AB}} \times \frac{(\tilde{A}\tilde{B}\tilde{C})_A (\tilde{A}\tilde{B}\tilde{C})_B}{(\tilde{A}\tilde{B}\tilde{C})_{AB}} \times \left[\frac{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_{AB}}{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_A \left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_B} \right] \times e^{\left(\frac{-\Delta_r E_0}{RT} \right)} \\
 &= \left[\frac{P^\ominus h^{\frac{9}{2}}}{\Pi^2 (k_B T)^4} \times (c)^{\frac{3}{2}} \right] \\
 &\quad \times \left[\frac{m_{AB}}{m_A m_B} \times \frac{\sigma_A \times \sigma_B}{\sigma_{AB}} \times \frac{(\tilde{A}\tilde{B}\tilde{C})_A (\tilde{A}\tilde{B}\tilde{C})_B}{(\tilde{A}\tilde{B}\tilde{C})_{AB}} \right] \times \left[\frac{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_{AB}}{\left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_A \left(\prod_K \frac{1}{1 - e^{-\left(\frac{\Theta_{V,K}}{T} \right)}} \right)_B} \right] \\
 &\quad \times e^{\left(\frac{-\Delta_r E_0}{RT} \right)}
 \end{aligned}$$

(4.10)

From equation (4.10), it is obvious that the term within the first square bracket is constant. The term $\frac{m_{AB}}{m_A m_B}$ is a fraction, the values of which may vary within the range $0 \leq \frac{m_{AB}}{m_A m_B} \leq 1$ [except

when H- atom is involved as one of the reacting species, when $\frac{m_{AB}}{m_A m_B} > 1$]. Smaller the value of either m_A or m_B , higher will be the value of $\frac{m_{AB}}{m_A m_B}$. The symmetry numbers σ_A , σ_B and σ_{AB} can be assumed to be 1 when none of A, B or AB are symmetric. Rotational constant [either $(\tilde{A}\tilde{B}\tilde{C})_A$ or $(\tilde{A}\tilde{B}\tilde{C})_B$] is common (when either A or B is common). Bigger the size of either of A or B (and hence AB), the values of either $(\tilde{A}\tilde{B}\tilde{C})_A$ or $(\tilde{A}\tilde{B}\tilde{C})_B$ [and hence $(\tilde{A}\tilde{B}\tilde{C})_{AB}$] will be smaller [as rotational constants are inversely proportional to moment of inertia (I), of the species. Contribution of vibrational partition function will depend on the number of strong or weak bonds [terms inside third square bracket in equation (4.10)] in the species and hence the values of the corresponding vibrational frequencies. It is expected that at 25 °C none of the three terms in the numerator and the denominator will vary much from 1.

However, in spite of some assumptions made (as discussed above) the numbers generated from the second and third square brackets will influence the value of K not that much as will be influenced by the value of the term $e^{\left(-\frac{\Delta_r E_0}{RT}\right)}$, because of its exponential nature. This is particularly true when either A (or B) is fixed in the equilibrium $A + B \rightleftharpoons AB$ (e.g., in a series of reactions where either the donor or the acceptor is fixed and the other reactant is variable). So, the trend of K will, in most of the cases, be mainly controlled by the $e^{\left(-\frac{\Delta_r E_0}{RT}\right)}$ term.

However, depending on A and B, quantities in second and third square brackets may, in some cases, alter the trend of K obtained only on the basis of last exponential term. This may happen in case of a series of reactions where the variable reactants differ widely from one another (in terms of strength and nature of bonds, structural parameters, etc.). Here, $\Delta_r E_0$ is defined as the difference of the molar ground state energies between the products and the reactants, i.e.,

$$\Delta_r E_0 = E_{0,m}(AB) - [E_{0,m}(A) + E_{0,m}(B)] \quad (4.11)$$

In equation (4.11), $E_{0,m}$ denotes the molar ground state energy of the corresponding species and is the sum of ground state electronic energy ($\varepsilon_{0,m}$) and the zero point energy (ZPE), So,

$$E_{0,m}(X) = \varepsilon_{0,m}(X) + ZPE(X) \quad (4.12)$$

The value of $\Delta_r E_0$ will be a negative quantity when adduct formation process, $A + B \rightleftharpoons AB$, lead to a stable adduct, AB. Hence from equation (4.11), we can argue that more negative is the value of $\Delta_r E_0$, higher will be the value of equilibrium constant K. Again, $\Delta_r E_0$ can be qualitatively related to $\Delta E_{SE(AB)}$ [equation (1.48)] as more is the stability of the adduct AB, more negative is the value of $\Delta E_{SE(AB)}$. So, it can be argued that more is the stabilization of the adduct (i.e., more negative is the value of $\Delta E_{SE(AB)}$) higher should be the value of K.

That means we can write, keeping in mind the above approximation and assumptions,

$$K \propto e^{\left(-\frac{\Delta E_{SE(AB)}}{RT}\right)} \quad (4.13)$$

The argument laid above regarding the correlation between K, $\Delta_r G^\ominus$ and $\Delta E_{SE(AB)}$ may be applicable in solution phase also, where solvent polarity will change the values of ϵ_0 , G_{corr} (and hence $\Delta_r G^\ominus$), $\Delta_r E_0$ and $\Delta E_{SE(AB)}$. However, for a series of adduct formation processes in a particular solvent these changes will be regular when either A or B varies keeping the other reactant fixed.

4.3. Computational Details:

Among the representative chemical systems chosen in the present study methyltrioxorhenium (MTO) acts as a Lewis acid (i.e., electron acceptor, A) and twenty-six different mono- and bidentate N-donor ligands as Lewis bases (i.e., electron donors). So, 26 different Lewis acid-base complexes are formed and in all these 26 complexes acceptor is common (i.e., MTO). The schematic diagram representing MTO-ligand adduct formation is shown in Figure 4.1, below,

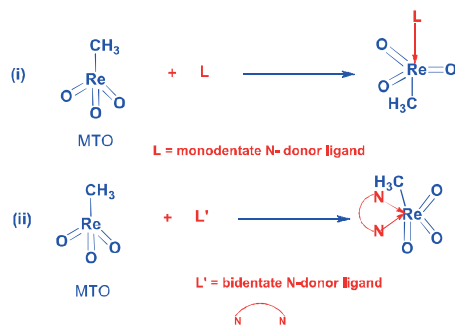
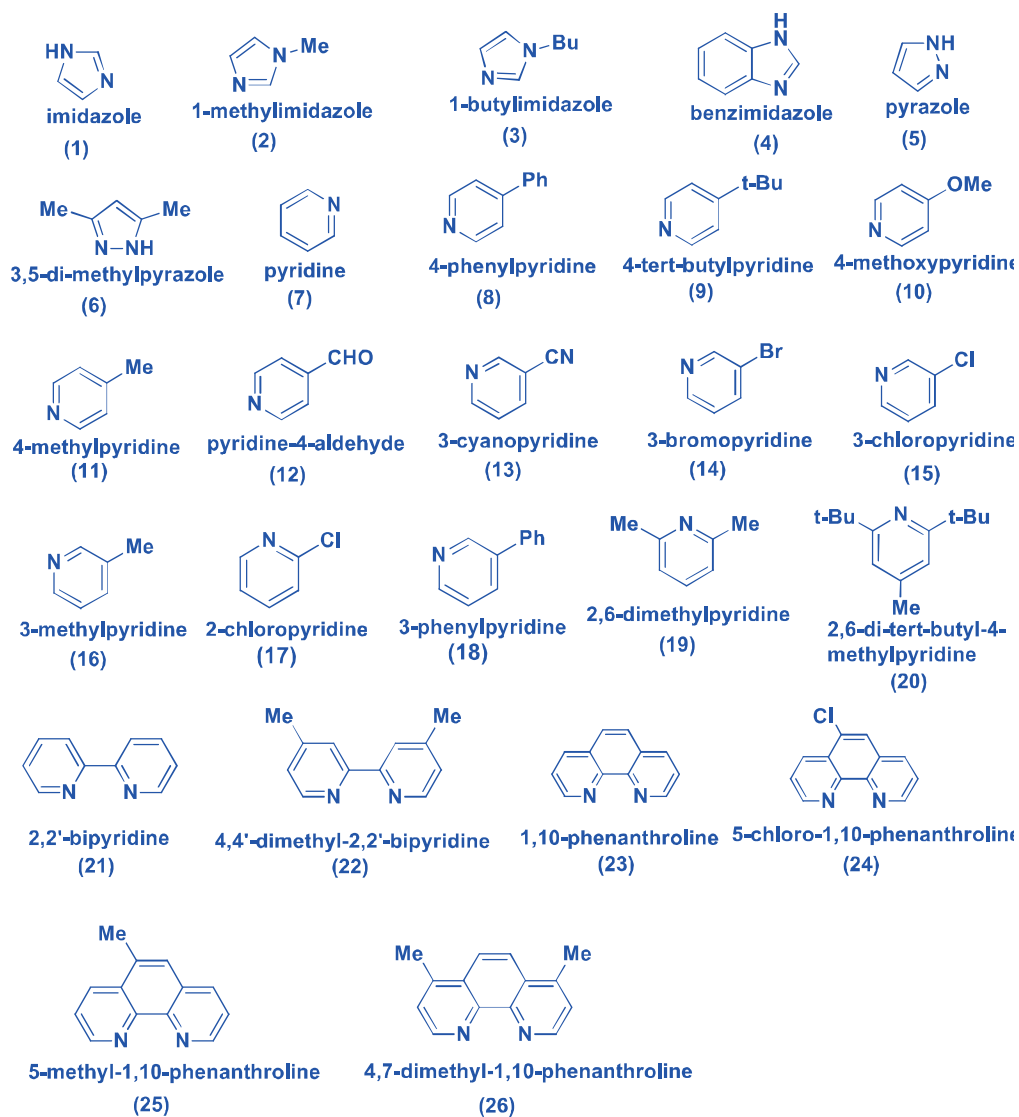


Figure 4.1. Schematic diagram representing the formation of MTO-ligand adduct with mono- and bidentate N- donor ligands.

The picture of all these ligands (donors) are given in Figure 4.2 below,



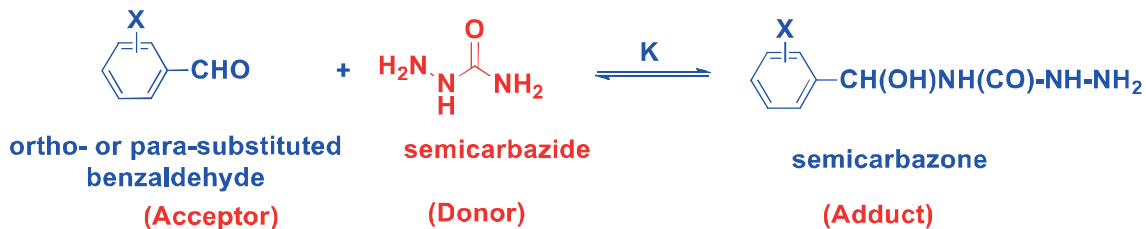
where,

-Me = -CH₃ group
 -Bu = -C₄H₉ group
 -Ph = -C₆H₅ group
 t-Bu = tert-butyl group

Figure 4.2. Structures of all mono and bi-dentate N-donor ligands.

Similarly, another two series of reactions are also chosen (Figure 4.3) where the donor is the common species semicarbazide. However, the acceptors in the first series are ortho-

substituted benzaldehydes and in the second series these are para-substituted benzaldehydes (Figure 4.4).



where, -X = -H, -OH, -Me, -OMe, -Cl, -NO₂

Figure 4.3. Schematic diagram representing the formation of semicarbazone (adduct) from ortho- or para- substituted benzaldehyde and semicarbazide.

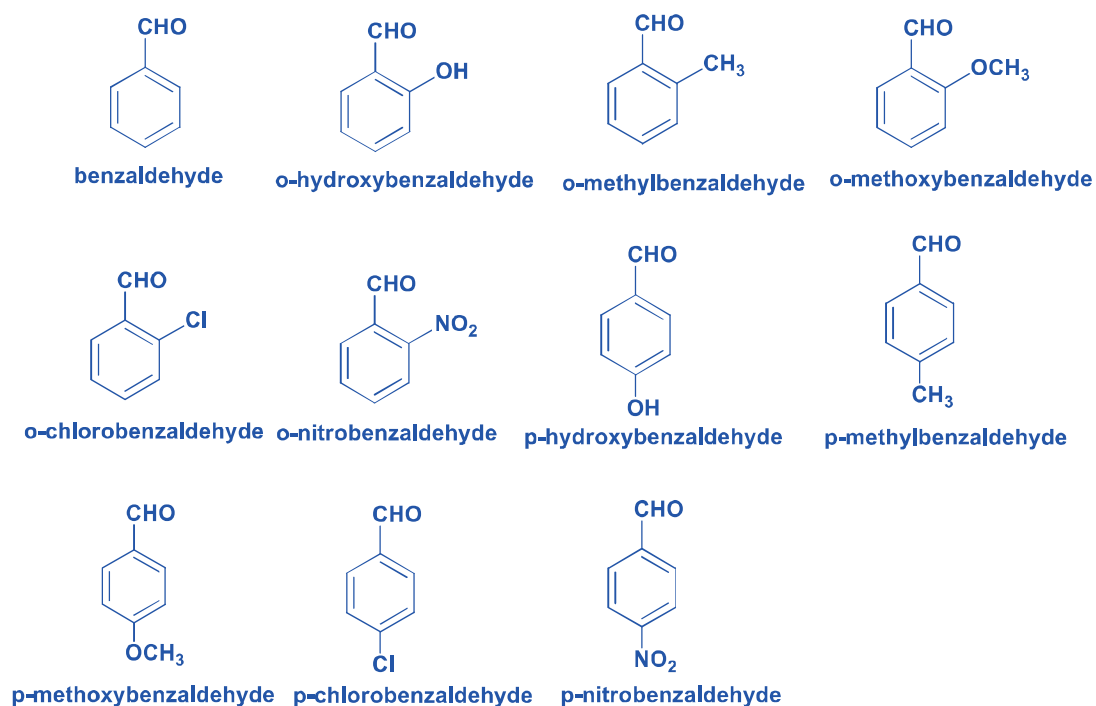


Figure 4.4. Structures of ortho- and para-substituted benzaldehydes (acceptors).

Geometry optimizations followed by frequency calculations (to ensure that no imaginary frequencies are present and hence the optimized structure is the most stable one) are carried out for all these structures using Gaussian09 program package.¹⁹ Once the optimization with

frequency check of the neutral structures is over, single point energy calculations of all the structures with monocationic and monoanionic charges at the optimized geometry of the corresponding neutral structures are carried out [this is required to compute $\Delta E_{SE(AB)}$, see section 4.1 (i.e., Introduction) and 4.2 (a)].

As there are wide variations in the structures of the ligands, they are segregated in different homologous series (to be discussed in section 4.4). This helps in understanding the cause of difference of Lewis basicity among the members in a particular series and so in comparing the K values with the corresponding $\Delta E_{SE(AB)}$ values. Presence of mono- and bidentate ligands also makes this segregation a necessary first step of analyzing stability factors. Similarly, to differentiate the effect of ortho- and para- substitutions on the reactivity of benzaldehyde with semicarbazide these reactions are also segregated in two different series.

To test the reliability and consistency of the generated data, all the calculations are carried out in two different methods: (i) B3LYP/6-31G(d,p), LANL2DZ (for Re atom) and (ii) M06-2X/6-31G(d,p), LANL2DZ (for Re atom). It is well known that M06-2X functional takes care of dispersion corrections.²⁰ This means that 6-31G(d,p) basis set is used for all other atoms of MTO other than rhenium (Re) as well as for all atoms of ligands (donors). Also, to take care of chemically inert core electrons of Re atom, LANL2DZ basis set with ECP is used, as this is effective in reducing computational cost.²¹ For reactions between semicarbazide and substituted benzaldehydes two different functionals B3LYP and M06-2X are used keeping the basis set same [i.e., 6-31G(d,p)]. Solvent effects are taken care implicitly. This means that geometry optimizations and single point calculations are all carried out using IEF-PCM model^{22, 23} (in both the methods) for all the series.

4.4. Results and Discussion:

The bonding between a Lewis acid and a Lewis base is coordinate covalent in nature, which fortifies the stability of overall adduct (complex). MTO, a Lewis acid in which rhenium (Re) atom is in +7 oxidation state, is having vacant orbitals in its structure. Conventionally, the coordinate covalent bonding occurs between nitrogen (N) atoms of the ligands (where nitrogen acts as a donor atom) and Re of MTO. The lone pair on N-atom of the ligand is donated to the empty orbitals of Re atom of MTO and thus reinforcing the stability of overall adduct. Although, the acceptor (MTO) molecule is fixed, the change of a base (ligand) has an impact on the

stability of adduct. As it is known that more basic is the ligand, greater is its electron donation ability towards the acid which results in the formation of stable adduct.

In reaction between semicarbazide and substituted benzaldehydes variation of Lewis acidity of later reactants will be reflected on the stability of the adduct. Thus, higher the Lewis acidity of the substituted benzaldehydes, as will be reflected in the values of their global electrophilicity (w),^{17,18} more stable will be the adduct. Which means higher the value of w of the Lewis acid, higher is the value of K , and more negative is the value of $\Delta E_{SE(AB)}$.

(a) Correlation of computed gas phase stabilization energy, $\Delta E_{SE(AB)}$ values with experimental equilibrium constant (K) values in solvent:

The calculated $\Delta E_{SE(AB)}$ values (in gas phase) are tabulated (Table 4.1) against the experimentally obtained equilibrium constant (K) values. It should be worth mentioning, here, that this comparison may not be exact as experimental K values reported here are obtained in conditions different from gas phase. Adduct formation with ligands numbering 1-10 and 21-26 are experimentally conducted in CHCl_3 solvent²⁴ and at 25 °C. For ligands 11-20 the experiments were conducted in CD_3NO_2 solvent at 24 °C.²⁵

In spite of this variation in experimental condition it is worth comparing the experimental K values with computed gas phase $\Delta E_{SE(AB)}$ values.

Also, as discussed in section 3, there is wide variation in the ligand structures (in terms of types of substitution, position of substitution causing variation in steric and electronic effects, number of donor N-atoms). Keeping all these factors in mind the ligands are segregated in seven different groups in Table 4.1.

Table 4.1. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of 1:1 adduct formation between MTO and twenty-six ligands (shown in Figure 4.2) at (i) B3LYP/6-31G(d,p), LANL2DZ (for Re atom) and (ii) M06-2X/6-31G(d,p), LANL2DZ (for Re atom) levels of theory. All the calculations are carried out in gas phase.

Group No.	Ligand	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p), LANL2DZ (for Re atom)	M06-2X/6-31G(d,p), LANL2DZ (for Re atom)
1	benzimidazole	300.80	-10.50	-11.54
	imidazole	714.90	-13.80	-15.40
	1-methylimidazole	1079.60	-14.11	-15.79
	1-butylimidazole	1999.50	-14.34	-16.20
2	pyrazole	28.40	-11.17	-11.35
	3,5-dimethylpyrazole	62.70	-13.80	-15.04
3	pyridine-4-aldehyde	36.80	-2.97	-2.76
	pyridine	196.60	-6.52	-7.50
	4-phenylpyridine	309.00	-7.23	-7.70
	4-tert-butylpyridine	677.40	-7.32	-8.32
	4-methylpyridine	732.00	-7.43	-8.72
	4-methoxypyridine	821.30	-8.11	-9.90
4	3-cyanopyridine	7.21	-2.93	-3.40
	3-chloropyridine	21.80	-5.88	-6.50
	3-bromopyridine	23.30	-6.32	-6.82
	3-phenylpyridine	156.00	-8.70	-9.20
	3-methylpyridine	254.00	-7.70	-8.60
5	2,2'-bipyridine	162.20	-7.50	-7.90
	4,4-dimethyl-2,2'-bipyridine	883.40	-8.50	-8.81
6	5-chloro-1,10-phenanthroline	1470.20	-7.17	-7.71
	1,10-phenanthroline	5464.30	-7.75	-8.40
	5-methy-1,10-phenanthroline	13097.00	-9.53	-10.52
	4,7-dimethy-1,10-phenanthroline	189234.40	-10.23	-11.30
7	2-chloropyridine	<1	-5.90	-6.45
	2,6-dimethylpyridine	<1	-8.90	-9.80
	2,6-di-tert-butyl-4-methylpyridine	<1	-9.65	-10.20

As can be seen the trends of experimentally obtained K values are matching with theoretically calculated $\Delta E_{SE(AB)}$ values in most of the cases and in both the methods. Among the Group-4 ligands experimental K values for 3-phenylpyridine.MTO complex (156 L mol^{-1}) is smaller than the 3-methylpyridine.MTO complex (254 L mol^{-1}). However, computed $\Delta E_{SE(AB)}$ values are found to be of opposite trend in both the methods. The experimental K-values of all adducts formed by Group-7 ligands are < 1 (exact values are not available) and so comparison of $\Delta E_{SE(AB)}$ values do not have much physical significance.

(b) Correlation of computed $\Delta E_{SE(AB)}$ values with experimental K values (in chloroform solvent):

To have physically more rational correlation the $\Delta E_{SE(AB)}$ values are computed implicitly in chloroform solvent and compared with K values obtained experimentally (again in chloroform). Ligands which are chosen for this purpose are from 1-10 and 21-26²⁴ (as complex formation of ligands 11-20 with MTO was studied in CD_3NO_2 solvent²⁵). The modified number of groups (after excluding ligands 11-20) are now 5 and are as shown in Table 4.2. It is worth mentioning here that the trends of $\Delta E_{SE(AB)}$ values are as expected from experimental K values in all 5 groups and in both the methods.

Table 4.2. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of 1:1 adduct formation between MTO and ligands [1-10 and 21-26] (shown in Figure 4.2) at (i) B3LYP/6-31G(d,p), LANL2DZ (for Re atom) and (ii) M06-2X/6-31G(d,p), LANL2DZ (for Re atom) levels of theory. All the calculations are carried out in chloroform.

Group No.	Ligand	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p), LANL2DZ (for Re atom)	M06-2X/6-31G(d,p), LANL2DZ (for Re atom)
1	benzimidazole	300.80	-11.85	-13.60
	imidazole	714.90	-16.20	-19.30
	1-methylimidazole	1079.60	-16.75	-19.54
	1-butylimidazole	1999.50	-16.90	-19.60
2	pyrazole	28.40	-12.71	-13.32
	3,5-dimethylpyrazole	62.70	-13.42	-15.31
3	pyridine	196.60	-6.96	-8.63
	4-phenylpyridine	309.00	-7.63	-9.00
	4-tert-butylpyridine	677.40	-7.70	-9.19
	4-methoxypyridine	821.30	-10.05	-11.24

4	2,2'-bipyridine	162.20	-7.60	-8.55
	4,4-dimethyl-2,2'-bipyridine	883.40	-8.35	-9.13
5	5-chloro-1,10-phenanthroline	1470.20	-7.50	-8.63
	1,10-phenanthroline	5464.30	-8.34	-9.45
	5-methyl-1,10-phenanthroline	13097.00	-9.01	-10.30
	4,7-dimethyl-1,10-phenanthroline	189234.40	-35.10	-40.10

(c) Correlation of computed $\Delta E_{SE(AB)}$ values with experimental K values (in CD_3NO_2 solvent):

The ligands which are considered for this correlation are numbered as 11-20 in Figure 4.2. The experimental K values are taken from the study of Espenson and Wang²⁵. Total 10 ligands are divided into three groups (Table 4.3). Group 1 comprises those ligands where H-atom at third position of the pyridine ring is substituted by other functional groups (like, -CN, -Cl, -Br, -C₆H₅ or -CH₃). Group 2 comprises pyridine-4-aldehyde and 4-methylpyridine, which are also derivatives of pyridine, where H-atom at fourth position of pyridine ring is replaced by -CHO and -CH₃ groups, respectively. In Group 3, there are three ligands which form very weak complex with MTO ($K < 1$). As the differences in K values between the members in this group are insignificant, it is not possible to correlate with computed $\Delta E_{SE(AB)}$ values. However, from the $\Delta E_{SE(AB)}$ values it is obvious that electronic factor play dominant role in stabilizing the adduct than the de-stabilizing steric factor. That is why $\Delta E_{SE(AB)}$ values follow the trend (including sign) 2,6-di-tert-butyl-4-methylpyridine < 2,6-dimethylpyridine < 2-chloropyridine. Also, 3-phenylpyridine (in Group 1) is an outlier.

Table 4.3. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of 1:1 adduct formation between MTO and ligands 11-20 (shown in Figure 4.2) at (i) B3LYP/6-31G(d,p), LANL2DZ (For Re atom) and (ii) M06-2X/6-31G(d,p), LANL2DZ (For Re atom) levels of theory. All the calculations are carried out in nitromethane.

Group No.	Ligand	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p), LANL2DZ (For Re atom)	M06-2X/6-31G(d,p), LANL2DZ (For Re atom)
1	3-cyanopyridine	7.21	-3.15	-4.31
	3-chloropyridine	21.80	-6.43	-7.85
	3-bromopyridine	23.30	-7.00	-8.10
	3-phenylpyridine	156.00	-9.83	-11.10
	3-methylpyridine	254.00	-8.50	-10.25
2	pyridine-4-aldehyde	36.80	-2.60	-2.70
	4-methylpyridine	732.00	-8.50	-10.25
3	2-chloropyridine	< 1	-6.25	-7.60
	2,6-dimethylpyridine	< 1	-10.33	-12.10
	2,6-di-tert-butyl-4-methylpyridine	< 1	-10.72	-12.11

(d) Correlation of computed $\Delta E_{SE(AB)}$ and w - values with experimental K-values for interaction between semicarbazide (as electron donor, B) and ortho- and para-substituted benzaldehydes (as electron acceptors, A):

Tables 4.4 – 4.8 demonstrate the correlation of generated $\Delta E_{SE(AB)}$ and w - values in gas phase with experimental K values in ethanol solvent.²⁶ Tables 4.8 – 4.11 demonstrate the same correlation when $\Delta E_{SE(AB)}$ and w values are computed in ethanol medium. From Tables 4.4, 4.5, 4.8 and 4.9 it is obvious that as the experimental K values increase in the series $\Delta E_{SE(AB)}$ values become more negative. Also, as the global electrophilicity (w) values of the Lewis acids (i.e., the electron acceptors) increase in a particular series experimental K values also increase. Similar trends are observed in ethanol medium. There are two outlier in these two series e.g., o-methoxybenzaldehyde and p-methoxybenzaldehyde. Theoretically generated $\Delta E_{SE(AB)}$ and w - values reflect comparatively weaker electron accepting power of these two Lewis acids than what is expected from experimental K values. The observation is similar when $\Delta E_{SE(AB)}$ and w - values are generated both in gas phase as well as in solution.

Table 4.4. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of semicarbazone (adduct) formation between semicarbazide and benzaldehyde and its ortho-derivatives (shown in Figure 4.3) at (i) B3LYP/6-31G(d,p) (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in gas phase.

Entry	Acceptor	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	o-hydroxybenzaldehyde	0.33	-1.77	-2.84
2	o-methylbenzaldehyde	1.05	-2.43	-2.94
3	benzaldehyde	1.32	-2.99	-3.10
4	o-methoxybenzaldehyde	1.67	-1.45	-1.56
5	o-chlorobenzaldehyde	19.0	-3.50	-3.56
6	o-nitrobenzaldehyde	27.1	-6.70	-7.02

Table 4.5. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of semicarbazone (adduct) formation between semicarbazide and benzaldehyde and its para-derivatives (shown in Figure 4.3) at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in gas phase.

Entry	Acceptor	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	p-hydroxybenzaldehyde	0.073	-1.54	-1.59
2	p-methylbenzaldehyde	0.62	-2.27	-2.74
3	p-methoxybenzaldehyde	1.05	-1.27	-1.37
4	benzaldehyde	1.32	-2.99	-3.10
5	p-chlorobenzaldehyde	4.14	-3.40	-3.50
6	p-nitrobenzaldehyde	27.1	-7.90	-7.88

Table 4.6. Global electrophilicity (w) values (in kcal mol⁻¹) of benzaldehyde and its ortho-derivatives (acceptors) at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in gas phase.

Entry	Acceptor	K (L mol ⁻¹)	w	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	o-hydroxybenzaldehyde	0.33	42.21	42.90
2	o-methylbenzaldehyde	1.05	46.40	48.95
3	benzaldehyde	1.32	47.91	49.20

4	o-methoxybenzaldehyde	1.67	40.80	41.85
5	o-chlorobenzaldehyde	19.0	53.10	53.90
6	o-nitrobenzaldehyde	27.1	75.90	75.90

Table 4.7. Global electrophilicity (w) values (in kcal mol⁻¹) of benzaldehyde and its para-derivatives (acceptors) shown in Figure 4.4 at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in gas phase.

Entry	Acceptor	K (L mol ⁻¹)	w	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	p-hydroxybenzaldehyde	0.073	40.00	40.81
2	p-methylbenzaldehyde	0.62	44.80	47.20
3	p-methoxybenzaldehyde	1.05	38.73	39.80
4	benzaldehyde	1.32	47.91	49.20
5	p-chlorobenzaldehyde	4.14	52.80	53.63
6	p-nitrobenzaldehyde	27.1	80.63	79.30

Table 4.8. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of semicarbazone (adduct) formation between semicarbazide and benzaldehyde and its ortho-derivatives (shown in Figure 4.3) at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in ethanol.

Entry	Acceptor	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	o-hydroxybenzaldehyde	0.33	-3.10	-3.60
2	o-methylbenzaldehyde	1.05	-4.27	-4.41
3	benzaldehyde	1.32	-5.14	-5.45
4	o-methoxybenzaldehyde	1.67	-2.86	-3.44
5	o-chlorobenzaldehyde	19.0	-5.45	-5.70
6	o-nitrobenzaldehyde	27.1	-10.62	-11.25

Table 4.9. Stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of semicarbazone (adduct) formation between semicarbazide and benzaldehyde and its para-derivatives (shown in Figure 4.3) at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in ethanol.

Entry	Acceptor	K (L mol ⁻¹)	$\Delta E_{SE(AB)}$	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	p-hydroxybenzaldehyde	0.073	-3.17	-3.16
2	p-methylbenzaldehyde	0.62	-3.93	-4.26
3	p-methoxybenzaldehyde	1.05	-2.47	-3.02
4	benzaldehyde	1.32	-5.14	-5.45
5	p-chlorobenzaldehyde	4.14	-5.25	-5.90
6	p-nitrobenzaldehyde	27.1	-11.3	-11.25

Table 4.10. Global electrophilicity (w) values (in kcal mol⁻¹) of benzaldehyde and its ortho-derivatives (acceptors) at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in ethanol.

Entry	Acceptor	K (L mol ⁻¹)	w	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	o-hydroxybenzaldehyde	0.33	74.32	80.10
2	o-methylbenzaldehyde	1.05	81.04	83.00
3	benzaldehyde	1.32	85.02	84.82
4	o-methoxybenzaldehyde	1.67	73.83	80.25
5	o-chlorobenzaldehyde	19.0	91.23	93.52
6	o-nitrobenzaldehyde	27.1	138.30	131.43

Table 4.11. Global electrophilicity (w) values (in kcal mol⁻¹) of benzaldehyde and its para-derivatives (acceptors) shown in Figure 4.4 at (i) B3LYP/6-31G(d,p) and (ii) M06-2X/6-31G(d,p) levels of theory. All the calculations are carried out in ethanol.

Entry	Acceptor	K (L mol ⁻¹)	w	
			B3LYP/6-31G(d,p)	M06-2X/6-31G(d,p)
1	p-hydroxybenzaldehyde	0.073	80.20	74.73
2	p-methylbenzaldehyde	0.62	84.67	82.20
3	p-methoxybenzaldehyde	1.05	80.00	74.30
4	benzaldehyde	1.32	85.02	84.82

5	p-chlorobenzaldehyde	4.14	93.20	93.52
6	p-nitrobenzaldehyde	27.1	137.96	130.80

4.5. Conclusions:

The present chapter tries to establish the correlation between equilibrium constant (K) and the stabilization energy [$\Delta E_{SE(AB)}$] computed through density functional reactivity theory (DFRT) based CDASE (Comprehensive Decomposition Analysis of Stabilization Energy) scheme. Thermodynamic relation between K and standard reaction Gibbs energy, $\Delta_r G^\ominus$ (and hence other electronic and thermochemical parameters e.g., ground state electronic energy, zero-point energy, thermal correction to free energy, etc.) is used to establish this correlation. Further, to make the correlation more obvious, analytical relation between K, partition functions and difference in ground state energies between the product (i.e., the adduct) and the reactants (i.e., adduct forming species) are invoked.

From the generated data it is obvious that there is clear correlation between K and $\Delta E_{SE(AB)}$ in both gas and solvent phase. This is expected because in solvent phase the $\Delta_r G^\ominus$ will be modified to some extent (depending on the dielectric constant of the solvent) after including free energy of solvation keeping the analytical relation between K and $\Delta_r G^\ominus$ [and hence $\Delta E_{SE(AB)}$] similar to that of gas phase.

In very few cases (numbers shown in bold font in different Tables), the trends of computed $\Delta E_{SE(AB)}$ values are not as expected from experimental K-values. There can be three plausible reasons for these irregular trends. These are: (i) $\Delta E_{SE(AB)}$ is computed using charge transfer component only. There are extended formalism to take care of electrostatic and dispersion interaction.²⁷ However, implementation of this extended formalism for interaction between polyatomic molecules seems not to be very practical one because it is based on ‘reactive site’ model (ii) other parameters in the statistical thermodynamic expression [equation (4.10)] may alter the trend obtained from just the values of $e^{-\frac{\Delta_r E_0}{RT}}$ [equation (4.10)] or $e^{-\frac{\Delta E_{SE(AB)}}{RT}}$ [equation (4.13)]. (iii) Although $\Delta_r E_0$ and $\Delta E_{SE(AB)}$ represent analogous parameters conceptually (i.e., net stabilization of the adduct with respect to the reactants) they are not same. This is because of the difference in conceptual origin of these two parameters. Also, computation of $\Delta_r E_0$ values need to be done carefully. As it is obvious from equation (4.11) it involves the

computation of the molar ground state energies of the product (AB) and of the reactants (A and B). Again molar ground state energy is the sum of molar ground state electronic and zero-point energies (ZPE) [equation (4.12)]. Conventionally, this is done through thermochemistry calculations and sensitivity of thermochemical parameters on methods and basis sets are well known.^{28,29} This might be one of the probable reasons for irregular trends of $\Delta_r E_0$ and $\Delta E_{SE(AB)}$ obtained for reaction between MTO and mono- and bidentate N-donor ligands (Tables 4.12 and 4.13).

Table 4.12. Reaction energy ($\Delta_r E_0$) and stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of adduct formation between MTO and different ligands (Groups 1 – 3, structures of which are shown in Figure 4.2) at B3LYP/6-31G(d,p), LANL2DZ (for Re atom) level of theory. All the calculations are carried out in gas phase.

Group No.	Ligand	$\Delta_r E_0$	$\Delta E_{SE(AB)}$
1	benzimidazole	-3.98	-10.50
	imidazole	-6.62	-13.80
	1-methylimidazole	-6.71	-14.11
	1-butylimidazole	-5.54	-14.34
2	pyrazole	-4.93	-11.17
	3,5-dimethylpyrazole	-4.99	-13.80
3	pyridine-4-aldehyde	-3.02	-2.97
	pyridine	-5.40	-6.52
	4-phenylpyridine	-2.71	-7.23
	4-tert-butylpyridine	-4.70	-7.32
	4-methylpyridine	-5.50	-7.43
	4-methoxypyridine	-5.32	-8.11

Table 4.13. Reaction energy ($\Delta_r E_0$) and stabilization energy [$\Delta E_{SE(AB)}$] values (in kcal mol⁻¹) in the process of adduct formation between MTO and different ligands (Groups 1 – 3, structures of which are shown in Figure 4.2) at B3LYP/6-31G(d,p), LANL2DZ (for Re atom) level of theory. All the calculations are carried out in chloroform.

GroupNo.	Ligand	$\Delta_r E_0$	$\Delta E_{SE(AB)}$
1	benzimidazole	-1.11	-11.85
	imidazole	-2.82	-16.20
	1-methylimidazole	-3.48	-16.75
	1-butylimidazole	-2.13	-16.90
2	pyrazole	-1.65	-12.71
	3,5-dimethylpyrazole	-1.59	-13.42

3	pyridine	-1.61	-6.96
	4-phenylpyridine	-0.12	-7.63
	4-tert-butylpyridine	-0.81	-7.70
	4-methoxypyridine	-0.03	-10.05

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