Density Functional Approach to Frontier Controlled Reactions

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Abstract: By using Density Functional Theory (DFT) for the description of the initial stages of the reaction between Lewis acid A and Lewis base :B, an expression for the amount of charge transfer is obtained. With this expression, it is shown that for the soft acid–soft base interaction this amount of charge transfer is controlled by the frontier orbitals, thus confirming the exclusive role frontier orbitals play in chemical reactivity.

Motivation

Density Functional Theory (DFT) proved to be a very valuable tool in providing a solid foundation for the basic concepts used in chemical reactivity theory. It is rather obvious that quantities like ionization potential (I) and electron affinity (A) are of primary importance for processes involving electron transfer. It was already realized by Mulliken that the linear combination in the form

$$\chi = \tfrac{1}{2}(I + A) \tag{1}$$

is characteristic of an escaping tendency for the electrons and therefore χ may serve as a basis for an electronegativity scale.[1] DFT confirmed this conclusion by identifying the finite difference formula for chemical potential $\mu = (\partial E/\partial N)_v$ with the negative of the Mulliken electronegativity.[2] Moreover, using DFT arguments Parr and Pearson were able to recognize the importance of a second derivative of E vs. N. The finite difference formula for this second derivative

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \simeq \frac{1}{2}(I - A) \tag{2}$$

was identified by them as an operational definition of an absolute hardness.[3] Therefore, DFT provided a quantitative measure for a qualitative concept that was so successfully used in a description of Lewis acids and bases.[4] Parr and Pearson also derived simple (but very valuable) expressions for the amount of charge transfer ΔN and energy change ΔE which accompany the formation of A:B complex from acid A and base :B. These expressions are

$$\Delta N = \frac{\chi_A^\circ - \chi_B^\circ}{2(\eta_A + \eta_B)} \tag{3}$$

$$\Delta E = \frac{-(\chi_A^\circ - \chi_B^\circ)^2}{4(\eta_A + \eta_B)} \tag{4}$$

Although eq 3 and 4 are incomplete, they have a great value in trying to predict a global change during the reaction with a minimum number of parameters. The shortcomings of eq 3 and 4 are known and were pointed out in the original derivation.[3] Thus the dependence of the chemical potential on the changing external field was neglected. Also, stereoselectivity of the reaction is not manifested through these expressions.

An extended version of eq 3 and 4 was obtained by Pearson[5] using a semiempirical molecular orbital approach. For example, for a two-atom two-electron system in which there is a bonding between A and B, the analogues of eq 3 and 4 are

$$\Delta N = \frac{\chi_A^\circ - \chi_B^\circ}{2(\eta_A + \eta_B) - 1/R - 2\beta/(N_A N_B)^{1/2}} \tag{5}$$

$$\Delta E = \frac{-(\chi_A^\circ - \chi_B^\circ)^2}{4[(\eta_A + \eta_B) - 1/R + 2\beta]} \tag{6}$$

In (5) and (6) R is the internuclear separation and β is the resonance integral.[5] For a fixed R, β is fixed and eq 5 and 6 have a form of eq 3 and 4. But according to the derivation in ref 5, ΔN and ΔE given by eq 5 and 6 are optimal changes along the reaction coordinate and therefore we are justified in considering them to be actual changes along this coordinate. In other words, ΔE and ΔN in (5) and (6) can be considered as functions of R. With this interpretation in mind, the orientational selectivity of the reaction is included in (5) and (6) through the exchange integral β. Therefore it may seem that MO theory can explain orientation and stereoselectivity of the reaction, while DFT is not able to do it. In what follows, we want to show that this is not the case. DFT is perfectly capable of explaining stereoselectivity. Moreover, it underlines the importance of frontier orbitals in this selectivity.

Density Functional Theory Description

Electronegativity and hardness defined by eq 1 and 2 are global quantities describing molecules. Understanding stereoselection requires quantities with local character. The first of such quantities was introduced by Parr and Yang.[6] The quantity they introduced depends on the orientational properties and was therefore called frontier or fukui function, $f(\vec{r})$, defined by eq 7.

$$f(\vec{r}) = \left.\frac{\delta \mu}{\delta v(\vec{r})}\right|_N = \left.\frac{\partial \rho(\vec{r})}{\partial N}\right|_v \tag{7}$$

Combining eq 2 and 7 one gets for the change in chemical potential eq 8.

$$d\mu = 2\eta\, dN + \int f(\vec{r})\, dv(\vec{r})\, d\vec{r} \tag{8}$$

This equation plays a prominent role in our discussion.

Consider a reaction between Lewis acid A and base :B. We shall consider the initial stage of the reaction so that even though we deal with one system A:B we still can distinguish two subsystems, acid A and base :B. From a DFT viewpoint, A and B being parts of the same system have to have the same value for the chemical potential, i.e.

$$\mu_A = \mu_B = \mu_{AB} \tag{9}$$

Now consider some motion of the reactants along some reaction coordinate, so that there is an electron flow from B to A, subject to the constraint in eq 10.

$$dN_A = -dN_B = dN \tag{10}$$

During this motion the external potential acting on the electronic cloud in A or B also changes. All this results in a change of the

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(6) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050.

chemical potential of A and B, but eq 9 remains valid. Therefore, for the change in chemical potential one can write

$$d\mu_A = 2\eta_A \, dN_A + \int f_A(\vec{r}) \, dv_A(\vec{r}) \, d\vec{r}$$
$$= 2\eta_B \, dN_B + \int f_B(\vec{r}) \, dv_B(\vec{r}) \, d\vec{r} = d\mu_B \qquad (11)$$

Because we consider the reaction in its earlier stages, we can replace η_i by η_i° and f_i by f_i°, where η_i° and f_i° are absolute hardness and fukui functions, respectively, of a free molecule (A or B). Equation 9 suggests a close analogy between the description of chemical reactions by DFT and the description of phase equilibrium in thermodynamics. In this analogy, the advancement of chemical reaction is a motion along an equilibrium line in $N,v(\vec{r})$ space, while in thermodynamics the equilibrium line is in T,P space. The equation describing the equilibrium curve in thermodynamics is the Clapeyron equation.[7] Our eq 11 is the closest analogue to the Clapeyron equation in the DFT description of chemical reactivity. The close analogy between thermodynamics and density functional description was pointed out more than once recently.[8]

In eq 11 dV_A is the change of the external potential acting on A, while dV_B is the same for B. In the first approximation two sources exist for a change in dV_A. Therefore

$$dV_A = dV_A^{(1)} + dV_A^{(2)} \qquad (12)$$

with the same equation for dV_B. The first source for a change in V_A is due to the motion of the nuclei

$$dV_A^{(1)}(\vec{r}) = dV^n(\vec{r}) \qquad (13)$$

where superscript n stands for nuclei.

The second source for a change in V_A is due to the electron flow from B to A

$$dv_A^{(2)}(\vec{r}) = \int \frac{\delta\rho_B(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' \qquad (14)$$

with

$$\delta\rho_B(\vec{r}') \simeq \left.\frac{\delta\rho_B(\vec{r}')}{\delta N_B}\right|_v dN_B = f_B^\circ(\vec{r}') \, dN_B \qquad (15)$$

where the last equality in eq 15 follows from eq 7. The same applies to dv_B. From eq 11–15 one gets

$$2\eta_A^\circ \, dN_A + \int f_A^\circ(\vec{r}) \, dv^n(\vec{r}) \, d\vec{r} +$$
$$\left[\int\int \frac{f_A^\circ(\vec{r})f_B^\circ(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'\right] dN_B = 2\eta_B^\circ \, dN_B +$$
$$\int f_B^\circ(\vec{r}) \, dv^n(\vec{r}) \, d\vec{r} + \left[\int\int \frac{f_A^\circ(\vec{r})f_B^\circ(\vec{r}') \, d\vec{r} \, d\vec{r}'}{|\vec{r} - \vec{r}'|}\right] dN_A \qquad (16)$$

Using charge conservation condition $dN_A = -dN_B$ we get from the last equation

$$[(2\eta_A^\circ - J_f) + (2\eta_B^\circ - J_f)] \, dN =$$
$$\int f_B^\circ(\vec{r}) \, dv^n(\vec{r}) \, d\vec{r} - \int f_A^\circ(\vec{r}) \, dv^n(\vec{r}) \, d\vec{r} \qquad (17)$$

In eq 17

$$J_f = \int\int \frac{f_A^\circ(\vec{r})f_B^\circ(\vec{r}') \, d\vec{r} \, d\vec{r}'}{|\vec{r} - \vec{r}'|} \qquad (18)$$

is the Coulomb integral between fukui functions. It is obvious that this Coulomb integral J_f has a strong orientational depen-

dency. From eq 17 we get for dN

$$dN = -\frac{\int [f_A^\circ(\vec{r}) - f_B^\circ(\vec{r})] \, dv^n(\vec{r}) \, d\vec{r}}{(2\eta_A^\circ + 2\eta_B^\circ) - 2J_f} \qquad (19)$$

Equation 19 is the final result in DFT language, but the analysis can be carried one step further. At this stage we use the approximation to fukui functions in terms of frontier orbitals[6]

$$f_A^\circ \simeq \rho_{LUMO}^A \qquad f_B^\circ \simeq \rho_{HOMO}^B \qquad (20)$$

and therefore

$$f_A^\circ(\vec{r}) - f_B^\circ(\vec{r}) \simeq \rho_{LUMO}^A - \rho_{HOMO}^B = \Delta\rho(\vec{r}) \qquad (21)$$

The combination of eq 21 with eq 19 results in the final expression for dN

$$dN = -\frac{\int \Delta\rho(\vec{r})\Delta v^n(\vec{r}) \, d\vec{r}}{2(\eta_A^\circ + \eta_B^\circ - J_f)} \qquad (22)$$

Equations 22 and 19 contain our final results. In these equations dN is the amount of electronic charge transferred between reactants during the small displacement along the reaction coordinate. As one can see from these equations the soft character of the reactants (η_A° and η_B° are small) facilitates such charge transfer, and the bonding has covalent character. Moreover, the orientational selectivity is evident in eq 22 and 19. The directional properties of frontier orbitals of both A and B determine the magnitude of Coulomb integral J_f and thus select the most favorable reaction coordinate. For large overlap J_f increases and that causes more effective electron transfer. The numerator of eq 22 also underlines the covalent character of the bonding. It quantifies the change in electronic attraction energy toward the nuclei[9] and indicates that during the reaction the electrons are redistributing themselves so that they can interact with nuclei more efficiently. The more efficient the redistribution is the stronger the covalent bonding is.

Concluding Remarks

Application of DFT to the description of the initial stages of the reaction between Lewis acid A and Lewis base :B results in a strongly orientation-dependent expression (eq 22) for the amount of electron transfer. This geometric dependence is dominated by the interaction of the *frontier* orbitals among themselves and with the nuclei (eq 19). Therefore DFT confirms the conclusion that frontier orbitals play a prominent role in the theory of chemical reactivity. One can see from eq 19 that frontier orbitals essentially control soft–soft reactions, where the bonding has covalent character. For hard–hard interactions dN is small and the reaction will be controlled by Coulomb interaction between the reagents.[10]

Finally, we would like to make some comments on the comparison of DFT results for the amount of electron transfer given by eq 3 and 19. Although they look somewhat similar, they describe different quantities. Thus eq 3 approximately describes the total amount of charge (ΔN) transferred in the reaction between Lewis acid A and Lewis base B, while eq 19 describes the differential amount of charge (dN) transferred during a small displacement of reactants along some reaction coordinate. Equation 19 and therefore eq 22 do not transform into eq 3. While deriving eq 3 one assumes that each reactant before the reaction is an independent system with its own chemical potential (electronegativity). After the reaction both reactants acquire the same chemical potential due to the transfer of charge ΔN. Thus eq 3 estimates the amount of the charge transferred in the reaction and points out the direction of electron transfer. In deriving eq 19, one considers from the start both reactants as a common system with a common chemical potential. During the small initial displacement along some path the chemical potential is changed,

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(8) Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631–656.

(9) Note that the minus sign in eq 19 takes care of the right direction of the electron flux. (Remember, the electron charge in DFT is positive.)
(10) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

but in such a way that the equality of chemical potentials of the reactants is preserved. This results in a transfer of the charge described by eq 19 or 22. The amount of charge transferred is now having strong dependence on the structure and orientation of the reactants.

Thus eq 3 and 19 illuminate different aspects of the acid–base reaction. The difference is reflected in different expressions for the numerator in eq 3 and 19. The common aspect of the equations is reflected by their denominator. Both equations show that soft–soft interaction facilitates the electron transfer, thus

predicting covalent character for the bonding.

(11) Tachibana, A., private communication.

Thermal Stability and Kinetic Lability of the Metal–Carbonyl Bond. A Theoretical Study on $M(CO)_6$ ($M = Cr, Mo, W$), $M(CO)_5$ ($M = Fe, Ru, Os$), and $M(CO)_4$ ($M = Ni, Pd, Pt$)

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Abstract: Molecular orbital calculations based on density functional theory have been carried out on the intrinsic mean bond energy $D(M-CO)$ of $Mn(CO)_m$ between M in the d^n valence configuration and m CO ligands, as well as the first CO ligand dissociation energy ΔH of $M(CO)_m$. The calculated values for $D(M-CO)$, all in kJ mol^{-1}, were $D(Cr-CO) = 211$, $D(Mo-CO) = 178$, $D(W-CO) = 210$ for $M(CO)_6$, $D(Fe-CO) = 216$, $D(Ru-CO) = 163$, $D(Os-CO) = 177$ for $M(CO)_5$, and $D(Ni-CO) = 179$, $D(Pd-CO) = 44$, $D(Pt-CO) = 59$ for $M(CO)_4$. The calculated values for the intrinsic mean bond energy revealed the ordering second row < third row < first row, for a series of homologous $M(CO)_m$ systems with metal centers from the same triad. The ordering for $D(M-CO)$ without the inclusion of relativistic effects was third row < second row < first row. The same trends were found in the calculated values for ΔH with $\Delta H_{Cr} = 147$, $\Delta H_{Mo} = 119$, $\Delta H_W = 142$ for $M(CO)_6$, $\Delta H_{Fe} = 185$, $\Delta H_{Ru} = 92$, $\Delta H_{Os} = 99$ for $M(CO)_5$, and $\Delta H_{Ni} = 106$, $\Delta H_{Pd} = 27$, $\Delta H_{Pt} = 38$ for $M(CO)_4$. The π-back-donation was found to be more important for the stability of the $M(CO)_m$ systems than the σ-donation. The π-back-donation is largest for the first row elements whereas σ-donation is largest for second and third row elements. The repulsive interactions between occupied nd metal orbitals and occupied σ_{CO} orbitals were found to weaken the M–CO bonds for the second and third row elements in the pentacarbonyls and tetracarbonyls compared to the homologous systems of the first row elements. Calculations are also presented on the M–CO bond strength in $V(CO)_6^-$, $Mn(CO)_6^+$ as well as the Ni–L bond strength in $Ni(CO)_3L$ for $L = CS, N_2, PH_3, PF_3, N(CH_3)_3, P(CH_3)_3$, and $As(CH_3)_3$.

I. Introduction

The extensive use of coordinatively saturated mononuclear metal carbonyls as starting materials in organometallic chemistry, along with their volatility and high molecular symmetry, has prompted numerous experimental[1-3] and theoretical[4,5] studies on their

structure and reactivity. Special attention has been given to the degree of σ-donation and π-back-donation in the synergic[4k] M–CO bond, and now, after some controversy,[4j] it seems well-established[4b-g,5a,5e] that π-back-donation is more pronounced in the M–CO bond than σ-donation.

There is, however, in spite of many experimental[2] investigations still a lack of basic data on the thermal stability and kinetic lability of the M–CO bond in essential metal carbonyls such as $M(CO)_6$ ($M = Cr, Mo, W$), $M(CO)_5$ ($M = Fe, Ru, Os$), and $M(CO)_4$ ($M = Ni, Pd, Pt$), in particular with respect to the carbonyls of the second- and third-row metals.

Theoretical methods have begun to play a role in determining the energetics of organometallics[5g] and ab initio type methods have recently been applied to calculation on the M–CO bond strength of $Cr(CO)_6$,[5d-e] $Fe(CO)_5$,[5a-c,f] and $Ni(CO)_4$,[5a,f] but not yet to the M–CO bond strengths of their second- and third-row homologues.

We shall here present calculations on the intrinsic mean bond energy $D(M-CO)$ and first CO dissociation energy ΔH of $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ as well as their second- and third-row homologues. Our calculations are based on the LCAO program system of Baerends et al.[6] as well as a new density

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