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A Possible Union of Chemical Bonding, Reactivity, and Kinetics

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In this communication, we report for the first time the reactivity behavior at the transition state, the connection between the equireactivity configuration and the activation barrier, and a possible principle of reactivity conservation along the reaction paths of typical thermoneutral and exo (endo) thermic reactions.

Chemical bonding, reactivity, and kinetics are three cornerstones of chemistry. An insight into a chemical reaction requires a proper understanding of all these aspects associated with the reaction. In this communication, we report for the first time the reactivity behavior at the transition state, the connection between the equireactivity configuration and the activation barrier, and a possible principle of reactivity conservation along the reaction paths of typical thermoneutral and exo (endo) thermic reactions.

A DFT[1,2] calculation (B3LYP/6-311+G(d,p)) has been performed to monitor the profiles of condensed Fukui functions,[3,4] f_k^α ($\alpha = +, -,$ and 0 refers to nucleophilic, electrophilic, and radical attacks, respectively, at the atom k), along the reaction paths of (1) a thermoneutral reaction[5,6] (symmetrical gas-phase S_N2-type nucleophilic substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$), (2) an endothermic reaction ($HNO \rightarrow HON$), and (3) an exothermic reaction ($H_2OO \rightarrow HOOH$) as prototypical examples. A chemical reaction comprises bond-making and bond-breaking processes, e.g., breaking of $C{-}F_b$, $H{-}N$, and $H{-}O(2)$ bonds and making of $F_a{-}C$, $H{-}O$, and $O(1){-}H$ bonds in the reactions 1, 2, and 3, respectively. Separate calculations are done for the N, $(N + 1)$, and $(N - 1)$ electron systems with the geometry of the $N -$ electron species, and a Mulliken population analysis scheme is used for the calculation of necessary charges. All the calculations are performed along the intrinsic reaction coordinate (IRC) which connects the reactant, the transition state (TS), and the product along the minimum-energy path on the potential energy surface.

Figure 1 shows the profiles of $f_{F_a}^-$ and $f_{F_b}^-$ along the IRC of the thermoneutral reaction: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$. Free F_a^- is the most reactive center (nucleophilicity) in the beginning of the reaction, which ultimately becomes the least reactive center as it gets bonded in the course of the reaction. An opposite behavior is observed for F_b^-. The energy profile is also superimposed in Figure 1. In the TS (IRC = 0), the energy is maximum. Both $f_{F_a}^-$ and $f_{F_b}^-$ pass through inflection points[5,6] around the TS. The profiles of $f_{F_a}^-$ and $f_{F_b}^-$ intersect in the TS implying that these two centers are equally reactive there, as is expected for a thermoneutral reaction. As we will see later, this equireactivity configuration has a bearing in chemical kinetics. Similar behavior for the bond order was observed in the past.[7,8] In Figure 1, we also plot $f_{F_a}^- + f_{F_b}^-$ which is shown to be roughly constant along the IRC. Therefore, there seems to exist a principle of reactivity conservation which may be considered to be a companion principle of bond order conservation.[7,8] A principle of helicity conservation is also known.[9] It may be noted that we consider reactivity of only two centers which are the most important in this reaction. The reactivity of free $f_{F_a}^-$ is the maximum to start with, which decreases as it gets bonded during the reaction and passes through an inflection point around the TS and then decreases rapidly to finally level off to its lowest value. On the other hand, the reactivity of $f_{F_b}^-$ is the minimum at the beginning which increases, passes through an inflection point around the TS, and then rapidly increases to finally level off to its highest value where it is more or less free. In the TS, both are equally reactive, and as they reverse their reactivity patterns along the reaction path, their total reactivity remains approximately constant.

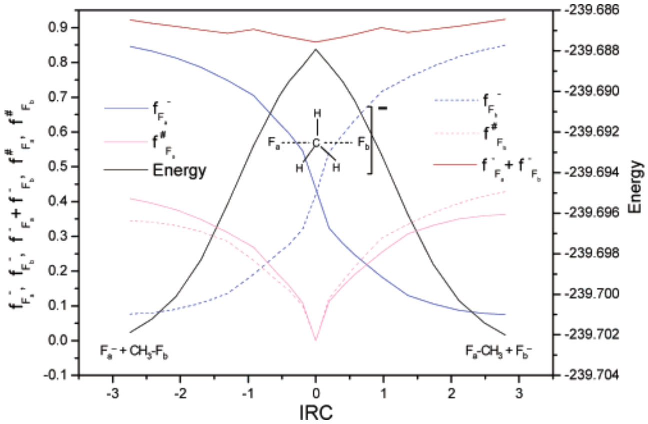

Figure 1. Profiles of different local reactivity descriptors (electrophilic attack) along the path of the gas-phase S_N2 substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$. Also shown is the energy profile.

To have a better understanding of the equireactivity configuration vis-à-vis its connection with the activation energy barrier, we define a descriptor $f_X^\# = |f_X^- - f_X^-(\mathrm{IRC_{eq}})|$ where $\mathrm{IRC_{eq}}$ is the IRC value at the equireactivity configuration (zero, the TS, for a thermoneutral reaction) and X = F_a, F_b. As the activation energy barriers for the forward and backward processes are the same for a symmetric reaction, the reactivity variation, $f_X^\#$, for these two processes (both F_a and F_b, Figure 1) are similar.

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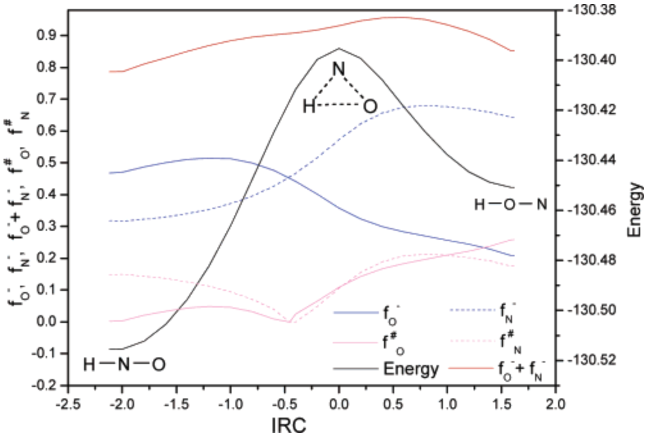

Figure 2. Profiles of different local reactivity descriptors (electrophilic attack) along the path of the gas-phase endothermic reaction: HNO → HON. Also shown is the energy profile.

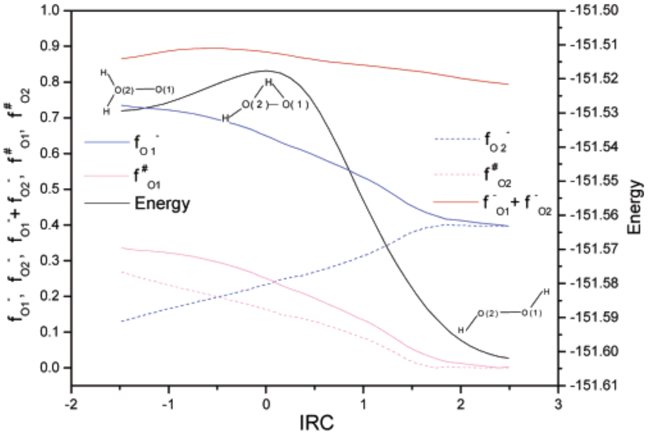

Figure 3. Profiles of different local reactivity descriptors (electrophilic attack) along the path of the gas-phase exothermic reaction: H_2OO → HOOH. Also shown is the energy profile.

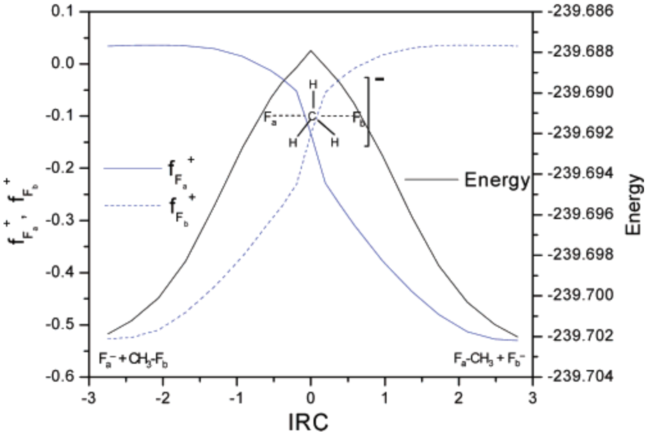

Figure 4. Profiles of different local reactivity descriptors (nucleophilic attack) along the path of the gas-phase S_N2 substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$. Also shown is the energy profile.

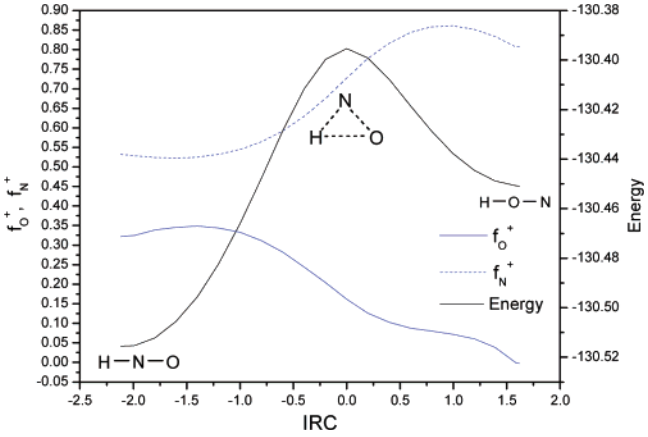

Figure 5. Profiles of different local reactivity descriptors (nucleophilic attack) along the path of the gas-phase endothermic reaction: HNO → HON. Also shown is the energy profile.

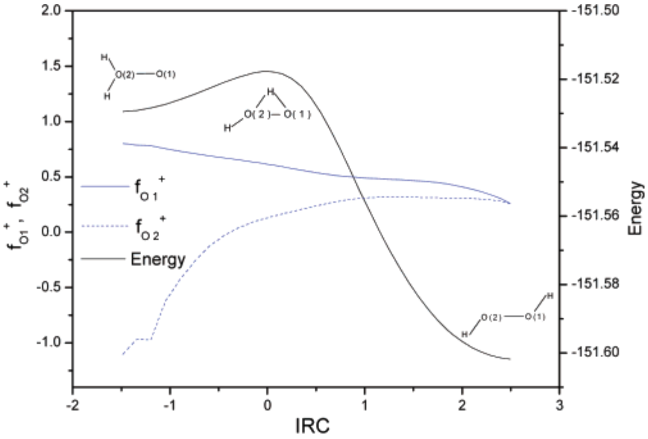

Figure 6. Profiles of different local reactivity descriptors (nucleophilic attack) along the path of the gas-phase exothermic reaction: H_2OO → HOOH. Also shown is the energy profile.

Figure 2 presents the profiles of f_O^-, f_N^-, $f_O^- + f_N^-$, E, $f_O^\#$, and $f_N^\#$ along the IRC of the endothermic reaction: HNO → HON. Here, f_O^- decreases and f_N^- increases, both passing through the inflection points and the IRC of the equireactivity configuration (where two curves intersect) is negative (toward the left of the TS). In general, the IRC_{eq} configuration will be different from that of the reactant, transition state, and product for an unsymmetrical reaction. Total reactivity of the reaction (considering other atoms to be spectators), $f_O^- + f_N^-$, remains roughly constant (in comparison to the variations in f_O^-, f_N^-, and E). The reactivity conservation principle is better obeyed in the case of the thermoneutral reaction. The reactivity-based Hammond postulate[10] may be envisaged as follows: For an endothermic reaction, the equireactivity configuration lies to the left of the TS so that the TS reactivity is productlike. Since the number of electrons (N) remains unaltered along the IRC and the geometry of the TS is productlike implying the similar external potential, $\upsilon(\vec{r})$, the Hamiltonian of the TS will be like that of the product and, hence, the wave function and all other properties including reactivity. For an endothermic reaction, the backward reaction is faster than the forward reaction, and $f_O^\#$ and $f_N^\#$ for the product side are larger than those of the reactant side. In general, a larger $f_X^\#$ (the product reactivity relative to that of the equireactivity value when compared to the corresponding quantity for the reactant) implies a faster reaction.

The profiles of $f_{O_1}^-$, $f_{O_2}^-$, $f_{O_1}^- + f_{O_2}^-$, E, $f_{O_1}^\#$, and $f_{O_2}^\#$ along the IRC of the exothermic reaction H_2OO → HOOH are depicted in Figure 3. While $f_{O_1}^-$ decreases, $f_{O_2}^-$ increases to reach an equireactivity configuration lying toward the right (positive IRC) of the TS so that the reactivity of the TS is reactantlike. An apparent conservation of $f_{O_1}^- + f_{O_2}^-$ is observed. Here, the forward reaction is faster than the backward reaction, and accordingly, $f_{O_1}^\#$ and $f_{O_2}^\#$ for the reactant side are greater than those of the product side. Relatively larger reactivity of the reactant implies a faster rate of the forward reaction.

For the sake of completeness, we also present the associated f_k^+ profiles corresponding to reactions 1, 2, and 3 along the IRC, in Figures 4, 5, and 6, respectively. The equireactivity configuration coincides with the TS for the thermoneutral reaction (Figure 4). For the exothermic reaction, the IRC_{eq} lies (Figure 6) toward the right of the TS, as would have been expected from the Hammond postulate. There is no intersection of the f_k^+ profiles for the endothermic reaction, and hence, the IRC_{eq} does not exist. The next best choice in this case would be the IRC, for which the difference of the two pertinent f_k^+ values is minimum (IRC_{min}) and the difference is zero at IRC_{eq} where it exists. For the endothermic reaction, the IRC_{min} lies to the left of the TS, confirming the validity of the Hammond postulate.

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