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Local Descriptors around a Transition State: A Link between Chemical Bonding and Reactivity

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In this communication, we report for the first time the possible existence of a point of inflection in the profile of a local reactivity descriptor around the transition state. The saddle point of the given reaction coincides with this inflection point which becomes transparent when two such profiles corresponding to bond making and bond breaking processes respectively intersect at the transition state for the thermoneutral reactions. The corresponding ramification of the Hammond postulate for the exo(endo) thermic reactions is also discussed.

Chemistry is the science of bond making and bond breaking. An understanding of these two processes lies at the heart of any reaction mechanism. In this communication, we report for the first time the possible existence of a point of inflection in the profile of a local reactivity descriptor around the transition state. The saddle point of the given reaction coincides with this inflection point which becomes transparent when two such profiles corresponding to bond making and bond breaking processes respectively intersect at the transition state for the thermoneutral reactions. The corresponding ramification of the Hammond postulate for the exo(endo) thermic reactions is also discussed. Similar studies using bond orders have been carried out in the past.[1−4] Several other descriptors are proposed in the present work. We also analyze how the most reactive center becomes the least reactive center and vice versa during the chemical reaction.

The condensed Fukui functions,[5,6] f_k^{α}, are the most important local reactivity descriptors where $\alpha = +, -$, and 0 refers to nucleophilic, electrophilic and radical attacks, respectively. Two related descriptors, viz, local softness,[7] $s_k^{\alpha}(\equiv S{\cdot}f_k^{\alpha})$, and philicity,[8] $\omega_k^{\alpha}(\equiv \omega{\cdot}f_k^{\alpha})$, are also introduced to tackle respectively the hard−soft and electrophile−nucleophile interactions better where S is the global softness[9] and ω is the global electrophilicity.[10]

A DFT calculation (B3LYP/6-311+G(d,p)) has been performed to monitor the profiles of these local descriptors along the reaction path of the symmetrical gas-phase S_N2 type nucleophilic substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$. Separate calculations are done for the N, (N + 1) and (N − 1) electron systems with the same geometry and a Mulliken population analysis scheme is used for the necessary charges.

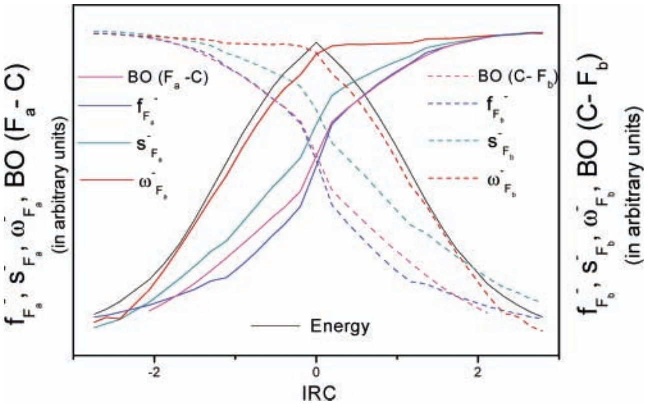

Figure 1. Profiles of different local reactivity descriptors along the path of the gas-phase S_N2 substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$. Also shown are the profiles of energy and bond order (BO).

Figure 1 shows the profiles of $f_{F_a}^-$ and $f_{F_b}^-$ along the intrinsic reaction coordinates (IRC) which connect the reactant, the transition state (TS) and the product along the minimum energy path on the potential energy surface. Also superimposed are the profiles of $s_{F_a}^-$, $s_{F_b}^-$, $\omega_{F_a}^-$, $\omega_{F_b}^-$, the bond order (BO), and the energy. The maximum in the energy profile (IRC = 0) corresponds to the TS. The nucleophilicity (propensity of electrophilic attack at that center) of F_a^- (F_b^-) gradually increases (decreases) and passes through an inflection point around the TS and then increases (decreases) suddenly to finally level off. Similar behavior is observed for $s_{F_a}^-$ ($s_{F_b}^-$) and $\omega_{F_a}^-$ ($\omega_{F_b}^-$) associated with the bond making (breaking) partner, because they are scaled Fukui functions though S and ω also vary along the reaction path and a comparison with the established indicators such as BO profiles reveals the usefulness of the conceptual DFT based local reactivity indices. This fact clearly demonstrates that the reactivity (selectivity) is not an absolute property of a (an) molecule (atom in a molecule) but it depends on the nature and the distance of the other species present in its vicinity and accordingly varies during the course of a chemical reaction. The reactivity/selectivity of F_a^- (with closed-shell noble gas configuration) is the least to start with which increases in the presence of $CH_3{-}F_b$ which induces reactivity into F_a^-. In the course of the reaction the F_b reactivity, decreases because it is in the process of breaking a bond (product) to ultimately attain a stable closed-shell configuration in F_b^- and the F_a reactivity increases because of the induction

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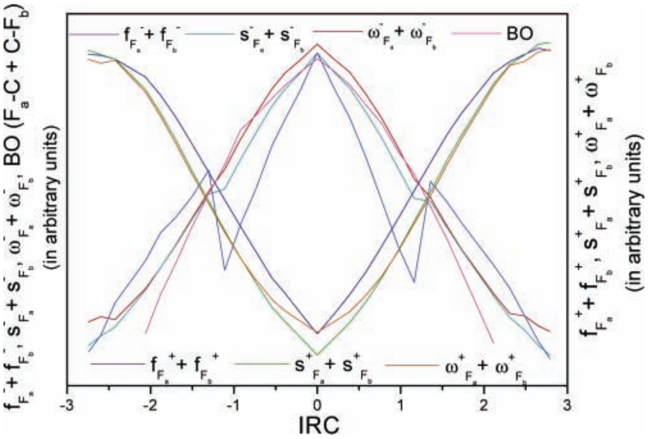

Figure 2. Profiles of different local reactivity descriptors along the path of the gas-phase S_N2 substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$.

by $CH_3{-}F_b$. In the TS, the reactivities of F_a and F_b are equal which implies that the system can go to the reactant side or to the product side with equal ease. Replacement of CH_3 by C_2H_5 does not alter the nature of these curves (not shown here). It becomes transparent how the reactivity can complement the pictures of bonding and interaction. In addition the concept of the corresponding activation quantities may lend additional insights into the kinetics as well. The intersection point between $f_{F_a}^-$ and $f_{F_b}^-$ (also $s_{F_a}^-$ and $s_{F_b}^-$ as well as $\omega_{F_a}^-$ and $\omega_{F_b}^-$) coincides with the saddle point of this S_N2 reaction and may be used to locate the transition state (IRC = 0) in a complementary way to the usual chemical reaction dynamics using the potential energy profile. In quest of an alternative local reactivity descriptor in identifying the TS, we propose $f_{F_a}^- + f_{F_b}^-$ (also $s_{F_a}^- + s_{F_b}^-$ as well as $\omega_{F_a}^- + \omega_{F_b}^-$). These quantities including the related BO are plotted as functions of IRC in Figure 2. It is heartening to note that all of them maximize at the TS implying that the system in the TS is the most reactive. This quantity may be utilized in locating the TS. Corresponding quantities for the electrophilic reactivity exhibit a somewhat mirror image relationship (Figure 2). Also the plot of $|f_{F_a}^- - f_{F_b}^-|$ ($f = f$, s, and w) shows a mirror image relationship with the corresponding ($f_{F_a}^- + f_{F_b}^-$) plot. However, the ($f_{F_a}^+ + f_{F_b}^+$) and $|f_{F_a}^+ - f_{F_b}^+|$ plots mimick each other (not shown here).

The profile of $r_{F_a-C} + r_{C-F_b}$ along the reaction path is parabolic in nature (Figure 3), r_{C-F} being the C−F bond length. As expected, it attains a minimum value at IRC equal to zero and may also be used to locate the TS. Figure 3 also depicts the profile of $|r_{F_a-C} - r_{C-F_b}|$ along the IRC. It is very easy to locate the TS at IRC equal to zero.

To check whether this behavior of local reactivity descriptors in the neighborhood of a saddle point in the potential energy surface is unique for symmetrical (thermoneutral) reactions only, we have also studied some exothermic and endothermic reactions including the profiles of the corresponding condensed electron localization functions, wherein the selectivity behavior becomes transparent. A variant of the Hammond postulate[11] may be envisaged as follows. For an endothermic reaction, the TS lies closer to the product in energy and geometry and the intersection point between $f_{F_a}^-$ and $f_{F_b}^-$ (likewise for s_k^- and ω_k^-) lies slightly left to the TS (toward the reactant) and at the TS it already crossed the intersection point conforming to the product reactivity pattern (cf. Figure 1) and for an exothermic reaction the TS lies closer to the reactant in energy and geometry and the corresponding intersection point lies slightly right to the TS (toward the product) as is demanded by the reactivity characteristics of the reactant. It deserves a careful scrutiny.

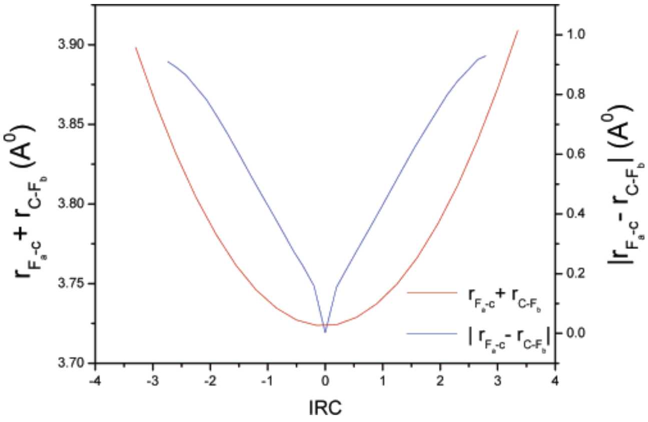

Figure 3. Profiles of ($r_{F_a-C} + r_{C-F_b}$) and $|r_{F_a-C} - r_{C-F_b}|$ along the IRC of the gas-phase S_N2 substitution: $F_a^- + CH_3{-}F_b \rightarrow F_a{-}CH_3 + F_b^-$.

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