

Should bond-formation lag behind bond-cleavage in radical-exchange reactions?

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MS received 30 December 1998; revised 22 April 1999

Abstract. A few simple concerted radical-exchange reactions ($\dot{A} + BC \rightarrow AB + \dot{C}$) are examined by the quantum-mechanical *ab initio* methods via calculations of bond orders and energies. Results reveal that, during these reactions, a small free valence develops on the migrating atom. As a result, the degree of bond-cleavage is more advanced than that of bond-formation with a common migrating atom at the transition state. The fact that bond-formation lags behind bond-cleavage is also examined by the configuration mixing of the reactant configurations at the early stages of the reaction.

Keywords. Bond-cleavage; bond-formation; free valence; asynchronous reaction.

1. Introduction

Simple concerted radical-exchange reactions ($\dot{A} + BC \rightarrow AB + \dot{C}$) are generally analysed in terms of bond-breaking and bond-forming processes¹. According to the Evans–Polanyi theory², the bond-breaking curve as a function of a common reaction coordinate crosses the bond-forming curve. The crossing point corresponds to the transition state where formation of the new bond is assumed to compensate exactly for breaking of the old one. In other words, the bond-forming and bond-breaking processes take place in unison. Dewar³ also observed, more recently, that one-bond reactions, which involve the breaking of one bond and the formation of another, are concerted and synchronous. On the basis of intuition³, however, activation energy in a simple reaction $\dot{A} + BC \rightarrow AB + \dot{C}$ arises because the new bond, AB, that is formed, cannot begin to form until the old one, BC, has weakened to a considerable extent. This intuition was not examined on a quantitative basis. Recently, we⁴ examined the simplest prototypical hydrogen transfer reaction $\dot{H} + H_2 \rightarrow H_2 + \dot{H}$ by the *ab initio* methods using the concept of bond order⁵. Our results reveal that the bond-cleavage process is slightly more advanced than the bond-formation process on the reaction path.

According to the conventional dictum^{6,7}, the sum of bond orders of the making and breaking bonds is believed to be constant and equal to unity along the minimum energy path (MEP) of a chemical reaction. Most chemists believe that the cleavage of a bond and the formation of a new one with a common migrating atom take place in unison. The success of such a conventional approach suggests that the difference, if any, in the extent of bond-formation and bond-cleavage is not significant. There are a number of definitions of bond orders^{5,8–12} for calculations from *ab initio* wavefunctions. As a general conclusion¹², one can state that all these definitions lead to similar bond orders which

correlate with bond lengths and provide a measure of strength of interaction between two atoms forming a bond. In our previous papers^{4,13}, we used Mayer's definition of bond order, free valence and atomic valence. Our results on radical-exchange reactions show that the sum of the bond orders of the bond being broken and that being formed during a radical exchange reaction is not exactly conserved to unity due to development of a small free valence on the migrating atom¹⁴. We have also shown that the free valence developed on the migrating hydrogen atom is almost equal to the square of the spin density on the same atom¹³, which is not negligibly small. Lendvay¹⁵ used Mayer's definition of bond orders and found that conservation of bond orders to unity holds good only approximately in a metathetical reaction because of the development of a small free valence on the migrating atom. Besides, he¹⁶ reported later on the isomerisation paths connecting C₃H₄ isomers and the reactions between different C₂H₂O isomers and observed that the processes of bond-formation and bond-rupture are not commensurate and that barriers are observed at different stages of development of different bonds in the same reaction. Whenever the bond-rupture and bond-formation processes in a reaction are found to be non-commensurate, the reactions are considered asynchronous^{4,16} though the reaction itself/may take place in a single kinetic step.

A continuous transformation from reactants to products along the reaction coordinate is provided by the concept of bond orders. Bond orders obtained in *ab initio* calculations do not always yield the same results on changing the basis sets. They are always close however to the corresponding classical values. On improving the energy calculations, bond orders do not converge the same way as energies do. This point has been emphasized in our earlier paper⁴ where we pointed out that the density matrices derived from multiconfiguration wavefunctions, an improvement over single configuration wave function, are not idempotent¹² and may lead to unreliable bond orders. Besides, with the improved treatment of electron correlation, there is no guarantee that bond orders will improve monotonically as energy does. The degrees of bond cleavage, I_1 , and of bond-formation, I_2 , were defined⁴ in terms of bond orders as

$$I_1 = 1 - (n_1/n_{1e}), \quad I_2 = (n_2/n_{2e}), \quad (1)$$

where n_1 and n_2 are, respectively, Mayer's bond orders of the breaking and forming bonds at a given stage of a reaction, while n_{1e} and n_{2e} are the respective equilibrium bond orders. We find that I_1 and I_2 are less sensitive to the basis sets than bond orders and remain nearly unchanged on correction for electron correlation. We therefore believe that our predictions based on calculated values of I_1 and I_2 for a series of simple metathetic reactions cannot be far from reality.

We examine the following elementary gas-phase metathetic (open-shell type) reactions which involve breaking of one bond and formation of another. They are:





All these reactions pass through nearly linear or linear transition states^{17–21}. Our motivation in this paper is to provide an insight into the detailed mechanism from calculations of I_1 and I_2 via the bond orders. We then address the question, whether or not the bond-formation process lags behind the bond-cleavage process from the point of view of interaction of molecular orbitals.

2. *Ab initio* calculations

We employed the Gaussian 92 program²² for *ab initio* calculations using the 6-31 G^{**} , 6-311 G^{**} and 6-31(+) G^{**} basis sets. We believe that the single configuration UHF (unrestricted Hartree–Fock) level describes the balance between the simultaneous formation of one bond and the breaking of another in the open-shell type of radical-exchange reactions. Earlier Fox and Schlegel²³ noted this with the 6-31 G^{**} basis set in many hydrogen abstraction reactions by methyl radicals. Geometry optimisations reveal that the transition state structures for reactions (A)–(G) are linear in agreement with many other previous *ab initio* calculations. For reactions involving F atoms, i.e. for reactions (B), (C), (F) and (G), the transition state structures have more than one negative eigenvalue in the matrix of the force constants. However, when the 6-311 G^{**} basis set is used instead of the 6-31 G^{**} basis, only one negative eigenvalue is obtained in the force constant matrix. For reactions (D) and (E), we employed the 6-31(+) G^{**} basis set which means split valence plus polarisation with diffuse functions namely, 's' 'p' and 'd' functions for calculations of the potential energy surface. The importance of diffuse functions in the reaction $\dot{\text{Cl}} + \text{HCl} \rightarrow \text{ClH} + \text{Cl}$ has recently been observed²⁴. For calculations of energies we employed MP2 = full in the UHF scheme where MP2 = full, means second-order Moller–Plesset perturbation theory²⁵ with all electron correlation. We use intrinsic reaction coordinate calculations to derive MEP and ensure that the eigenvalue of the spin operator S^2 remains close to 0.75 of the variation of the reaction coordinate, which corresponds to an asymmetric stretch for a linear triatomic system.

We then derive the density matrix from the single-configuration UHF wavefunctions and use Mayer's formalism⁸ for calculations of bond orders, valence and free valence⁸. We consider the following relation for an open-shell system between bond orders n_1 and n_2 , free valence, F_A and valence V_A on the migrating atom A ,

$$V_A = F_A + n_1 + n_2. \quad (2)$$

V_A can be obtained from (2) as well as from the density matrix and is always estimated at values close to unity. It should be noted that (2) is valid for the three-atom reactions dealt with in this paper. We normalise bond orders, free valence and valence in (2) by dividing with V_A and obtain

$$1 = \frac{F_A}{V_A} + \frac{n_1}{V_A} + \frac{n_2}{V_A},$$

$$1 = \Delta + \chi_1 + \chi_2 \quad (3)$$

Here, χ_1 and χ_2 are respectively the normalised bond orders of the breaking and forming bonds in a reaction and Δ is the free valence on the migrating atom.

3. Results and discussion

For all reactions (A) to (G) the sum of bond orders χ_1 and χ_2 decreases along the MEP of the corresponding reaction to a minimum value and then increases, while Δ increases from zero to a maximum value and then decreases to zero along the reaction path. The maximum in the Δ -profile coincides with the saddle point of the energy profile for the corresponding reaction. For reaction (A), such a plot was shown in figure 1 of the ref. [4]. Figure 1 of this paper shows a similar plot for the reaction (E). Table 1 gives the transition state bond orders χ_1^\ddagger and χ_2^\ddagger , free valence Δ^\ddagger on the migrating atom, the calculated bond dissociation energies and activation barriers for all reactions (A) ~ (G) at the levels indicated. Results show that the transition state bond orders are always less than 0.5 for symmetric thermoneutral reactions for which the transition state bond orders are equal due to symmetry. The barriers are not located exactly half-way between the reactants and products. This follows from the fact that in the reaction (A), for example, the reactant bond order $\chi_1 = 1$ is decreased to $\chi_1^\ddagger = 0.47$ in the transition state. The magnitude of the decrease is 0.53 which is not exactly compensated for by the corresponding increase in the value of χ_2^\ddagger from zero, since $\chi_2^\ddagger = 0.47$. It may be important here to note that, according to bond energy bond order (BEBO) theory⁷, the transition state bond order is 0.5 for any symmetrical thermoneutral reaction but it does not lead to

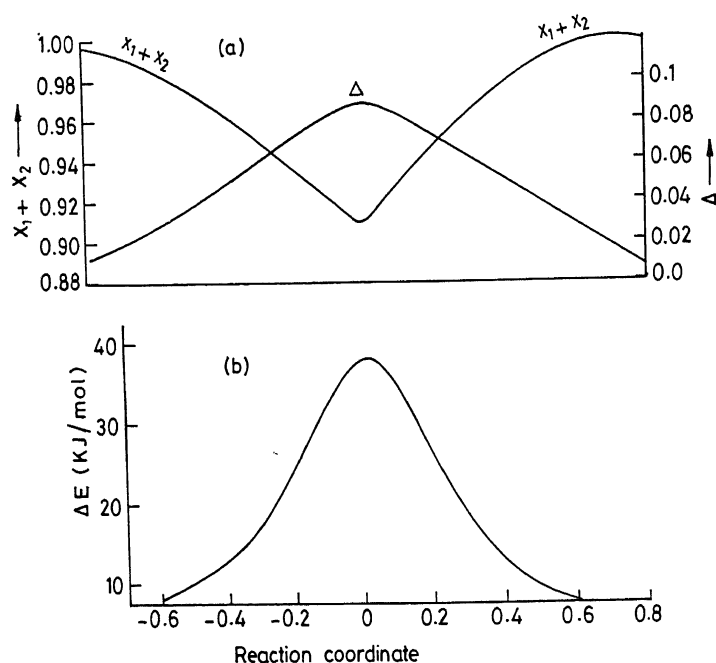


Figure 1. (a) Plots of the sum of bond orders ($\chi_1 + \chi_2$) and free valence Δ against the reaction coordinate for the reaction $\dot{\text{C}}\text{l} + \text{HCl} \rightarrow \text{ClH} + \dot{\text{C}}\text{l}$. (b) The energy change ΔE (kJ/mol) against the reaction coordinate for the same reaction as in (a).

Table 1. Transition state bond-orders and free valence on the migrating atom, calculated bond-dissociation energies and activation barriers for all reactions. All calculations are made at the level indicated.

Reactions	$\chi_1^\#$	$\chi_2^\#$	$\Delta^\#$	D kJ/mol	E_a kJ/mol
(A) $H + H_2 \rightarrow H_2 + H$ [UHF/6-311G**/MP2]	0.466	0.466	0.07	432	50
(B) $H + FH \rightarrow HF + H$ [UHF/6-311G**/MP2]	0.460	0.460	0.08	564	199
(C) $F + HF \rightarrow FH + F$ [UHF/6-311 G**/MP2]	0.469	0.469	0.062	564	84
(D) $Cl + HCl \rightarrow ClH + Cl$ [UHF/6-31(+) <i>G</i> **/MP2]	0.459	0.459	0.08	428	59
(E) $H + ClH \rightarrow HCl + H$ [UHF/6-31(+) <i>G</i> **/MP2]	0.430	0.430	0.14	428	102
(F) $H_2 + F \rightarrow H + HF$ [UHF/6-311G**/MP2]	0.59	0.34	0.07	$D_1 = 432$ $D_2 = 564$	8
(G) $H + HF \rightarrow H_2 + F$ [UHF/6-311G**/MP2]	0.34	0.59	0.07	$D_1 = 564$ $D_2 = 432$	162

any barrier for such reactions¹. Although the BEBO theory can be modified as suggested by us^{14,26} to predict the activation barrier for a symmetric radical-exchange reaction, the improved BEBO model based on the principle of conservation of bond orders without developing a free valence on the migrating atom in the transition state is not without limitations. For two similar radical-exchange reactions like $A-X + A \rightarrow A + X-A$ and $X-A + X \rightarrow X + A-X$ where two similar bonds are broken and formed, the BEBO model leads to the same barrier. But these two reactions have different observed as well as computed barriers.

The development of small free valence $\Delta^\#$ (or spin density) on the migrating atom in a transition state of a radical-exchange reaction is not an artifact of *ab initio* calculations¹⁴. It can be easily understood from the valence bond wave functions of a three-electron exchange process outlined in our previous paper¹³. The cause for development of free valence on the migrating atom is therefore rooted in quantum mechanics. We now define I_1 and I_2 in terms of χ_1 and χ_2 as

$$I_1 = 1 - (\chi_1/\chi_{1e}), \quad I_2 = (\chi_2/\chi_{2e}), \quad (4)$$

where χ_{1e} and χ_{2e} are the equilibrium bond orders in the reactant and product respectively. One should note that (1) and (4) are not exactly equivalent because 'n' and ' χ ' are slightly different. Henceforth, we follow (4) for further discussion. It is to be noted that $\chi_{1e} = \chi_{2e} = 1$ as no free valence is observed in the reactant and product molecules. Initially, $I_1 = 0$ and increases gradually to unity when the bond-breaking is complete, i.e. $\chi_1 = 0$. On the other hand, $I_2 = 0$ initially, because $\chi_2 = 0$ and then I_2 increases to unity when the bond-formation is complete, i.e. $\chi_2 = \chi_{2e}$. For all reactions in table 1, $I_1^\#$ is

always greater than I_2^\ddagger where I_1^\ddagger and I_2^\ddagger refer to the values of I_1 and I_2 , respectively, in the transition state. One can therefore write from (4),

$$I_1^\ddagger - I_2^\ddagger = 1 - \frac{\chi_{1e}^\ddagger}{\chi_{1e}} - \frac{\chi_{2e}^\ddagger}{\chi_{2e}} = 1 - \chi_{1e}^\ddagger - \chi_{2e}^\ddagger = \Delta^\ddagger, \quad (5)$$

since $\chi_{1e} = \chi_{2e} = 1$. Thus, owing to the development of free valence on the migrating atom, a difference develops in the degrees of the bond-breaking and bond-forming processes with a common migrating atom. Since $I_1^\ddagger > I_2^\ddagger$ for all reactions (from (5)), the extent of bond-cleavage is higher than that of bond-formation in the reaction path. Figure 2 shows the variation of I_1 and I_2 with the reaction coordinate for the reactions (C) and (D). Results reveal that the curves do not overlap. The bond-formation and bond-rupture processes do not develop exactly to the same degree in the reaction, and the bond-formation process lags behind the bond-cleavage process except at the reactant and product stages. Similar plots are observed for other reactions in table 1. The plot for the reaction (1) was shown in our earlier paper⁴.

We then plot the energy change ΔE along the MEP against I_1 and I_2 characterising the bond-cleavage and bond-forming processes respectively. Figure 3 shows one such plot for the reaction (D). The plot is convex and differs from the usual energy profile. It shows that the maximum in the ΔE vs I_1 is located to the right of the similar plot of ΔE vs I_2 . Therefore, the barrier is observed at different stages of the bond-forming and bond-breaking processes. From figure 2, we observe that

$$\frac{dI_1}{dR} > \frac{dI_2}{dR},$$

where the variable I_1 is more advanced than I_2 along the reaction path. This can be shown otherwise from (3). On differentiating (3) with respect to R , we have

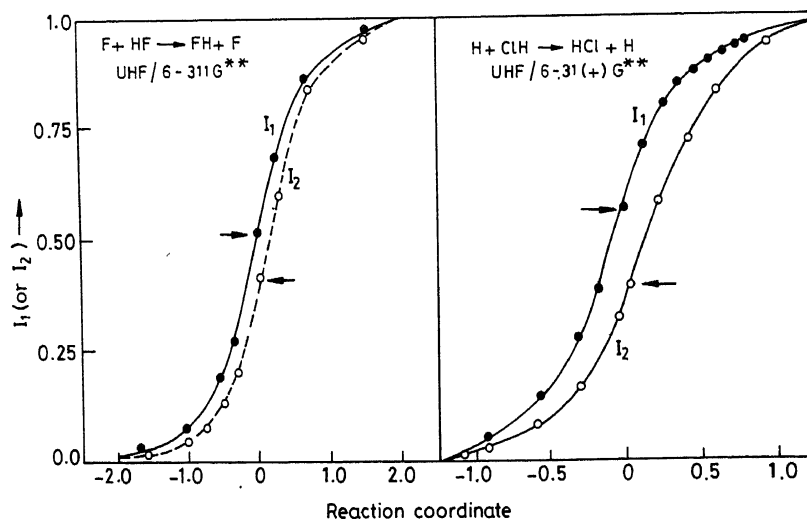


Figure 2. Plots of I_1 and I_2 vs reaction coordinate for the reaction indicated in the figure, (a) $F + HF$, (b) $H + ClH$, where I_1 and I_2 are obtained from bond orders using the density matrix.

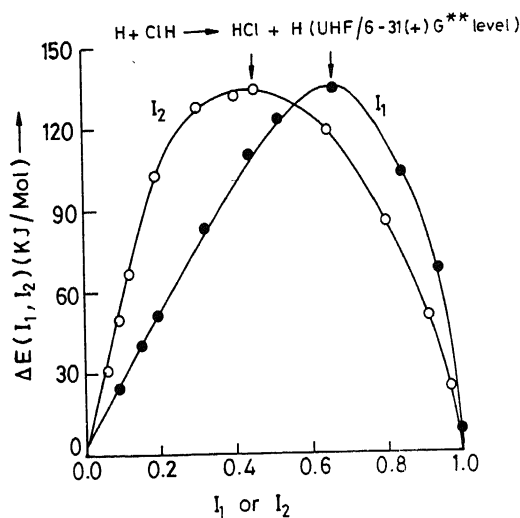


Figure 3. Variation of energies $\Delta E(I_1, I_2)$ [kJ/mol] with I_1 and I_2 for the reaction indicated in the figure.

$$\frac{d\chi_1}{dR} + \frac{d\chi_2}{dR} + \frac{d\Lambda}{dR} = 0,$$

$$\text{or } \frac{dI_1}{dR} - \frac{dI_2}{dR} = - \left[\frac{d\chi_1}{dR} + \frac{d\chi_2}{dR} \right] = \frac{d\Lambda}{dR}.$$

Before reaching the saddle point from the reactant, $d\Lambda/dR$ is positive. There seems to be no guarantee that this is always positive but for all the three-atom reactions considered in this paper, it is positive. We may, therefore, say that until the saddle point is reached where $d\Lambda/dR = 0$, we have

$$\frac{dI_1}{dR} > \frac{dI_2}{dR}.$$

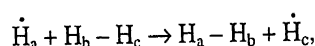
If the free valence does not develop at all on the migrating atom, $(dI_1/dR) = (dI_2/dR)$ at all points on the reaction path. In that case, bond-formation and bond-cleavage occur in unison in chemical reactions. But our present analysis shows that the bond-cleavage process is expected to be more advanced than is the bond-formation process in a radical-exchange reaction owing to the development of free valence on the migrating atom. We thus notice that the conclusions derived from energy calculations are consistent with those derived from bond order calculations.

We cannot use Pauling's relation between bond order and bond length here as Pauling's bond order is conceptually different from the quantum mechanical bond order. Besides, the concept of free valence is absent in Pauling's relation. So we refrain from using Pauling's relation here for predicting an imbalance between bond-cleavage and bond-formation. In a previous paper²⁷, we have shown that intrinsic activation barriers for thermoneutral reaction arise from the greater degree of bond cleavage in the reactant than of bond-formation in the product at the saddle point.

If there are more than one bond in a reacting molecule, one has to be careful because the total energy is not just a sum of the bond energies due to the bond–bond interactions. Besides, the extra bonds may not be passive during reactions. That the extent of bond-cleavage is more advanced than that of bond-formation in the transition state is valid for simple one-bond reactions. This is unlikely to hold good for reactions involving polyatomic molecules. For example, in the $\dot{\text{C}}\text{H}_3 + \text{CH}_4 \rightarrow \text{CH}_4 + \dot{\text{C}}\text{H}_3$ reaction, which passes through a linear transition state, $\text{H}_3\text{C}\text{I}\cdots\text{H}\text{I}\cdots\text{C}_2\text{H}_3$, our *ab initio* calculations²⁸ with the 6-31 G^{**} basis set show that the bond orders of the other C2–H bonds in the methyl radical and that of the other C1–H bonds in methane also change slightly during the reaction besides those of the reacting C1–H1 and C2–H1 bonds, leading to deviations from the above observations.

4. Why should bond-formation lag behind the bond-cleavage process?

This question can be examined using the interaction diagrams of molecular orbitals of $(\text{H}_b\text{--H}_c)$ and (H_a) for the reaction (A)



without invoking the concept of bond order. We assume that the three atoms are always collinear in the reaction. Figure 4 shows the interaction diagram of the fragment orbitals (reactant orbitals) to produce the molecular orbitals of the product, where ϕ 's are the atomic orbitals centred on the atoms indicated by the subscripts. The stretching of the $\text{H}_b\text{--H}_c$ bond (stretching is a part of the reaction coordinate) leads to an increase of energy of the σ -orbital and a decrease of energy of the corresponding σ^* orbital until they become doubly degenerate, while the n -orbital located on H_a (i.e. the ϕ_a orbital) is not affected. Figure 4 shows the interaction of orbitals n with σ and σ^* to produce a bonding molecular orbital (m.o.) Ψ_1 and an antibonding m.o. Ψ_3 of $\text{H}_a\text{--H}_b$ and an orbital Ψ_2 centred on H_c . The coefficients a , b and a_1 , b_1 are greater than zero.

Using the fragment m.o.'s of figure 4, we construct the following configurations:

$$\begin{aligned} {}^2\Psi_0 &= |n\sigma\bar{\sigma}|, \\ {}^2\Psi_1 &= |n\bar{n}\sigma|, \\ {}^2\Psi_2 &= 1/\sqrt{2} [| \sigma\bar{\sigma}^*n| + | \sigma^*\bar{\sigma}n|], \\ {}^2\Psi_2' &= 1/\sqrt{6} [| 2|\sigma\bar{n}\sigma^*| + |\sigma\bar{\sigma}^*n| - |\sigma^*\bar{\sigma}n|], \\ {}^2\Psi_3 &= | \sigma\bar{\sigma}\sigma^*|, \\ {}^2\Psi_4 &= |n\sigma^*\bar{\sigma}^*|, \\ {}^2\Psi_5 &= | \sigma\sigma^*\bar{\sigma}^*|, \\ {}^2\Psi_6 &= |n\bar{n}\sigma^*|, \end{aligned} \tag{8}$$

which include singly and doubly excited configurations from ${}^2\Psi_0$. It should be noted that two linearly independent doublet state wavefunctions Ψ_2 and Ψ_2' are possible for the

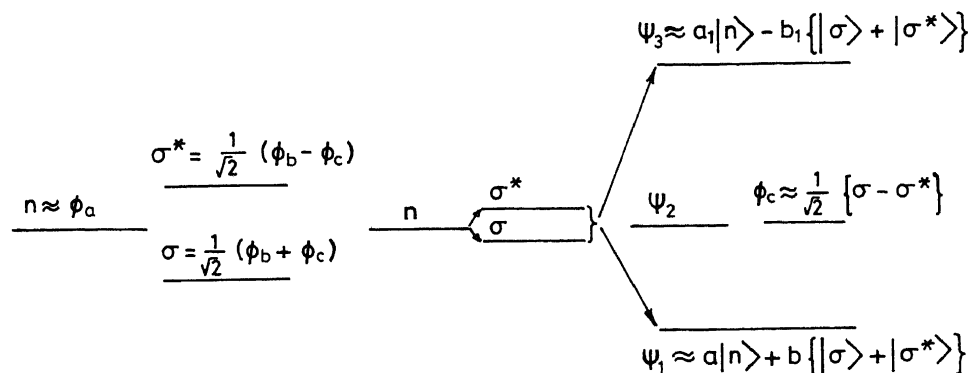


Figure 4. Interaction diagrams of molecular orbitals of the reactants at the early stages of the reaction $H_a + H_b - H_c \rightarrow H_a - H_b + H_c$.

configuration $|n\sigma\sigma^*\rangle$. We then determine the matrix elements of the total Hamiltonian. The n -orbital is not strictly orthogonal to the σ and σ^* orbital of H_2 . However, the orthogonality integral between the two wavefunctions, ${}^2\Psi_0$ and ${}^2\Psi_1$, is given by

$$\langle {}^2\Psi_0 | {}^2\Psi_1 \rangle = \langle \sigma | n \rangle [1 - \langle \sigma | n \rangle^2], \quad (9)$$

which depends on the interfragment overlap. We consider R_1 , the distance between H_a and H_b , and R_2 , the distance between H_b and H_c . At large R_1 , R_2 is the equilibrium bond length in the H_b-H_c molecule (i.e. R_2 1.4 au). For large values of R_1 , the interfragment overlap is negligible. So we neglect not only the interfragment overlap $\langle \sigma | n \rangle$ but also the two-centre differential overlap σn in the two-electron repulsion integrals. If we decompose the total Hamiltonian H into one-electron part V and two electron part (e^2/r_{12}), we have

$$\begin{aligned} \langle {}^2\Psi_0 | H | {}^2\Psi_1 \rangle &= \langle \sigma | v | n \rangle, \\ \langle {}^2\Psi_0 | H | {}^2\Psi_2 \rangle &= \sqrt{2} \langle n | \sigma \sigma^* \rangle, \\ \langle {}^2\Psi_0 | H | {}^2\Psi_3 \rangle &= 0, \\ \langle {}^2\Psi_0 | H | {}^2\Psi_4 \rangle &= 0, \\ \langle {}^2\Psi_0 | H | {}^2\Psi_5 \rangle &= \langle \sigma \sigma^* | \sigma \sigma^* \rangle, \\ \langle {}^2\Psi_0 | H | {}^2\Psi_6 \rangle &= 0, \end{aligned} \quad (10)$$

where $\langle n | \sigma \sigma^* \rangle = \iint n(1) n(2) |e^2/r_{12}| \sigma(1) \sigma^*(2) dv_1 dv_2$.

We decompose the σ and σ^* orbitals which are localised on H_2 , as

$$\sigma = 1/\sqrt{2} (\phi_b + \phi_c),$$

$$\sigma^* = 1/\sqrt{2} (\phi_b - \phi_c),$$

while $n \approx \phi_a$.

At a large value of R_1 it is evident from (10) that ${}^2\Psi_0$ can mix with ${}^2\Psi_4$ as its mixing coefficient does not depend on R_1 . We therefore represent the ground state reactant configuration ${}^2\Psi_G$ as

$${}^2\Psi_G = [{}^2\Psi_0 + \lambda {}^2\Psi_4]/(1 + \lambda^2)^{1/2}, \quad (11)$$

where λ is a very small quantity for the equilibrium bond length in H_2 . The configuration, ${}^2\Psi_4$, can mix with ${}^2\Psi_2$, ${}^2\Psi_5$ and ${}^2\Psi_6$ of (8). In the present approximation, the ground state reactant wavefunction, ${}^2\Psi_G$, can interact with the excited state configurations as,

$$\begin{aligned} \langle {}^2\Psi_G | H | {}^2\Psi_1 \rangle &= \frac{\langle \sigma | \nu | n \rangle}{(1 + \lambda^2)^{1/2}} = \frac{\langle \phi_a | \nu | \sqrt{2}(\phi_b + \phi_c) \rangle}{(1 + \lambda^2)^{1/2}}, \\ \langle {}^2\Psi_G | H | {}^2\Psi_2 \rangle &= \sqrt{2} \left(\frac{\lambda + 1}{(1 + \lambda^2)^{1/2}} \right) \langle n | \nu | \sigma^* \rangle, \\ &= \frac{1}{2} \left[\frac{\sqrt{2}(\lambda + 1)}{(1 + \lambda^2)^{1/2}} \right] [\langle \phi_a \phi_a | \phi_b \phi_b \rangle - \langle \phi_a \phi_a | \phi_c \phi_c \rangle], \quad (12) \end{aligned}$$

$$\langle {}^2\Psi_G | H | {}^2\Psi_5 \rangle = \frac{\lambda}{(1 + \lambda^2)^{1/2}} \langle n | \nu | \sigma \rangle = \frac{\lambda}{(1 + \lambda^2)^{1/2}} \langle \phi_a | \nu | 1/\sqrt{2}(\phi_b + \phi_c) \rangle,$$

$$\langle {}^2\Psi_G | H | {}^2\Psi_6 \rangle = -\frac{\lambda}{(1 + \lambda^2)^{1/2}} \langle n | \nu | \sigma^* \rangle = -\frac{\lambda}{(1 + \lambda^2)^{1/2}} \langle \phi_a | \nu | 1/\sqrt{2}(\phi_b - \phi_c) \rangle.$$

We ignore λ^2 but not λ . We find that in (12), ${}^2\Psi_G$ interacts with ${}^2\Psi_2$, ${}^2\Psi_1$, ${}^2\Psi_5$ and ${}^2\Psi_6$. Table 2 shows how the integrals $\langle n | \nu | \sigma \rangle$ and $\langle n | \nu | \sigma^* \rangle$ vary with R_1 in the three-hydrogen atom system at large R_1 .

Results show that, at $R_1 = 12$ au, the magnitude of $\langle n | \nu | \sigma^* \rangle$ is 20 times greater than that of $\langle n | \nu | \sigma \rangle$. For $R_1 > 12$ au, the chemical forces are absent and the wavefunctions used are not appropriate. However, qualitatively, we see that at an early stage of the reaction (A), the ground state reactant wavefunction mixes slightly with ${}^2\Psi_2$ which involves

Table 2. The values in atomic units of the integrals $\langle n | \nu | \sigma \rangle$ and $\langle n | \nu | \sigma^* \rangle$ for the reaction (A) for large values of R_1 , while $R_2 = 1.4$ au in H_2 .

R_1 (au)	$\langle n \nu \sigma^* \rangle$	$\langle n \nu \sigma \rangle$
6	0.013	-0.029
8	0.0095	-0.005
10	0.0050	-0.001
12	0.004	-0.0002
13	0.004	-0.0001

weakening of the H_b-H_c bond. At lower values of R_1 , the reactant wavefunction mixes with ${}^2\Psi_1$, ${}^2\Psi_5$ and ${}^2\Psi_6$ when the overlap $\langle\sigma|n\rangle$ begins to develop but mixing with ${}^2\Psi_5$ and ${}^2\Psi_6$ can be neglected in comparison to the mixing with ${}^2\Psi_1$. This means that the formation process of a covalent bond between ϕ_a and ϕ_b begins to take place after the cleavage process of the H_b-H_c bond has already started in the reaction path. At a later stage of the reaction, R_1 decreases and R_2 increases from its equilibrium bond length. This leads to decrease of the energy gap between the σ and σ^* orbitals of H_2 . So mixing with ${}^2\Psi_2$ also increases. The above argument shows that before the reactants are prepared for bonding between H_a and H_b , the bond cleavage process in H_b-H_c starts. Thus, the bond formation process lags behind the bond-cleavage process in a simple metathetic reaction due to polarisation of the bonding σ orbital with the corresponding antibonding σ^* orbital at an early stage when the overlap between the σ and the n -orbital is negligible.

4. Conclusions

In radical-exchange reactions where one bond is formed and another is broken, the conservation of bond orders of the breaking and forming bonds to unity does not hold good owing to development of a small free valence on the migrating atom in the transition state. The cause for development of this free valence is rooted in quantum mechanics. As a result of the free valence, the bond-formation process lags behind the bond-cleavage process. The same conclusion can be drawn qualitatively from consideration of the configuration mixing of the reactant configurations at the early stages of the reaction.

Acknowledgement

The author thanks the Council of Scientific and Industrial Research, Government of India, New Delhi for an emeritus fellowship.

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