

Orbital Interaction and Chemical Bonds. Exchange Repulsion and Rehybridization in Chemical Reactions

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Abstract: The roles of the exchange interaction in chemical reactions are studied by the use of the molecular orbital method. The redistribution of electrons due to the interaction is divided into two terms, the overlap repulsion and orbital mixing effects. It is shown that the rehybridization of the reaction sites is performed under the efficient cooperation of the two effects. The overlap repulsion gives rise to the forces which thrust the reaction centers and the adjacent atoms away from the attacking reagent, while the orbital mixing yields the force elements which tend to detain the reaction centers. The outcome of the exchange interaction in chemical reactions is compared with those of the delocalization and polarization interactions.

Investigations of reaction mechanisms utilizing the orbital concept are very popular these days. Among the several methods proposed so far, the orbital interaction approach seems to be most useful in dealing with a variety of chemical reactions in a unified manner.¹⁻⁷ It is also endowed with chemical lucidity which allows us to partition the interaction energy into several terms.⁸⁻¹⁰ The sources of the formation and breaking of chemical bonds in the course of chemical reactions were studied in detail on the basis of the orbital interaction concept.¹¹⁻¹³ The roles of the delocalization and polarization interactions were clarified. On the other hand, Salem introduced the repulsive interaction between the occupied MOs in his perturbation approach to the molecular orbital theory of chemical interactions.³ The contribution of overlap repulsion to the stability of aromatic systems was discussed by Epiotis and Yates.¹⁴ Very recently, Houk made an interesting suggestion that the closed-shell repulsion would be a significant factor for differentiating the symmetrical two-bond transition state from the unsymmetrical one-bond transition state in cycloadditions.¹⁵

The progress of chemical reactions is visualized by the harmonious changes in the reactant skeletons along the reaction coordinates. The displacements of the nuclei lead to the rehybridization of reaction sites, as well as the formation and breaking of bonds. The importance of the exchange interaction in bringing about the changes in the nuclear configuration around the reaction sites has been noticed fragmentarily in molecular orbital calculations.^{16,17} The interaction is intensified markedly with the progress of reactions, since it appears through the orbital overlaps between the reactants. With a view to getting clearer insights into the nature of chemical bonds in reactions, we undertook an analysis of the exchange interaction, focusing our attention on the local properties of chemical interactions, in particular, on the rehybridization of reaction sites.

The Exchange Interaction in Chemical Reactions

Since Heitler and London, the exchange of electrons has been recognized as an important source of the chemical binding in the hydrogen molecule.^{18,19} In the interaction between two closed-shell systems, the exchange interaction serves as a repulsive term.²⁰ The exchange interaction has been studied extensively for the short-range interactions of two small species, like hydrogen, helium, and so on.²¹ It has also been shown that the interaction brings about the redistribution of electrons.²²⁻²⁴ Then, the interaction should naturally play a significant role in organic reactions of larger systems to determine the favorable reaction pathways.^{15,25}

Let us examine first the exchange interaction between two closed-shell molecules, A and B. The wave function of the in-

teracting system is given by the linear combination of various electron configurations.^{9,12}

$$\Psi = \sum_p C_p \Psi_p \quad (1)$$

The dominant term at an early stage of the interaction is the original configuration Ψ_0 , shown in Figure 1. The initial electron configurations of the two systems A and B are retained in Ψ_0 . The electron density of the interacting system is given by

$$\rho(1) = \rho_{0,0}(1) + \sum_p \sum_q C_p C_q (\rho_{p,q}(1) - S_{p,q} \rho_{0,0}(1)) \quad (2)$$

where

$$\begin{aligned} \rho_{p,q}(1) &= M \int \Psi_p^*(1, 2, \dots, M) \\ &\quad \times \Psi_q(1, 2, \dots, M) d\xi_1 d\tau_2 \dots d\tau_M \\ S_{p,q} &= 1/M \int \rho_{p,q}(1) dv(1) \end{aligned}$$

Of the electron configurations other than 0, the roles of the electron-transferred and locally excited configurations were discussed in our previous papers.^{12,13}

The wave function Ψ_0 is represented by the antisymmetrized product of the occupied MOs ϕ_i of A and the occupied MOs ψ_k of B due to Pauli's exclusion principle.²⁶ It is important to note here that the MOs ϕ_i are not orthogonal to the MOs ψ_k , in general. The existence of the intermolecular orbital overlaps leads to the redistribution of electrons, defined as the exchange density ρ_K . We may divide the density ρ_K into two contributions, the overlap repulsion term ρ_K^R and the orbital mixing term ρ_K^M , given by

$$\rho_K(1) = \rho_{0,0}(1) - \rho_A(1) - \rho_B(1) = \rho_K^R(1) + \rho_K^M(1) \quad (3)$$

$$\begin{aligned} \rho_K^R(1) &\approx 2 \sum_i^{\text{occ}} \left\{ \sum_k^{\text{occ}} (s_{ik} \phi_i(1)^2 - \phi_i(1) \psi_k(1)) s_{ki} \right\} \\ &\quad + 2 \sum_k^{\text{occ}} \left\{ \sum_i^{\text{occ}} (s_{ki} \psi_k(1)^2 - \psi_k(1) \phi_i(1)) s_{ik} \right\} \quad (4) \end{aligned}$$

$$\begin{aligned} \rho_K^M(1) &\approx \sum_k^{\text{occ}} \sum_i^{\text{occ}} \sum_{i' \neq i}^{\text{occ}} (\phi_i(1) \phi_{i'}(1) + \phi_{i'}(1) \phi_i(1)) s_{ik} s_{i'k} \\ &\quad + \sum_i^{\text{occ}} \sum_k^{\text{occ}} \sum_{k' \neq k}^{\text{occ}} (\psi_k(1) \psi_{k'}(1) + \psi_{k'}(1) \psi_k(1)) s_{ki} s_{k'i} \quad (5) \end{aligned}$$

where

$$s_{ik} = \int \phi_i(1) \psi_k(1) dv(1)$$

The physical meanings of ρ_K^R and ρ_K^M will be discussed separately in the next section with reference to several sorts of organic reactions.

In the orbital approaches to reaction mechanisms, we have

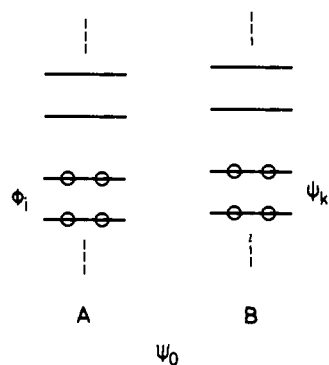


Figure 1. The original electron configuration in the interaction of two closed shell systems.

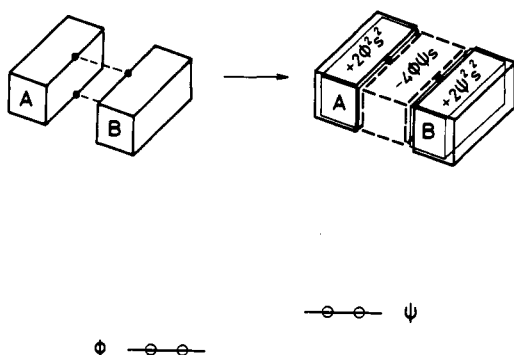


Figure 2. A schematic representation of the electron redistribution associated with the overlap repulsion.

been accustomed to consider the regio- and stereospecificities of chemical reactions in terms of the MOs which are obtained by solving the Fock-Roothaan equations or their simplified versions.^{27,28} Now, we may keep on adopting the MOs delocalized over the constituent atomic orbitals to examine the effects of the exchange interaction. All the numerical results given in this paper have been calculated by the use of the MOs with the STO-3G basis set.²⁹

Overlap Repulsion and Orbital Mixing

The exchange of a pair of electrons with the same spin, say α , between the doubly occupied MO ϕ_i and the doubly occupied MO ψ_k gives rise to the overlap density $\sim -(\phi_i \psi_k s_{ki} + \psi_k \phi_i s_{ik})$. The same is also true for the exchange of the pair of electrons with the spin β . The integration of the overlap density over all the space yields $\sim -4s_{ik}^2$. This means that the interaction of two doubly occupied MOs leads to the reduction of the electron density in the intermolecular region between the two systems. By definition, ρ_K represents the redistribution of electrons. The total number of electrons must be kept constant throughout the interaction. Equation 4 indicates that the electron population evacuated from the region between A and B is shared evenly by the two systems, irrespective of the donor-acceptor relation between them. One-half of the electron population expelled from the intermolecular region is accommodated in the MO ϕ_i to give the density term $2s_{ik}^2 \phi_i^2$ and the other half is received by the MO ψ_k to yield the density term $2s_{ki}^2 \psi_k^2$. Figure 2 illustrates schematically the deformation of the density cloud due to the interaction between ϕ_i and ψ_k .

To achieve the formation of chemical bonds between the two systems, the reaction sites of A and B must approach each other. The negative overlap density in the intermolecular region produces the forces which tend to hinder such displacements of reaction sites so as to form new chemical bonds between the

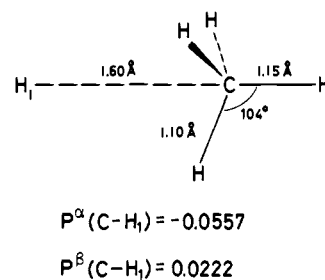


Figure 3. Overlap populations in methane-hydrogen interacting system.

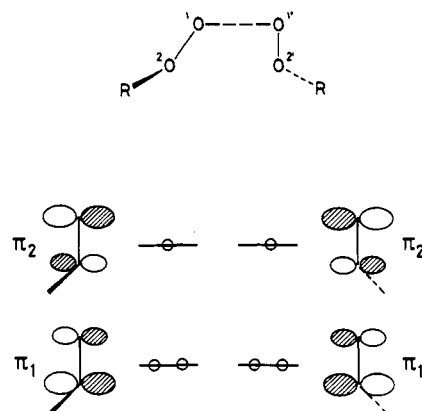


Figure 4. Orbital interactions in the self-reaction of peroxy radicals. The hatched and unhatched areas symbolize the positive and negative regions of the MOs, respectively.

two systems. Thus, the orbital overlap between the two doubly occupied MOs results in the repulsive interaction and, hence, the interaction may be called the "overlap repulsion".

It should be noted here that there exists another effect associated with the overlap repulsion. The MOs ϕ_i and ψ_k are occupied and mostly bonding between the reaction sites and the adjacent atoms in A and in B. Therefore, the increase in the electron populations of ϕ_i and ψ_k by absorbing the electron density from the intermolecular region strengthens the bonds in A and in B. Equation 4 signifies that the overlap term ρ_K^R suppresses the progress of chemical reactions first by giving rise to the repulsive intermolecular forces and second by tightening the chemical bindings onto the reaction sites from the adjacent atoms in each of the reactants.

The significance of the overlap term can be recognized very clearly when we apply a similar discussion to the reactions of radicals with closed-shell molecules. Figure 3 gives the overlap populations of the methane-hydrogen reacting system.³⁰ We assigned without loss of generality the spin α to the odd electron. The overlap population between the carbon atom of methane and the incoming hydrogen is negative for the α spin electrons and is positive for the β spin electrons. Since the hydrogen 1s AO overlaps efficiently with the occupied MOs of methane, the odd electron produces a strong overlap repulsion between the reaction sites. Thus, the positive overlap population created by the delocalization interaction is offset by the negative overlap population due to the repulsion in regard to the α spin electrons. The electrons with the spin β , on the other hand, have no overlap repulsion in this case, giving the net positive overlap population. The trend in the overlap populations has been shown to be a common feature of the interactions between a radical and a closed-shell system.³¹

An interesting cooperation of the exchange interaction with the delocalization interaction is found in the self-reaction of peroxy radicals. As shown in Figure 4, the π_2 - π_2' stabilizing interaction is large when two radicals approach in a parallel

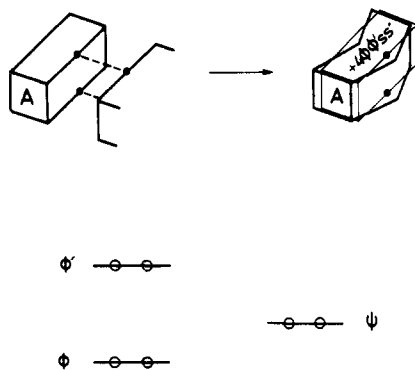


Figure 5. A schematic representation of the electron redistribution due to the orbital mixing in the exchange interaction.

fashion. However, such an approach yields a strong repulsion between the oxygen atoms 2 and 2' due to the $\pi_1-\pi_1$ overlap interaction. Our recent calculation suggested that the interaction would not be the four-centered type, since the decrease in the delocalization stabilization could be compensated by the decrease in the exchange repulsion.³² Thus, the termination of autoxidations by means of the coupling of tertiary alkylperoxy radicals gives peroxides and oxygen molecule via tetroxide.³³ The two-centered interaction between the radicals is plausible. On the other hand, secondary and primary alkylperoxy radicals yield carbonyl compounds and alcohols in the reaction presumably through six-centered interactions.³⁴ The six-centered transition state is considered to be formed via precursory two-centered interaction between the terminal oxygen atoms of peroxy radicals.³²

The other term of importance in the exchange interaction is the mixing of the occupied MOs in A and in B.³⁵ In most chemical reactions, the reagent and reactant are sizable systems and, therefore, possess many occupied MOs. Then, the overlap interaction between them is accompanied by the orbital mixings. The first term on the right-hand side of eq 5 shows that the occupied MO ϕ_i of A mixes with another occupied MO $\phi_{i'}$ of the same system through the overlap interactions with the occupied MO ψ_k of B. To make efficient the MO mixing, the MO ψ_k should have large overlaps both with ϕ_i and with $\phi_{i'}$. In a similar manner, the MO ψ_k of B mixes with another MO $\psi_{k'}$ through the overlaps with the MO ϕ_i , as given by the second term on the right-hand side of eq 5. The integration of each term in ρ_K^M over all the space obviously vanishes. That is, it represents the redistribution of electrons inside of A and of B, as illustrated schematically in Figure 5. The MO mixings lead to the accumulation of electron density around the reaction sites on the side of mutual approach of A and B. That is, the s and p AOs recombine with each other through the MO mixings, giving rise to the forces onto the reaction sites to oppose the overlap repulsion. The following examples demonstrate the circumstances.

In order to examine the relative strengths of the overlap repulsion and orbital mixing effects, we carried out a numerical calculation first on a reaction model of bimolecular nucleophilic substitution. The reaction is suitable for our study since it involves a notable change in the hybridization and the concerted formation and breaking of chemical bonds at the reaction site.³⁶ The substrate and the attacking nucleophile were tentatively represented by methyl fluoride and fluoride ion for the sake of simplicity. Figure 6 shows the exchange density (see Appendix for numerical calculations). It is divided into two terms, the overlap repulsion term and the orbital mixing term. By the overlap repulsion, the hydrogen atoms of the substrate are thrust away. The carbon under attack is also repelled. Incidentally, the carbon-fluorine bond to be broken is strengthened.

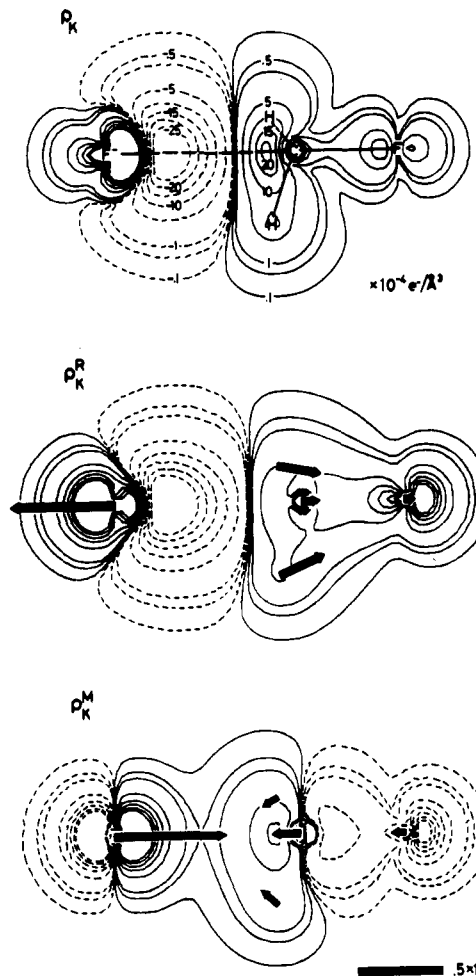


Figure 6. The exchange density and its fragments in a bimolecular nucleophilic substitution reaction. Each arrow shows the force exerted on the nucleus from the interference density divided by the mass of the atom.

Figure 6 indicates that the orbital mixing term gives the forces which counteract the overlap repulsion. Equation 5 is helpful in understanding the situation. Let us consider the orbital mixing in the fluoride ion. The basis orbitals of the anion of interest here are the 2s and 2p_x AOs. These AOs intermix through the overlaps with the occupied MOs of methyl fluoride having the a_1 symmetry. We may take the signs of the 2s and 2p_x AOs as to possess positive overlaps with the substrate MOs as shown in Figure 7. Then eq 5 shows that these AOs should intermix with positive sign. That is, the s and p_x AOs hybridize so as to increase the electron density on the side of attack.

The MOs of methyl fluoride are delocalized over the constituent atoms. The 2s and 2p AOs of the carbon atom, however, have their largest amplitudes in different MOs. The 4a₁ MO having the large component of the carbon 2s AO lies lower than the 5a₁ MO having the large component of the carbon 2p_x AO. These MOs intermix with each other with positive sign through the overlaps with the 2s and 2p_x AOs of the attacking anion. The orbital mixing leads to the accumulation of the electron density on the backside of the carbon-fluorine bond to be displaced. It is interesting to note that the force exerted on the carbon nucleus due to the orbital mixing overrides the one due to the overlap repulsion, as shown in Figure 6. The hydrogen atoms of the substrate are repelled away by the overlap repulsion with the incoming nucleophile, while the orbital mixing tends to detain the carbon atom. The calculation suggests that the inversion at the reaction site is an outcome of the beautiful cooperation between the overlap repulsion and orbital mixing effects.

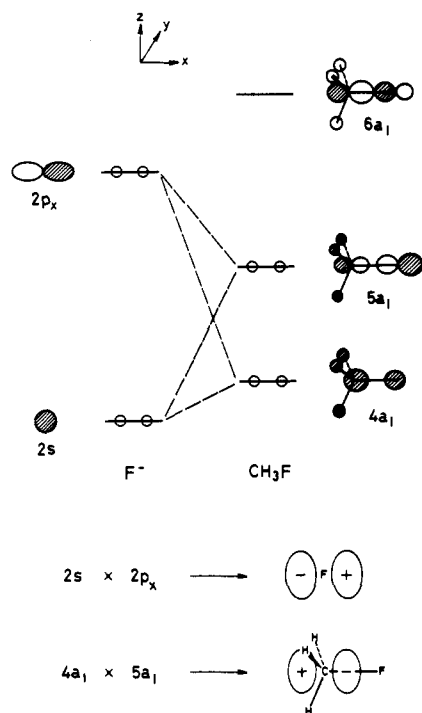


Figure 7. Some orbitals of methyl fluoride and fluoride ion relevant for orbital interactions. The signs + and - stand for the regions of the increase and decrease in the electron density, respectively.

The rehybridization of the reaction sites in the reactions of planar conjugated systems may be discussed in a similar manner. The reaction sites and the adjacent atoms are placed under the overlap repulsion from the approaching reagent. Then the occupied σ and π MOs of conjugated systems intermix through the overlaps with the reagent occupied orbitals to counteract the overlap repulsion onto the reaction centers. The reaction sites are retained, while the adjacent atoms are repelled away.

Figure 8 shows the exchange interaction in the addition of methyl radical to ethylene.³⁷ We assigned the α spin to the odd electron. There exists a strong overlap repulsion of the α spin electrons, since the odd electron orbital of methyl radical overlaps effectively with the $p\pi$ orbital of the carbon atom of ethylene under attack. Concurrently, the orbital mixing through the exchange interaction gives rise to the forces which contend with the overlap repulsion at the reaction site of each system. As for the β spin electrons, on the other hand, the orbital mixing effect is negligibly small. This is obviously due to the fact that the relevant orbital of methyl radical is vacant. The overlap repulsions of the β spin electrons onto the reaction sites and the neighboring atoms are naturally much weaker than the overlap repulsions of the α spin electrons.

Our recent calculation has shown that the exchange repulsion is reduced markedly by the pyramidization of the reaction sites in the recombination of methyl radicals to give ethane.³⁸ The increase in the delocalization stabilization has been found to be rather minor. In some radicals the radical center does not have the sp^2 planar structure. For example, the C_2-H bond in 2-norbornyl radical is known to be tilted in the endo direction.^{39,40} Then, the approach of a reagent, e.g., halogen molecule, from the exo side should be favorable to reduce the overlap repulsion.

Comparison of the Exchange Effect with the Delocalization and Polarization Effects

Before closing our discussion on the roles of the exchange interaction in chemical reactions, we may refer to the delo-

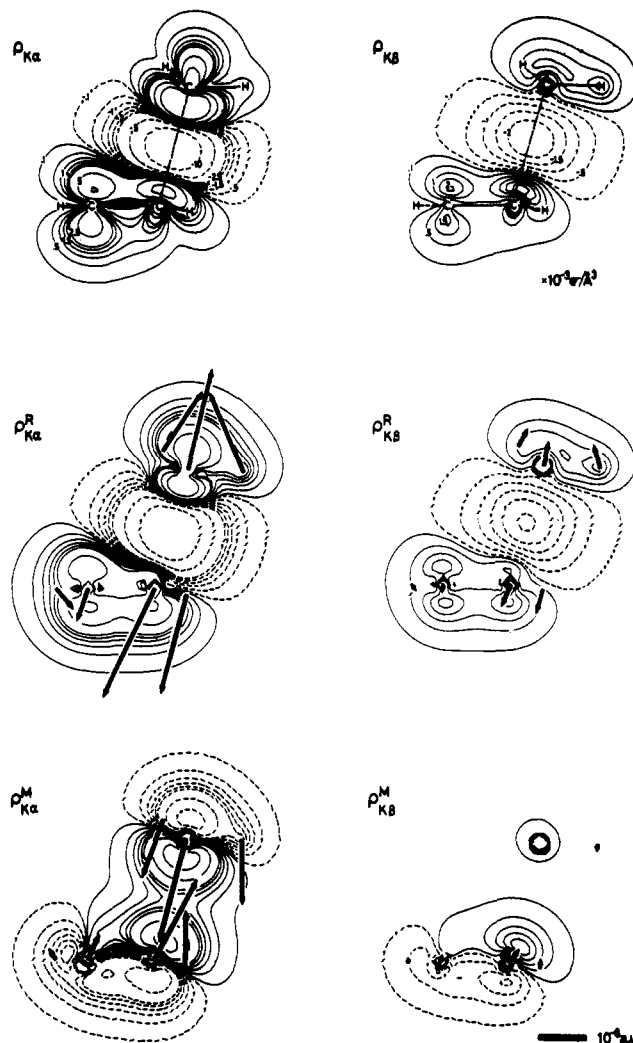


Figure 8. The overlap repulsion and orbital mixing effects in the exchange interaction between ethylene and methyl radical.

calization and polarization interactions. The wave function of the interacting system is given by the linear combination of various electron configurations, involving the electron-transferred and locally excited configurations in addition to the original one Ψ_0 .^{41,42} The electron-transfer interaction is the major origin of the formation of chemical bonds between the reaction sites of two systems.¹² Thus, the delocalization interaction must take place efficiently in order to produce positive overlap populations between the reaction sites of the two systems by overcoming the overlap repulsion. The electron transfer interaction is also a source of the bond weakening between the reaction sites and the adjacent atoms in each of the reactants.⁴³ Therefore, with respect to the formation and breaking of chemical bonds, there seems to be an intense competition between the delocalization interaction and the exchange interaction. In fact, calculations have shown that the exchange repulsion tends to cancel with the delocalization stabilization for the most part in many cases.^{44,45} Then, the favorable reaction path may be defined as that in which the noticeable increase in the delocalization stabilization is gained, while the increase in the exchange repulsion is kept moderate.

The distinction between the symmetry-allowed reactions and the symmetry-forbidden reactions⁷ can be clarified in terms of the exchange and delocalization interactions. For example, the concerted $[4_s + 2_s]$ cycloaddition of butadiene and ethylene does not suffer the strong overlap repulsion, because the overlap between the highest occupied MOs of diene

and dienophile vanishes in the symmetric reaction path.^{12,15} On the other hand, the overlap repulsion between the occupied π MOs of olefins makes the concerted [$2_s + 2_s$] cycloaddition unfavorable. In order to avoid the bumping of the highest occupied MO of an addend into the highest occupied MO of the other, electron(s) should be shifted from the highest occupied MO to the lowest unoccupied MO by some adequate means.¹² Cycloaddition of olefins in the first excited state or in the ground state via three-centered interaction is the case. The combination of the exchange interaction and the delocalization interaction leads us to a general statement of the stereoselection rules that the symmetry-allowed processes are characterized by the large delocalization stabilization with the small overlap repulsion, while the symmetry-forbidden processes are characterized by the large overlap repulsion with the small delocalization stabilization.

The addition of singlet methylene to an ethylenic double bond along the symmetric least-motion pathway brings about the strong overlap repulsion between the ethylenic π MO and the lone-pair hybrid of methylene.⁴⁴ Then, the reaction may proceed along the non-least-motion path,⁴⁶ because the tilt of methylene results in the decrease of the exchange repulsion and also in the increase of the delocalization stabilization.⁴⁴ Because of the differences in the nodal properties and the density distributions of the highest occupied MO and the lowest unoccupied MO, the reaction course with a large delocalization stabilization can often be the one with the small overlap repulsion.^{44,47} This may be one of the reasons why the frontier orbital theory based simply on the delocalization interaction has been successful. As we have seen above, however, the inclusion of the exchange interaction yields a more reasonable rationalization of reaction mechanisms.

The intermixings of MOs take place through the delocalization and polarization interactions, in addition to that caused by the exchange interaction.^{12,13} Each of them shows several effects, partially similar, but for the most part different from the effects of others. The occupied and unoccupied MOs of reactant intermix under the influence of approaching reagent.¹³ Thus, the polarization interaction is responsible for the relaxation of the interacting system. On the other hand, the occupied MOs ϕ_i and $\phi_{i'}$ of A can mix with each other through the electron transfer interaction with an unoccupied MO, ψ_j , of B.¹³ When we choose the overlap integrals $s_{ii'}$ and $s_{j'j}$ to be positive, the intermixing of ϕ_i and $\phi_{i'}$ carries a factor -1 in the ground state.⁴⁸ That is, the intermixing of the occupied MOs through the delocalization interaction is opposite in sign to the orbital mixing through the exchange interaction. This means that the electron redistribution caused by the exchange interaction, if unfavorable for the progress of chemical reactions, will be compensated by that caused by the delocalization interaction or vice versa.⁴⁹

In nonpolar reactions, all the exchange, delocalization, and polarization interactions are roughly similar in magnitudes of their effects on the local redistribution of electrons ($\sim s^2$). Then, the rearrangement of reactant skeletons in reactions is likely to be governed by the balance of these interactions. We have observed such a circumstance actually in the numerical analysis of the potential gradient of the methane-tritium system along a reaction coordinate.¹⁶ In studying reaction courses by means of MOs, much attention has been paid to the delocalization interaction. It has been clarified above that the exchange interaction possesses important effects on the redistribution of electrons and, hence, on the changes in the nuclear configuration of reagent and reactant. We hope that the present study can offer an insight into the theoretical aspects of chemical bonds in reactions.

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Appendix

The electron densities of the isolated reactants A and B are defined by

$$\rho_A(1) = 2 \sum_i^{\text{occ}} \phi_i(1)^2 \quad (6)$$

$$\rho_B(1) = 2 \sum_k^{\text{occ}} \psi_k(1)^2 \quad (7)$$

The electron density of the original configuration Ψ_0 is given by

$$\begin{aligned} \rho_{0,0}(1) = 2 \left\{ \sum_i^{\text{occ}} \sum_{i'}^{\text{occ}} \phi_i(1) \phi_{i'}(1) D_{i,i'} \right. \\ \left. + \sum_k^{\text{occ}} \sum_{k'}^{\text{occ}} \psi_k(1) \psi_{k'}(1) D_{m+k,m+k'} \right\} / D \\ + 4 \sum_i^{\text{occ}} \sum_k^{\text{occ}} \phi_i(1) \psi_k(1) D_{i,m+k} / D \quad (8) \end{aligned}$$

In eq 8 D is the determinant of the overlap integrals between the occupied MOs of A ($i = 1, 2, \dots, m$) and the occupied MOs of B ($k = m + 1, m + 2, \dots, m + n$):

$$D = \begin{vmatrix} 1 & (s_{ik}) \\ (s_{ki}) & 1 \end{vmatrix} \quad (9)$$

and $D_{p,q}$ means the minor of D with respect to the (p,q) element, including the factor $(-1)^{p+q}$. By subtracting ρ_A and ρ_B from $\rho_{0,0}$ and neglecting the terms with higher order overlap integrals than s^2 , we get eq 4 and 5. The orbital mixing term ρ_K^M consists of the off-diagonal elements ($i \neq i', k \neq k'$) of the density terms in the braces on the right-hand side of eq 8. If we adopt the zero-differential overlap approximation, eq 8 shows that $\rho_{0,0}$ is given simply by the sum of ρ_A and ρ_B . The exchange density ρ_K disappears. That is, the interference between the wave function of A and that of B does not take place within the framework of the approximation. The density ρ_K accounts for the basic statistical property of electrons by taking the wave function as the antisymmetrized product of the one-electron spin orbitals.

References and Notes

- (1) (a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology", P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 513; (b) H. Fujimoto and K. Fukui, "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley-Interscience, New York, N.Y., 1974, p 23.
- (2) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
- (3) (a) L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968); (b) A. Devaquet and L. Salem, *ibid.*, **91**, 3793 (1969).
- (4) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).
- (5) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).
- (6) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).
- (7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1969.
- (8) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. R. Soc. London, Ser. A*, **284**, 566 (1965).
- (9) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968).
- (10) Morokuma devised the method of partitioning the interaction energy within the framework of the Fock-Roothaan variation scheme. See K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976); W. A. Lathan, G. R. Pack, and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 6624 (1975).
- (11) H. Fujimoto, S. Inagaki, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 2670 (1976).
- (12) H. Fujimoto and T. Sugiyama, *J. Am. Chem. Soc.*, **99**, 15 (1977).
- (13) H. Fujimoto and S. Inagaki, *J. Am. Chem. Soc.*, **99**, 7424 (1977).
- (14) N. D. Epiotis and R. L. Yates, *J. Am. Chem. Soc.*, **98**, 461 (1976).
- (15) P. Caramella, K. N. Houk, and L. N. Domeismith, *J. Am. Chem. Soc.*, **99**, 4511 (1977).
- (16) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).
- (17) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 7208 (1976).
- (18) H. Heitler and London, *Z. Phys.*, **44**, 455 (1927).
- (19) As for the further refinements in order to give an agreement with the observed result, see, for example, C. A. Coulson, "Valence", Clarendon

- Press, Oxford, 1961.
- (20) The interaction between two closed-shell anions may give the negative exchange energy. See ref 8.
- (21) (a) J. C. Slater, *Phys. Rev.*, **32**, 349 (1928); (b) G. Gentile, *Z. Phys.*, **63**, 795 (1930); (c) E. A. Mason and L. Monchick, *Adv. Chem. Phys.*, **12**, 329 (1967).
- (22) (a) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962); (b) W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl.*, **12**, 546 (1973).
- (23) (a) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955); (b) L. Salem, *Proc. R. Soc. London, Ser. A*, **264**, 379 (1961); (c) V. Magnasco, *Theor. Chim. Acta*, **21**, 267 (1971).
- (24) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **44**, 2936 (1971).
- (25) K. Fukui, H. Fujimoto, and S. Yamabe, *J. Phys. Chem.*, **76**, 232 (1972).
- (26) W. Pauli, *Z. Phys.*, **31**, 765 (1925).
- (27) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 74 (1951).
- (28) The division of the intramolecular part in ρ_K into two terms ρ_K^A and ρ_K^B may be affected by the transformation of the basis MOs into other sets of MOs, e.g., localized orbitals. In any event, ρ_K is invariant toward such transformations within the occupied MOs of A and/or of B, and, therefore, the conclusion derived in this paper on the exchange interaction is independent of the choice of the basis MOs. The overlap repulsion in chemical reactions has usually been discussed by the use of the canonical MOs delocalized over the component atoms. See, for example, ref 3.
- (29) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) R. F. Stewart, *ibid.*, **52**, 431 (1970).
- (30) The MOs were calculated by means of the unrestricted open-shell Hartree-Fock method. See J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).
- (31) H. Fujimoto, S. Yamabe, T. Minato, and K. Fukui, *J. Am. Chem. Soc.*, **94**, 9205 (1972).
- (32) T. Minato, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, to be published.
- (33) P. O. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799 (1967).
- (34) (a) R. Hiatt and L. Zigmund, *Can. J. Chem.*, **48**, 3967 (1970); (b) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
- (35) The orbital mixing term in the exchange interaction was omitted in our previous paper,¹² because it does not contribute directly to the intermolecular overlap populations.
- (36) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, p 418.
- (37) The reaction model was taken after Hoyland. See J. R. Hoyland, *Theor. Chim. Acta*, **22**, 229 (1971).
- (38) S. Yamabe, T. Minato, H. Fujimoto, and K. Fukui, to be published.
- (39) H. Fujimoto and K. Fukui, *Tetrahedron Lett.*, 5551 (1966).
- (40) (a) J. Glaux, M. Guglielmi, and H. Lemaire, *Mol. Phys.*, **17**, 425 (1969); **19**, 833 (1970); (b) R. Marx and L. Bonazzola, *ibid.*, **19**, 899 (1970); (c) T. Kawamura, T. Koyama, and T. Yonezawa, *J. Am. Chem. Soc.*, **92**, 7222 (1970); **95**, 3220 (1973).
- (41) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).
- (42) H. Fujimoto, S. Kato, S. Yamabe, and K. Fukui, *J. Chem. Phys.*, **60**, 572 (1974).
- (43) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **42**, 3399 (1969).
- (44) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 2424 (1972).
- (45) (a) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **95**, 7563 (1973); (b) S. Yamabe and K. Morokuma, *ibid.*, **97**, 4458 (1975).
- (46) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
- (47) H. Fujimoto, M. Katata, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 1320 (1972).
- (48) See eq 4 in ref 13.
- (49) In the reaction of planar electron-deficient species, e.g., CH_3^+ , BH_3 , etc., with electron donors, the orbital mixing term ρ_K^M is of minor importance. The delocalization interaction, as well as the overlap repulsion term, may be responsible, in part, for the rehybridization of reaction site in that case.

Photoelectron and Charge-Transfer Spectra of Benzobicycloalkenes. Relationships between Through-Space Interactions and Reactivity

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Abstract: Photoelectron and charge-transfer spectra of a variety of bicyclic and tricyclic alkenes fused to phenyl rings have been measured. The molecules studied are the benzo derivatives of norbornene, bicyclo[3.2.1]oct-6-ene, bicyclo[4.2.1]non-7-ene, norbornadiene, 2,6-bicyclo[3.2.1]octadiene, 2,7- and 3,7-bicyclo[4.2.1]nonadiene, 2,4,5-bicyclo[4.2.1]nonatriene, *exo*- and *endo*-tricyclo[4.2.1.0^{2,5}]non-7-ene, tricyclo[3.2.1.0^{2,4}]oct-6-ene, and *exo*- and *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene. As the through-space interactions between the benzene ring and the alkene moieties increase, the photochemical di- π -methane and electrophilic reactivities increase.

Introduction

The interactions between nonconjugated alkene moieties in polycyclic hydrocarbons have been thoroughly explored by photoelectron spectroscopy,² but little attention has been paid to the through-space interactions between phenyl and alkene moieties. Because of our interests in the photochemistry and electrophilic reactivity of these systems, we have studied the photoelectron, ultraviolet absorption, and charge-transfer spectra of benzonorbornadiene and related compounds, 1-13, containing phenyl groups and alkene, diene, or cyclopropyl moieties not conjugated with the benzene ring. The extent of interaction between these nonconjugated moieties has been estimated, and the relationships between these interactions and the reactivities of these compounds have been explored.

Experimental Section

Preparations of the compounds studied here have been reported elsewhere.³ Photoelectron spectra were recorded on a Perkin-Elmer

PS-18 photoelectron spectrometer operating with a resolution of 25-35 meV. Four to five spectra of each sample were recorded using xenon and argon as internal calibrants. Ultraviolet absorption spectra were recorded in 95% ethanol or hexane. Charge-transfer spectra were recorded on a Cary 118 UV-vis spectrophotometer, using dichloromethane as reference. Solutions were prepared by dissolving 50-100 mg of each hydrocarbon in 3 mL of a 3.90×10^{-3} M solution of tetracyanoethylene (resublimed) in dichloromethane.

Molecular Orbitals of Benzobicycloalkenes

The degenerate highest occupied orbitals of benzene, which give rise to ionization potentials (IPs) of 9.24 eV, are split by ortho dialkylation. The influence of dialkylation is larger on the "Ph_S" orbital than the "Ph_A", because the hyperconjugative interaction of the alkyl group is larger with the orbital with larger coefficients at the site of substitution. For example, *o*-xylene has IPs of 8.57 (the Ph_S, or b₁ IP) and 9.10 eV (the Ph_A, or a₂ IP), shifted by 0.67 and 0.14 eV, respectively,⁴ from the IP of benzene.