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An MO-theoretical Interpretation of the Nature of Chemical Reactions III. Bond Interchange

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The wave functions of a system composed of two mutually-interacting molecules have been expressed in terms of configuration interaction wave functions. The electron configurations have been taken into account with respect to the states of adiabatic interaction, delocalization interaction, and polarization interaction. The electron populations in all of these states have been obtained separately. It has been demonstrated that the adiabatic interaction between two closed-shell molecules can not be the origin of the bond interchange in chemical reactions. The inclusion of charge-transferred states has been shown to be of great importance in explaining the formation of new bonds and the weakening of old bonds in the case of chemical interaction between two molecules. On the basis of the results of numerical calculations on some typical reaction models, the important role of the orbital overlapping interaction of the highest occupied molecular orbital and the lowest unoccupied molecular orbital has been pointed out.

The interaction energy between two mutually-reacting molecules has been investigated by partitioning it into the Coulomb-interaction, exchange-interaction, delocalization, and polarization terms on the assumption of no nuclear configuration change.[1] Expressions for these four energy terms have been derived. The important role of electron delocalization in determining the favorable position and spatial direction of chemical interaction with respect to each of the two reacting molecules has been pointed out on the basis of the three governing principles of chemical interaction.[2] The significance of the cooperation of the charge-transfer and the nuclear configuration change has been stressed in relation to the nodal properties of the highest occupied (HO) molecular orbital (MO) and of the lowest unoccupied (LU) MO. The purpose of the present paper is to show how and why the formation of new bonds and the cleavage of old bonds take place in chemical reactions. This seems to be one of the most fundamental problems in understanding the nature of chemical reactions.

Wave Functions

Let us consider the chemical interaction between the molecules A and B. Here we set limits to the case in which both A and B have closed-shell structures in the isolated state. Only a slight modification should be needed for other systems. We represent the wave function of the combined system of the two molecules, A and B, by the configuration interaction (CI) wave function;

$$\Psi = C_0\Psi_0 + \sum_i^{\mathrm{occ}}\sum_l^{\mathrm{uno}} C_{i\to l}\Psi_{i\to l} + \sum_k^{\mathrm{occ}}\sum_j^{\mathrm{uno}} C_{k\to j}\Psi_{k\to j} + \sum_i^{\mathrm{occ}}\sum_j^{\mathrm{uno}} C_{i\to j}\Psi_{i\to j} + \sum_k^{\mathrm{occ}}\sum_l^{\mathrm{uno}} C_{k\to l}\Psi_{k\to l} + \cdots \qquad (1)$$

The meanings of the wave functions Ψ_0, $\Psi_{i\to l}$, $\Psi_{i\to j}$, $\cdots$ are the same as those in Ref. 1. These wave functions are constructed by means of the Slater determinants, composed of the MO's, a_i's, and a_j's of the molecule A and the b_k's and b_l's of the molecule B, according to each electron configuration. Other highly-transferred and highly-excited configurations can be neglected, provided the interaction is not too strong. The coefficients, C_0, $C_{i\to l}$, $C_{i\to j}$, $\cdots$, can be obtained by solving the secular equations. The integrals which are necessary in constructing the secular determinant have already been derived in Ref. 1. The coefficients of the wave function, Ψ, are taken so as to satisfy the normalization condition:

$$\int \Psi^2 d\tau = 1 \qquad (2)$$

In order to obtain the expressions of the electron populations of the interacting systems by the use of Ψ, it is convenient to represent them as the sum of the electron populations in each of the terms appearing in Eq. (1). For this purpose, we present the first-order density matrices[3] of some of the terms in Appendix. In the following

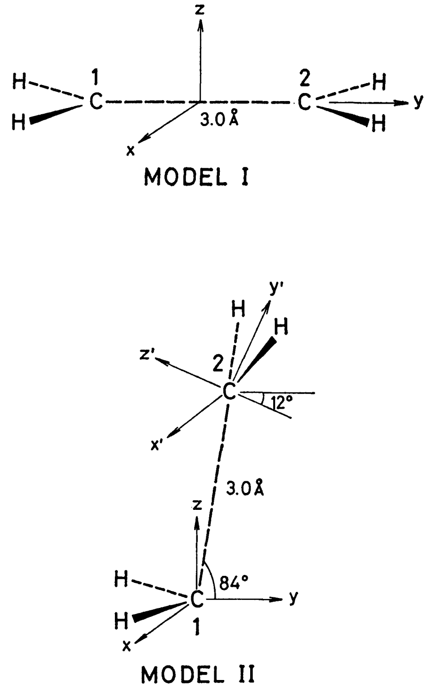

Fig. 1. A schematic representation of assumed models of the dimerization of methylenes.

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[1] K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).

[2] K. Fukui and H. Fujimoto, *ibid.*, **42**, 3399 (1969).

[3] R. McWeeny, *Proc. Roy. Soc.* (London), **A223**, 63 (1954); **A232**, 114 (1955).

discussions, the contribution from polarized configurations may be disregarded so long as we concentrate our attention on the intermolecular charge-transfer between *A* and *B*. The off-diagonal terms $\rho_{JJ'}$ $(J \neq J')$ (see Appendix), in which neither J nor J' is 0, are put equal to zero in a first approximation.

The example taken here to show the numerical results is the dimerization of singlet methylenes to form ethylene. This system was discussed by Hoffmann and his coworkers in order to demonstrate the preference of the non-least motion to the least motion in the mutual approach of methylenes by the use of the extended Hückel calculation.[4] We will compare the two modes of approach by means of our method, from the standpoint of mutual electron-donating and electron-accepting interactions. The two models are schematically illustrated in Fig. 1. The relative nuclear positions of the two methylenes are the same as those determined by Hoffmann. In Tables 1 and 2 we present the coefficients, C_0, $C_{i\to l}$'s, and $C_{k\to j}$'s, with respect to the two models in Fig. 1. The method of calculation and the approximations employed are the same as those adopted in our previous calculation.[5] It is clear that the charge-transfer interaction is by far more effective in Model II than in Model I.

Table 1. The coefficients of the ground-state CI wave function of model I

$C_0 = 0.9925$

		π'	σ_4'	σ_5'
$\lvert C_{i\to l}\rvert$	σ_1	0	0.0223	0
	σ_2	0	0	0.0025
	σ_3	0	0.0544	0

		π	σ_4	σ_5
$\lvert C_{k\to j}\rvert$	σ_1'	0	0.0223	0
	σ_2'	0	0	0.0025
	σ_3'	0	0.0544	0

The MO's of methylenes are termed as follows.

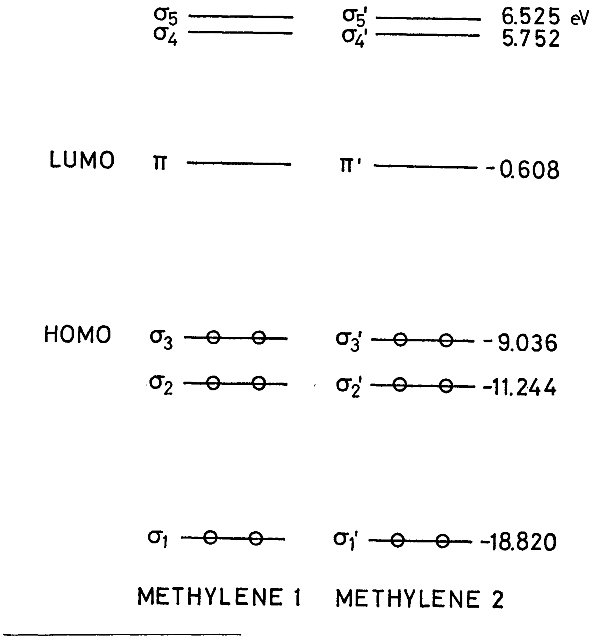

Table 2. The coefficients of the ground-state CI wave function of model II

$C_0 = 0.9231$

		π'	σ_4'	σ_5'
$\lvert C_{i\to l}\rvert$	σ_1	0.0038	0.0240	0
	σ_2	0	0	0.0039
	σ_3	0.0601	0.0035	0

		π	σ_4	σ_5
$\lvert C_{k\to j}\rvert$	σ_1'	0.0466	0.0266	0
	σ_2'	0	0	0.0111
	σ_3'	0.2879	0.0480	0

Formation of New Bonds

Let us divide the electron populations into two parts, intermolecular and intramolecular. First, let us try to connect this concept to the origins of the formation of new bonds between *A* and *B*. The AO bond population between the AO *t* of *A* and the AO *u* of *B* is given by:

$$\phi_{tu} = \phi_{tu}^{(E)} + \phi_{tu}^{(D)} \tag{3}$$

$\phi_{tu}^{(E)}$ is the AO bond population between *t* and *u* due to the exchange interaction:

$$\phi_{tu}^{(E)} \cong C_0{}^2(\phi_{tu}^{(E)})_0 + \sum_i^{\text{occ}} \sum_l^{\text{uno}} C_{i\to l}^2 (\phi_{tu}^{(E)})_{i\to l} + \sum_k^{\text{occ}} \sum_j^{\text{uno}} C_{k\to j}^2 (\phi_{tu}^{(E)})_{k\to j} \tag{4}$$

$$(\phi_{tu}^{(E)})_0 \cong -4(M!)\mathcal{N}_0{}^2 \sum_i^{\text{occ}} \sum_k^{\text{occ}} c_t^{(i)} c_u^{(k)} s_{tu} S_{ik} \tag{5}$$

where $c_t^{(i)}$ is the coefficient of the AO *t* in the MO a_i and where s_{tu} is the overlap integral between the AO's, *t* and *u*.

$$(\phi_{tu}^{(E)})_{i\to l} \cong -2(M!)\mathcal{N}_{i\to l}^2 \Big(2\sum_{i'}^{\text{occ}} \sum_k^{\text{occ}} c_t^{(i')} c_u^{(k)} s_{tu} S_{i'k} - \sum_k^{\text{occ}} c_t^{(i)} c_u^{(k)} s_{tu} S_{ik} + \sum_{i'}^{\text{occ}} c_t^{(i')} c_u^{(l)} s_{tu} S_{i'l} - 2c_t^{(i)} c_u^{(l)} s_{tu} S_{il}\Big) \tag{6}$$

$(\phi_{tu}^{(E)})_0$, $(\phi_{tu}^{(E)})_{i\to l}$, and $(\phi_{tu}^{(E)})_{k\to j}$ indicate the AO bond populations of a bond newly formed between the AO *t* of *A* and the AO *u* of *B* due to the electron exchange in Ψ_0, $\Psi_{i\to l}$, and $\Psi_{k\to j}$ states respectively.

The quantity $\phi_{tu}^{(D)}$ implies the AO bond population between *t* and *u* due to the electron delocalization:

$$\phi_{tu}^{(D)} \cong \sum_i^{\text{occ}} \sum_l^{\text{uno}} \{(\phi_{tu}^{(D)})_{0,i\to l} + (\phi_{tu}^{(D)})_{i\to l,0}\} C_0 C_{i\to l} + \sum_k^{\text{occ}} \sum_j^{\text{uno}} \{(\phi_{tu}^{(D)})_{0,k\to j} + (\phi_{tu}^{(D)})_{k\to j,0}\} C_0 C_{k\to j} \tag{7}$$

$$(\phi_{tu}^{(D)})_{0,i\to l} \cong \sqrt{2}\, c_t^{(i)} c_u^{(l)} s_{tu} \tag{8}$$

In Table 3 are given $(\phi_{tu}^{(E)})_0$ and $\phi_{tu}^{(E)}$ with respect

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[4] R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970).

[5] H. Fujimoto, S. Yamabe, and K. Fukui, This Bulletin, **44**, 971 (1971).

Table 3. The intermolecular AO bond populations due to the exchange

		Carbon of Methylene 1			
		s	x	y	z
Carbon of Methylene 2	s'	−0.0038	0	−0.0000	−0.0001
		(−0.0035)	(0)	(−0.0000)	(0)
	x'	0	−0.0001	0	0
		(0)	(−0.0001)	(0)	(0)
	y'	−0.0051	0	−0.0000	0.0005
		(−0.0048)	(0)	(−0.0000)	(0)
	z'	0.0000	0	0.0000	0
		(0)	(0)	(0)	(0)

The values in parentheses indicate $(\phi_{tu}^{(E)})_0$.

Table 4. The intermolecular AO bond populations due to the electron delocalizations from methylene 1 to methylene 2 and from methylene 2 to methylene 1

		Carbon of Methylene 1			
		s	x	y	z
Carbon of Methylene 2	s'	−0.0021	0	0.0000	0
		−0.0035	0	0.0003	0.0139
	x'	0	0.0001	0	0
		0	−0.0002	0	0
	y'	0.0015	0	0.0000	0
		−0.0052	0	0.0003	0.0372
	z'	0.0002	0	0.0014	0
		0	0	0	0

The upper value in each set indicates the AO bond population due to the electron delocalization from methylene 1 to methylene 2 and the lower value that arising from the electron delocalization from methylene 2 to methylene 1.

to Model II. The contribution of mono-transferred states to $\phi_{tu}^{(E)}$ is negligibly small. It can be seen that the sum of $\phi_{tu}^{(E)}$'s over all the pairs of the t of A and the u of B is negative. This demonstrates an antibonding contribution of the exchange interaction in the chemical interaction between two methylenes. Table 4 shows the $\phi_{tu}^{(D)}$ due to the electron delocalization from methylene 1 to methylene 2 and that due to the electron delocalization from methylene 2 to methylene 1. Adding $\phi_{tu}^{(D)}$ to $\phi_{tu}^{(E)}$, we can find the positive atomic bond population arising in the region between the carbon atoms of two methylenes. It should be noted that the greatest contribution comes from the combination of the p_z orbital of methylene 1 and $p_{y'}$, orbital of methylene 2, and that the next largest is that of the p_z orbital of methylene 1 and the 2s orbital of methylene 2.

The intermolecular chemical bonding can be interpreted in terms of the mixing of charge-transferred states into the Ψ_0 state. Thus, the importance of delocalization interaction in the process of bond formation is clear.

Weakening of Old Bonds

The changes in the bond populations of the intramolecular AO pairs in A and B due to the electron-exchange interaction may be given by:

$$\varphi_{tt'}^{(E)} = C_0{}^2(\varphi_{tt'}^{(E)})_0 + \sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}^2(\varphi_{tt'}^{(E)})_{i\to l} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}^2(\varphi_{tt'}^{(E)})_{k\to j} \tag{9}$$

$$\varphi_{uu'}^{(E)} = C_0{}^2(\varphi_{uu'}^{(E)})_0 + \sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}^2(\varphi_{uu'}^{(E)})_{i\to l} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}^2(\varphi_{uu'}^{(E)})_{k\to j} \tag{10}$$

$$(\varphi_{tt'}^{(E)})_0 \cong 4(M!)\mathcal{N}_0{}^2 \sum_i^{\text{occ}}\sum_k^{\text{occ}} c_t^{(i)}c_{t'}^{(i)}s_{tt'}S_{ik}^2 \tag{11}$$

$$(\varphi_{tt'}^{(E)})_{i\to l} \cong 2(M!)\mathcal{N}_{i\to l}^2\{\sum_{i'}^{\text{occ}} c_t^{(i')}c_{t'}^{(i')}s_{tt'}(2\sum_k^{\text{occ}} S_{i'k}^2 + S_{i'l}^2) - c_t^{(i)}c_{t'}^{(i)}s_{tt'}(\sum_k^{\text{occ}} S_{ik}^2 + 2S_{il}^2)\} \tag{12}$$

$$(\varphi_{tt'}^{(E)})_{k\to j} \cong 2(M!)\mathcal{N}_{k\to j}^2\{\sum_i^{\text{occ}} c_t^{(i)}c_{t'}^{(i)}s_{tt'}(2\sum_{k'}^{\text{occ}} S_{ik'}^2 - S_{ik}^2) + c_t^{(j)}c_{t'}^{(j)}s_{tt'}(\sum_{k'}^{\text{occ}} S_{jk'}^2 - 2S_{jk}^2)\} \tag{13}$$

The changes in the AO bond populations of A and of B due to the mixing of charge-transferred states into Ψ_0 are given by:

$$\varphi_{tt'}^{(D)} \cong 2(-\sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}^2 c_t^{(i)}c_{t'}^{(i)}s_{tt'} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}^2 c_t^{(j)}c_{t'}^{(j)}s_{tt'} - 2\sqrt{2}\,C_0\sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}c_t^{(i)}c_{t'}^{(i)}s_{tt'}S_{il}) \tag{14}$$

$$\varphi_{uu'}^{(D)} \cong 2(-\sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}^2 c_u^{(k)}c_{u'}^{(k)}s_{uu'} + \sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}^2 c_u^{(l)}c_{u'}^{(l)}s_{uu'} - 2\sqrt{2}\,C_0\sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}c_u^{(k)}c_{u'}^{(k)}s_{uu'}S_{kj}) \tag{15}$$

Table 5. The changes in the AO bond populations of the C–H bond of methylene 1 and methylene 2

Methylene 1

	Carbon			
	s	x	y	z
Hydrogen s	−0.0035	0.0000	−0.0012	0

Methylene 2

	Carbon			
	s'	x'	y'	z'
Hydrogen s'	0.0053	0.0000	−0.0083	0

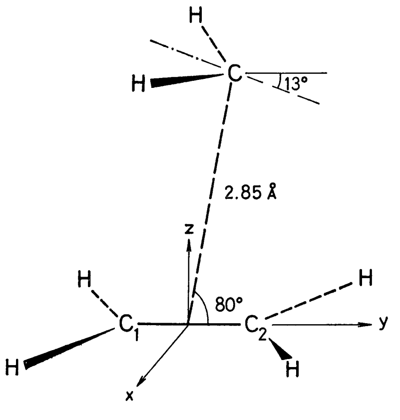

Fig. 2. A schematic representation of assumed model of the addition of methylene to ethylene.

Table 6. The changes in the bond populations of the carbon-carbon bond of ethylene due to the interaction with methylene

		Carbon 1			
		s	x	y	z
Carbon 2	s	−0.0020	0	0.0002	0
	x	0	0.0003	0	0
	y	−0.0002	0	−0.0003	0
	z	0	0	0	−0.0397

Table 5 shows the changes in the AO bond populations in methylenes. However, the numerical values are too small to show the importance of the bond weakening caused by electron delocalization, since carbon-hydrogen bonds in methylenes never break down in the process of dimerization to form an ethylene molecule. In order to obtain a more distinct result, we had better proceed to the addition of singlet methylene to ethylene[6) (Fig. 2). The results of the calculation of the changes in the AO bond populations of the carbon-carbon bond of ethylene are shown in Table 6. We can find that the AO bond population between the $2p_z$ orbital of the carbon 1 and the $2p_z$ orbital of the carbon 2 decreases conspicuously, while the others remain almost unchanged. This demonstrates the start of the disappearance of the π bond in ethylene to form σ bonds with methylene.

Extending Mulliken's concept of population analysis[7) to an AO pair between two interacting molecules, the electrons flow into the intermolecular region through the orbital overlapping between the AO t of A and the AO u of B may be divided into two, one of which reverts to the AO t, and the other, to the AO u. Therefore, the changes in the AO populations of AO t and AO u due to the electron delocalization are given by:

$$\Delta N_t^{(D)} = \frac{1}{2}\Big(\sum_u^B \phi_{tu}^{(D)} + \sum_{t'}^A \varphi_{tt'}^{(D)}\Big) \tag{16}$$

$$\Delta N_u^{(D)} = \frac{1}{2}\Big(\sum_t^A \phi_{tu}^{(D)} + \sum_{u'}^B \varphi_{uu'}^{(D)}\Big) \tag{17}$$

Table 7 shows the changes in the AO populations of methylenes in Model II. We can see that methylene 2 serves as an electron donor, and methylene 1, as an electron acceptor.

Table 7. The changes in AO populations of methylene 1 and methylene 2

Methylene 1

Carbon				Hydrogen
s	x	y	z	
−0.0053	0.0000	−0.0034	0.1088	0.0042

Methylene 2

Carbon				Hydrogen
s'	x'	y'	z'	
−0.0070	0.0000	−0.0961	0.0045	−0.0050

Intramolecular Electron Rearrangement Due to Interaction

The other terms in the diagonal elements of Eqs. (A. 1), (A. 3), and (A. 5), which have not appeared in Eqs. (4)—(17), stand for the reorganization of the electron populations in both A and B caused by the mutual interaction. We may define the partial AO populations of the AO t as:

$$n_t^{(ii')} + n_t^{(i'i)} = (p_t^{(ii')} + v_t^{(ii')}) + (p_t^{(i'i)} + v_t^{(i'i)}) \tag{18}$$

$$p_t^{(ii')} = c_t^{(i)} c_t^{(i')} \qquad (i \neq i')$$

$$v_t^{(ii')} = \sum_{t'}^A c_t^{(i)} c_{t'}^{(i')} s_{tt'} \qquad (t \neq t')$$

where $p_t^{(ii')}$ stands for the valence-inactive part, and $v_t^{(ii')}$ for the valence-active part.[8) The quantity $n_t^{(ii')} + n_t^{(i'i)}$ gives a non-zero value, in general, although the sum over all the t's of the molecule A vanishes. We represent the changes in the AO bond populations in the molecules A and B by $\varphi_{tt'}^{(R)}$ and $\varphi_{uu'}^{(R)}$ respectively. Therefore, the changes in the AO populations of the AO's t and u resulting from the intramolecular electron rearrangement may be given by:

$$\Delta N_t^{(R)} = \frac{1}{2}\sum_{t'}^A \varphi_{tt'}^{(R)} \tag{19}$$

$$\Delta N_u^{(R)} = \frac{1}{2}\sum_{u'}^B \varphi_{uu'}^{(R)} \tag{20}$$

The changes in the AO populations and AO bond populations caused by the electron rearrangement are shown in Table 8 with respect to Model II. Although the changes in the electron populations due to the intramolecular electron rearrangement are small in comparison with the other terms discussed above, they are hardly negligible in the systems where one or both of the reactants involve highly-polarized bonds. In Fig. 3 we present the changes in the atomic popula-

Table 8. The changes in AO populations and in AO bond populations of methylene 1 and methylene 2 due to the intramolecular electron rearrangement

Methylene 1

	Carbon				Hydrogen
	s	x	y	z	
Hydrogen	0.0046	0.0003	−0.0002	0	−0.0024
	−0.0035	0.0000	0.0001	0	—

Methylene 2

	Carbon				Hydrogen
	s'	x'	y'	z'	
Hydrogen	−0.0059	−0.0001	0.0025	0	0.0018
	0.0006	0.0000	0.0012	0	—

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6) a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968). b) K. Fukui, H. Fujimoto, and S. Yamabe, to be published.

7) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

8) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

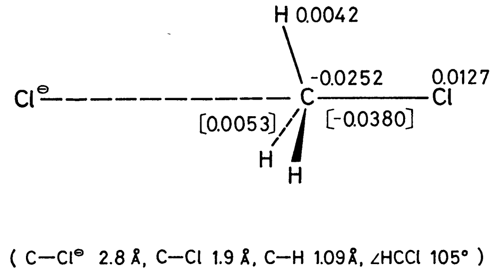

Fig. 3. The changes in atomic populations and in atomic bond populations due to the intramolecular electron rearrangement. The values in [ ] indicate the changes in atomic bond populations.

tions and in the atomic bond populations due to the intramolecular electron rearrangement with regard to the chemically-interacting system shown in the figure.[5] It is interesting to see that the carbon-chlorine bond is loosened and that electron migration takes place in the direction from carbon to chlorine.

Changes in Electron Populations

The difference in the population of the AO t before and after interaction will be:

$$\varDelta N_t \cong \frac{1}{2}\sum_{u}^{B}\phi_{tu} + \frac{1}{2}\sum_{t'}^{A}(\varphi_{tt'}^{(D)}+\varphi_{tt'}^{(E)}+\varphi_{tt'}^{(R)}) \tag{21}$$

Similarly, the change in the AO bond population between the AO's t and t' of A is given by:

$$\varphi_{tt'} \cong \varphi_{tt'}^{(D)} + \varphi_{tt'}^{(E)} + \varphi_{tt'}^{(R)} \tag{22}$$

Summing up the changes in AO populations and AO bond populations discussed above gives the final results on Model I and Model II for the dimerization of methylenes shown in Fig. 4.

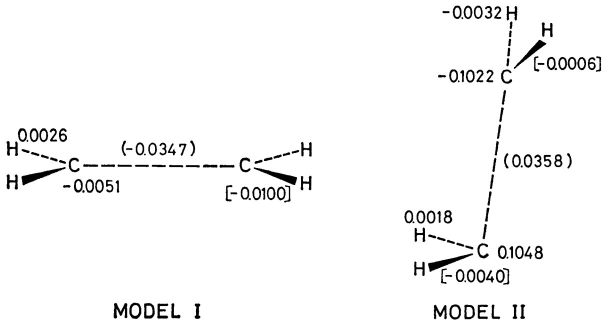

Fig. 4. The changes in atomic populations and in atomic bond populations due to the interaction. The values in ( ) indicate the intermolecular atomic bond populations and the values in [ ] stand for the changes in atomic bond populations.

As has been discussed above, the delocalization interaction has a close connection to the bond-interchange in chemical reactions of two closed-shell molecules. It has been demonstrated that the formation of new bonds between reagent and reactant and the weakening of old bonds in both can be interpreted only by the inclusion of charge-transferred configurations. Among various charge-transferred terms, the orbital interaction between the HO MO of the reactant and the LU MO of the reagent, and the reverse interaction, play the most dominant role. Those electron configurations which have been omitted in the present calculation can also be included in a similar fashion in the population calculation, although it will take too much computer time to be performed. It is believed that the main consequences would not be seriously different from those presented here.

This calculation has been limited to the cases in which both reactant and reagent are closed-shell systems. Extension to other cases is now in progress.

The authors wish to express their appreciation to the Data Processing Center of Kyoto University for the generous permission to use the FACOM 230–60 computer.

Appendix

Taking the terms up to the second order of the overlap integrals S_{ab} between the MO's, a's of the molecule A and b's of the molecule B, we have the first order spinless density matrix given by:

$$\begin{aligned}\rho(1'|1)_{0,0} &= M\int\varPsi_0(1',2,\cdots,M)\varPsi_0(1,2,\cdots,M)\mathrm{d}\xi_1\mathrm{d}\tau_2\cdots\mathrm{d}\tau_M\\ &\cong 2\sum_{i}^{\mathrm{occ}}i(1')i(1) + 2\sum_{k}^{\mathrm{occ}}k(1')k(1)\\ &\quad + \{2\sum_{i}^{\mathrm{occ}}\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}i(1')i'(1)S_{ik}S_{i'k}\\ &\quad + 2\sum_{k}^{\mathrm{occ}}\sum_{k'}^{\mathrm{occ}}\sum_{i}^{\mathrm{occ}}k(1')k'(1)S_{ik}S_{ik'}\\ &\quad - 2\sum_{i}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}(i(1')k(1)+k(1')i(1))S_{ik}\}\mathscr{N}_0^{2}(M!)\end{aligned} \tag{A.1}$$

where M is the total number of electrons of the system composed of A and B, $i(1')k(1)$, for instance, is the abbreviation of $a_i(1')b_k(1)$, and the normalization factor for $\varPsi_0$ is:

$$\mathscr{N}_0 \cong (1-2\sum_{i}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}S_{ik}^{2})^{-1/2}(M!)^{-1/2} \tag{A.2}$$

With respect to $\varPsi_{i\to l}$, we have

$$\begin{aligned}\rho(1'|1)_{i\to l,i\to l} &\cong 2\sum_{i'}^{\mathrm{occ}}i'(1')i'(1)\\ &\quad + 2\sum_{k}^{\mathrm{occ}}k(1')k(1) - i(1')i(1) + l(1')l(1)\\ &\quad + \{i(1')i(1)(\sum_{k}^{\mathrm{occ}}S_{ik}^{2}+2S_{il}^{2}) + l(1')l(1)(\sum_{i'}^{\mathrm{occ}}S_{i'l}^{2}-2S_{il}^{2})\\ &\quad - 2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}(i'(1')k(1)+k(1')i'(1))S_{i'k}\\ &\quad + \sum_{k}^{\mathrm{occ}}(i(1')k(1)+k(1')i(1))S_{ik}\\ &\quad - \sum_{i'}^{\mathrm{occ}}(i'(1')l(1)+l(1')i'(1))S_{i'l} + 2(i(1')l(1)+l(1')i(1))S_{il}\\ &\quad + \sum_{i'}^{\mathrm{occ}}\sum_{i''}^{\mathrm{occ}}i'(1')i''(1)(2\sum_{k}^{\mathrm{occ}}S_{i'k}S_{i''k}+S_{i'l}S_{i''l})\\ &\quad - \sum_{i'}^{\mathrm{occ}}(i(1')i'(1)+i'(1')i(1))(\sum_{k}^{\mathrm{occ}}S_{ik}S_{i'k}+2S_{il}S_{i'l})\\ &\quad + \sum_{k}^{\mathrm{occ}}\sum_{k'}^{\mathrm{occ}}k(1')k'(1)(2\sum_{i'}^{\mathrm{occ}}S_{i'k}S_{i'k'}-S_{ik}S_{ik'})\\ &\quad + \sum_{k}^{\mathrm{occ}}(k(1')l(1)+l(1')k(1))(\sum_{i'}^{\mathrm{occ}}S_{i'k}S_{i'l}-2S_{ik}S_{il})\}\mathscr{N}_{i\to l}^{2}(M!)\end{aligned} \tag{A.3}$$

and

$$\mathscr{N}_{i\to l} \cong \Big(1-2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}S_{i'k}^2+\sum_{k}^{\mathrm{occ}}S_{ik}^2-\sum_{i'}^{\mathrm{occ}}S_{i'l}^2+2S_{il}^2\Big)^{-1/2}(M!)^{-1/2} \tag{A.4}$$

The next to be considered is the term which represents the mixing in of monotransferred configuration into zero-configuration. Neglecting the terms smaller than $S_{ab}{}^2$, we have:

$$\begin{aligned}\rho(1'|1)_{0,i\to l} \cong{}& \sqrt{2}\,S_{il}\Big(2\sum_{i'}^{\mathrm{occ}}i'(1')i'(1)+2\sum_{k}^{\mathrm{occ}}k(1')k(1)\Big)\\ &-\sqrt{2}\Big(\sum_{i'}^{\mathrm{occ}}i(1')i'(1)S_{i'l}+\sum_{k}^{\mathrm{occ}}k(1')l(1)S_{ik}-i(1')l(1)\Big)\end{aligned} \tag{A.5}$$

Similar expressions are obtained from $\Psi_{k\to j}$. The elements of the density matrix due to the mixing in of the monoexcited states are:

$$\begin{aligned}\rho(1'|1)_{i\to j,i\to j} \cong{}& 2\sum_{i'}^{\mathrm{occ}}i'(1')i'(1)\\ &+2\sum_{k}^{\mathrm{occ}}k(1')k(1) - i(1')i(1) + j(1')j(1)\\ &+\Big\{j(1')j(1)\sum_{k}^{\mathrm{occ}}S_{jk}^2+i(1')i(1)\sum_{k}^{\mathrm{occ}}S_{ik}^2\\ &+2\sum_{i'}^{\mathrm{occ}}\sum_{i''}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}i'(1')i''(1)S_{i'k}S_{i''k}\\ &-\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}(i(1')i'(1)+i'(1')i(1))S_{ik}S_{i'k}\\ &+\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}(j(1')i'(1)+i'(1')j(1))S_{jk}S_{i'k}\\ &-2\sum_{k}^{\mathrm{occ}}(j(1')i(1)+i(1')j(1))S_{jk}S_{ik}\\ &+\sum_{k}^{\mathrm{occ}}\sum_{k'}^{\mathrm{occ}}k(1')k'(1)\Big(2\sum_{i'}^{\mathrm{occ}}S_{i'k}S_{i'k'}-S_{ik}S_{ik'}+S_{jk}S_{jk'}\Big)\\ &-2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}(i'(1')k(1)+k(1')i'(1))S_{i'k}\\ &+\sum_{k}^{\mathrm{occ}}(i(1')k(1)+k(1')i(1))S_{ik}\\ &-\sum_{k}^{\mathrm{occ}}(j(1')k(1)+k(1')j(1))S_{jk}\Big\}\mathscr{N}_{i\to j}^2(M!)\end{aligned} \tag{A.6}$$

and:

$$\mathscr{N}_{i\to j} \cong \Big(1-2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}S_{i'k}^2+\sum_{k}^{\mathrm{occ}}S_{ik}^2-\sum_{k}^{\mathrm{occ}}S_{jk}^2\Big)^{-1/2}(M!)^{-1/2} \tag{A.7}$$

and;

$$\begin{aligned}\rho(1'|1)_{0,i\to j} \cong{}& \sqrt{2}\Big\{\Big(2\sum_{i'}^{\mathrm{occ}}i'(1')i'(1)\\ &+2\sum_{k}^{\mathrm{occ}}k(1')k(1)\Big)\Big(-\sum_{k}^{\mathrm{occ}}S_{ik}S_{jk}\Big)\\ &+\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}i(1')i'(1)S_{jk}S_{i'k} + \sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}i'(1')j(1)S_{ik}S_{i'k}\\ &+\sum_{k}^{\mathrm{occ}}\sum_{k'}^{\mathrm{occ}}k(1')k'(1)S_{ik}S_{jk'} - \sum_{k}^{\mathrm{occ}}i(1')k(1)S_{jk}\\ &-\sum_{k}^{\mathrm{occ}}k(1')j(1)S_{ik}\Big\} + \sqrt{2}\,i(1')j(1)\Big(1-2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}S_{i'k}^2\Big)^{1/2}\\ &\times\Big(1-2\sum_{i'}^{\mathrm{occ}}\sum_{k}^{\mathrm{occ}}S_{i'k}^2+\sum_{k}^{\mathrm{occ}}S_{ik}^2-\sum_{k}^{\mathrm{occ}}S_{jk}^2\Big)^{-1/2}\end{aligned} \tag{A.8}$$

and similar formulas corresponding to the contributions from $\Psi_{k\to l}$.