A Molecular Orbital Calculation of Chemically Interacting Systems. Addition of Singlet Methylene to Ethylene

Hiroshi Fujimoto, Shinichi Yamabe, and Kenichi Fukui
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received March 31, 1972)

A semi-empirical self-consistent-field molecular orbital calculation of the addition of singlet methylene to ethylene was carried out on the basis of an isolated molecule approximation. The calculation was made with respect to two modes of approaches of methylene to ethylene which were proposed by Hoffmann. A calculation of the electron populations by use of the configuration interaction wave function showed that singlet methylene added to ethylene double bond in an electrophilic fashion with a quasi-synchronous formation of two σ bonds to yield cyclopropane. The present calculation revealed the important roles of the interaction between the highest occupied molecular orbital of ethylene and the lowest unoccupied molecular orbital of methylene and of the interaction between the highest occupied molecular orbital of methylene and the lowest unoccupied molecular orbital of ethylene, in interpreting the formation of new σ bonds between ethylene and methylene and the disappearance of the π bond of ethylene.

Molecular orbital (MO) theory has achieved a fair success in interpreting the orientation and stereoselection in various sorts of chemical reactions.[1,2] In dealing with chemical reactions by MO methods, there exist two kinds of approaches. One is to apply MO methods, regarding the whole system composed of two reacting species as if it were one molecule, while the other intends to express the energy and the electron populations of a reacting system by use of the MO's which are obtained with respect to the two reactants in their isolated states. Although the application of the latter approach is usually limited to the cases of weak interaction, it is capable of providing us with some basic information on the nature of chemical reactions. Murrell and his collaborators extended the theory of long range force to the interaction with small orbital overlap and divided the interaction energy into several terms.[3] Their theory has been applied to some weak interactions, such as hydrogen bonding and molecular complexes.[4,5] In one of our previous papers, we have discussed the interaction energy between two reacting systems, by partitioning it into the Coulomb, exchange, delocalization, and polarization terms and have pointed out the importance of the delocalization interaction in promoting reactions.[6] An investigation of the delocalization energy has led us to a supposition that the interaction between the highest occupied (HO) MO of one reactant and the lowest unoccupied (LU) MO of the other reactant is almost solely responsible for the determination of the favorable paths of a majority of chemical reactions.[7] The concept of the HOMO-LUMO interaction now seems to be a well established and powerful means to disclose the detailed mechanisms of chemical reactions.[8-10] It is interesting to examine how such particular orbital interaction explains bond formation, bond loosening and charge-transfer, since these are characteristics of chemical reactions.

In this paper, we show the results of calculation on the addition of singlet methylene to ethylene. This reaction was studied by Hoffmann mainly from an energetic viewpoint, using the extended Hückel MO method.[11] Therefore, it will be a test of our configuration interaction (CI) approach to chemical reactions to compare our result with that of Hoffmann.

Interaction between Two Systems

In order to calculate the electron distribution of chemically interacting system of two molecules, by use of the MO's obtained for each of them in an isolated state, we proceed in the following way; (1) we make a self-consistent-field (SCF) calculation on each of the two reactants separately and determine the MO's, (2) we construct the Slater determinantal wave functions for the combined system which represent the original and charge-transferred electron configurations, using the MO's obtained in (1), and (3) then we calculate the wave function for the lowest energy state of the interacting system by solving the secular equation by the usual CI procedure of the electron configurations given in (2), with respect to a given nuclear framework of the system composed of the two reactants.[12]

The wave function of the interacting system is ap-

---

[1] (a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Eds., Academic Press, New York, N. Y. (1964). (b) K. Fukui, "Modern Quantum Chemistry. Istanbul Lectures, Part I," O. Sinanoğlu, Ed., Academic Press, New York, N. Y. (1965). (c) K. Fukui, "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. B. Wiberg, Eds., Yale University Press, New Haven, Conn. (1970).

[2] (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 395, 2511 (1965). (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965). (c) R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed.* (*Engl*)., **8**, 781 (1969). (d) M. J. S. Dewer, *Tetrahedrcn Suppl.*, **8**, *Part I*, 75 (1966). (e) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1969). (f) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970). (g) K. Fukui and H. Fujimoto, This Bulletin, **40**, 2018 (1967).

[3] J. N. Murrell, M. Randić, and D. R. Williams, *Proc. Roy. Soc., Ser. A.* **284**, 566 (1965).

[4] F. B. van Duijneveldt and J. N. Murrell, *J. Chem. Phys.*, **46**, 1759 (1967).

[5] J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969).

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

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

[8] G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

[9] R. G. Pearson, *Theor. Chim. Acta.* **16**, 107 (1970).

[10] K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

[11] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[12] H. Fujimoto, S. Yamabe, and K. Fukui, This Bulletin, **44**, 2936 (1971).

proximately given by;

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

where Ψ_0 is the original electron configuration with the adiabatic interaction, $\Psi_{i\to l}$ is the charge-transferred state in which an electron in the ith occupied MO of one reactant is shifted into the lth unoccupied MO of another, and $\Psi_{k\to j}$ is the charge-transferred state in the converse fashion. The symbols $\overset{\mathrm{occ}}{\sum}$ and $\overset{\mathrm{uno}}{\sum}$ imply the summation over all the occupied and unoccupied MO's respectively. The local-excited states are less important than the charge-transferred states and can be neglected in a first approximation.[12]

Calculation on Isolated Reactants

The MO's of ethylene and methylene were calculated by a semi-empirical all valence-electrons SCF MO method as before.[13] The nuclear configurations of these species were chosen as the same as those adopted by Hoffmann.[11] The calculated MO energy levels of ethylene and methylene are shown in Fig. 1. The calculated ionization potential of ethylene is 10.2 eV, which is 0.2~0.4 eV smaller than the observed values.[14] The HOMO of methylene is a lone-pair like orbital and the LUMO is a purely p atomic orbital (AO) of the carbon atom. We tentatively term the MO's as shown in Fig. 1.

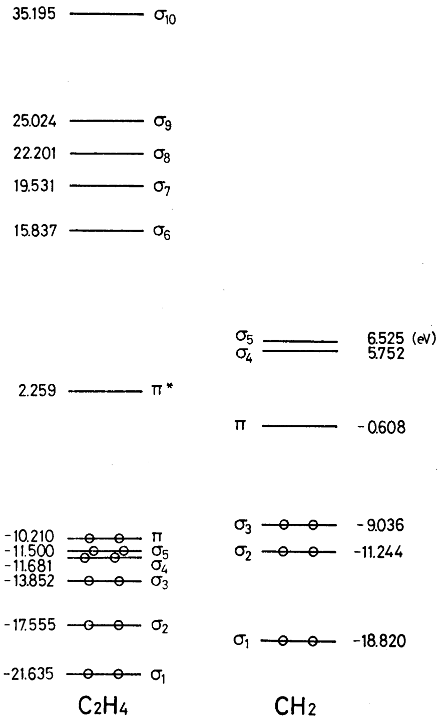
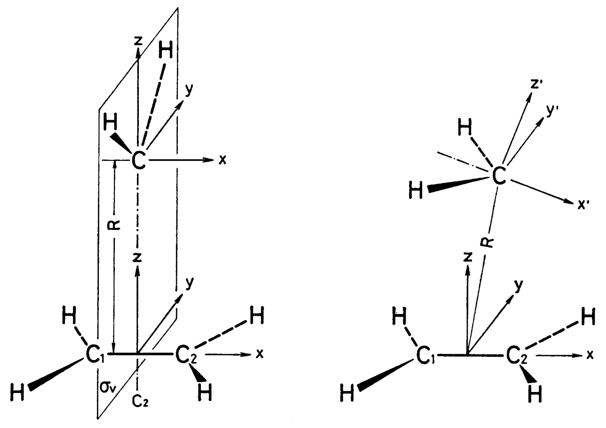


Fig. 1. MO energy levels of ethylene and methylene.

Electron Populations

Hoffmann proposed two modes of approaches of methylene to ethylene.[11] Those are schematically illustrated in Fig. 2 in order to define the variables and coordinates. In Model I, methylene approaches ethylene on the C_2 principal axis, directing the lone-pair orbital toward ethylene. In Model II, the carbon atom of methylene locates away from the bisecting axis of the ethylene C–C bond. We follow the paths suggested by Hoffmann.[11] In this context, we distinguish each model only by specifying the value of R in Fig. 2. It is convenient to choose different Cartesian coordinate systems for methylene and for ethylene in Model II as shown in Fig. 2. The integrals which are necessary for the calculation of the matrix elements of the secular equation were estimated in the same way as in our previous calculation.[13]



Model I Model II

Fig. 2. A schematic representation of assumed reaction models.

Table 1 gives the coefficients of the CI wave function, C_0, $C_{i\to l}$'s and $C_{k\to j}$'s in Eq. (1), for the lowest root of the secular equation, with respect to Models Ia (R=3.0 Å), IIa (R=3.0 Å), and IIb (R=2.85 Å). By comparing Models Ia and IIa, it is clear that the mixing in of charge-transferred electron configurations is much more effective in the latter than in the former. In Models IIa and IIb, the most dominant term except Ψ_0 is the charge-transferred electron configuration from the HOMO of ethylene to the LUMO of methylene, and the next dominant is the one from the HOMO of methylene to the LUMO of ethylene. Comparison of these two models elucidates that the mixings of the charge-transferred electron configuration from the HOMO of ethylene to the LUMO of methylene and of the one from the HOMO of methylene to the LUMO of ethylene become more and more dominant over other charge-transferred electron configurations with the progress of the reaction.

The electron densities of the combined system of ethylene and methylene are given by

$$\rho(1) = M\int \Psi^*(1,2,\cdots,M)\Psi(1,2,\cdots,M)\mathrm{d}\xi_1\mathrm{d}\tau_2\cdots\mathrm{d}\tau_M \qquad (2)$$

where M is the total number of electrons of the system

---

13) K. Fukui, H. Fujimoto, and S. Yamabe, *J. Phys. Chem.*, **76**, 232 (1972).

14) (a) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
(b) W. C. Walker and G. L. Weissler, *ibid.*, **23**, 1547 (1955).

TABLE 1. THE COEFFICIENTS OF THE GROUND-STATE CI WAVE FUNCTION

Model Ia			$C_0=0.9967$				
					i		
		σ_1	σ_2	σ_3	σ_4	σ_5	π
$\lvert C_{i\to l}\rvert$	l π	0	0.0240	0	0	0	0
	σ_4	0.0130	0	0	0.0013	0	0.0313
	σ_5	0	0	0.0104	0	0	0
					j		
		π_*	σ_6	σ_7	σ_8	σ_9	σ_{10}
$\lvert C_{k\to j}\rvert$	k σ_1	0	0	0	0.0021	0	0
	σ_2	0	0.0008	0	0	0	0
	σ_3	0	0	0	0.0013	0	0

Model IIa			$C_0=0.9555$				
					i		
		σ_1	σ_2	σ_3	σ_4	σ_5	π
$\lvert C_{i\to l}\rvert$	l π	0.0406	0.0185	0	0.0062	0	0.1947
	σ_4	0.0072	0.0011	0	0.0086	0	0.0048
	σ_5	0	0	0.0014	0	0.0091	0
					j		
		π^*	σ_6	σ_7	σ_8	σ_9	σ_{10}
$\lvert C_{k\to j}\rvert$	k σ_1	0.0121	0	0.0008	0.0015	0	0.0002
	σ_2	0	0.0023	0	0	0.0002	0
	σ_3	0.0600	0	0.0025	0.0015	0	0.0000

Model IIb			$C_0=0.9215$				
					i		
		σ_1	σ_2	σ_3	σ_4	σ_5	π
$\lvert C_{i\to l}\rvert$	l π	0.0493	0.0173	0	0.0001	0	0.2650
	σ_4	0.0070	0.0003	0	0.0102	0	0.0027
	σ_5	0	0	0.0039	0	0.0110	0
					j		
		π^*	σ_6	σ_7	σ_8	σ_9	σ_{10}
$\lvert C_{k\to j}\rvert$	k σ_1	0.0130	0	0.0011	0.0009	0	0.0003
	σ_2	0	0.0039	0	0	0.0003	0
	σ_3	0.0851	0	0.0042	0.0024	0	0.0005

i and j denote the MO's of ethylene and k and l stand for those of methylene.

composed of ethylene and methylene (=18). By calculating the terms appearing in Eq. (2) separately, we can disclose the origin of the formation of the intermolecular σ bonds between ethylene and methylene and of the disappearance of the π bond of ethylene. This is an advantage of the present CI method over the usual variational approaches to chemically interacting systems. In order to visualize this circumstance, we show the results of calculation on Models Ib and IIc in which R is 2.7 Å. Figure 3 shows the electron densities of Model IIc in the x—z cross section at $y=0$. Figure 3 (a) indicates the simple sum of the electron densities of ethylene and methylene without interaction and Fig. 3 (b) shows the electron densities of the state of adiabatic interaction, ρ_0. It is noted that the electron densities in the intermolecular region between ethylene and methylene in the Ψ_0 state decrease in comparison with $\rho_{\mathrm{CH_2}}+\rho_{\mathrm{CH_2CH_2}}$, due to the electron exchange interaction in that state. This is essential to the interaction between two closed shell systems.[12,15] Figure 4 demonstrates ρ. By comparing Figs. 3 and 4, it is clear that the mixing of charge-transferred electron configurations into Ψ_0 is of importance in interpreting the chemical bond formation

---

15) V. Magnasco, *Theor. Chim. Acta*, **21**, 267 (1971),

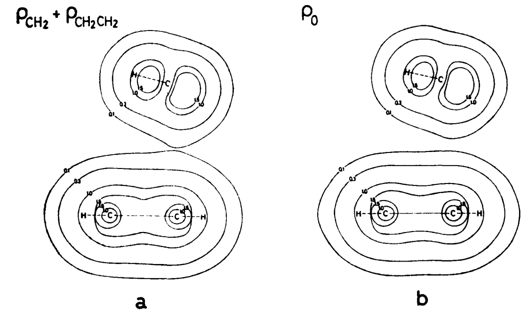


Fig. 3. Electron densities of Model II in the $x-z$ cross section at $y=0$ ($e^-/Å^3$).
(a): the simple sum of the electron densities of ethylene and methylene.
(b): without charge-transfer interaction.

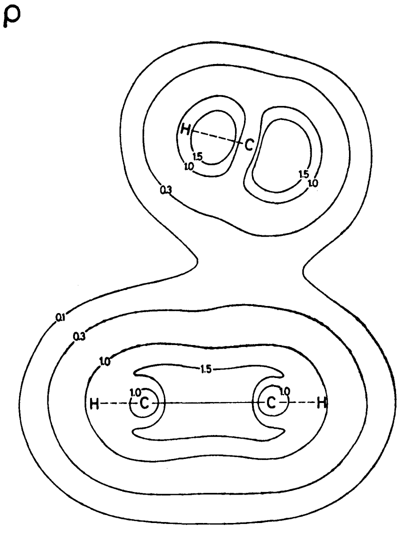


Fig. 4. Electron densities of Model II in the $x-z$ cross section at $y=0$, with charge-transfer interaction.

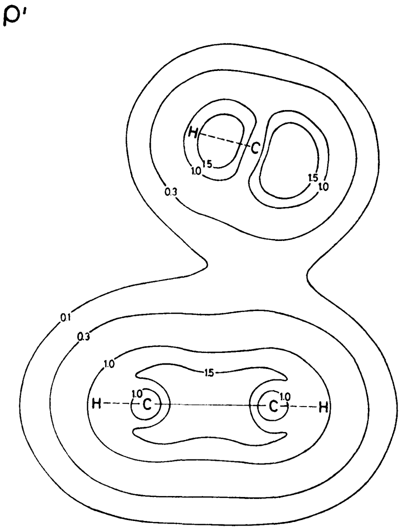


Fig. 5. Electron densities of Model II in the $x-z$ cross section at $y=0$, in which only the HOMO-LUMO interactions are included.

between ethylene and methylene, as well as the weakening of the π bond of ethylene. Figure 5 shows the electron densites in Ψ' state, in which only the charge-transfer interaction from the HOMO of ethylene into the LUMO of methylene and that from the HOMO of methylene into the LUMO of ethylene are taken into consideration. Comparison of Figs. 4 and 5 indicates that the changes in the electron densities due to the mixing in of charge-transferred electron configurations are almost covered by only introducing the HOMO-LUMO interactions. This signifies the mobility of π electrons in case of chemical reactions and suggests the pertinency of the π electrons approximation in discussing the chemical reactivity of conjugated molecules.[1,2] In this calculation, the nuclear configuration of ethylene was kept unchanged. As ethylene loses its planarity with the progress of the reaction, the $\sigma-\pi$ interaction takes place.[16] The σ part and the π part of ethylene will also mix through the orbital overlap interaction with the MO's of methylene.

Figure 6 shows the electron densities of Model Ib. The left of the vertical line presents the simple sum of the electron densities of ethylene and methylene and the right gives the electron densities of the interacting state, ρ. We can see that the bond formation between ethylene and methylene is not effective, indicating the disadvantage of such an approach of methylene to ethylene as Model I. This conclusion is consistent with the results of the extended Hückel MO calculation by Hoffmann.[11]

Figure 7 shows the changes in atomic populations and in atomic bond populations of ethylene and methylene due to the interaction with respect to Models Ia and IIa. We can see that ethylene becomes positively charged, while methylene gets negatively charged in Model II. This agrees with the experimental observations that singlet methylenes add to olefinic double bonds in an electrophilic fashion.[17] Both of the atomic bond populations between the carbon of methylene and the carbons 1 and 2 of ethylene are positive, demonstrating a synchronous character of

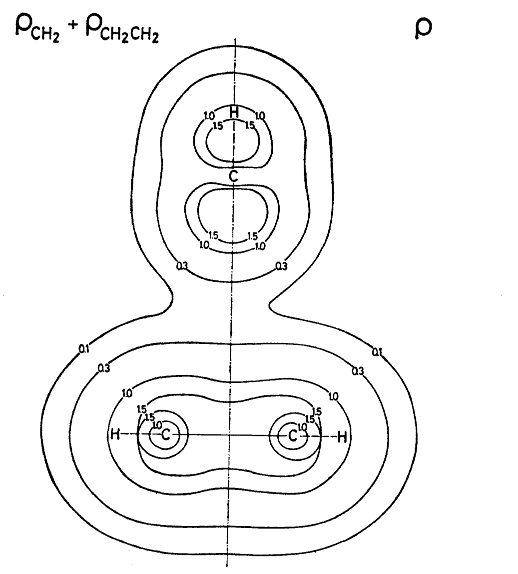


Fig. 6. Electron densities of Model I in the $x-z$ cross section at $y=0$.

---

[16] K. Fukui and H. Fujimoto, This Bulletin, **39**, 2116 (1966).

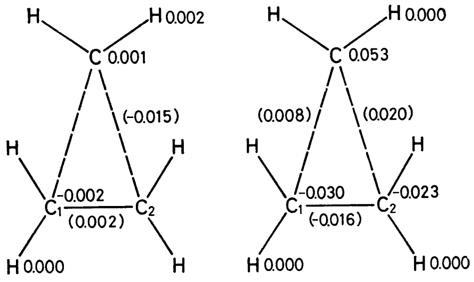


Fig. 7. Changes in atomic populations and in atomic bond populations due to the interaction (the values in parentheses denote the changes in atomic bond populations).

this reaction.

Here let us investigate the mode of charge-transfer in some details. As has been mentioned above, there exist two modes of charge-transfer, *i.e.*, from ethylene to methylene and the converse. Tables 2 and 3 give the changes in AO populations of ethylene and of methylene, due to the charge-transfer from ethylene to methylene and from methylene to ethylene, with respect to Model IIa. The values in the second column in Table 2 indicate the changes in the electron populations of the AO's of ethylene by the charge-transfer from ethylene to methylene, and those in the third column are the changes in the AO populations due to the charge-transfer from methylene to ethylene. Table 3 can be similarly understood. The negative values in the columns of accepted electrons in Tables 2 and 3 may appear strange at first sight. This is caused by the negative intermolecular overlap population of the AO t (t belongs to the molecule A), which is not recovered by the increase in intramolecular populations of that AO, in case of the electron delocalization from the molecule B to the molecule A.[12] We can recognize that the apparent changes in AO populations are only overall results of mutual electron donating and electron accepting interactions. This may be a characteristic feature of chemical interaction between two electronically neutral systems. The AO bond populations between the AO's of ethylene and the AO's of methylene are given in Table 4 with respect to Model IIa. The results indicate that the most contributing term to the bond formation is the combination of the $p\pi$ orbitals of ethylene and the vacant p orbital of methylene. Table 5 shows the changes in the AO bond populations of the C–C bond of ethylene. We can see that the weakening of the π bond is conspicuous, although the σ bond remains almost unchanged. Tables 4 and 5 may be helpful to understand how the double bond of ethylene is converted into the single bonds with methylene in the course of the addition of singlet methylene to ethylene.

TABLE 2. THE CHANGES IN THE AO POPULATIONS OF ETHYLENE DUE TO THE ELECTRON DELOCALIZATION INTERACTION IN MODEL IIa

AO	Electrons donated	Electrons accepted	Net change
$1C_s$	0.0028	−0.0001	−0.0029
$1C_x$	0.0003	0.0000	−0.0003
$1C_y$	0.0000	0.0000	0.0000
$1C_z$	0.0290	0.0023	−0.0267
$2C_s$	0.0016	0.0000	−0.0016
$2C_x$	0.0004	0.0001	−0.0003
$2C_y$	0.0001	0.0000	−0.0001
$2C_z$	0.0248	0.0036	−0.0212

TABLE 3. THE CHANGES IN THE AO POPULATIONS OF METHYLENE DUE TO THE ELECTRON DELOCALIZATION INTERACTION IN MODEL IIa

AO	Electrons donated	Electrons accepted	Net change
C_s	0.0003	−0.0008	−0.0011
$C_{x'}$	0.0048	0.0001	−0.0047
$C_{y'}$	0.0000	0.0002	0.0002
$C_{z'}$	0	0.0585	0.0585

TABLE 4. THE INTERMOLECULAR AO BOND POPULATIONS BETWEEN METHYLENE AND ETHYLENE IN MODEL IIa

		Methylene			
		C_s	$C_{x'}$	$C_{y'}$	$C_{z'}$
Ethylene	$1C_s$	−0.0008	−0.0003	0	0.0008
	$1C_x$	0.0003	0.0000	0	0.0000
	$1C_y$	0	0	−0.0002	0
	$1C_z$	−0.0048	0.0010	0	0.0116
	$2C_s$	−0.0032	−0.0001	0	0.0032
	$2C_x$	0.0001	0.0000	0	−0.0001
	$2C_y$	0	0	−0.0001	0
	$2C_z$	−0.0015	0.0017	0	0.0200

TABLE 5. THE CHANGES IN THE AO BOND POPULATIONS OF THE CARBON-CARBON BOND OF ETHYLENE DUE TO THE INTERACTION IN MODEL IIa

	$1C_s$	$1C_x$	$1C_y$	$1C_z$
$2C_s$	−0.0008	0.0002	0	0
$2C_x$	−0.0001	0.0000	0	0
$2C_y$	0	0	0.0001	0
$2C_z$	0	0	0	−0.0151

Conclusion

We have made an approximate MO calculation on the addition of singlet methylene to ethylene by an isolated molecule CI method. The electron populations of the system, composed of ethylene and methylene, have been calculated by use of the SCF MO's of the two species. The results of the present calculation have proved the important role of the HOMO-LUMO interactions in determining the favorable path of the addition of singlet methylene to ethylene. The analysis of the electron populations

---

17) (a) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956). (b) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

has demonstrated an interesting feature of chemical interactions between two electronically neutral systems that stronger electron donating and electron accepting interactions take place than simply expected from the apparent changes in electron populations. The present calculation suggests that the CI approach to chemically reacting systems is promising for a better understanding of the mechanisms of chemical reactions.

It is a pleasure to express our gratitude to the Data Processing Center, Kyoto University for its generous permission to use the FACOM 230–60 computer.