Molecular Orbital Calculation of Chemically Interacting Systems. Interaction between Radical and Closed-Shell Molecules

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Abstract: An approximate molecular orbital (MO) calculation has been carried out on the interaction between methyl radicals and methane and that between methyl radicals and ethylene. The changes in the electron distributions due to the chemical interactions were calculated from the wave functions of the combined systems of radicals and closed-shell molecules which were obtained by the configuration interaction (CI) method of the electronic states of the adiabatic interaction and the charge-transfer interaction. These electronic states were described by the use of the MO's of reactant and reagent in an isolated state. The exchange interaction contributes to the bonds which are newly formed between reactant and reagent in an antibonding fashion, while the charge-transfer interaction is shown to be the main origin of the formation of new bonds as well as the loosening of the bonds to be broken in the reactions. The orbital interactions between the singly occupied (SO) MO of the radical and the highest occupied (HO) MO and the lowest unoccupied (LU) MO of the closed-shell molecule were found to be of importance.

Quantum chemical study of radical reactions may be suitable for an elucidation of the basic nature of chemical reactions, because they are less influenced by the environment of reactions than ionic reactions. The chemical reactivity index, free valence, was derived as a measure of the chemical reactivities of conjugated molecules toward the reagent radical.[1] Szwarc and Binks related the localization energies to the methyl affinities of aromatic and olefinic compounds.[2] In the frontier orbital theory, the important role of the orbital overlap interactions between the SOMO of the radical and the HOMO and the LUMO of the closed-shell system was pointed out.[3–8] The reactivity indices, frontier electron density, superdelocalizability, and delocalizability were defined in order to discuss the reactivities of unsaturated and saturated molecules with radicals in the frame of the isolated-molecule approximation. Recently, some MO calculations of the addition of methyl radical to ethylene and butadiene[9,10] and of the reaction of hydrogen with methane were performed.[11]

Here, it may be interesting to investigate, in detail, how the bond formation between reagent and reactant begins to take place, accompanied by the electron spin transfer, in the chemical reactions between the radical and closed-shell molecule. The aim of the present calculation is not to search for the accurate potential energy surface and to reproduce the experimental activation energy of some specified radical reaction but to discuss, rather qualitatively, the characteristic features of radical reactions by the employment of semiempirical MO's.

Interaction between Radicals and Closed-Shell Molecules

Some theoretical treatments of chemical interactions have been developed.[12–18] Klopman pointed out the importance of the Coulomb interaction and the electron transfer interaction in ionic reactions.[13] He thus used the terms "charge-controlled" and "frontier-controlled" in classifying some kinds of donor–acceptor interactions. Salem discussed thermal and photochemical interactions between two conjugated systems, applying the MO perturbation theory.[14,15] Chemical interaction between the two systems was studied by the present authors by partitioning the interaction energy into several terms in which the Coulomb interaction energy and the charge-transfer interaction energy were included.[18] The important role of the charge-transfer interaction between reagent and reactant in interpreting the formation of new bonds and the weakening of the bonds to be broken in the reaction was pointed out by the use of a CI wave function of a chemically interacting system of two closed shells.[19] In this paper, we present the results of an MO calculation on the chemical interaction of radical with closed-shell molecules, following the line mentioned in our previous papers.[18,19]

The CI method is convenient in order to express the

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(16) A. Devaquet, *Mol. Phys.*, **18**, 233 (1970).

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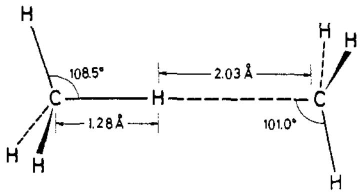

Figure 1. Interaction model of methane and methyl radical.

interacting system by the use of the MO's which are obtained for reactant and reagent in their isolated states. To a first approximation, we may take the electron configurations, representing the adiabatic, one-electron transfer, and local one-electron excitation interactions. Then, the wave function is given by eq 1, where 0 indicates the original state in which

$$\psi = C_0\psi_0 + \sum_i^{\text{occ}}\sum_l^{\text{uno}} C_{i\to l}\psi_{i\to l} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} C_{k\to j}\psi_{k\to j} + \sum_i^{\text{occ}} C_{i\to o}\psi_{i\to o} + \sum_j^{\text{uno}} C_{o\to j}\psi_{o\to i} + \sum_i^{\text{occ}}\sum_j^{\text{uno}} C_{i\to j}\psi_{i\to j} + \sum_k^{\text{occ}}\sum_l^{\text{uno}} C_{k\to l}\psi_{k\to l} + \sum_k^{\text{occ}} C_{k\to o}\psi_{k\to o} + \sum_l^{\text{uno}} C_{o\to l}\psi_{o\to l} \quad (1)$$

neither electron transfer nor electron excitation takes place, i and j are the occupied and unoccupied MO's of the closed-shell molecule, say A, in its isolated state, k, l, and o mean the occupied, unoccupied, and singly occupied MO's of the radical, say B, respectively. The symbols Σ^{occ} and Σ^{uno} imply the summation over occupied and unoccupied MO's, respectively, and $i \to l$, for instance, stands for the one-electron shift from the ith originally occupied MO of A to the lth originally unoccupied MO of B. The coefficients, C_0, $C_{i\to l}$, ..., in eq 1 can be obtained by solving the simultaneous equations

$$\sum_{p'} C_{p'}(H_{p,p'} - S_{p,p'}E) = 0 \qquad (p, p' = 0, i \to l, \ldots) \quad (2)$$

where

$$H_{p,p'} = \int \psi_p{}^* H \psi_{p'} \mathrm{d}\tau$$

$$S_{p,p'} = \int \psi_p{}^* \psi_{p'} \mathrm{d}\tau$$

The interaction energy between the two systems is approximately given by the sum of the four energies: Coulomb (ϵ_Q), exchange (ϵ_K), delocalization (D), and polarization (Π) interaction terms:

$$\Delta W \cong \epsilon_Q + \epsilon_K - D - \Pi \quad (3)$$

The formulas of these energy terms can be obtained rather in a straightforward manner, as in our previous paper.[18] The electron density of the interacting system is calculated by the use of eq 1

$$\rho(1) = M\int \psi^*(1,2,\ldots,M) \times \psi(1,2,\ldots,M)\, \mathrm{d}\xi_1 \mathrm{d}\tau_2 \ldots \mathrm{d}\tau_M \quad (4)$$

where ψ is assumed to be normalized so as to make the integration of $\rho(1)$ overall space, with respect to the electron referred to as 1, give the total electrons, M, of the interacting system. In the following, we will investigate the change in the electron distribution due to the interaction in detail, since this, we believe, reflects most distinctly what happens in chemical reactions.

Results of the Calculation

The calculation was performed by the use of a semiempirical all-valence electron SCF–MO method including overlap integrals.[20] The method of calculation and the approximations adopted are the same as those in our previous paper.[21] The matrix elements in eq 2 were calculated to the second order of overlap integrals by the use of the Mulliken approximation.[22]

Hydrogen Abstraction of Methane by Methyl Radical. As the first example, we show the result of the calculation on the interaction between methane and methyl radical. The reaction model was assumed to be as shown in Figure 1, making reference to the MINDO calculation by Dewar[23] and our preliminary calculation by the extended Hückel MO method.[24] Although the interaction between a radical and a closed-shell molecule was expressed by the use of restricted open-shell MO's in our previous paper,[18] they cannot necessarily reproduce chemically interesting quantities of radical, such as ionization potential, electron affinity, etc. It may be better to employ the MO's which reflect the properties of independent reactants. We here approximate them by the MO's of the unrestricted open-shell method.[25] The unrestricted MO wave function has a deficiency that it is not the eigenfunction of the operator S^2, but the contamination of higher multiplets to doublet is negligibly small for the present purpose. The vertical ionization potentials of methane (T_d) and methyl radical (assumed to be D_{3h}) obtained by our MO method are 12.79 and 10.41 eV, in fair agreement with the observed values, 12.99 and 9.86 eV, respectively.[26,27] The electron affinity of the methyl radical is calculated to be −1.00 eV, which is about 2 eV smaller than the observed value.[28]

The contributions of local-excited states to the wave function given by eq 1 are usually so small in comparison with those of charge-transferred states that they can be neglected with no serious influence upon the results.[29] We may assume here without loss of generality that the methyl radical has four valence electrons with spin α and three valence electrons with spin β. Then, the electron densities of two spins of the system composed of methane and methyl without any interaction may be given by

$$\rho_A{}^\alpha + \rho_B{}^\alpha = \sum_i^{\text{occ}}(a_i)^2 + \sum_k^{\text{occ}}(b_k)^2 + (b_o)^2 \quad (5)$$

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(20) T. Yonezawa, K. Yamaguchi, and H. Kato, *Bull. Chem. Soc. Jap.*, **40**, 536 (1967).

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(26) K. Watanabe, *ibid.*, **26**, 542 (1957).

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and

$$\rho_A{}^\beta + \rho_B{}^\beta = \sum_i^{\text{occ}}(a_i)^2 + \sum_k^{\text{occ}}(b_k)^2 \qquad (6)$$

where a_i is the ith occupied MO of A, b_k is the kth occupied MO of B, and b_0 is the MO of the unpaired electron. Here we have

$$\int\{\rho_A{}^\alpha(1) + \rho_B{}^\alpha(1) + \rho_A{}^\beta(1) + \rho_B{}^\beta(1)\}\mathrm{d}v_1 = M \qquad (7)$$

Figure 2 presents the simple sum of the electron densities of methane and methyl in one of the σ_v planes of the C_{3v} symmetry. The difference between the distributions of the two spins is obviously attributable to the unpaired electron which is almost localized to the atomic orbital (AO) of the carbon of methyl, having the extension in the direction along the principal axis.

The wave function ψ_0 may be given by a single determinant which is constructed by a_i's, b_k's, and b_o

$${}^1/_2\psi_0 = \mathfrak{N}\mathfrak{A}[a_1\bar{a}_1\ldots a_i\bar{a}_i\ldots a_m\bar{a}_m b_1\bar{b}_1\ldots b_k\bar{b}_k\ldots b_n\bar{b}_n b_o] \qquad (8)$$

where $\mathfrak{N}\mathfrak{A}$ means the normalization-antisymmetrization operator. Taking the terms up to the second order of the overlap integrals of the MO's of A and B (when they are integrated over all space), the electron densities of spin α and spin β in the state of the adiabatic interaction, ψ_0, are given by

$$\begin{aligned}\rho_o{}^\alpha \cong {} & \sum_i^{\text{occ}}\sum_{i'}^{\text{occ}} a_i a_i{}'\left(\sum_k^{\text{occ}} s_{ik}s_{i'k} + s_{io}s_{i'o}\right) + \\ & \left\{\sum_k^{\text{occ}}\sum_{k'}^{\text{occ}} b_k b_{k'}\sum_i^{\text{occ}} s_{ik}s_{ik'} + (b_o)^2\sum_i^{\text{occ}} s_{io}{}^2 + \right. \\ & \left. \sum_k^{\text{occ}}(b_k b_o + b_o b_k)\sum_i^{\text{occ}} s_{ik}s_{io}\right\} - \\ & 2\left\{\sum_i^{\text{occ}}\sum_k^{\text{occ}} a_i b_k s_{ik} + a_i b_o s_{io}\right\} + \rho_A{}^\alpha + \rho_B{}^\alpha \qquad (9)\end{aligned}$$

$$\begin{aligned}\rho_0{}^\beta \cong {} & \sum_i^{\text{occ}}\sum_{i'}^{\text{occ}} a_i a_{i'}\sum_k^{\text{occ}} s_{ik}s_{i'k} + \\ & \sum_k^{\text{occ}}\sum_{k'}^{\text{occ}} b_k b_{k'}\sum_i^{\text{occ}} s_{ik}s_{ik'} - 2\sum_i^{\text{occ}}\sum_k^{\text{occ}} a_i b_k s_{ik} + \rho_A{}^\beta + \rho_B{}^\beta \qquad (10)\end{aligned}$$

where

$$s_{ik} = \int a_i(1)b_k(1)\mathrm{d}v_1$$

There appear the terms which represent the distortion of the electron cloud, originating from the electron exchange interaction between the two systems. The exchange interaction between two closed-shell molecules results in the decrease in the electron densities of the intermolecular region and the increase in the electron densities in the neighborhood of the two molecules.[19,30] The same is true for the interaction of a radical with a closed-shell molecule. The third terms in eq 9 and 10 imply the decrease in the electron densities in the region between the two systems, leading to an antibonding contribution to the bonds to be formed between them. The extent of the change in electron distribution is parallel to the sum of the squares of overlap integrals of doubly and singly occupied MO's. In Figure 3 are illustrated $\rho_0{}^\beta$ and $\rho_0{}^\beta$, corresponding to the ψ_0 state. The change in the electron distribution of α spin is conspicuous, while that of spin β is not. The marked change in the electron densities of spin α

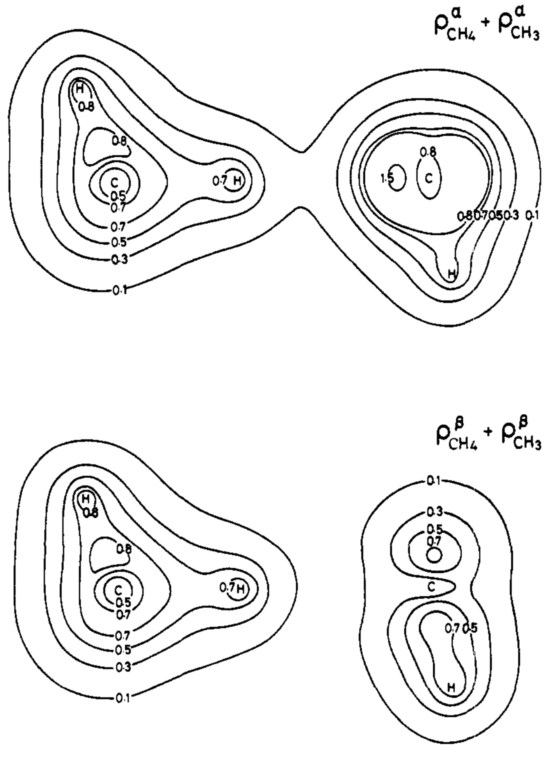

Figure 2. Sum of the electron densities of methane and methyl radical without interaction (in e/Å³). Note that the difference between Figure 2 and Figure 3 or Figure 4 is significant.

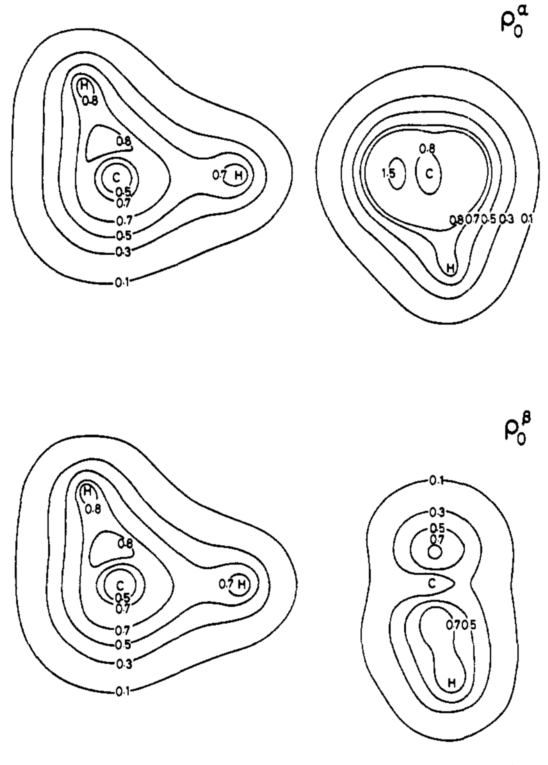

Figure 3. Electron densities of the system composed of methane and methyl radical with adiabatic interaction.

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(30) V. Magnasco, *Theor. Chim. Acta*, **21**, 267 (1971). See, also, M. Dreyfus and A. Pullman, *ibid.*, **19**, 20 (1970); L. Salem, *Proc. Roy. Soc., Ser. A*, **264**, 379 (1961).

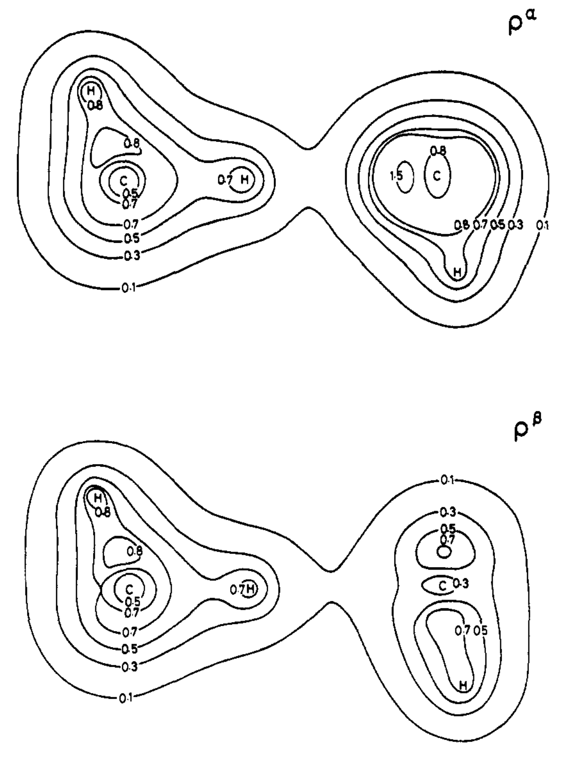
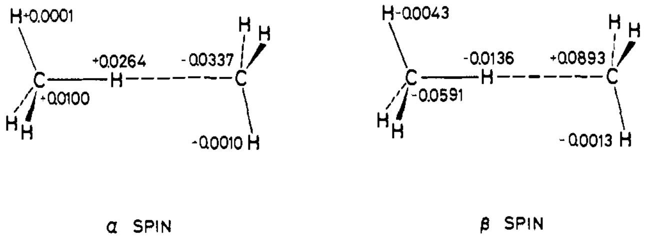


Figure 4. Electron densities of the system composed of methane and methyl radical with adiabatic and charge-transfer interactions.



α SPIN

β SPIN

Figure 5. Changes in atomic populations of methane and methyl radical due to interaction.

is clearly owing to the large overlap between a_i^{α}'s and b_o^{α}.

The electron densities ρ^{α} and ρ^{β} of the lowest energy state which is represented by the linear combination of ψ_0 and the charge-transferred electron configurations are shown in Figure 4. The terms to the second order of overlap integrals are taken into consideration. Among the various charge-transferred electron configurations, the one in which an electron is transferred from the HOMO (a_1) of deformed methane (C_{3v}) to b_o^{β} of methyl was calculated to be the most important and the one from b_o^{α} to the LUMO (a_1) of methane was found to be the next important. The cross terms of the charge-transferred states and the ψ_0 state in eq 4 are responsible for the increase in electron densities in the intermolecular region which stands for the formation of new bonds between two species.[19,31] However, the increase in the electron densities of spin α in the region between methane and methyl through the charge-transfer interaction is almost cancelled by the decrease caused by the electron exchange interaction. Therefore, the net contribution of α-spin electrons to the bond formation between the hydrogen of methane and the carbon of methyl is of a minor importance in the present model. On the other hand, the growing of the β electron densities in the region between methane and methyl, coming from the introduction of the charge-transferred states, obviously serves as the major origin of the formation of the new carbon-hydrogen bond. Comparison of Figure 4 with Figure 2 indicates that the decrease in the electron densities in the neighborhood of the carbon-hydrogen bond of methane to be broken in the reac-

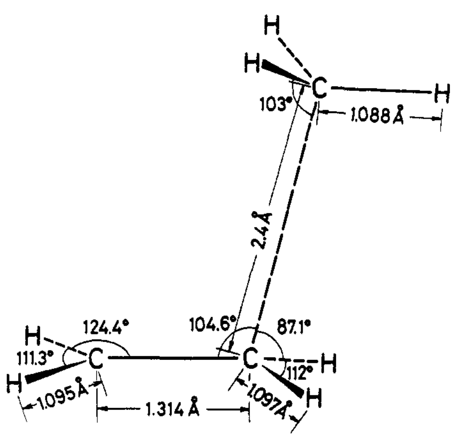


Figure 6. Interaction model of ethylene and methyl radical after Hoyland.[10]

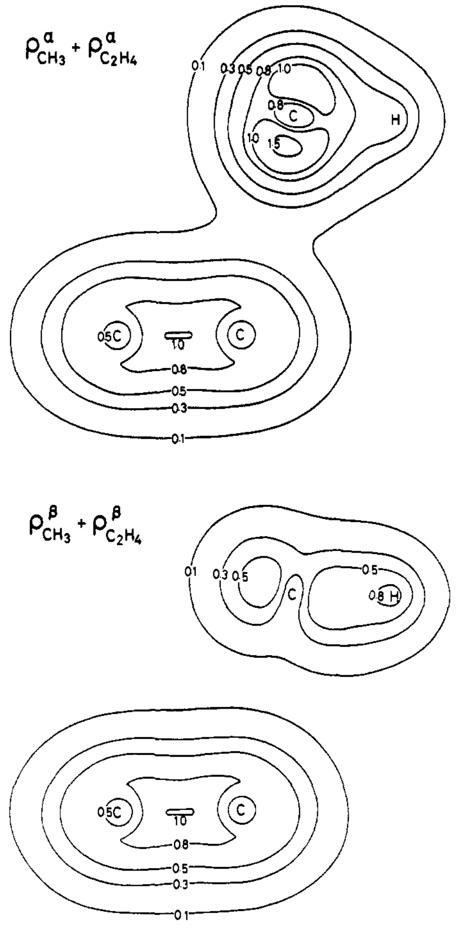


Figure 7. Sum of the electron densities of ethylene and methyl radical without interaction.

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(31) H. Fujimoto, S. Yamabe, and K. Fukui, *Tetrahedron Lett.*, 443 (1971).

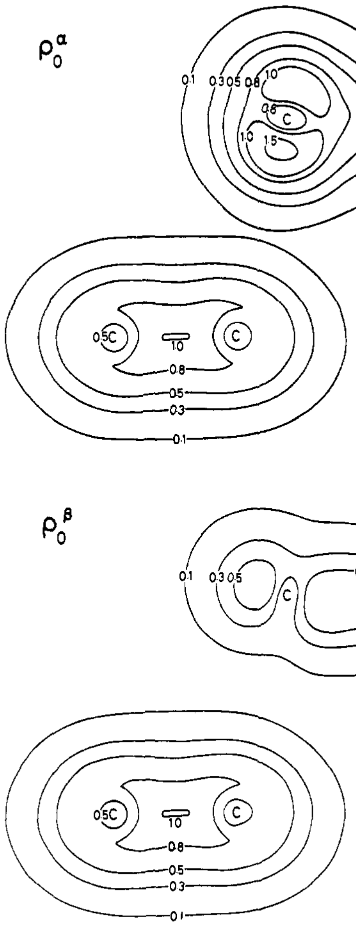

Figure 8. Electron densities of the system composed of ethylene and methyl radical with adiabatic interaction.

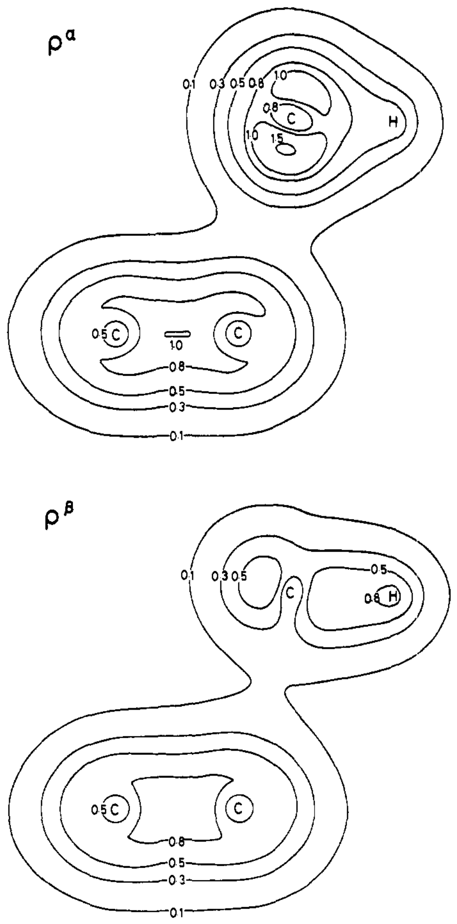

Figure 9. Electron densities of the system composed of ethylene and methyl radical with adiabatic and charge-transfer interactions.

tion is also caused mainly by β-spin electrons. From the above result, we can recognize the interesting behavior of β-spin electrons of methane which tend to form an electron pair with the unpaired electron of methyl.

Methane is the acceptor of the electrons with spin α and the donor of the electrons with spin β. On the contrary, methyl is the donor of the electrons with spin α and the acceptor of the electrons with spin β. The calculated changes in atomic populations, applying the Mulliken population analysis[32] to the AO pairs of methane and methyl, are shown in Figure 5. The amount of electrons with spin α donated from methyl to methane and that with spin β donated from methane to methyl are not the same in the present calculation. This result might be inherent to the approximations used for the calculation of matrix elements of the secular equation. However, it is in agreement with the result of a variational calculation on the whole system composed of methane and a methyl radical that the hydrogen of methane to be abstracted by a methyl radical migrates carrying slightly positive net charge. The essential difference in the behaviors of electrons of opposite spins mentioned above is believed to be independent of the crudeness of approximations, in a qualitative sense.

Addition of Methyl Radical to Ethylene. In order to see if the discussion given above holds for other chemical interactions between a radical and a closed-shell system, we proceed here to another example, the addition of methyl radical to ethylene. The course of the reaction was thoroughly examined by Basilevsky[9] and by Hoyland.[10] They gave good calculated values of the activation energy of the reaction by the use of semiempirical MO methods.[9,10,33]

Figure 6 shows the reaction model employed for the calculation by Hoyland.[10] The simple sums of the electron densities of methyl and ethylene without interaction on the bisecting plane are shown in Figure 7. Here, methyl is assumed to have 4 valence electrons with spin α.

By introducing the electron exchange interaction between the two species, a conspicuous change in the distribution of the electrons with spin α takes place due to the strong repulsive interaction between the unpaired electron of methyl and the π electrons (not in a strict sense) of ethylene as shown in Figure 8. The change in the distribution of the electrons with spin β is relatively small.

Figure 9 demonstrates that the strong antibonding contribution of α-spin electrons to the bond to be newly formed between the carbons of methyl and ethylene, originating from the electron exchange interaction, is barely recovered by the inclusion of charge-transferred states. The important role of β-spin electrons in the formation of the carbon–carbon bond is clearly

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(32) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(33) M. V. Basilevsky, V. A. Tikhomirov, and I. E. Chlenov, *Theor. Chim. Acta*, **23**, 75 (1971).

recognized from Figures 7 and 9. Among the various electron configurations except ψ_0, the configuration in which an electron is transferred from the SOMO of methyl to the LUMO of ethylene is calculated to be the most dominant, and the one from the HOMO of ethylene to the SOMO of methyl is the next dominant. The present calculation suggests that methyl is positively charged, while ethylene is negatively charged in the interaction. This tendency seems to be in an agreement with the Szwarc's proposition that a methyl radical adds to olefinic double bonds in a nucleophilic fashion.[34]

Conclusion

A configuration interaction treatment of chemical interactions between methyl and methane and between methyl and ethylene revealed interesting features of the unpaired electron of the radical and the electrons of closed-shell systems with opposite spin. The contribution of an unpaired electron to the formation of new bonds through charge-transfer interaction was found to be cancelled either partly or entirely by the exchange interaction. On the contrary, the charge-transfer interaction from a closed-shell molecule to a radical to form an electron pair with the odd electron contributed significantly to bond formation. Such a behavior of the unpaired electron will have a profound importance in understanding the nature of radical reactions, because the SOMO has the greatest amplitude in the neighborhood of the most reactive position of radical, in general. To estimate quantitatively the ratio of the contribitions of the two spins to the formation of new bonds and the weakening of old bonds is hardly possible at the present time because of the crudeness of the calculation. More elaborate calculations will be needed for such a purpose. Nucleophilicity and electrophilicity of radicals will have a concern with this problem.

Acknowledgment. We would like to express our gratitude to the Data Processing Center, Kyoto University, for its generous permission to use the FACOM 230-60 computer.

(34) A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **251**, 394 (1959).

The Failure of Some Commonly Accepted Spectroscopic–Enthalpy Correlations for Chloroform Adducts[1a]

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Abstract: In this article we demonstrate that neither the change in the nmr proton chemical shift nor the change in the C–D infrared stretching frequency in chloroform or deuteriochloroform upon complexation with a series of Lewis bases can be used as a reliable estimate of the enthalpy of adduct formation. No linear correlation was found to exist between the enthalpy of adduct formation with the change in infrared stretching frequency although a linear correlation between the enthalpy and the hydrogen bonding chemical shift did exist for a limited number of donors. It is shown that $\Delta\nu_{CD}$ for deuteriochloroform adducts do not fall on a constant base line and a plot of $\Delta\nu_{CD}$ *vs.* $\Delta\nu_{OH}$ (phenol) is not linear. These relationships have been shown to be requirements for a constant acid plot with slope similar to the alcohols. The enthalpies of interaction are nicely correlated by our double scale enthalpy equation. The principal contribution to the interaction of chloroform with the donors studied comes from the "electrostatic" term rather than from the "covalent" interaction term.

In a previous report from this laboratory, a series of Lewis bases were shown to give rise to straight line plots of $-\Delta H$ *vs.* $\Delta\nu_{OH}$, the infrared stretching frequency, when either the hydrogen bonding acid was held constant and the base varied (constant acid plots) or when the base was held constant and the hydroxy acid varied (constant base plots). The correlation encompassed data for phenol,[2] a series of substituted phenols,[3] 1,1,1,3,3,3-hexafluoro-2-propanol,[4] 2-methyl-2-propanol[5] and 2,2,2-trifluoroethanol.[6] By combining equations describing constant acid and constant base plots, we were able to show that any new acid that satisfied both plots would have to give rise to an additional straight line plot with zero intercept when $(\Delta\nu_{O-H})_x$ for a series of bases with this acid were plotted against $\Delta\nu_{OH}$ for any acid (*e.g.*, phenol) already in the correlation[7]

$$\Delta\nu_{OH}(X) = \frac{(n_x - L)\Delta\nu_{OH}(\text{phenol})}{(M_0 - M_x)\Delta\nu_{OH}(\text{phenol}) + (n_0 - L)}$$

where M_0 and M_x are the slopes of the constant acid plots for phenol and the new acid X (these slopes were found to be equal within experimental error for the above acids), n_0 and n_x are the intercepts for the constant acid plots of the reference acid and the new acid

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(1) (a) Abstracted in part from the Ph.D. Thesis of F. L. Slejko, University of Illinois, Urbana, Illinois, 1972. (b) National Science Foundation Predoctoral Fellow 1969–1972.

(2) T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967).

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(7) M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 7086 (1970).