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A Molecular Orbital Calculation of Chemically Interacting Systems. Recombination of Two Methyl Radicals

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A molecular orbital (MO) approach to a radical-radical reacting system is proposed within the isolated molecule approximation. The interaction energy, ΔW, is defined as the sum of four components, Coulomb, exchange, charge transfer and polarization energies. The four terms are calculated in the recombination of two methyl radicals. The origin of the deformation of methyl radical ($D_{3h}\rightarrow C_{3v}$) and the rotational barrier (staggered→eclipsed) in the course of the recombination was found to be the exchange energy caused by the interaction of both doubly occupied MO's. The difference-density map shows the characteristic role of exchange and charge transfer interactions for charge redistribution.

The molecular orbital (MO) method has been found to be fairly satisfactory for describing a reasonable reaction path and the activation energy of ionic[1)] and addition[2)] reactions, but not those of radical-radical reactions. Multi-determinantal wave functions such as those obtained by the MCSCF[3)] and natural orbital[4)] methods have also been utilized. However, enormous computer time is required for molecules with size of chemical interest, and difficulty in convergence is sometimes encountered. In addition, the methods give no vivid orbital picture which appeals to organic chemists as regards the interpretation of reactivity. In view of the fact that the path of the radical-radical reaction does not yet seem to be understood theoretically,[5)] a new means to analyze the mechanism with a clear orbital concept is desirable.

In 1968, two of us (K.F. and H.F.) proposed a method for the general reactivity index ("ΔW method") based on the isolated molecule approximation.[6)] Various calculations of model reacting systems showed that the ΔW method is effective for interpreting the reactivity of closed-shell molecules.[7)]

In view of the applicability of this method to the elucidation of the reaction mechanism and the necessity to investigate the radical-radical reaction theoretically, an extension of the method was carried out, the aim of the work being to simulate and analyze the reaction within the framework of the MO calculation. Since the ΔW method is based on the *static* model, dynamic processes in the reaction such as the relaxation of vibration energy are beyond the scope of the present approach.

Definition of Interaction Energy

The derivation of the interaction energy (ΔW) is based on the configuration interaction (CI) procedure in terms of the electronic structure of two independent radicals, essentially similar to the case of the reaction between two closed-shell molecules.[6)] The wave function ($\Psi^{s,t}$) of the whole reacting system is represented by a linear combination of various configuration functions (Fig. 1).

$$\Psi^{s,t} = C_0\Psi_0^{s,t} + \sum_{p} C_p\Psi_p^{s,t} \qquad (1)$$

Each Slater determinant of $\Psi_0^{s,t}$ and $\Psi_p^{s,t}$ is composed of the MO's, a_l,[8)] a_o, b_k, and b_o, which are the solutions of the doublet spin state of two *independent* radicals. Once they are included within one Slater determinant and the electron exchange between them is allowed, the non-orthogonality condition makes the evaluation of expected values difficult. The tedious derivation was carried out in this work. Configurations other than $\Psi_0^{s,t}$ in Eq. 1 are all possible one-electron transferred (from i→l to o→o') and excited (from i→j to o'→l) ones which have the forms as the eigenstate of the spin augular momentum $\mathbf{S}^2$. The minimum total energy of $\langle\Psi^{s,t}|\mathbf{H}|\Psi^{s,t}\rangle/\langle\Psi^{s,t}|\Psi^{s,t}\rangle$ is determined by the secular equation according to the usual CI procedure. In order to get a succinct expression of the interaction energy (ΔW), the secular determinant is expanded perturbationally. We obtain ΔW in the following partitioned form.

$$\Delta W = E_Q + E_K - D - \Pi \qquad (2)$$

E_Q is the classical Coulombic energy and E_K the exchange energy caused by the overlap of the electron cloud between two radicals. These two are the first-order energies in the sense of the Rayleigh-Schrödinger perturbation. On the other hand, fourteen terms of the second-order perturbation form corresponding to the electron configurations (except $\Psi_0^{s,t}$) (Fig. 1) are divided into two groups, D and Π, according to the type of electron jumping. D is the stabilization energy due to the mixing of the one-electron transferred configurations and Π the stabilization energy by the one-electron excited configurations. ΔW is a general index of the reactivity for both singlet and triplet radical-radical interactions. This simplified form of interaction energy which can be grasped intuitively is based on the idea of *isolated molecule approximation.* The mode of molecular interaction is entirely dependent on the electronic structure of two monomers. In order to get a more explicit form of the four terms in Eq. 2, we rewrite them as the sum of various molecular integrals, taking into account the possible permutation of electrons within each Slater determinant. Thus, E_K, D, and Π are generally represented as a power series of the MO overlap (s_{lk}). As long as the interaction is weak enough to be dealt with by perturbation, the MO overlap of the high order caused by the multiple permutation is negligible. The validity of this

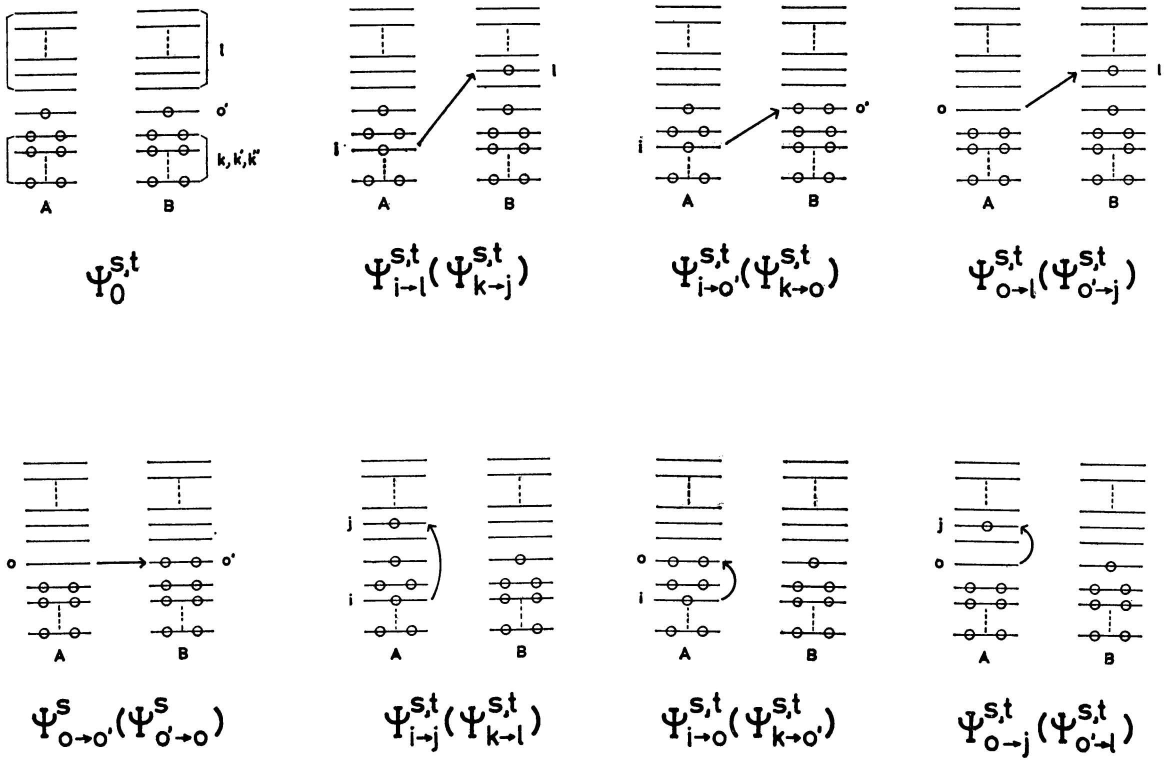


Fig. 1. Electronic configurations adopted for the present CI procedure. The "zero confiuration." $\Psi_0^{s,t}$, retains the original electronic structure at the infinite separation between two radical monomers, A and B.

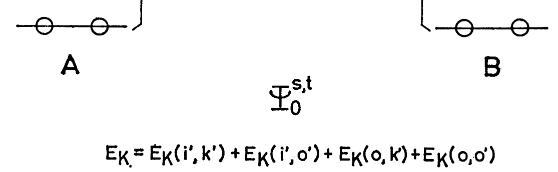


Fig. 2. The schematic representation of four types of exchange interaction. The reason why the doubly occupied MO's, i and k, have the prime in the figure is that exchange energy is caused by the electron permutation for which the prime is imposed on MO's.

truncation can be confirmed numerically by calculating some terms of MO overlap.

Coulomb Energy E_Q. This energy depends only on the occupation number of electrons in each MO regardless of the spin multiplicity of the system. The derivation is straightforward.

Exchange Energy E_K. In the present scheme, E_K can be partitioned into four pairs of occupied MO's.

$$E_K = E_K(i', k') + E_K(i', o') + E_K(o, k') + E_K(o, o') \quad (3)$$

Their schematic representation is shown in Fig. 2. $E_K(i',k')$ expresses the interaction between doubly occupied MO's, working repulsively. Both $E_K(i',o')$ and $E_K(o,k')$ are also repulsive energies (>0). Whether $E_K(o,o')$ is repulsive or attractive depends on the spin multiplicity of the system. When the spin coupling between the electrons of MO's, a_0 and $b_{0'}$, gives the singlet state, $E_K(o,o')$ represents attraction, when it gives the triplet state, $E_K(o,o')$ represents repulsion.

Charge Transfer Energy D. D consists of eight different terms of the second-order perturbational form corresponding to charge-transferred configurations (Fig. 1). The difference in the normalization factors (*e.g.*, $<\Psi_{i\to l}^{s,t}|\Psi_{i\to l}^{s,t}>$ and $<\Psi_0^{s,t}|\Psi_0^{s,t}>$) for expected values are explicitly considered. For the sake of convenience, D is represented as the sum of eight components.

$$D = D(i\to l) + D(k\to j) + D(i\to o') + D(k\to o)$$
$$+ D(o\to l) + D(o'\to j) + D(o\to o') + D(o'\to o) \quad (4)$$

In line with the fact that $\Psi_{o\to o'}$ and $\Psi_{o'\to o}$ have only singlet spin state that can not mix with Ψ_0^t, the stabilization energies $D(o\to o')$ and $D(o'\to o)$ are zero for triplet. D is usually positive, acting as the stabilization energy in ΔW of Eq. 2. The denominator of each component of Eq. 4 becomes negative in some cases.[9]

Polarization Energy Π. In Eq. 2, the residual part of the second-order perturbational form, Π, consists of six different terms corresponding to local one-electron excited configurations (Fig. 1). Π can be represented by the sum of six components.

$$\Pi = \Pi(\mathrm{i}\rightarrow\mathrm{j}) + \Pi(\mathrm{k}\rightarrow\mathrm{l}) + \Pi(\mathrm{i}\rightarrow\mathrm{o}) + \Pi(\mathrm{k}\rightarrow\mathrm{o}') + \Pi(\mathrm{o}\rightarrow\mathrm{j}) + \Pi(\mathrm{o}'\rightarrow\mathrm{l}) \tag{5}$$

Difference Density. The difference density map of the radical-radical reaction system visualizes the change of the electron density during the course of reaction. Here, the case of singlet interaction is dealt with. The spinless difference density $\Delta\rho(1|1)_{E_K}$ which includes the exchange interaction is derived by the use of Eq. (A.3),[10] and is partitioned into four components according to the decomposition of E_K in Eq. 3.

$$\Delta\rho(1|1)_{E_K} = \Delta\rho(1|1)_{E_K(\mathrm{i}',\mathrm{k}')} + \Delta\rho(1|1)_{E_K(\mathrm{i}',\mathrm{o}')} + \Delta\rho(1|1)_{E_K(\mathrm{o},\mathrm{k}')} + \Delta\rho(1|1)_{E_K(\mathrm{o},\mathrm{o}')} \tag{6}$$

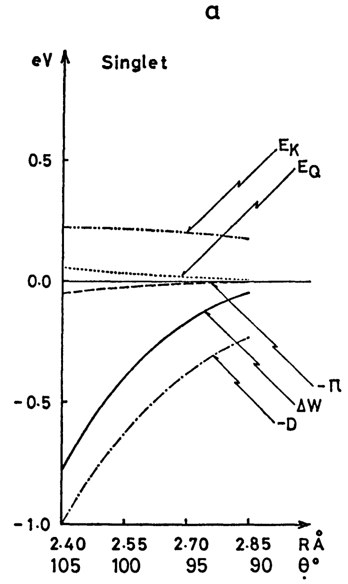
The difference density including the exchange and charge-transfer interactions, $\Delta\rho(1|1)$, is also given as

$$\Delta\rho(1|1) = \mathrm{M}\int \Psi'^{\mathrm{s}}(1,2,\cdots,\mathrm{M})\Psi'^{\mathrm{s}}(1,2,\cdots,\mathrm{M})\mathrm{d}\xi_1\mathrm{d}\tau_2\cdots\mathrm{d}\tau_{\mathrm{M}} - \rho(1|1)_{\mathrm{A}} - \rho(1|1)_{\mathrm{B}} \tag{7}$$

where $\Psi'^{\mathrm{s}}(1,2,\ldots,\mathrm{M})$ is the wavefunction of Eq. 1 without the six polarization-type configurations and M the total number of electrons of the system. $\Delta\rho(1|1)$ can be obtained numerically.[11]

Recombination of Methyl Radicals

As a test of the ΔW method, the recombination between two methyl radicals was examined. In the assumed model of the D_{3d} symmetry (*i.e.*, elongated staggered ethane), two variables (R and θ) are changed to simulate the reaction. R is the C···C distance and θ is the <HCC angle. The C–H bond length (1.079 Å)[12] of the monomer radical is kept constant throughout the calculation. The interaction energy is computed approximately in terms of the semi-empirical all-valence-electron UHF MO including overlap integrals. In a strict sense, the RHF MO which is the doublet spin eigenfunction should be employed as MO's, i, k, j, and so forth (Fig. 1). However, the MO gives unacceptable physical properties such as ionization potential and electron affinity. Since the orbital energy is crucial to evaluate the second-order terms (D and Π), we are obliged to use the UHF MO instead of the RHF MO. The former MO, although somewhat deviated from the spin eigenfunction, can reproduce the property well. The way of estimating semi-empirical parameters to evaluate MO integrals is the same as that used in a previous paper.[7a] Calculated results of the singlet ΔW along the approaching path of two radicals with plausible values of R and θ are given in Fig. 3a and Table 1 and those of the triplet ΔW in Fig. 3b and Table 2. R is restricted to the range 2.85 Å—2.40 Å, since the perturbational expansion of the CI matrix elements was used in this work. The two methyl radicals approach in an eclipsed manner (D_{3h}), the other models having D_{3d} symmetry.



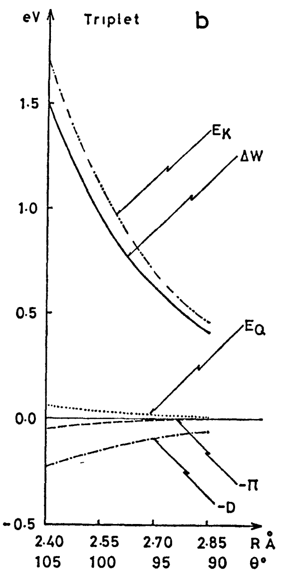


Fig. 3a. The change of the singlet interaction energies along the adopted staggered path with the deformation of the methyl-radical geometry. The deformation of methyl radical is found to smooth the increase of the global E_K as R becomes smaller, and consequently the stabilization of the system becomes large.

3b. The change of the triplet interaction energies along the adopted staggered path with the deformation of the methyl-radical geometry.

First, the singlet ΔW is examined. E_Q is found to have a positive (repulsive) and small value throughout the adopted models (Table 1). Since the present neutral system consists of only carbon and hydrogen atoms, E_Q is obviously small, the positive value being caused by the C···C electrostatic repulsion, overcoming the C···H attraction.

The singlet E_K in Eq. 2 is also positive. Of its four components the largest (absolute value) at $R=$

Table 1. Caluculated singlet interaction energies for the recombination of two methyl radicals

R/Å	2.85	2.85(E)[b]	2.40	2.40
θ/°	90.00	90.00	105.00	90.00
E_Q[a]/eV	0.0134 (0.0216)	0.0145 (0.0235)	0.0626 (0.0858)	0.0269 (0.0435)
$E_K(\mathrm{i}', \mathrm{k}')$	0.1678	0.1821	0.3779	0.7401
$E_K(\mathrm{i}', \mathrm{o}')$, $E_K(\mathrm{o}, \mathrm{k}')$	0.0756	0.0757	0.2703	0.3251
$E_K(\mathrm{o}, \mathrm{o}')$	−0.1372	−0.1373	−0.6964	−0.5730
E_K/eV	0.1818	0.1962	0.2221	0.8173
$D(\mathrm{i}\rightarrow\mathrm{l})$, $D(\mathrm{k}\rightarrow\mathrm{j})$	0.0004	0.0001	0.0113	0.0072
$D(\mathrm{o}\rightarrow\mathrm{l})$, $D(\mathrm{o}'\rightarrow\mathrm{j})$	0.0008	0.0008	0.0002	0.0099
$D(\mathrm{i}\rightarrow\mathrm{o}')$, $D(\mathrm{k}\rightarrow\mathrm{o})$	0.0283	0.0283	0.0937	0.1130
$D(\mathrm{o}\rightarrow\mathrm{o}')$, $D(\mathrm{o}'\rightarrow\mathrm{o})$	0.0842	0.0842	0.3962	0.3170
D/eV	0.2274	0.2268	1.0028	0.8942
$\Pi(\mathrm{i}\rightarrow\mathrm{j})$, $\Pi(\mathrm{k}\rightarrow\mathrm{l})$	0.0002	0.0002	0.0044	0.0012
$\Pi(\mathrm{i}\rightarrow\mathrm{o})$, $\Pi(\mathrm{k}\rightarrow\mathrm{o}')$	0.0019	0.0019	0.0205	0.0269
$\Pi(\mathrm{o}\rightarrow\mathrm{j})$, $\Pi(\mathrm{o}'\rightarrow\mathrm{l})$	0.0000	0.0000	0.0003	0.0006
Π/eV	0.0042	0.0042	0.0504	0.0574
ΔW/eV	−0.0364	−0.0203	−0.7685	−0.1074

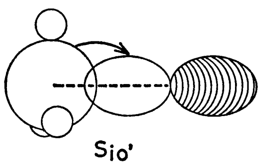
a) Values in parentheses evaluated by net charge approximation. b) Eclipsed approach model with $R=$ 2.85 Å.

TABLE 2. CALCULATED TRIPLET INTERACTION ENERGIES FOR THE RECOMBINATION OF TWO METHYL RADICALS

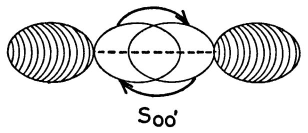
R/Å	2.85	2.40
θ/°	90.00	105.00
E_Q/eV	0.0134 (0.0216)	0.0626 (0.0858)
E_K(i′, k′)	0.1696	0.3994
E_K(i′, o′), E_K(o, k′)	0.0764	0.2857
E_K(o, o′)	0.1386	0.7361
E_K/eV	0.4610	1.7069
D(i→l), D(k→j)	0.0004	0.0123
D(o→l), D(o′→j)	0.0008	0.0002
D(i→o′), D(k→o)	0.0288	0.1017
D(o→o′), D(o′→o)	0	0
D/eV	0.0600	0.2284
Π(i→j), Π(k→l)	0.0002	0.0044
Π(i→o), Π(k→o′)	0.0019	0.0223
Π(o→j), Π(o′→l)	0.0000	0.0000
Π/eV	0.0042	0.0534
ΔW/eV	0.4102	1.4877

2.85 Å is E_K(i′,k′), while that at R=2.40 Å is E_K(o,o′). This shows that a_0-$b_{0'}$ MO interaction grows discriminatively along the progress of the reaction. Such remarkable growth of a particular MO interaction plays a key role to determine the reaction path. Thus, the repulsive character of the exchange energy which is unfavorable to the enhancement of the reaction is considerably weakened by E_K(o,o′).

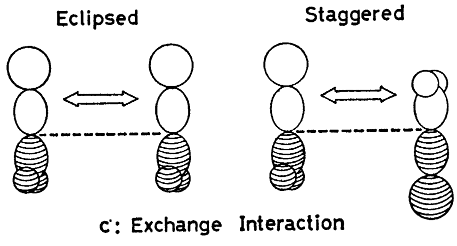
D is found to give the largest attractive energy throughout the adopted staggered models, the increase of the energy along the C···C approach being drastically large. It is noteworthy that D(i→l) [or D(k→j)] has a small value in spite of many (a_i,b_l) pairs. This is because both a_i and b_l do not have their spatial extension toward the intermolecular C···C region, the MO overlap between them thus being small. The strength of the MO overlap is a crucial criterion to determine the extent of the (a_i→b_l) charge transfer (CT) interaction. Since the "symmetry-forbidden" CT interaction (*e.g.*, from the a_1-symmetry MO of one radical to the *e*-symmetry MO of the other) has no contribution to D, the non-zero components of D(i→l) are actually limited to three. D(o→l) and D(o′→j) have also small values for the following reason. The singly occupied (SO) MO's, a_0 and $b_{0'}$, which are of $a_1(\sigma)$-symmetry, can overlap only one unoccupied a_1 MO with its spatial extension localized on three hydrogens. However, owing to the largest separation between the density of a_0 (or $b_{0'}$) and that of the one σ type a_1 MO, no effective CT interaction occurs. As for D(i→o′) [or D(k→o)] there is only one occupied $a_1(\sigma)$ MO with its substantial localization on the carbon 2s atomic orbital,[13] which is able to mix with the a_1 type MO, a_0 or $b_{0'}$. Contrary to the case of D(i→l), the combination of a_i and $b_{0'}$ gives an appreciable MO overlap, $s_{io'}$, resulting in the large value of D(i→o′) (Fig. 4a). The largest two equivalent CT terms, D(o→o′) and D(o′→o), have their common origin from the huge MO overlap, $s_{oo'}$, shown in Fig. 4b. In view of this, the MO overlap, $s_{oo'}$, is a crucial factor to give the large stabilization energies, D(o→o′) and D(o′→o) as well as E_K(o,o′) in the case of singlet interaction. Thus, the important role of the particular MO interaction to control the reaction is demonstrated.



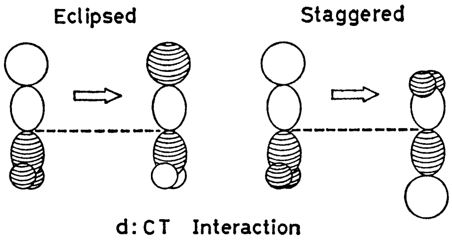
a: (i→o') CT Interaction



b: (o→o') and (o'→o) CT Interaction



c: Exchange Interaction



d: CT Interaction

Fig. 4. Schematic representation of the mode of dominant MO interactions.

The polarization energy Π (Table 1) has the smallest absolute value among the four terms of ΔW regardless of the C···C distance R, reflecting the "neutral" character of the system without heteroatoms.

Summing up E_Q, E_K, D, and Π according to Eq. 2, we obtain the total singlet energy, ΔW (Table 1). Its value indicates that the electronic interaction energy gives considerable stabilization energy at the perturbational region between two radicals. Comparing the two ΔW's (θ=90° and 105°) at R=2.40 Å, we see a remarkable difference in E_K. Thus, the geometrical deformation of methyl radical (planar→pyramidal) in the course of the reaction brings about the decrease in the exchange repulsion resulting in the decrease of ΔW and ease in recombination. Terms other than E_K are not influenced so much by the θ variation. Of the four terms of E_K, E_K(i′,k′) of θ=90° differs a great deal from that of $\theta=105°$ at $R=2.40$ Å. Thus, for the progress of the reaction it is very important to avoid the exchange repulsion of doubly occupied MO's by deformation. The enlargement of lobes of SOMO's (a_o and $b_{o'}$) which makes $E_K(o,o')$, $D(o\rightarrow o')$ and $D(o'\rightarrow o)$ more attractive terms is found to be a secondary factor for this acceleration. Even if the geometrical deformation is accompanied by the destabilization of the monomer total energy in its isolated state, it is covered entirely by the electronic stabilization energy.[14]

A comparison of the interaction energy between the D_{3d} staggered and the D_{3h} eclipsed models is made at $R=2.85$ Å. As expected, the staggered path gets more stabilization energy ($\Delta W=-0.0364$ eV) than the eclipsed path ($\Delta W=-0.0203$ eV). What is the origin of this rotational barrier in the course of the reaction? Comparing all the components of ΔW, we find that the sole component, E (i′,k′), gives the energy difference. This is because the σ type MO overlap such as $s_{oo'}$ is insensitive to the rotation of the π type electronic cloud around the C⋯C σ axis. Only the π-π' type exchange interaction which is included in $E_K(i',k')$ depends on the rotation angle. The mode of the MO overlap, the origin of $E_K(i',k')$,[15] for the two approaching models is shown in Fig. 4c. It is evident that the eclipsed approach gets the larger MO overlap than the staggered one. On the other hand, CT interaction does not give a large energy difference between the two approaches (Fig. 4d). The negligible difference in CT interaction arises from the nodal property of the π type unoccupied MO. Sovers and his coworkers made an extensive study on the internal rotation barrier of ethane by use of the bond-orbital wavefunction and concluded that the main source of the barrier is the overlap repulsion between localized C–H bond orbitals with the closed shell.[16] Although ethane itself is not dealt with in this work, the present result seems to help to elucidate the origin of the rotational barrier.

The sharp increase of ΔW is due mostly to E_K (Fig. 3b). This indicates that the triplet interaction makes the recombination (D_{3d}) path unfavorable. The triplet E_K (Table 2) differs considerably from the singlet E_K (Table 1). The greater destabilization due to the triplet E_K is ascribed to the change of the sign attached to $E_K(o,o')$. The minor difference of $E_K(i',k')$, $E_K(i',o')$ and $E_K(o,k')$ between singlet and triplet is due to that of the normalization factor of Ψ_0. Contrary to the case of singlet, the triplet a_o-$b_{o'}$ MO interaction contributes to the exchange energy as repulsive. The triplet D is much smaller than the singlet D, which is mostly due to the absence of both $\Psi^{t}_{o\rightarrow o'}$ and $\Psi^{t}_{o'\rightarrow o}$ configurations in Eq. 1. However, the triplet Π is almost the same as the singlet Π. The global term, ΔW, of triplet is positively large. This reflects the fact that two electrons with parallel spins can not occupy the same space (along the C⋯C axis) according to the Pauli exclusion principle.

The density distribution is analyzed in terms of the various difference densities given by Eqs. 6 and 7. Of the four terms of Eq. 6, $\Delta\rho(1|1)_{E_K(i',k')}$ of the singlet radical-radical interaction is shown in Fig. 5a. This is regarded as the electron rearrangement through the mutual overlap between both doubly occupied MO's, i′ and k′. We see a large amount of decreased density in the C⋯C region. This quantity corresponding to the positive $E_K(i',k')$ usually appears when the exchange interaction is taken up in the system of closed-shell molecules. Instead, the electron density, shifting from the central C⋯C region, is piled up around respective carbon and hydrogen atoms. In the case of $\Delta\rho(1|1)_{E_K(i',o')}$ (Fig. 5b), $E_K(i',o')$ is the repulsive energy (Table 1). The repulsive character is reflected in the large area of the negative density along the C⋯C line (Fig. 5b). However, the center of the negative part is located almost at the left end of the C⋯C region. The shift of the region of the intermolecular decreased density is due to the fact that the differential MO overlap, i′(1)o′(1), which is the main origin of the $\Delta\rho(1|1)_{E_K(i',o')}$ has a maximum in the region. The trend always appears in the overlap between the s type and p type orbitals.[17] The counterpart of the decreased density is accumulated at each carbon site, which is similar to the case of $\Delta\rho(1|1)_{E_K(i',k')}$. As regards $\Delta\rho(1|1)_{E_K(o,o')}$ (Fig. 5c), since $E_K(o,o')$ is a considerable stabilization energy, $\Delta\rho(1|1)_{E_K(o,o')}$ is expected to give the large bonding density at the central C⋯C region, competing with the decrease by $\Delta\rho(1|1)_{E_K(i,'k')}$, $\Delta\rho(1|1)_{E_K(i',o')}$ and $\Delta\rho(1|1)_{E_K(o,k')}$. An egg-shaped increased density is observed in the middle of the C⋯C line. This also demonstrates the important role of the a_o-$b_{o'}$ MO interaction on bond formation. The decreased quantity opposing the drastic bonding density is found just around each carbon atom. Thus, the change in density distribution is interpreted as follows. The MO overlap, $s_{oo'}$, absorbs the electron density from the MO's a_o and $b_{o'}$.

Of the four components of $\Delta\rho(1|1)_{E_K}$ the origin of the geometrical deformation. ($D_{3h}\rightarrow C_{3v}$) of methyl radical is brought about by $\Delta\rho(1|1)_{E_K(i',k')}$ (Fig. 5-a).[18] The other three difference densities exhibit a nearly equivalent electron redistribution around both hydrogen and carbon atoms or represent only the motion of translation of the C–H bond. However, $\Delta\rho(1|1)_{E(i',k')}$ has a positive contour line just around the front side of the pyramidal methyl carbon which pulls the carbon atom so as to decrease the C⋯C distance,[19] whereas the hydrogen atom does not move toward any direction. The discussion based on the "force" criterion[20] is in line with the result of interaction energy. $E_K(i',k')$ affects mostly nuclear deformation of the methyl radical among the four energy terms of E_K.

The change of the electron distribution due to the exchange and CT interactions in Eq. 7 is shown in Fig. 5d. No polarization interaction is taken into account in the present analysis, since the reacting system is neutral and the interaction is not so important. A huge accumulation of the intermolecular bonding density in the central C⋯C region is noteworthy. As compared with that of $E_K(o,o')$, the global bonding density in the C⋯C region is much more increased. This indicates the significant role of the $a_o\rightarrow b_{o'}$ and

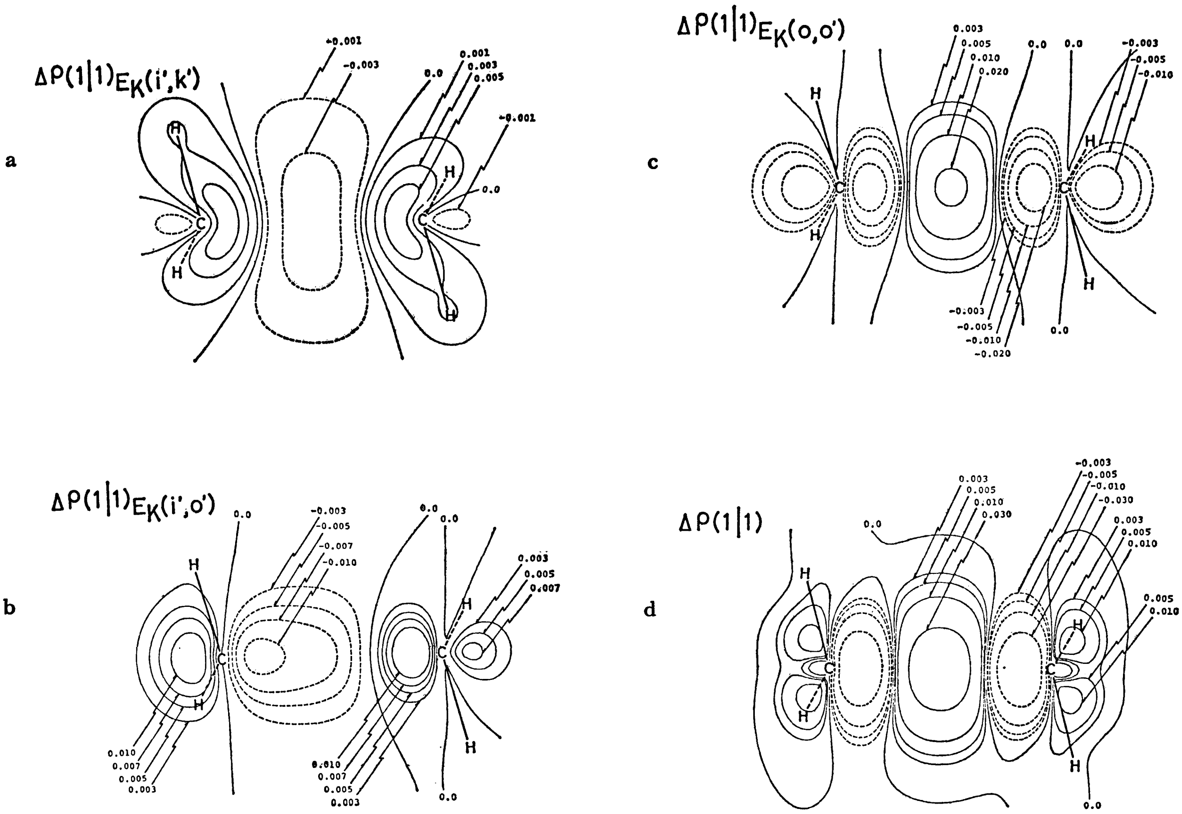


Fig. 5a. The difference density map of $\Delta\rho(1|1)_{E_K(i',k')}$ for the singlet interaction. The value attached to each contour line is in e/Å^3.

5b. The difference density map of $\Delta\rho(1|1)_{E_K(i',o')}$ for the singlet interaction. The map of $\Delta\rho(1|1)_{E_K(o,k')}$ is obtained through the 180° rotation of this figure around the center of C···C line in the cut plane.

5c. The difference density map of $\Delta\rho(1|1)_{E_K(o,o')}$ for the singlet interaction.

5d. The difference density map due to the singlet exchange and charge transfer interactions in Eq. 7.

its reverse $b_{o'}\rightarrow a_o$ CT interactions to pile up the density. The decreased density which sandwiches the central increased density arises, to a great extent, from the exchange interaction, $\Delta\rho(1|1)_{E_K(o,o')}$.

Conclusion

In the present work, a means to investigate the mode of interaction between two radicals has been proposed. The interaction energy, ΔW, has been partitioned into four terms, E_Q, E_K, D, and Π.

As a result of analysis of its four components for the $CH_3\cdots CH_3$ reaction, the ease of the recombination in this neutral system is attributed to the SOMO–SOMO interaction. If the deformation ($D_{3h}\rightarrow C_{3v}$) is added to each methyl radical, the singlet W gains a greater stabilization. The deformation enlarges the a_o-$b_{o'}$ MO interaction and reduces the exchange repulsion between both doubly occupied MO's. The latter effect in particular is remarkable. The rotational barrier between staggered and eclipsed approaches was examined and found to be almost due to the exchange interaction of both doubly occupied MO's.

A density map of the same system has been constructed, in order to examine the role of the four components of E_K. Accumulation of the bonding density in the $\Delta\rho(1|1)_{E_K(o,o')}$ is remarkable, contributing to the new C–C bond formation.

Since the present study is made within the scope of perturbation procedure with the use of semi-empirical MO, each term calculated so far should be regarded as qualitative. The ΔW method employed simplifies the reaction as a static model, the energy obtained thus having hardly anything to do with measurable property. In spite of these handicaps, the present method seems to give an idea of how to interpret and understand the radical-radical reaction in terms of the partitioned energies. Applicability of the orbital picture to this reaction could be successfully demonstrated. We may take up two important types of interaction contributing to the progress of recombination, $E_K(i',k')$ which has a role to deform the monomer radical, and the a_o-$b_{o'}$ MO overlap [$E_K(o,o')$, $D(o\rightarrow o')$, and $D(o'\rightarrow o)$] which operates to make the new C···C bond.

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