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A Molecular Orbital Study of the Electrophilicity of Hydroxyl Radical in Hydrogen Abstraction Reaction

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The electrophilicity of the hydroxyl radical in hydrogen abstraction from methane was studied by the CNDO/2 method. The stabilization energy due to the delocalization of the electrons (SEDE) between methane and the radical at a close distance was calculated. The electrophilicity defined by the SEDE from methane to the hydroxyl radical was larger than the nucleophilicity defined by that from the hydroxyl radical to methane. This result is consistent with the electrophilicity observed in hydrogen abstraction by the hydroxyl radical from a series of substituted methanes. For sulfhydryl radical, the electrophilicity was also suggested by the calculation for hydrogen abstraction from methane. The calculations were also carried out for various radicals which have low electron affinity (hydrogen atom and methyl radical), and the SEDE from methane to the radical was found to be large compared with that from the converse case.

Various kinds of radicals have been shown to react as electrophiles in reactions such as addition, substitution, or abstraction. A typical instance was given by Anbar *et al.*,[1,2] who determined the rate constants for reactions of hydroxyl radical with one series of aromatic and two series of aliphatic compounds (substituted methanes and acetate ions) in gamma-irradiated aqueous solutions. They concluded from the ρ values in the Hammett equation that the hydroxyl radical reacts as an electrophile in these reactions.

Recently, in order to explain the electrophilicity observed in radical reactions, theoretical attempts have been made by some workers. Nagase *et al.*[3] suggested the electrophilicity of a radical in hydrogen abstraction by an intermolecular perturbation approach and proposed a three-stage model which gives an insight into the mechanism of radical reactions.[4,5] Imamura has developed the molecular orbital (MO) method, which defines the polarity of the radical (nucleophilicity or electrophilicity) from the comparison of the stabilization energy due to delocalization of electrons (SEDE) between a substrate and the radical at a close distance.[6] According to this procedure, the nucleophilicity of the radical is evaluated by the SEDE from the occupied MO's of the radical to the vacant MO's of the substrate and the electrophilicity by that from the occupied MO's of the substrate to the vacant MO's of the radical. The electrophilicity of the hydroxyl radical in addition reactions with a series of mono-substituted benzenes was well understood by the differences in the SEDE.[6]

In the present work, as a first step in the investigation of the Hammett equation, we applied the MO method to hydrogen abstractions by the hydroxyl radical, sulfhydryl radical, hydrogen atom, and methyl radical from methane. The SEDE which corresponds to the electrophilicity is larger than that related to the nucleophilicity, and it can be concluded that these radicls react with methane as electrophiles.

Method of Calculation

The total energies for the reacting systems were calculated by the UHF method[7] in the CNDO/2 approximation.[8,9] The values of the parameters included in the CNDO-UHF calculation are the same as those used in the original papers.[8,9]

Procedure of Analysis. For the analysis of the polarity of a radical, a calculation should be carried out to obtain the MO's of substrate RH and radical X in the supposed model, in which they interact electrostatically with each other but are prohibited from any overlapping of MO's between them. Therefore the delocalization of electrons is prohibited in the model. These MO's can be obtained by the SCF calculation after dropping the resonance integrals I_{rs} between the atomic orbitals (AO's) of RH, χ_r, and AO's of X, χ_s, as given by

$$I_{rs} = \frac{1}{2}(\beta_r+\beta_s)S_{rs}. \tag{1}$$

Then the MO's for the reacting system [R$\cdots$H$\cdots$X] are classified into the MO's localized on RH and those localized on X:

$$\phi_{RHi} = \sum_r C_{RHi,r}\chi_r, \tag{2}$$

$$\phi_{Xj} = \sum_s C_{Xj,s}\chi_s. \tag{3}$$

ϕ_{RHi} is the i-th MO localized on RH and $C_{RHi,r}$ is the coefficient of AO's in the i-th MO, and ϕ_{Xj} and $C_{Xj,s}$ are for X. From Eq. 2, one obtains

$$\begin{aligned}\sum_i C_{RHi,r_1}\phi_{RHi} &= \sum_r\sum_i C_{RHi,r_1}C_{RHi,r}\chi_r \\ &= \sum_r \chi_r \sum_i C_{RHi,r_1}C_{RHi,r}.\end{aligned} \tag{4}$$

Since a set of ϕ_{RHi},s is orthonormal,

$$\sum_i C_{RHi,r_1}C_{RHi,r} = \delta_{rr_1}, \tag{5}$$

and thus

$$\chi_r = \sum_i C_{RHi,r}\phi_{RHi}, \tag{6}$$

$$\chi_s = \sum_j C_{Xj,s}\phi_{Xj}. \tag{7}$$

From Eqs. 6 and 7, one obtains the relation between the I_{rs} represented by the AO basis of χ_r, χ_s, and the I_{ij} by the MO basis of ϕ_{RHi}, ϕ_{Xj}:

$$\begin{aligned}I_{rs} = \int\chi_r h^\circ\chi_s \mathrm{d}\tau &= \sum_i\sum_j C_{RHi,r}C_{Xj,s}\int\phi_{RHi}h^\circ\phi_{Xj}\mathrm{d}\tau \\ &= \sum_i\sum_j C_{RHi,r}C_{Xj,s}I_{ij}.\end{aligned} \tag{8}$$

Instead of Eq. 8, the I_{rs} in Eq. 9 is used in the SCF calculation in order to include the delocalization of electrons between particular orbital sets (i_1, j_1):

$$I_{rs} = \sum_{(i_1-j_1)} C_{RHi_1,r} C_{Xj_1,s} I_{i_1j_1}, \qquad (9)$$

where $\sum_{(i_1-j_1)}$ denotes the summation over the sets (i_1, j_1). From Eq. 9, it is easily proved that the I_{ij} reduces to zero except for the $I_{i_1j_1}$ term, which has the same value as that obtained by using Eq. 8.

The procedure of the calculations is written as follows.

(i) The total energy of the reacting system without the delocalization of electrons is calculated by the SCF calculation after dropping the I_{rs} in Eq. 1. Thus we obtain the MO's in Eqs. 2 and 3.

(ii) By using the MO's obtained in the step (i), the modified resonance integrals between AO's are calculated according to Eq. 9 in order to take the delocalization of electrons between particular MO's into account.

(iii) The I_{rs} in Eq. 9 is employed to calculate the total energy of the reacting system with the delocalization of electrons, which corresponds to the nucleophilic or the electrophilic nature of the radical in question.

(iv) A measure of the nucleophilicity of the radical defined by the SEDE from the radical to the substrate, N, or the electrophilicity defined by the SEDE from the substrate to the radical, E, is evaluated by the difference between the two energies obtained in the steps (i) and (iii).

Results

Figure 1 shows a model for hydrogen abstraction by the hydroxyl radical from methane. The hydrogen atom of the hydroxyl radical lies at the opposite direction to the C^1–H^2 bond with regard to the C^1–H^5 bond. We examined the energy dependence of the CH_4–OH system upon the angle H^5OH in the intermolecular distance of 1.46 Å ;the result is given in Table 1. The minimum energy was situated at the angle between 100.45 and 104.45°. Therefore we assumed that the hydroxyl radical approaches to the H^5 atom of methane along the extension of the C^1–H^5 bond, maintaining the angle H^5OH at 104.45° (bond angle of water), and abstracts the H^5 atom.

Figure 2 shows the potential curves of the CH_4–OH system calculated by assuming that the HCH angle of the CH_3 group is not varied throughout the reaction. In this figure, we specify the reaction path with a notation (r_1, r_2), where r_1 is the distance (in Å) between C^1 and H^5 atoms and r_2 is that between H^5 and hydroxyl oxygen atoms in Fig. 1. As the energy of the system increases monotonously, the geometry of the transition state is not obvious. However, it can be assumed that a more favorable reaction path for H^5 atom abstraction goes through the following points: A, B, C, and D, which are specified respectively by the sets of r_1 and r_2 indicated in the parenthesis: A(1.09, 1.46), B(1.20, 1.35), C(1.30, 1.25), D(1.40, 1.15).

TABLE 1. THE ENERGY DEPENDENCE OF CH_4-OH SYSTEM[a] UPON THE ANGLE H^5OH

H^5OH angle (°)	Total energy
96.45	−28.0226
100.45	−28.0229
104.45	−28.0229
108.45	−28.0227
112.45	−28.0226
180.00	−28.0056

a) The calculation was carried out at point A(1.09, 1.46) by the INDO method.[15] Atomic units.

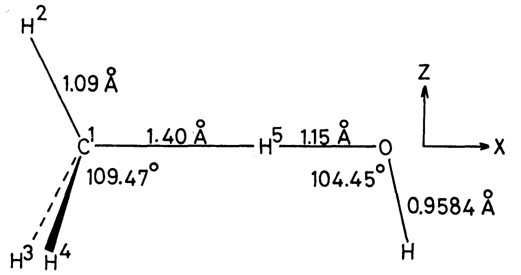


Fig. 1. Coordinate system for hydrogen abstraction by the hydroxyl radical from methane.

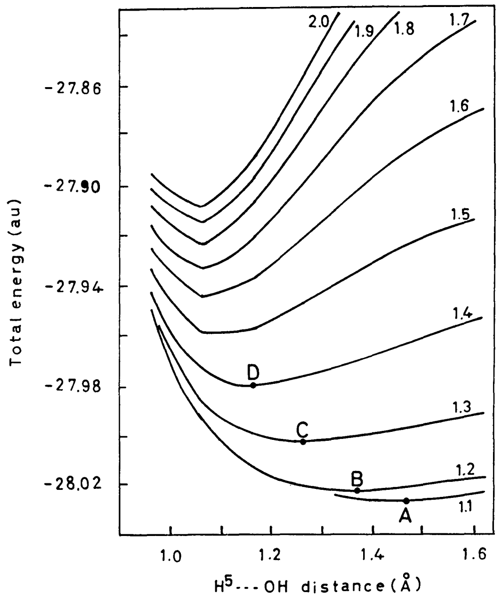
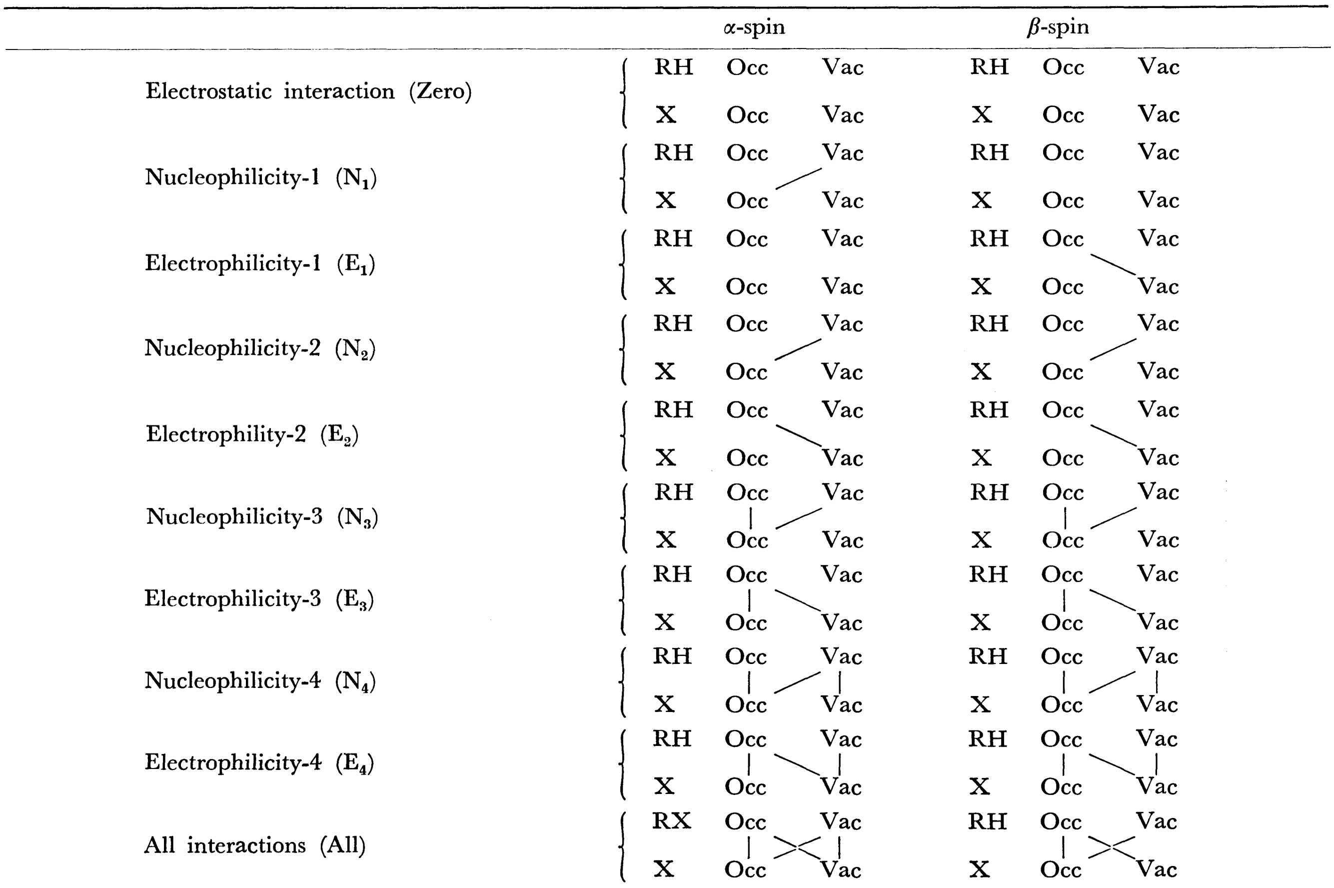


Fig. 2. Potential curves as a function of H^5-O distance at various C^1-H^5 distances in CH_4-OH system. 1.1 and others in figure correspond to C^1-H^5 distances in Å. INDO method.[15]

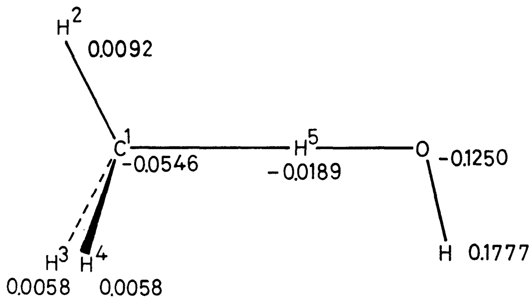
Table 2 shows the schematic representation of the intermolecular interaction between the MO's of RH and X obtained by dropping the I_{rs} in Eq. 1. Here, Occ and Vac represent occupied and vacant MO's respectively; N or E denotes the nucleophilicity or the electrophilicity of the radical defined previously. Among them, N_1, N_2, E_1, and E_2 include the effect of the delocalization of electrons only, while N_3, N_4, E_3, and E_4 include the interaction between occupied MO's in addition to the effect of the delocalization. It can be noticed from the electron distribution shown

Table 2. The schematic representation of the orbital interaction between substrate RH and radical X[a)]

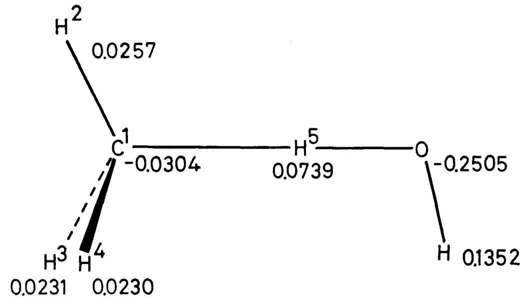


		α-spin			β-spin	
Electrostatic interaction (Zero)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilicity-1 (N_1)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilicity-1 (E_1)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilicity-2 (N_2)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophility-2 (E_2)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilicity-3 (N_3)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilicity-3 (E_3)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilicity-4 (N_4)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilicity-4 (E_4)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
All interactions (All)	RX	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac

a) The symbol for the orbital interaction used in the text is given in the parentheses. The interaction which includes the $I_{i_1j_1}$ is represented by a solid line.



Nucleophilicity-1



Electrophilicity-1

Fig. 3. The electron distribution of CH_4-OH system by the orbital interaction N_1 or E_1 defined in Table 2.

in Fig. 3 that the delocalization of electrons occurs from the hydroxyl radical to methane by the interaction N_1, while that from methane to the hydroxyl radical occurs by the interaction E_1. These results are summarized in Table 3. The ratios of E_1/N_1 are 2.7, 2.1, 1.8, and 1.5 at the points A, B, C, and D, respectively. As is shown in N_3 and E_3, the SEDE including the interaction of occupied MO's is larger than that including the delocalization of electrons only. This energy can be considered to include the redistribution energy as well as the delocalization energy. It should be noticed that the stabilization energy by delocalization is much larger than that by the redistribution effect, although the absolute magnitude of the latter is not negligibly small. Consequently, if we can determine the polarity of a radical from the viewpoint of the SEDE, it will be possible to conclude that the hydroxyl radical reacts as an electrophile in hydrogen abstraction from methane. The HOMO-LUMO interaction plays an important role in E_1 and the electrophilicity of the hydroxyl radical is closely related with this interaction.

As organic sulfur compounds are recognized to have high levels of HOMO and low levels of LUMO, it is interesting to determine the polarity of the sulfhydryl radical. Figure 4 shows a model for hydrogen abstraction by the sulfhydryl radical from methane.

TABLE 3. THE ELECTROPHILICITY OF THE HYDROXYL RADICAL IN HYDROGEN ABSTRACTION FROM METHANE

Path point	Orbital[a)] interaction	Total[b)] energy	Stabilization[b)] energy	ET[c)]
(A)	Zero	−29.0560	0	0
	N_1	−29.0667	0.0107	0.0114
	E_1	−29.0848	0.0288	−0.0423
	All	−29.1062	0.0502	−0.0372
(B)	Zero	−29.0253	0	0
	N_1	−29.0439	0.0186	0.0208
	E_1	−29.0646	0.0393	−0.0610
	All	−29.1031	0.0778	−0.0518
(C)	Zero	−28.9653	0	0
	N_1	−28.9943	0.0290	0.0341
	E_1	−29.0170	0.0517	−0.0845
	All	−29.0836	0.1183	−0.0736
(D)	Zero	−28.8765	0	0
	N_1	−28.9202	0.0437	0.0527
	HOMO-LUMO	−28.8998	0.0233	0.0378
	E_1	−28.9440	0.0675	−0.1253
	HOMO-LUMO	−28.9378	0.0613	−0.1095
	N_2	−28.9422	0.0657	0.0707
	E_2	−28.9445	0·0680	−0.1158
	N_3	−28.9591	0.0826	0.0659
	E_3	−28.9609	0.0844	−0.1561
	N_4	−28.9790	0.1025	0.0913
	E_4	−28.9720	0.0955	−0.1700
	All	−29.0620	0.1855	−0.1028

a) See Table 1. b) Atomic units. c) Electron transfer quantities due to delocalization of electrons. Positive values correspond to those from the radical to substrate and negatives, *vice versa.*

TABLE 4. THE ELECTROPHILICITY OF THE SULFHYDRYL RADICAL IN HYDROGEN ABSTRACTION FROM METHANE

Path point	Orbital[a)] interaction	Total[b)] energy	Stabilization[b)] energy	ET[c)]
(C)	Zero	−21.5850	0	0
	N_1	−21.5857	0.0007	0.0014
	E_1	−21.5871	0.0021	−0.0038
	N_2	−21.5860	0.0010	0.0015
	F_2	−21.5878	0.0028	−0.0048
	All	−21.5883	0.0033	−0.0033
(D)	Zero	−17.2002	0	0
	N_1	−17.2226	0.0224	0.0494
	E_1	−17.4292	0.2297	−0.3095
	N_2	−17.2354	0.0352	0.0673
	E_2	−17.4412	0.2410	−0.3459
	N_3	−17.4284	0.2282	−0.5974
	E_3	−17.6064	0.4062	−0.6706
	N_4	−17.4446	0.2444	−0.5321
	E_4	−17.6315	0.4313	−0.5184
	All	−17.7315	0.5313	−0.6110

a), b), c) See the notes in Table 3.

Figure 5 shows the energy dependence of the CH_4–SH system upon the intermolecular H^5–S distance, with the C^1–H^5 distance fixed at 1.09 Å, while Fig. 6 shows that upon the C^1–H^5 distance with variations of the C^1–S distance. The result of calculations (Table 4) at the points C (1.40, 2.74) and D(1.40, 1.524) in Fig. 6 confirms the electrophilicity of the sulfhydryl radical.

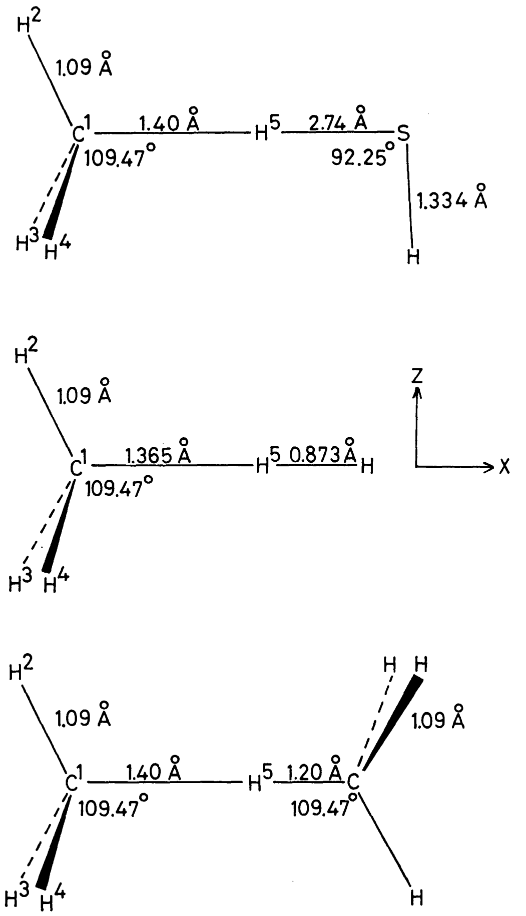


Fig. 4. Coordinate system for hydrogen abstraction by the doublet radical from methane.

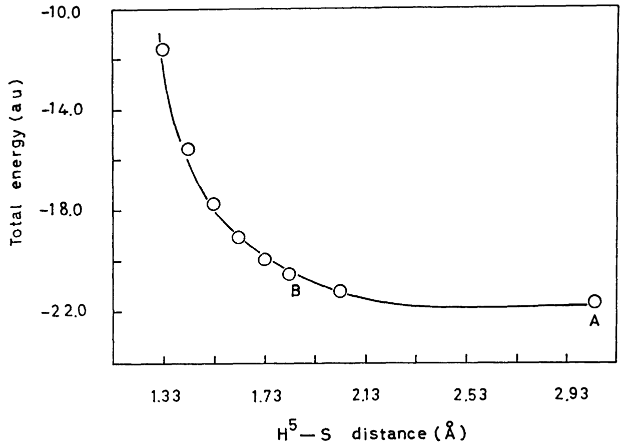


Fig. 5. Potential curve as a function of H^5–S distance in CH_4–SH system.

Calculations were carried out for the radicals of low electron affinities, such as hydrogen atom and methyl radical. For hydrogen atom, the result is given in Table 5. The ratio of E_1/N_1 calculated in the coordinate system (Fig. 4) which corresponds to the transition state deduced from *ab initio* MO method[10)] represents the electrophilicity.

The electrophilicity of the methyl radical was clarified by Fujimoto *et al.*[11)] using the semiempirical MO

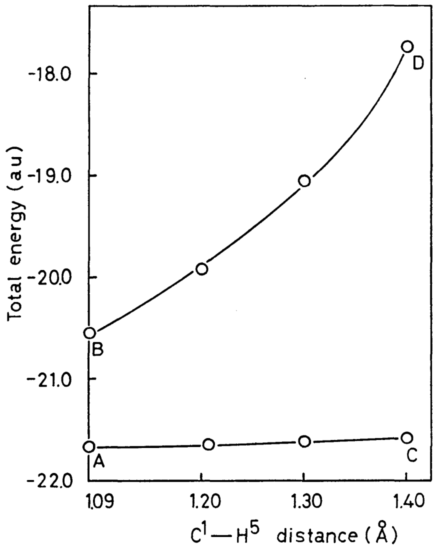


Fig. 6. Potential curves as a function of C^1-H^5 distance, with C^1-S distance varied in CH_4-SH system.

TABLE 5. THE ELECTROPHILICITY OF THE HYDROGEN ATOM IN HYDROGEN ABSTRACTION FROM METHANE

Orbital[a) interaction	Total[b) energy	Stabilization[b) energy	ET[c)
Zero	−10.5959	0	0
N_1	−10.6078	0.0120	0.0249
E_1	−10.6723	0.0765	−0.1338
All	−10.7001	0.1043	−0.0953

a), b), c) See the notes in Table 3.

TABLE 6. THE ELECTROPHILICITY OF THE METHYL RADICAL IN HYDROGEN ABSTRACTION FROM METHANE

Orbital[a) interaction	Total[b) energy	Stabilization[b) energy	ET[c)
Zero	−18.9894	0	0
N_1	−19.0358	0.0464	0.0822
E_1	−19.1336	0.1442	−0.2029
N_2	−19.0455	0.0561	0.0895
E_2	−19.1342	0.1448	−0.2036
N_3	−19.0758	0.0864	0.1836
E_3	−19.1438	0.1544	−0.2212
N_4	−19.0769	0.0875	0.1812
E_4	−19.1624	0.1730	−0.1980
All	−19.2782	0.2888	−0.0263

a), b), c) See the notes in Table 3.

method including overlap integrals; it is also confirmed by our analysis (Table 6), which was carried out in the strong interaction region, as is shown in Fig. 4.

Discussion

As the present analysis is based on the zero differential overlap approximation, the quantitative evaluation of the polarity of a radical is hardly possible because of the crudeness of the calculation. The aim of this work is to discuss qualitatively the polarity of a radical from the viewpoint of the SEDE between a substrate and a radical. Despite these inaccuracies, we believe that the results obtained here may still be useful as a working tool for understanding radical reactions. It is concluded that not only the hydroxyl radical but also the hydrogen atom or the methyl radical reacts as an electrophile in hydrogen abstraction from methane, in spite of its low electron affinity. The polarity of a radical is derived properly from the rate constants for reactions with a series of substrates. However, it is essentially dependent on the substrate, and thus a relative property given to individual reactions. The direction of the delocalization of electrons in an individual reaction may not necessarily accord with the electrophilicity defined by the ρ value.

Sakurai *et al.*[12) reported the linear relationship of the electron affinities of the radicals and the negative ρ values for hydrogen abstractions by various radicals from substituted toluenes. The electrophilicity defined in the present work is related to the electron affinity of the radical; therefore, the negative ρ values may be expected to correlate with the SEDE from a substrate to the radical calculated for individual reactions. Isopropyl and *t*-butyl radicals have recently been found to react as nucleophiles in hydrogen abstractions from substituted toluenes by Pryor *et al.*[13) The positive ρ value increases with a decrease in the ionization potential (*IP*) of the radical (i-C_3H_7: $\rho=0.8$, $IP=7.90$ eV, t-C_4H_9: $\rho=1.0$, $IP=7.07$ eV[14)). As the nucleophilicity defined in the present work is related with the ionization potential of the radical, SEDE from the radical to a substrate will provide a way to explain the reactions of positive ρ values. Further calculations of the SEDE are in progress for hydrogen abstractions by various kinds of radicals.

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