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Polarity of Free Radicals in Hydrogen Abstraction Reactions

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The electrophilicity of the CF_3 radical in hydrogen abstraction reactions was studied theoretically by the CNDO/2 method. The activation energy for hydrogen abstraction by the CF_3 radical from aliphatic hydrocarbons decreases with an increase in the electron density on the hydrogen atom to be abstracted. The origin of the electrophilicity of the CF_3 radical can be well understood by the stabilization energy due to delocalization of electrons (SEDE) between the radical and substrate. The electrophilic stabilization energy defined by the SEDE from substrate to the radical governs the relative reactivities of aliphatic hydrocarbons, $CH_4 < CH_3CH_3 < CH_3CH_2CH_3 < (CH_3)_3CH$, which corresponds to the order of the increase in the electron density. The results indicate that the radical is an electrophile if the relative reactivities of substrates are governed by the electrophilic stabilization energy, and a nucleophile when the reactivities are governed by the nucleophilic stabilization energy (the SEDE from the radical to substrate). SEDE was calculated for the reactions of the OH and the CH_3 radicals with CH_4 and CH_3CN; the results indicated that the OH radical is electrophilic and the CH_3 radical nucleophilic. These polarities of radical reagents are discussed in connection with their physicochemical properties such as ionization potentials and electron affinities.

The reactions of free radicals often show substituent effects[1–5] which resemble those of ionic reactions. A number of radical reactions can be correlated with the Hammett or Taft equation[1,2,5,6] and the polarity of a radical (nucleophilicity or electrophilicity) has been investigated. In rationalizing the observed trends, the polar effects concept[1,2,7] (substituent effect on the transition state) has been widely accepted for a hydrogen abstraction reaction (Eq. 1), which can be described by the three resonance structures shown in Eq. 2[8] (RH: hydrogen donor, X: radical):

$$\mathrm{RH} + \mathrm{X} \longrightarrow \mathrm{R} + \mathrm{HX}, \tag{1}$$

$$[\underset{1}{\mathrm{R}\cdot\dot{\mathrm{H}}\cdot\mathrm{X}} \longleftrightarrow \underset{2}{\mathrm{R}\overset{-}{:}\dot{\mathrm{H}}\,{}^{+}\mathrm{X}} \longleftrightarrow \underset{3}{\mathrm{R}^{+}\dot{\mathrm{H}}\overset{-}{:}\mathrm{X}}] \tag{2}$$

According to Pryor *et al.*,[8] if R^+ is more stable than X^+ and X^- is more stable than R^-, then the structure 3 makes a more important contribution to the stability of the transition state than does the structure 2 and the electrophilicity would be expected. The negative ρ values were obtained for reactions of hydrogen abstractions with substituted toluenes by the radicals that were thought to be electrophilic, such as CH_3, C_6H_5, Br, and Cl, and this result has supported the polar effects concept. Moreover, Sakurai *et al.*[9] reported a linear relationship of negative ρ values for CH_3, C_6H_5, *t*-BuO, and Cl (for these radicals, HX bonds formed in Eq. 1 have nearly equal bond dissociation energies) and the electron affinities of the radicals. This evidence supports the importance of the structure 3 in the transition state. In connection with the polarity of a radical, however, quantitative investigation of structures 2 or 3 has not yet been made. Imamura has recently developed a molecular orbital (MO) method[10] which determines the polarity of a radical on the basis of the stabilization energy due to delocalization of electrons (SEDE) between a substrate and a radical. This method was applied to the reaction of OH and H radicals with benzene derivatives, and OH and H radicals were found to behave as electrophiles, in good correspondence with the experimental facts.[10] Moreover, the polarities of various radical reagents in the reaction of hydrogen and chlorine abstractions were studied by using SEDE; the interesting conclusion was reached that a radical reagent with an electrophilic nature changes its SEDE for the electrophilicity from substrate to substrate remarkably, while a radical reagent with a nucleophilic nature changes its SEDE for the nucleophilicity. That is, the electrophilicity or the nucleophilicity can be determined not by the absolute value of SEDE but by the change in SEDE from substrate to substrate.[11,12]

In the present work, along the above-mentioned line, we calculated the SEDE in hydrogen abstraction by CF_3 radical from aliphatic hydrocarbons by the MO method and attempted to clarify the factors determining the polarity of the radical. This radical is interesting from a theoretical point of view since the fluorine atoms have large electronegativity, leading to the strong electrophilicity of the radical reagent. The calculations of SEDE correspond to the evaluation of the contribution of the structure 2′ or 3′ to the stabilization of the reacting system. That is, the structure 2′ or 3′ correlates with the nucleophilicity or the electrophilicity of the radical.

$$[\underset{2'}{\overset{\delta-}{\mathrm{R}\cdots}\mathrm{H}\cdots\overset{\delta+}{\mathrm{X}}} \longleftrightarrow \underset{3'}{\overset{\delta+}{\mathrm{R}\cdots}\mathrm{H}\cdots\overset{\delta-}{\mathrm{X}}}] \tag{2'}$$

If the relative reactivities of RH are governed by the SEDE corresponding to the structure 3′, the radical is an electrophiles; it is a nucleophile when the reactivities are governed by the SEDE corresponding to the structure 2′.

Method of Calculation

The total energies for the reacting system were calculated by the UHF method[13] in the CNDO/2 approximation.[14,15] The values of the parameters included in the method are the same as those used in the original papers.[14,15]

Geometries used for calculation are as follows: for CH_4,[16] $r(C\text{–}H)=1.09$ Å; for CH_3CN,[17] $r(C\text{–}H)=1.107$, $r(C\text{–}C)=1.468$, and $r(C\text{–}N)=1.159$ Å; for CH_3CH_3, $CH_3CH_2CH_3$, and $(CH_3)_3CH$, $r(C\text{–}H)=1.09$ and $r(C\text{–}C)=1.54$ Å. The bond angle HCH for these compounds is assumed to be 109.47°.

Procedure of Analysis. The magnitude of the contribution of 2 in Eq. 2 to the reacting system is evaluated by the SEDE from a radical to substrate. This energy is a measure for the nucleophilic character of the radical, so it is defined as the nucleophilic stabilization energy. Similarly, the contribution of 3 in Eq. 2 is evaluated by the electrophilic stabilization energy (the SEDE from substrate to the radical). Here, we may mention the method of calculating the SEDE in connection with hydrogen abstraction:

$$\mathrm{R}{\uparrow}{\downarrow}\mathrm{H} + {\uparrow}\mathrm{X} \longrightarrow [\mathrm{R}\cdots{\uparrow}{\downarrow}\cdots\mathrm{H}\cdots{\uparrow}\mathrm{X}] \longrightarrow \mathrm{R}{\uparrow} + \mathrm{HX},$$

where RH and X denote a substrate (hydrogen donor) and a radical, respectively. The SEDE (ΔE) is defined by Eq. 3;

$$\Delta E = E(\mathrm{R}\cdots{\uparrow}{\downarrow}\cdots\mathrm{H}\quad{\uparrow}\mathrm{X}) - E(\mathrm{R}\cdots{\uparrow}{\downarrow}\cdots\mathrm{H}\cdots{\uparrow}\mathrm{X}), \tag{3}$$

where the first term on the right in Eq. 3 denotes the energy of the reacting system in which the delocalization of electrons between RH and X is forbidden (absence of the dotted line between H and X). The second term includes the delocalization of electrons. The first term is obtained by the SCF calculation after dropping the resonance integrals I_{rs} between atomic orbitals (AO's) of RH, χ_r, and AO's of X, χ_s, given by Eq. 4:

$$I_{rs} = \frac{1}{2}(\beta_r+\beta_s)S_{rs}, \tag{4}$$

β denotes the bonding parameter in the CNDO/2 method.[11,13] The MO's of the reacting system (R···H···X) thus obtained are classified into the MO's localized on R···H and the ones localized on X in Eqs. 5 and 6, respectively:

$$\psi_{\mathrm{RH}i} = \sum_{r} C_{\mathrm{RH}i,r}\chi_r, \tag{5}$$

$$\psi_{\mathrm{X}j} = \sum_{s} C_{\mathrm{X}j,s}\chi_s, \tag{6}$$

$\psi_{\mathrm{RH}i}$ is the i-th MO localized on R···H and $C_{\mathrm{RH}i,r}$ is the coefficient of AO in the i-th MO, and $\psi_{\mathrm{X}j}$ and $C_{\mathrm{X}j}$'s are for the radical X.

From Eq. 5, one obtains

$$\sum_{i}^{\text{all}} C_{\mathrm{RH}i,r_1}\psi_{\mathrm{RH}i} = \sum_{r}\sum_{i}^{\text{all}} C_{\mathrm{RH}i,r_1}C_{\mathrm{RH}i,r}\chi_r$$
$$= \sum_{r}\chi_r \sum_{i}^{\text{all}} C_{\mathrm{RH}i,r_1}C_{\mathrm{RH}i,r}. \tag{7}$$

Since a set of $\psi_{\mathrm{RH}i}$'s is orthonormal,

$$\sum_{i}^{\text{all}} C_{\mathrm{RH}i,r_1}C_{\mathrm{RH}i,r} = \delta_{rr_1}. \tag{8}$$

Namely

$$\chi_r = \sum_{i}^{\text{all}} C_{\mathrm{RH}i,r}\psi_{\mathrm{RH}i}, \tag{9}$$

$$\chi_s = \sum_{j}^{\text{all}} C_{\mathrm{X}j,s}\psi_{\mathrm{X}j}. \tag{10}$$

From Eqs. 9 and 10, one obtains the relation between the I_{rs} represented by the AO basis (χ_r, χ_s) and the I_{ij} by the MO basis ($\psi_{\mathrm{RH}i}$, $\psi_{\mathrm{X}j}$):

$$I_{rs} = \int \chi_r h^{\circ}\chi_s \mathrm{d}\tau = \sum_{i}^{\text{all}}\sum_{j}^{\text{all}} C_{\mathrm{RH}i,r}C_{\mathrm{X}j,s}\int \psi_{\mathrm{RH}i}h^{\circ}\psi_{\mathrm{X}j}\mathrm{d}\tau$$
$$= \sum_{i}^{\text{all}}\sum_{j}^{\text{all}} C_{\mathrm{RH}i,r}C_{\mathrm{X}j,s}I_{ij}. \tag{11}$$

Instead of Eq. 11, the modified resonance integrals between AO's. I'_{rs} in Eq. 12 are used in the SCF calculation in order to include the delocalization of electrons between a particular orbital set (i_1, j_1).

$$I'_{rs} = \sum_{(i_1-j_1)} C_{\mathrm{RH}i_1,r}C_{\mathrm{X}j_1,s}I_{i_1j_1}, \tag{12}$$

where $(\Sigma_{i_1-j_1})$ denotes the summation over the set. From Eq. 12, it is easily proved that the modified resonance integrals between MO's, I'_{ij}, reduces to zero except for the $I_{i_1j_1}$, which has the same value as that obtained by using Eq. 11 (I_{ij}). The proof is as follows.

$$I'_{ij} = \sum_{r}\sum_{s} C_{\mathrm{RH}i,r}C_{\mathrm{X}j,s}I'_{rs}$$
$$= \sum_{r}\sum_{s} C_{\mathrm{RH}i,r}C_{\mathrm{X}j,s}\sum_{(i_1-j_1)} C_{\mathrm{RH}i_1,r}C_{\mathrm{X}j_1,s}I_{i_1j_1}$$
$$= \sum_{(i_1-j_1)} I_{i_1j_1}\sum_{r} C_{\mathrm{RH}i,r}C_{\mathrm{RH}i_1,r}\sum_{s} C_{\mathrm{X}j,s}C_{\mathrm{X}j_1,s}$$
$$= \sum_{(i_1-j_1)} I_{i_1j_1}\delta_{ii_1}\delta_{jj_1}. \tag{13}$$

The procedure of the calculation is written as follows. (i) The total energy of the reacting system without the delocalization of electrons is calculated with the unrestricted SCF method in the CNDO/2 approximation after dropping all the resonance integrals between AO's on the fragment RH and those on the fragment X. Thus we obtain the value for the first term in Eq. 3, as well as the MO's localized on the fragments given by Eqs. 5 and 6. (ii) By using the MO's obtained in step (i), the modified resonances integrals between AO's are calculated according to Eq. 12 in order to take the delocalization of electrons between particular MO's into account. (iii) The modified resonance integrals are 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 reagent in question. (iv) A measure of the nucleophilicity or the electrophilicity of the radical reagent can be obtained by calculating the difference between the two energies obtained in the steps (i) and (iii), as is shown in Eq. 3.

When the vacant MO's of the substrate and the

TABLE 1. THE SCHEMATIC REPRESENTATION OF THE ORBITAL INTERACTION BETWEEN SUBSTRATE RH AND RADICAL X[a)]

Interaction		α-spin			β-spin	
Electrostatic (Zero)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilic (N)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilic (E)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac

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

occupied MO's of the radical are chosen for i_1 and j_1, respectively, in Eq. 12, ΔE in Eq. 3 corresponds to the SEDE from radical to substrate. Thus, ΔE should be the nucleophilic stabilization energy; it is represented by the symbol N. When the occupied MO's of the substrate and the vacant MO's of the radical are chosen for i_1 and j_1, respectively, ΔE is the electrophilic stabilization energy; it is represented by the symbol E. Table 1 shows the schematic representation of intermolecular interaction between the MO's of RH and X obtained by dropping the resonance integrals I_{rs} (they interact electrostatically with each other but the delocalization of electrons is prohibited).

Results and Discussion

The coordinate system assumed for a hydrogen abstraction reaction by the CF_3 radical from aliphatic hydrocarbons is shown in Fig. 1. In a previous paper,[11] we examined the reaction path of the CH_4–OH system by the INDO method, and the geometry in Fig. 1 might be roughly approximated as the transition state. Moreover, the electrophilicity of the OH radical in the reaction with methane deduced from the SEDE was not dependent on the reaction paths: A(1.09, 1.46), B(1.20, 1.35), C(1.30, 1.25), D(1.40, 1.15) which are specified respectively by the sets of C^1–H^5 and H^5–O distances indicated in the parenthesis. For the OH and the CH_3 radicals, therefore, we used the same geometries as in the previous paper to determine the polarity in the reaction with a series of substrates. Although the geometry in Fig. 1 is tentatively chosen for the reaction of the CF_3 radical, we believe that the result need not be revised when the geometry is changed slightly.

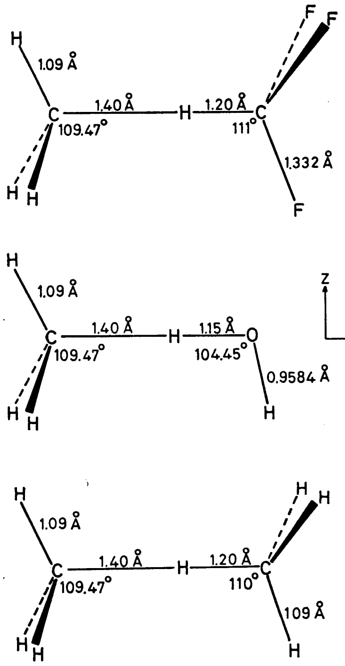

Fig. 1. The coordinate system assumed for hydrogen abstraction by the CF_3 radical from methane.

We may assume here without loss of generality that the CF_3 radical has thirteen valence electrons with α-spin and twelve valence electrons with β-spin. It is noticed from the electron distribution shown in Fig. 2 that the delocalization of electrons occurs from the CF_3 radical to methane by the orbital interaction N, while it occurs from methane to the CF_3 radical by the interaction E. Thus the stabilization energy defined by N or E corresponds to the direction of the delocalization of electrons occurring between a substrate and a radical. The structure 2′ or 3′ in Eq. 2′ is considered to correspond to N or E. Figure 3a shows the correlation of the activation energy[18] and the electron density on the hydrogen atom. The activation energy decreases with an increase in the electron density. The origin of the electrophilicity of the CF_3 radical can be understood by N and E, as summarized in Table 2. E increases with the increasing

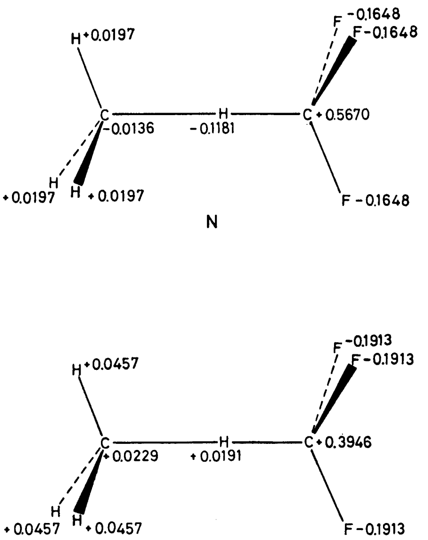

Fig. 2. The electron distribution of CH_4–CF_3 system by the orbital interaction corresponding to the nucleophilic (N) and the electrophilic (E) stabilization energy.

TABLE 2. THE ELECTROPHILICITY OF THE CF_3 RADICAL IN HYDROGEN ABSTRACTION WITH ALIPHATIC HYDROCARBONS

Substrates	Orbital interaction[a]	Total energy[b]	SEDE[b]	ET[c]
	Zero	−100.0340	0	0
CH_4(11.3)[d]	N	−100.0845	0.0505	0.0726
	E	−100.1534	0.1194	−0.1793
CH_3CH_3 (7.5)	Zero	−108.7335	0	0
	N	−108.7827	0.0492	0.0711
	E	−108.8568	0.1233	−0.1927
$CH_3CH_2CH_3$(5.1)	Zero	−117.4275	0	0
	N	−117.4758	0.0483	0.0708
	E	−117.5540	0.1265	−0.2035
$(CH_3)_3CH$(3.6)	Zero	−126.1176	0	0
	N	−126.1652	0.0476	0.0702
	E	−126.2469	0.1293	−0.2141

a) See the notes in 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*. d) Activation energy (kcal/mol).[18]

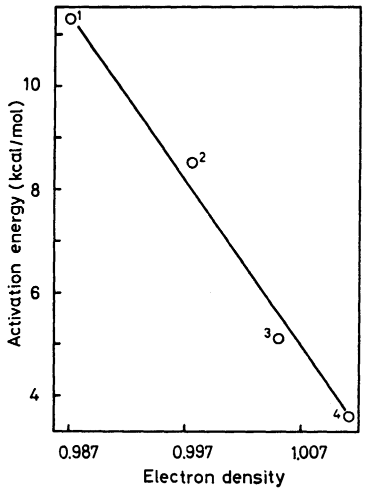

Fig. 3a. The correlation of the activation energy and the electron density for hydrogen abstraction by the CF_3 radical from aliphatic hydrocarbons. 1: CH_4, 2: CH_3CH_3, 3: $CH_3CH_2CH_3$, 4: $(CH_3)_3CH$.

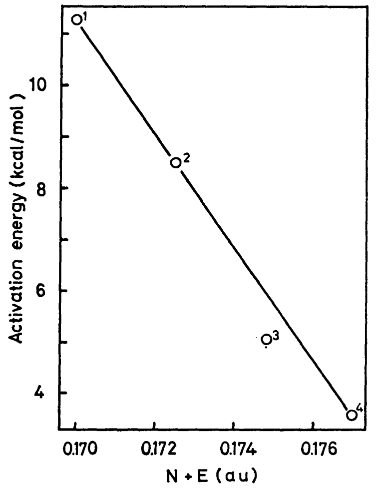

Fig. 3b. The correlation of the activation energy and the sum of the nucleophilic and the electrophilic stabilization energy ($N+E$). 1—4, see the caption in Fig. 3a.

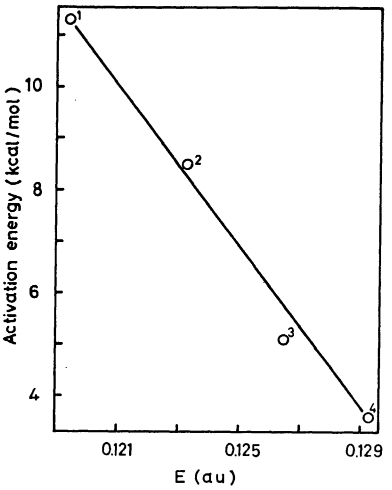

Fig. 3c. The correlation of the activation energy and the electrophilic stabilization energy E. 1—4, see the caption in Fig. 3a.

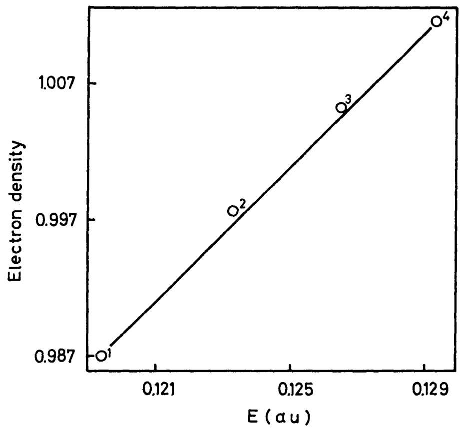

Fig. 3d. The correlation of the electron density and the electrophilic stabilization energy E. 1—4, see the caption in Fig. 3a.

number of electron-donating CH_3 groups, while N decreases. The reactivities of aliphatic hydrocarbons correlate linearly with the sum of N and E, as is shown in Fig. 3b. It should be pointed out that both N and E contribute in determining the reactivity, but the increase of E from molecule to molecule is much larger than the decrease of N. Hence E governs the relative reactivities, as is shown in Fig. 3c. The electrophilicity of the CF_3 radical suggested by the electron density is ascribable to the correlation of the electron density and E shown in Fig. 3d. The electrophilic stabilization energy is closely related with the electron affinity of a radical. Therefore the linear relationship of the negative ρ values and the electron affinities of the radical[9] supports the present conclusion that the radical is an electrophile if the relative reactivities of the substrates are governed by E.

For the study of factors which determine the polarity of radical reagents, the polarities of the OH and CH_3 radicals were subjected to the analysis by the above-mentioned procedure for the reaction with CH_4 and CH_3CN. Fig. 4 shows the difference in the polarity

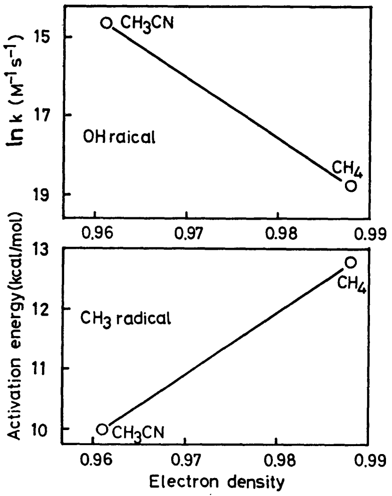

Fig. 4. The difference in the polarity between the OH and the CH_3 radicals.

Table 3. The difference in the polarity between the OH and the CH_3 radicals

	Substrates	Orbital interaction[a)]	Total energy[b)]	SEDE[b)]	ET[c)]
OH radical	$CH_3CN(0.0212)$[d)]	Zero	−46.6568	0	0
		N	−46.7480	0.0912	0.1067
		E	−46.6616	0.0048	−0.0093
	$CH_4(1.43)$[d)]	Zero	−28.8765	0	0
		N	−28.9422	0.0657	0.0527
		E	−28.9445	0.1180	−0.1253
CH_3 radical	$CH_3CN(10.0)$[e)]	Zero	−36.7689	0	0
		N	−36.8312	0.0623	0.1038
		E	−36.9112	0.1423	−0.2029
	CH_4 (12.8)[e)]	Zero	−18.9882	0	0
		N	−19.0441	0.0559	0.0892
		E	−19.1339	0.1457	−0.2048

a), b), c) See the notes in Table 2. d) Rate constant (10^8 M^{-1} s^{-1}).[6e)] e) Activation energy (kcal/mol).[19)]

between the OH and the CH_3 radicals in hydrogen abstraction.[19)] Although only two points are available, a distinct tendency is observed: the OH is electrophilic while the CH_3 radical is nucleophilic. This result is in good agreement with our previous studies on the polarity of the OH and the CH_3 radicals in the reaction with methane and a series of chloromethanes, respectively.[12)] It is evident that the correlation in Fig. 4 is not explained by the bond dissociation energy of the C–H bond broken, D_{C-H}, only (D_{C-H} in CH_3CN: 86 kcal/mol,[9)] CH_4: 104 kcal/mol[20)]) but by the significant contribution of the polar effects. As Table 3 shows, the relative reactivities are interpreted by the sum of *N* and *E*. For the OH radical, the increase of *E* is larger than the decrease of *N* when the substrate changes from CH_3CN to CH_4, so that *E* governs the reactivities. This tendency is consistent with that of the CF_3 radical. The electrophilicity of the OH radical determined by the SEDE is in agreement with the one reported by Anbar *et al.*[6e)] on the basis of the Hammett equation. For the CH_3 radical, on the other hand, the increase of *E* is smaller than the decrease of *N*, hence *N* governs the reactivities. As the difference of the ionization potential between the

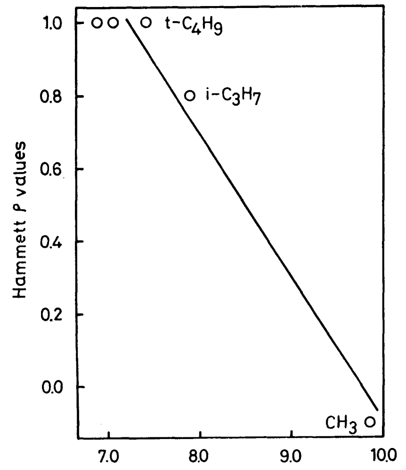

Fig. 5. The correlation of the Hammett ρ values and the ionization potentials of alkyl radicals.

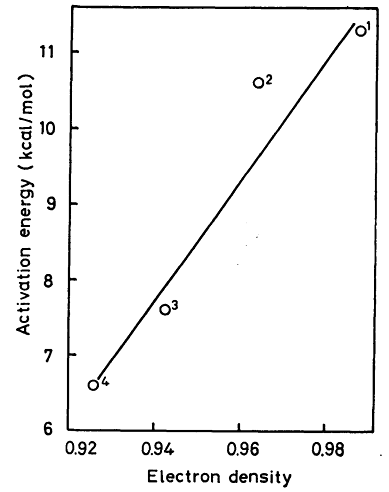

Fig. 6a. The correlation of the activation energy and the electron density for hydrogen abstraction by the CF_3 radical from chloromethane. 1: CH_4, 2: CH_3Cl, 3: CH_2Cl_2, 4: $CHCl_3$.

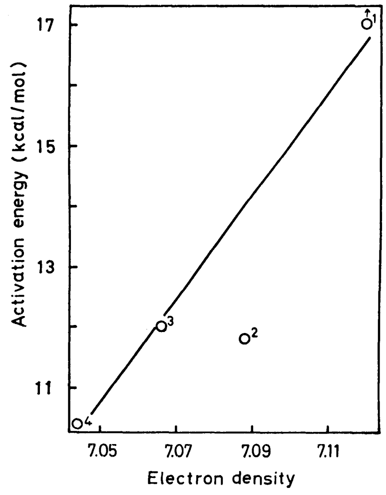

Fig. 6b. The correlation of the activation energy and the electron density for chlorine abstraction by the CF_3 radical from chloromethanes. 1: CH_3Cl, 2: CH_2Cl_2, 3: $CHCl_3$, 4: CCl_4.

OH and the CH_3 radicals (OH: 13.18,[21] CH_3: 9.86 eV[21]) is larger than that of the electron affinity[22] (OH: 1.83, CH_3: 1.4 eV), the former seems to play a dominant role in determining the polarity of the radical. The nucleophilicity of the CH_3 radical is based on its low ionization potential. In fact, i-C_3H_7 and t-C_4H_9 radicals having low potentials[21] (i-C_3H_7: 7.90, t-C_4H_9: 6.90, 7.07, 7.42 eV) have recently been found by Pryor *et al.*[8c] to react as nucleophiles in hydrogen abstractions from substituted toluenes. As Fig. 5 shows, the positive ρ value increases with a decrease in the ionization potential of a radical. This supports the conclusion that the radical is a nucleophile if the relative reactivities of the substrates are governed by N.

According to Pryor *et al.*, the CH_3 radical is slightly electrophilic in hydrogen abstraction with substituted toluenes ($\rho = -0.1$[23]), while it abstracts electron deficient α hydrogen 7.8-fold faster than β hydrogen in the reaction with propionic acid.[24] Similarly, the CF_3 radical is nucleophilic in hydrogen abstraction or chlorine abstraction with chloromethanes, as is shown in Figs. 6a and 6b.[25] The electron affinity of the CF_3 radical is nearly equal to that of the electrophilic OH radical (CF_3: 1.85, OH: 1.83 eV),[22] while its ionization potential (10.18, 8.90 eV)[21] is lower than that of the OH radical (13.18 eV[19]) and approximately the same as that of the CH_3 radical (9.86 eV).[21] This may account for the two different behaviors of the CF_3 radical in the polarity. These results show that the polarity of a radical seems to be primarily determined by its physicochemical properties (ionization potential or electron affinity), but also to depend on the nature of the substrate.

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