October, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (10), 2801—2807 (1979) 2801

A Molecular Orbital Study on the Nucleophilicity and the Electrophilicity of Free Radicals in Abstraction Reactions

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(Received February 14, 1979)

The polarities (nucleophilicity and electrophilicity) of free radicals in abstraction reactions were studied by the comparison of the stabilization energies due to delocalization of electrons (SEDE) between a radical and a substrate. The stabilization energies were calculated by the CNDO/2 method for several substrate–radical systems. For the reactions of the methyl radical with chlorinated methanes, the nucleophilicity of the radical was well interpreted by the SEDE from the radical to the substrate. Similarly, the nucleophilicity of the hydrogen atom in chlorine abstraction from chlorinated methanes was indicated by the SEDE from the hydrogen atom to the substrate. In an electrophilic reaction such as hydrogen abstraction by the methyl radical from aliphatic hydrocarbons, the activation energy was found to decrease linearly with an increase in the SEDE from the substrate to the radical. This result is consistent with the electrophilic tendency of the reaction. The SEDE calculated for the reactions of a radical with a series of substrate thus indicates the polarity of the free radical in the abstraction reactions.

The polarity of a free radical has been an interesting subject in organic chemistry ever since a number of observations were published on the polar effect in radical reactions.1) The Hammett and the Taft equations allow the quantitative study of polar effects in radical reactions as well as ionic reactions. On the basis of ρ values, various kinds of radicals have been found to react as electrophiles in abstraction reactions,1–8) while a few radicals undergo the nucleophilic reactions.9–16) The argument about the polarity of the radical, however, was generally empirical and no successful theoretical elucidation of the factors determining the polarity has been given.

The theory of chemical reactivity has succeeded in explaining the relative reactivity of the substrate toward a given radical. The Evans-Polanyi relationship17) and the delocalizability18) in the frontier electron theory developed by Fukui and his coworkers are typical theories. In the Evans-Polanyi relationship, the resonance stabilization energy of the formed radical is an important factor in determining the reactivity. On the other hand, the delocalizability is a measure of the stabilization energy due to delocalization of electrons (SEDE) between a substrate and a radical, and is recognized as an excellent reactivity index. Imamura has recently developed a molecular orbital (MO) method which evaluates semiempirically the SEDE from a substrate to a radical or *vice versa*.19)

In the present work, an attempt was made to explain the polarity of free radicals in terms of the SEDE, which was calculated by the CNDO/2 method for the substrate–radical system. In the nucleophilic reactions, such as hydrogen abstraction by the methyl radical from chlorinated methanes20) and chlorine abstraction by the hydrogen atom from chlorinated methanes,21) the SEDE from the radical to the substrate was found to correlate linearly with the activation energy. The SEDE from the substrate to the radical also correlates with the activation energy in electrophilic reactions such as the hydrogen abstraction by the methyl radical from aliphatic hydrocarbons.21) For several kinds of radicals, the polarity in abstraction reactions is discussed on the basis of both the SEDE and their physical properties.

Method of Calculation

The total energies for the isolated molecule as well as the reacting system were calculated by the UHF method22) in the CNDO/2 approximation.23,24) The values of the parameters included in the method are the same as those used in the original papers.23,24)

Geometries. Geometries used for the calculation are as follows: for CH_4,25) r(C–H) = 1.09 Å; for CH_3Cl,26) r(C–H) = 1.103 Å and r(C–Cl) = 1.782 Å; for CH_2Cl_2,27) r(C–H) = 1.082 Å and r(C–Cl) = 1.772 Å; for $CHCl_3$,27) r(C–H) = 1.10 Å and r(C–Cl) = 1.758 Å; for CCl_4,27) r(C–Cl) = 1.755 Å; for aliphatic hydrocarbons, r(C–H) = 1.09 Å and r(C–C) = 1.54 Å. The bond angles for chlorinated methanes and aliphatic hydrocarbons are assumed to be the same as that of methane (109.47°).

Stabilization Energy Analysis. To calculate the SEDE, it was assumed that in a hydrogen abstraction by a radical from a substrate the reaction proceeds through the following steps:

$$\mathrm{RH} + \mathrm{X} \longrightarrow [\mathrm{R}\cdots\mathrm{H}\cdots\mathrm{X}] \longrightarrow \mathrm{R} + \mathrm{HX}$$

where RH and X denote a substrate (hydrogen donor) and a radical, respectively. The SEDE (ΔE) is defined by Eq. 1

$$\Delta E = E(\mathrm{R}\cdots\mathrm{H}\quad\mathrm{X}) - E(\mathrm{R}\cdots\mathrm{H}\cdots\mathrm{X}) \tag{1}$$

where the first term on the right hand side in Eq. 1 denotes the energy of the reacting system in which the delocalization of electrons between RH and X is forbidden. The second term includes the delocalization of electrons. The SEDE is calculated as follows. (i) The total energy of the reacting system [R⋯H⋯X] without delocalization of electrons is calculated with the UHF method in the CNDO/2 approximation after dropping all the resonance integrals (I_{rs}) between atomic orbitals (AO's) on the fragment RH and those on the fragment X. Thus we obtain the MO's localized on the fragments RH and X. (ii) By using the MO's obtained in step (i), the modified resonance integrals between AO's (I'_{rs}) are calculated according to Eq. 2

in order to take the delocalization of electrons between particular MO's into account:

$$I'_{rs}=\sum_{(i_1-j_1)} C_{RHi_1,r}C_{Xj_1,s}I_{i_1j_1}, \tag{2}$$

where $C_{RHi_1,r}$ is the coefficient of AO in the i_1-th MO of substrate RH and $C_{Xj_1,r}$ is for radical X. $\sum_{(i_1-j_1)}$ denotes the summation over a particular orbital set (i_1-j_1). (iii) I'_{rs} 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) When the vacant MO's of the substrate and the occupied MO's of the radical are chosen for i_1 and j_1, respectively, in Eq. 2, the difference between the two energies obtained in steps (i) and (iii) corresponds to the SEDE from radical to substrate. This energy 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, the electrophilic stabilization energy E is obtained. Table 1 shows the schematic representation of intermolecular interaction between the MO's of RH and X obtained by dropping the I_{rs} (they interact electrostatically with each other, but the delocalization of electrons is prohibited).

TABLE 1. THE SCHEMATIC REPRESENTATION OF THE ORBITAL INTERACTIONS 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-1 ($1N$)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilic-1 ($1E$)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Nucleophilic-2 ($2N$)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
Electrophilic-2 ($2E$)	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac
All	RH	Occ	Vac	RH	Occ	Vac
	X	Occ	Vac	X	Occ	Vac

a) The symbols for the orbital interactions used in the text are given in the parentheses. An interaction including the $I_{i_1j_1}$ is represented by a solid line.

Results

A. Hydrogen Abstraction Reaction by the Methyl Radical. A-1: The Nucleophilicity of the Methyl Radical in Hydrogen Abstractions with Chlorinated Methanes:[20)] The coordinate system assumed for the reaction of the methyl radical with methyl chloride is shown in Fig. 1 as an example. Without loss of generality, it is assumed that the methyl radical has four valence electrons with α-spin and three valence electrons with β-spin. The electron distribution shown in Fig. 2 indicates that the delocalization of electrons occurs from the methyl radical to methyl chloride by the interaction $1N$, and from methyl chloride to the methyl radical by $1E$. Thus the stabilization energy represented by N or E corresponds to the direction of the delocalization of electrons occurring between a substrate and a radical. Figure 3a shows the correlation between the activation energy[20)] and the electron density on the hydrogen atom to be abstracted. The activation energy decreases with a decrease in the electron density, and thus the methyl radical reacts as a nucleophile. The nucleophilicity of the methyl radical is explained essentially by the SEDE, as summarized in Table 2. In the reactions with chlorinated methanes the electrophilic stabilization energy $2E$ decreases with the increasing number of chlorine atoms, while the nucleophilic stabilization energy $2N$ increases. As is shown

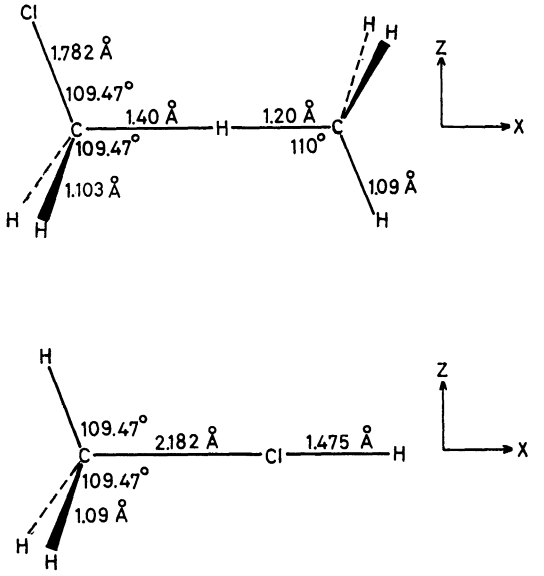


Fig. 1. Interaction models for hydrogen and chlorine abstraction reactions by radicals.

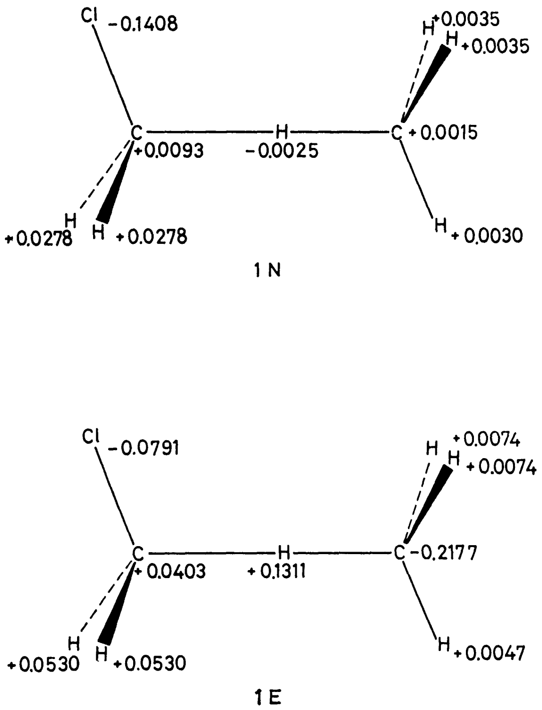


Fig. 2. The electron distribution of CH_3Cl–CH_3 system by the nucleophilic and the electrophilic interactions.

in Fig. 3b, the reactivities of chlorinated methanes are correlated with the sum of $2N$ and $2E$ calculated by the present procedure. It should be noted that the change of $2N$ from molecule to molecule is much larger than that of $2E$, although $2E$ is larger than $2N$. This suggests that the nucleophilic stabilization energy governs the relative reactivities (Fig. 3c). The conclusion is consistent with the linear relation between the electron density and $2N$, as is shown in Fig. 3d.

The electrophilic stabilization energy depends mainly on the delocalization of electrons with β-spin from the occupied MO's of the substrate to the vacant MO's of the methyl radical, because the stabilization energy for the $2E$ interaction is almost the same as that for the $1E$ interaction, as indicated in Table 2. On the other hand, the nucleophilic stabilization energy depends not only on the delocalization of electrons with α-spin from the occupied MO's of the methyl radical to the vacant MO's of the substrate, but also on the delocalization of

TABLE 2. THE NUCLEOPHILICITY OF THE METHYL RADICAL IN HYDROGEN ABSTRACTION REACTIONS WITH CHLOROMETHANES

Substrate	Orbital[a)] interaction	Total[b)] energy	Stabilization[b)] energy	ET[c)]
CH_4 (12.8)[d)]	Zero	−18.9882	0	0
	$1N$	−19.0345	0.0463	0.0822
	$1E$	−19.1333	0.1451	−0.2043
	$2N$	−19.0441	0.0559	0.0892
	$2E$	−19.1339	0.1457	−0.2048
	All	−19.2779	0.2897	−0.0276
CH_3Cl (9.4)	Zero	−34.3920	0	0
	$1N$	−34.4449	0.0529	0.0985
	$1E$	−34.5321	0.1401	−0.1982
	$2N$	−34.4555	0.0635	0.1065
	$2E$	−34.5328	0.1408	−0.1987
	All	−34.6894	0.2974	0.0004
CH_2Cl_2 (7.2)	Zero	−49.8072	0	0
	$1N$	−49.8659	0.0587	0.1126
	$1E$	−49.9436	0.1364	−0.1945
	$2N$	−49.8773	0.0701	0.1212
	$2E$	−49.9442	0.1370	−0.1952
	All	−50.1120	0.3048	0.0162
$CHCl_3$ (5.8)	Zero	−65.2482	0	0
	$1N$	−65.3124	0.0642	0.1264
	$1E$	−65.3817	0.1335	−0.1918
	$2N$	−65.3245	0.0763	0.1354
	$2E$	−65.3823	0.1341	−0.1923
	All	−65.5601	0.3119	0.0269

a) See Table 1. b) Atomic units. c) Electron transfer quantity due to delocalization of electrons. Positive values correspond to that from the radical to the substrate and negatives, *vice versa*. d) The values denote the activation energy (kcal/mol). Ref. 20.

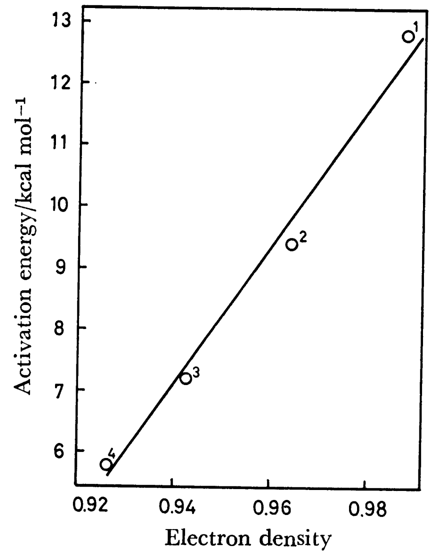


Fig. 3a. The correlation of the activation energy[20)] and the electron density for hydrogen abstraction by the methyl radical from chloromethanes. 1: CH_4, 2: CH_3Cl, 3: CH_2Cl_2, 4: $CHCl_3$.

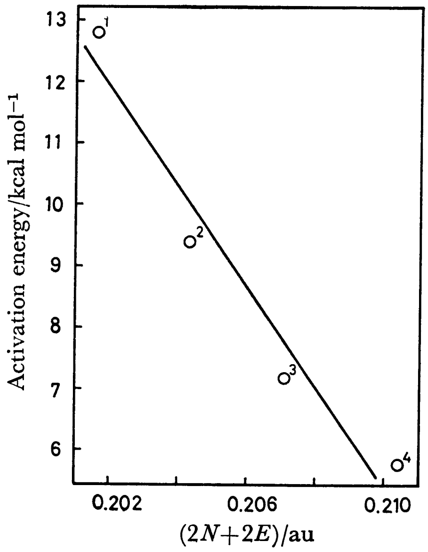


Fig. 3b. The correlation of the activation energy[20)] and $(2N+2E)$ for hydrogen abstraction by the methyl radical from chloromethanes. 1—4, see the caption in Fig. 3a.

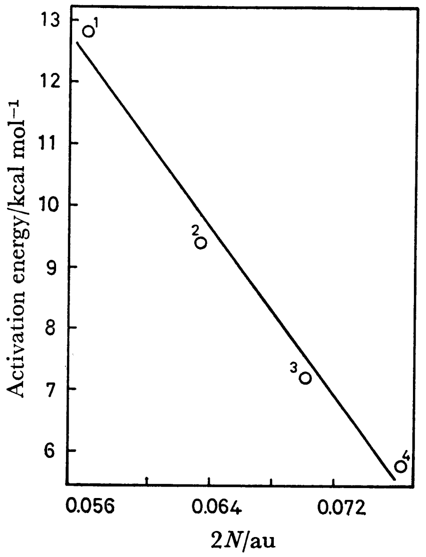


Fig. 3c. The correlation of the activation energy[20)] and $2N$ for hydrogen abstraction by the methyl radical from chloromethanes. 1—4, see the caption in Fig. 3a.

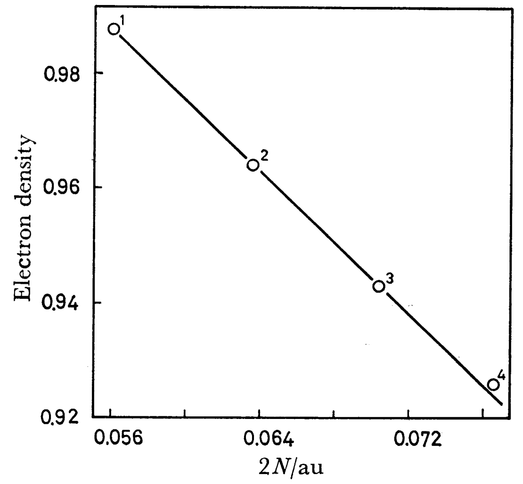
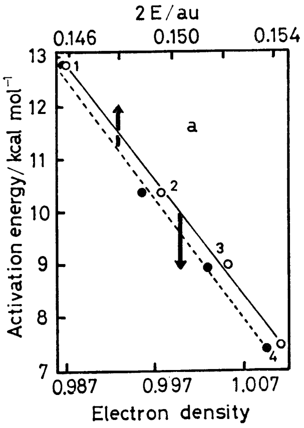


Fig. 3d. The correlation of the electron density and $2N$ for hydrogen abstraction by the methyl radical from chloromethanes. 1—4, see the caption in Fig. 3a.

electrons with β-spin, although the former contribution is larger than the latter. The total stabilization energy including the interaction between the occupied MO's of the substrate and the methyl radical ("All" in Table 2) is larger than that due to the delocalization of electrons, as is shown in Table 2. This energy can be considered to include the redistribution energy in addition to the delocalization energy, which is much larger than the redistribution energy and comes to about 70% of "All". As the ratio of $(2N+2E)$ to "All" is nearly constant for every substrate, a good correlation between the activation energy and "All" is also observed in Table 2.

A-2: The Electrophilicity of the Methyl Radical in Hydrogen Abstraction Reactions with Aliphatic Hydrocarbons:[21] The coordinate system assumed for the reaction is the same as that used in Fig. 1. Figure 4a shows the correlation between the activation energy and the electron density on the hydrogen atom. Contrary to the methyl chloride–methyl radical system, the activation energy decreases with an increase in the electron density and, in this case, the methyl radical reacts as an electrophile. The electrophilic stabilization energy $2E$ was found to correlate linearly with the activation energy, as is shown in Fig. 4a. The results suggest that the electrophilic stabilization energy gives a theoretical basis for the electrophilicity of the methyl radical. A linear relation between the electron density and $2E$ is also shown in Fig. 4b.

On the basis of the results obtained above, the polarity of a free radical can be defined as follows: If the reactivity of the radical toward a series of substrates



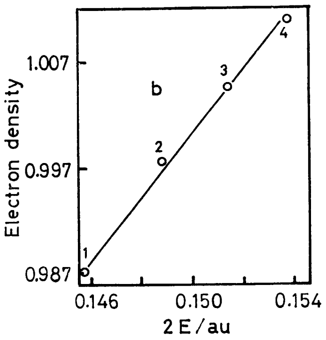


Fig. 4a. The correlation of the activation energy[21] with the electron density and $2E$ for hydrogen abstraction by the methyl radical from aliphatic hydrocarbons.
1: CH_3-H, 2: CH_3CH_2-H, 3: $(CH_3)_2CH$-H, 4: $(CH_3)_3C$-H. For the reaction of the methyl radical with CH_4, 12.8 kcal/mol of the activation energy was used in the present work as the average value in Ref. 12 and 42.

Fig. 4b. The correlation of the electron density with $2E$.

TABLE 3. THE ELECTROPHILICITY OF THE METHYL RADICAL IN HYDROGEN ABSTRACTION REACTIONS WITH ALIPHATIC HYDROCARBONS

Substrate	Orbital[a] interaction	Total[b] energy	Stabilization[b] energy	ET[c]
CH_3CH_3	Zero	−27.6864	0	0
(10.4)[d]	$2N$	−27.7421	0.0551	0.0902
	$2E$	−27.8353	0.1489	−0.2160
	All	−27.9821	0.2957	−0.0341
$CH_3CH_2CH_3$	Zero	−36.3794	0	0
(9.0)	$2N$	−36.4350	0.0556	0.0910
	$2E$	−36.5309	0.1515	−0.2246
	All	−36.6806	0.3012	−0.0377
$(CH_3)_3CH$	Zero	−45.0686	0	0
(7.5)	$2N$	−45.1234	0.0557	0.0920
	$2E$	−45.2224	0.1538	−0.2334
	All	−45.3749	0.3063	−0.0403

a—d) See the notes in Table 2. The activation energy is cited from Ref. 21.

TABLE 4. THE NUCLEOPHILICITY OF THE HYDROGEN ATOM IN CHLORINE ABSTRACTION REACTIONS WITH CHLOROMETHANES

Substrate	Orbital[a] interaction	Total[b] energy	Stabilization[b] energy	ET[c]
CH_3Cl	Zero	−25.8786	0	0
(7.9)[d]	$1N$	−25.9415	0.0629	0.1233
	$1E$	−25.9342	0.0556	−0.0861
	All	−26.0565	0.1779	0.0568
CH_2Cl_2	Zero	−41.2827	0	0
(6.0)	$1N$	−41.3478	0.0651	0.1302
	$1E$	−41.3375	0.0548	−0.0845
	All	−41.4663	0.1836	0.0593
CH_3Cl	Zero	−56.7160	0	0
(4.3)	$1N$	−56.7828	0.0668	0.1359
	$1E$	−56.7700	0.0540	−0.0834
	All	−56.9052	0.1892	0.0606
CCl_4	Zero	−72.1550	0	0
(3.5)	$1N$	−72.2232	0.0680	0.1404
	$1E$	−72.2086	0.0536	−0.0828
	All	−72.3487	0.1937	0.0621

a—d) See the notes in Table 2. The activation energy is cited from Ref. 20.

increases with an increase in the nucleophilic stabilization energy, the radical is a nucleophile. Similarly, the radical is an electrophile when the reactivity increases with the increase in the electrophilic stabilization energy.

B: *Chlorine Abstraction Reactions by the Hydrogen Atom.* Nagai *et al.*[11] reported the nucleophilicity of the triethylsilyl and phenyldimethylsilyl radicals in chlorine abstractions with polychloroalkanes. If the present analysis is applied to the reactions, the information on the theoretical basis of the Taft equation will be obtained from the reactivities of polychloroalkanes toward these radicals. Unfortunately, the molecules and the radicals are too large for the calculation to be carried out. Thus the chlorinated methane–hydrogen atom system[20] was taken as a model case. As will be discussed below, the nucleophilic nature of a radical in hydrogen abstraction depends on the ionization potential of the radical. When the ionization potential is rather low, the nucleophilicity is observed. If the hydrogen atom, which is known to have a high ionization potential (13.6 eV),[28] reacts as a nucleophile in chlorine abstractions with chlorinated methanes, the silyl radical would be expected to react as a nucleophile, because its ionization potential is lower than that of the hydrogen atom. The coordinate system assumed for the reaction is given in Fig. 1. As shown in Fig. 5, the nucleophilic stabilization energy $1N$ correlates with the relative reactivity, so that the hydrogen atom reacts as a nucleophile. The result suggests that the nucleophilicity of the silyl radicals in chlorine abstractions from polychloroalkanes will be interpreted by the SEDE, if the energy is calculated for the reacting system.

C: *Hydrogen Abstraction Reactions by Various Kinds of Radicals.*[29] For the hydrogen abstractions involving several radicals with hydrocarbons, the activation energy is plotted against the reciprocal of the difference between the ionization potentials of the hydrocarbons and the electron affinities of the radicals in Fig. 6. The reciprocal of the difference between the ionization potential of hydrocarbon and the electron affinity of the radical is not directly related to the electrophilic stabilization energy, but is qualitatively associated with it. From the linear correlation shown in Fig. 6, it may be inferred that the electrophilic stabilization energy is an important factor in determining the reaction rates for the radicals with low electron affinity (H: 0.80 eV, CH_3O: 0.38 eV)[28] and with high electron affinity (CF_3: 1.85 eV, OH: 1.83 eV).[28] The correlation in Fig. 6 is also consistent with the order of reactivity of the C–H bonds (primary<secondary<tertiary). The result supports the significance of the electrophilic stabilization energy in hydrogen abstractions from aliphatic hydrocarbons, although the important role of the dissociation energy of the C–H bond should also be taken into consideration.[30]

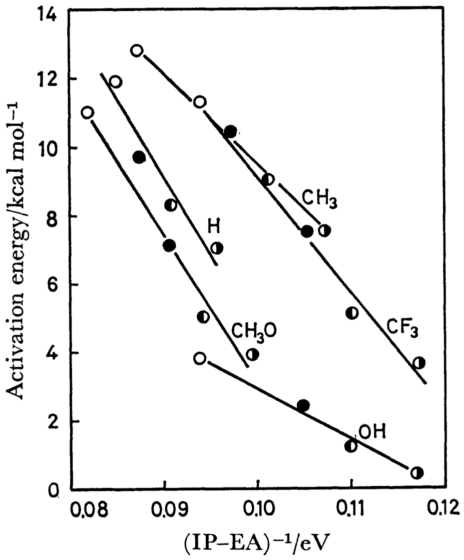


Fig. 6. The correlation between the activation energy[28] and 1/(IP–EA) for hydrogen abstractions by various kinds of radicals from aliphatic hydrocarbons. EA: electron affinity of the radical, IP: ionization potential of the aliphatic hydrocarbon. ○: CH_4, ●: CH_3CH_3, ◐: $CH_3CH_2CH_3$, ◑: $(CH_3)_3CH$.

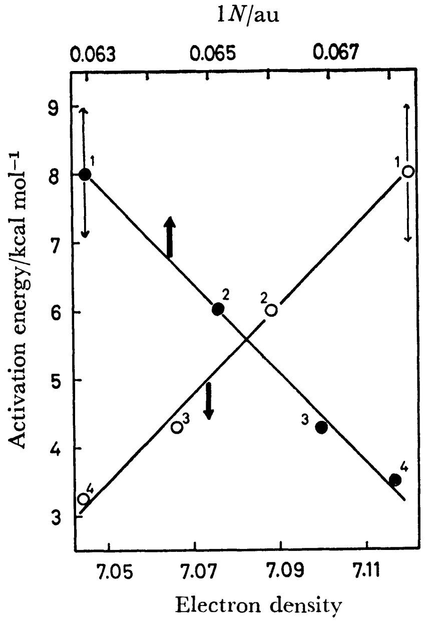


Fig. 5. The correlation of the activation energy[20] with the electron density and $1N$ for chlorine abstraction by the hydrogen atom from chloromethanes. 1: CH_3Cl, 2: CH_2Cl_2, 3: $CHCl_3$, 4: CCl_4.

Figure 7 shows the difference in the polarity between the phenyl[31] and the hydroxyl[32] radicals in the reactions with chlorinated methanes. In spite of its high electron affinity (2.20 eV),[28] the phenyl radical reacts as a nucleophile, while the hydroxyl radical and the chlorine atom (3.61 eV)[33] react as electrophiles in the reactions. The difference in behavior is interpreted by the ionization potentials of the radicals (C_6H_5: 9.90 eV,[28] OH: 13.18 eV,[28] Cl: 13.01 eV[34]). The low ionization potential of the phenyl radical is a cause of the nucleophilicity. A radical with a high ionization potential, such as the hydroxyl radical, on the other hand, reacts as an electrophile. Although the stabilization energy analysis was not carried out for these radicals, the correlation between the electron density and the SEDE in Figs. 3d, 4, and 5 indirectly interprets the nucleo-

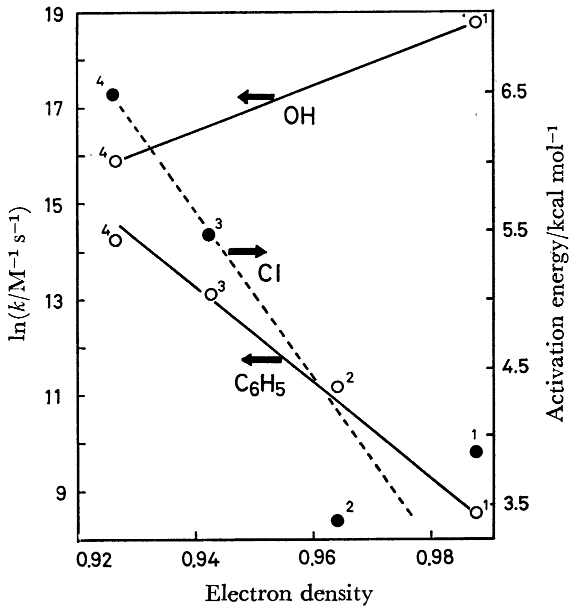


Fig. 7. The nucleophilicity of the phenyl radical and the electrophilicity of the hydroxyl radical or the chlorine atom in hydrogen abstractions with chloromethanes.

philicity of the phenyl radical[35] and the electrophilicity of the hydroxyl radical or the chlorine atom.

Discussion

The polar effect may explain the substituent effect in hydrogen abstraction reactions[1,2,5–7] where an empirical linear energy relation such as the Hammett or the Taft equation holds. In the present work, the electron density on the hydrogen atom was found to correlate with the activation energy. However, for a more fundamental understanding, the polarity of a radical in hydrogen abstraction should be explained by a quantity derived from the reaction system, not one taken from an individual reactant. The stabilization energy due to delocalization of electrons (SEDE), calculated by the CNDO/2 method for the reaction system which consists of a substrate and a radical, is a more essential quantity. As described above, the change of the electrophilic stabilization energy indicates the electrophilic tendency of the radical, and the nucleophilic stabilization energy corresponds to the nucleophilicity.

Since the electron affinity or the ionization potential of a radical can be related with the electrophilic or the nucleophilic stabilization energy,[36] respectively, the Hammett ρ values are expected to correlate with the physicochemical properties of the radical. In fact, Sakurai *et al.*[37] reported a linear relation between the negative ρ values and the electron affinity of the radical for hydrogen abstraction from substituted toluenes. Pryor *et al.*[38] revealed that the isopropyl and the t-butyl radicals react as nucleophiles. The positive ρ values increase with the decreasing ionization potentials (IP) of the radicals (CH_3: $\rho=-0.10$,[39] IP$=9.86$ eV,[28] i-C_3H_7: $\rho=0.8$, IP$=7.90$ eV,[28] t-C_4H_9: $\rho=1.0$, IP$=7.07$ eV[28]). The quantitative correlation may be given by the SEDE, because it is calculated for the reacting system and includes both reactants.

The present analysis is based on the zero differential overlap approximation,[23,24] and thus the quantitative treatment is not sufficient. Furthermore, the SEDE were not calculated for the transition state in the reacting system. The geometries shown in Fig. 1 were tentatively chosen as interaction models, because the reaction path could not be obtained by the CNDO/2 method. However, the essential features of the radical reagent obtained in the present work will probably be valid, because for an argument on the polarity[40] the absolute value of the stabilization energy is not necessarily required but a relative one is sufficient. For a more elaborate approach, the *ab initio* MO method might be adapted to the present analysis. The method of Kitaura and Morokuma,[41] which divides the intermolecular interaction energy into the electrostatic, the polarization, the exchange, and the delocalization energies, will make it possible to apply the *ab initio* method to the present analysis.

We would like to express our gratitude to the Computer Center of Tokyo University for the generous permission to use the HITAC 8700/8800 computer.

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$$E = \sum_{i=1}^{m} \sum_{j=p+1}^{q} \frac{(\sum_{\mathrm{r}}\sum_{\mathrm{s}} C_{\mathrm{RH}i,\mathrm{r}} C_{\mathrm{X}j,\mathrm{s}} I'_{\mathrm{rs}})^2}{\varepsilon_j - \varepsilon_i} \tag{3}$$

$$N = \sum_{i=m+1}^{n} \sum_{j=1}^{p} \frac{(\sum_{\mathrm{r}}\sum_{\mathrm{s}} C_{\mathrm{RH}i,\mathrm{r}} C_{\mathrm{X}j,\mathrm{s}} I'_{\mathrm{rs}})^2}{\varepsilon_i - \varepsilon_j} \tag{4}$$

where the occupied MO's of RH are denoted by 1, 2,$\cdots$, m and the vacant MO's by $m+1$, $m+2$,$\cdots$, n, while 1, 2,$\cdots$, p and $p+1$, $p+2$,$\cdots$,q denote the occupied and the vacant MO's of X, respectively. ε_i or ε_j is the i-th or the j-th MO energy.

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