The Origin of the Polarity of a Radical in Hydrogen Abstraction Reactions

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The electrophilicity of the H atom in hydrogen abstraction reactions was studied by the CNDO/2 method. The origin of the electrophilicity of the H atom was well understood using the stabilization energy due to the delocalization of electrons (SEDE) between the radical and substrate; this energy was calculated along the reaction path. The electrophilic energy (SEDE from the substrate to the radical) governs the relative reactivities of substrates, $CH_4 < CH_3CH_3 < CH_3CH_2CH_3 < (CH_3)_3CH$, which correspond to the order of the increase in the electron density. The electrophilic energy is also important in hydrogen abstraction by the H atom from aliphatic alcohols. In the case of the Cl_2^- radical, the nucleophilic energy (SEDE from the radical to the substrate) determines the relative reactivities of substrates, $CH_3OH < C_2H_5OH < i\text{-}C_3H_7OH$. The polarity of a free radical is tentatively clarified by using its ionization potential.

The polarities of free radicals in abstraction reactions (nucleophilicity or electrophilicity) have been examined experimentally by the Hammett or the Taft equation.[1-4] Although the equation does allow the determination of the polarity, its origin has not been clarified theoretically. In previous papers,[5] we attempted to explain the polarity of a free radical by the stabilization energy due to the delocalization of electrons (SEDE) between the radical and substrate; this was calculated by the CNDO/2 method.[6,7] The nucleophilic stabilization energy, defined by the SEDE from the radical to substrate (contribution of the structure **1** in the reacting system R···H···X), and the electrophilic stabilization energy, defined by the SEDE from substrate to the radical (structure **2** in Eq. 2), contribute in determining the relative reactivities of substrates (RH: hydrogen donor, X: radical).

$$RH + X \longrightarrow [R\cdots H\cdots X] \longrightarrow R + HX \tag{1}$$

$$\underset{\textbf{1}}{[\overset{\delta-}{R}\cdots H\cdots \overset{\delta+}{X}} \longleftrightarrow \underset{\textbf{2}}{\overset{\delta+}{R}\cdots H\cdots \overset{\delta-}{X}]} \tag{2}$$

The polarity of a free radical is correlated with the relative importance of these structures. Thus the radical is a nucleophile if the relative reactivities of substrates are governed by the nucleophilic energy (nucleophilic stabilization energy) and an electrophile when the reactivities are governed by the electrophilic energy (electrophilic stabilization energy). The electrophilicity of the OH and CH_3 radicals in hydrogen abstractions with methane derivatives or the nucleophilicity of the CH_3 radical in hydrogen abstraction with chlorinated methanes is well understood by using the SEDE.[5]

In the present work, we examined the polarity of the H atom in hydrogen abstractions with aliphatic hydrocarbons. The hydrocarbon–H system is useful to check our ideas on the polarity because the reaction path for CH_4–H system was deduced by the *ab initio* MO method,[8] which enabled us to calculate the SEDE in detail along the reaction path. The electrophilic energy changes remarkably from one substrate to another substrate, compared with the change in nucleophilic energy. The former thus plays a dominant role in determining the relative reactivities of substrates, $CH_4 < CH_3CH_3 < CH_3CH_2CH_3 < (CH_3)_3CH$, which correspond to the order of the increase in the electron density. On the other hand, in hydrogen abstractions by the Cl_2^- radical from aliphatic alcohols, the nucleophilic energy changes remarkably compared with the electrophilic energy, although the absolute magnitude of these energies changes with a change of the geometry in the reacting system. The ionization potential of the radical is found to be the important factor determining the polarity, judging from the present results obtained in the reactions of the H atom and Cl_2^- radical.

Method of Calculation

The total energies for the reacting systems were calculated by the UHF method[9] in the CNDO/2 approximation.[6,7] The values of the parameters included in the method are the same as those used in the original papers.

Geometries used for calculation are as follows: for CH_4,[10] CH_3CH_3, $CH_3CH_2CH_3$, and $(CH_3)_3CH$, $r(C\text{–}H) = 1.09$ Å and $r(C\text{–}C) = 1.54$ Å; for CH_3OH,[11] C_2H_5OH, and $i\text{-}C_3H_7OH$, $r(C\text{–}H) = 1.094$ Å, $r(C\text{–}O) = 1.425$ Å, $r(O\text{–}H) = 0.945$ Å, $\angle COH = 108.53°$. The bond angles HCH for these compounds were assumed to be 109.47°.

Procedure of Analysis.[5] (i) The total energy of the reacting system [R···H···X] without the 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 fragment RH and those on the fragment 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. 3 in order to take the delocalization of electrons between particular MO's into account.

$$I'_{rs} = \sum_{(i_1-j_1)} C_{RHi_1,r} C_{Xj_1,s} I_{i_1 j_1}, \tag{3}$$

where $C_{RHi_1,r}$ is the coefficient of AO in the i-th MO of the substrate RH and $C_{Xj_1,s}$ is for the radical X. $\sum_{(i_1-j_1)}$ denotes the summation over a particular orbital

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 $I_{i_1 j_1}$ is represented by a solid line. The symbol for the interaction used in the text is given in the parentheses.

set (i_1, j_1). (iii) I'_{rs} values 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 in question. (iv) When the vacant MO's of the substrate and occupied MO's of the radical are chosen for i_1 and j_1, respectively, in Eq. 3, the difference between two energies obtained in steps (i) and (iii) corresponds to the SEDE from the radical to the substrate. This energy should be the nucleophilic 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 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).

Results and Discussion

The Electrophilicity of the H Atom. The coordinate system for a hydrogen abstraction reaction by the H atom from aliphatic hydrocarbons is shown in Fig. 1. We specify the reaction path with a notation (r_1, r_2), where r_1 is the distance (in Å) between the carbon atom C^1 and the hydrogen atom H^5 to be abstracted, while r_2 is the distance between this hydrogen atom H^5 and the incoming H atom. Calculations were carried out at six path points: A(1.2, 1.1), B(1.3, 0.95), C(1.365, 0.873), D(1.38, 0.85), E(1.5, 0.80), and F(1.7, 0.75), which are very nearly on the potential valley deduced by *ab initio* calculations.[8)] Figure 2a shows the correlation of the activation energy[12)] 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 H atom can be understood by N and E, as summarized in Tables 2a—2f. E is about 6—10 times larger than N before transition state (C) and after the state, the difference becomes nearly constant as the reaction proceeds. When the substrate changes from CH_4 to CH_3CH_3, $CH_3CH_2CH_3$, or $(CH_3)_3CH$, E increases remarkably with the increasing number of electron donating CH_3 groups, while N does not change significantly in any substrate. The contribution of the structure **2** in the reacting system is an important factor in determining the relative reactivities of substrates, and thus the reactivities are explained by E, as is shown in Fig. 2b. The electrophilicity of the H atom suggested by the electron density is ascribable to the correlation of the electron density and E in Fig. 2c.

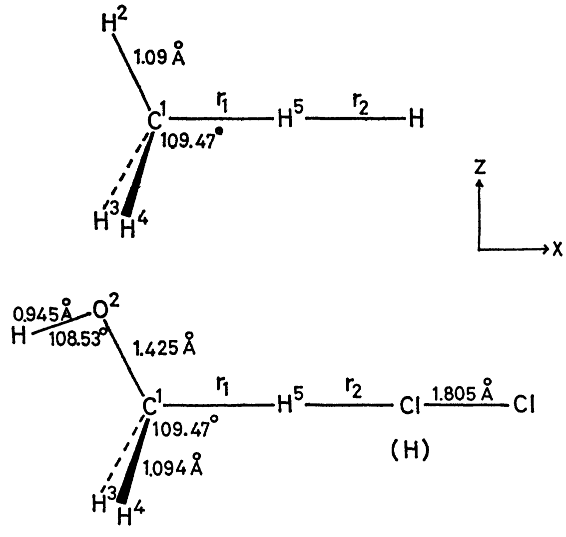

Fig. 1. The coordinate systems for hydrogen abstractions by the H atom and the Cl_2^- radical from CH_4 and CH_3OH, respectively.

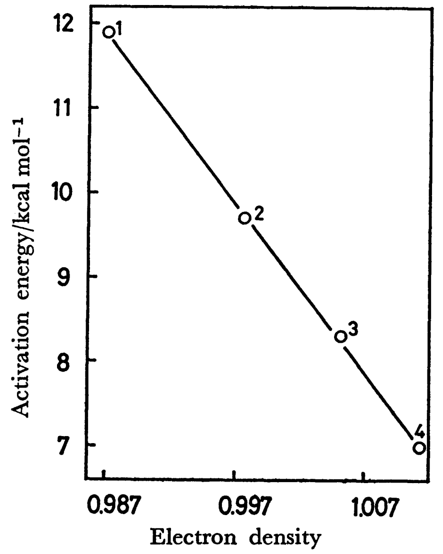

Fig. 2a. The correlation of the activation energy[12)] and the electron density in hydrogen abstraction by the H atom from aliphatic hydrocarbons. 1: CH_4, 2: CH_3CH_3, 3: $CH_3CH_2CH_3$, 4: $(CH_3)_3CH$.

The Nucleophilicity of the Cl_2^- Radical. Radical anions (Br_2^-, $(CNS)_2^-$, CO_3^-, and Cl_2^-) are known as the free radical probes which attack specific residues in enzymes[13,14)] and give the information on the active sites. In comparison with OH radical, the radical anions are highly selective in reactions with amino acid residues. The polarity of the radical anion is

TABLE 2a. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT A(1.2, 1.1)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4	Zero	−10.7030	0	0
	N	−10.7075	0.0045	0.0079
	E	−10.7473	0.0443	−0.0718
CH_3CH_3	Zero	−19.3987	0	0
	N	−19.4033	0.0046	0.0081
	E	−19.4437	0.0450	−0.0762
$CH_3CH_2CH_3$	Zere	−28.0894	0	0
	N	−28.0941	0.0047	0.0083
	E	−28.1349	0.0455	−0.0801
$(CH_3)_3CH$	Zero	−36.7764	0	0
	N	−36.7811	0.0047	0.0085
	E	−36.8223	0.0459	−0.0829

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.*

TABLE 2b. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT B(1.3, 0.95)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4	Zero	−10.6445	0	0
	N	−10.6530	0.0085	0.0168
	E	−10.7085	0.0640	−0.1087
CH_3CH_3	Zero	−19.3414	0	0
	N	−19.3500	0.0086	0.0170
	E	−19.4066	0.0652	−0.1158
$CH_3CH_2CH_3$	Zero	−28.0332	0	0
	N	−28.0419	0.0087	0.0170
	E	−28.0993	0.0661	−0.1209
$(CH_3)_3CH$	Zero	−36.7213	0	0
	N	−36.7300	0.0087	0.0173
	E	−36.7882	0.0669	−0.1263

a)—c) See the notes in Table 2a.

TABLE 2c. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT C(1.365, 0.873)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4 (11.9)[d)]	Zero	−10.5959	0	0
	N	−10.6078	0.0120	0.0249
	E	−10.6723	0.0765	−0.1338
CH_3CH_3 (9.7)	Zero	−19.2936	0	0
	N	−19.3056	0.0120	0.0252
	E	−19.3717	0.0781	−0.1426
$CH_3CH_2CH_3$	Zero	−27.9862	0	0
(8.3)	*N*	−27.9983	0.0121	0.0256
	E	−28.0656	0.0794	−0.1489
$(CH_3)_3CH$	Zero	−36.6751	0	0
(7.0)	*N*	−36.6873	0.0121	0.0260
	E	−36.7556	0.0805	−0.1554

a)—c) See the notes in Table 2a. d) Activation energy (kcal/mol).[12)]

TABLE 2d. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT D(1.38, 0.85)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4	Zero	−10.5808	0	0
	N	−10.5939	0.0131	0.0276
	E	−10.6616	0.0808	−0.1418
CH_3CH_3	Zero	−19.2789	.	0
	N	−19.2920	0.0131	0.0279
	E	−19.3613	0.0824	0.1510
$CH_3CH_2CH_3$	Zero	−27.9716	0	0
	N	−27.9849	0.0133	0.0283
	E	−28.0555	0.0839	−0.1577
$(CH_3)_3CH$	Zero	−36.6607	0	0
	N	−36.6740	0.0133	0.0282
	E	−36.7457	0.0850	−0.1645

a)—c) See the notes in Table 2a.

TABLE 2e. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT E(1.5, 0.80)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4	Zero	−10.5051	0	0
	N	−10.5251	0.0200	0.0462
	E	−10.5950	0.0898	−0.1680
CH_3CH_3	Zero	−19.2051	0	0
	N	−19.2250	0.0199	0.0465
	E	−19.2973	0.0922	−0.1791
$CH_3CH_2CH_3$	Zero	−27.8997	0	0
	N	−27.9195	0.0198	0.0469
	E	−27.9937	0.0940	−0.1883
$(CH_3)_3CH$	Zero	−36.5903	0	0
	N	−36.6102	0.0199	0.0475
	E	−36.6859	0.0959	−0.1962

a)—c) See the notes in Table 2a.

TABLE 2f. THE SEDE FOR HYDROCARBON-H SYSTEM IN THE PATH POINT F(1.7, 0.75)

Substrates	Orbital[a)] interaction	Total[b)] energy	SEDE[b)]	ET[c)]
CH_4	Zero	−10.3827	0	0
	N	−10.4176	0.0349	0.0913
	E	−10.4857	0.1030	−0.2156
CH_3CH_3	Zero	−19.0863	0	0
	N	−19.1213	0.0350	0.0925
	E	−19.1929	0.1066	−0.2289
$CH_3CH_2CH_3$	Zero	−27.7841	0	0
	N	−27.8191	0.0350	0.0936
	E	−27.8934	0.1093	−0.2393
$(CH_3)_3CH$	Zero	−36.4776	0	0
	N	−36.5130	0.0354	0.0947
	E	−36.5890	0.1114	−0.2474

a)—c) See the notes in Table 2a.

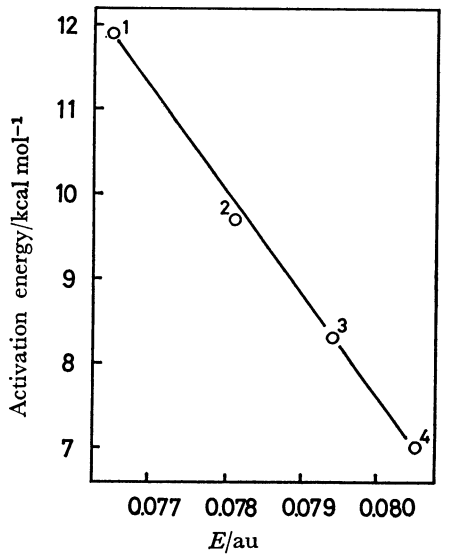

Fig. 2b. The correlation of the activation energy and the electrophilic energy E (in path point C) in hydrogen abstraction by the H atom from aliphatic hydrocarbons. 1—4, see the caption in Fig. 2a.

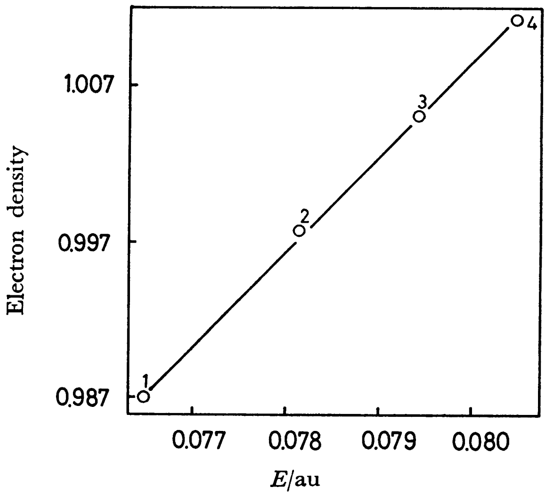

Fig. 2c. The correlation of the electron density and the electrophilic energy E (in path point C) in hydrogen abstraction by the H atom from aliphatic hydrocarbons. 1—4, see the caption in Fig. 2a.

interesting from a theoretical point of view since it has a negative charge, unlike a neutral radical. In the present work, we calculated the SEDE in hydrogen abstraction by the Cl_2^- radical from aliphatic alcohols[15] by assuming the following reaction paths: A(1.2, 1.4), B(1.3, 1.4), C(1.4, 1.3), and D (1.5, 1.27). Calculations were also carried out for hydrogen abstraction by the H atom from aliphatic alcohols[16] to study the factors which determine the polarity of a radical. The coordinate systems for these reactions are shown in Fig. 1. The optimized Cl–Cl distance of the Cl_2^- radical is 1.805 Å. It is slightly longer than that of Cl_2 molecule (1.75 Å).[17] Table 3 shows the result for the H atom. As is shown in the previous section, the electrophilic energy governs the relative reactivities of alcohols, which confirms the electrophilicity of the H atom (Fig. 3). Although the points A, B, C, and D were tentatively chosen for the reaction of the Cl_2^- radical, an interesting result was obtained, as is shown in Table 4. When the C^1–H^5 bond is not elongated far from the equilibrium C–H bond distance, the electrophilic energy is larger than the nucleophilic

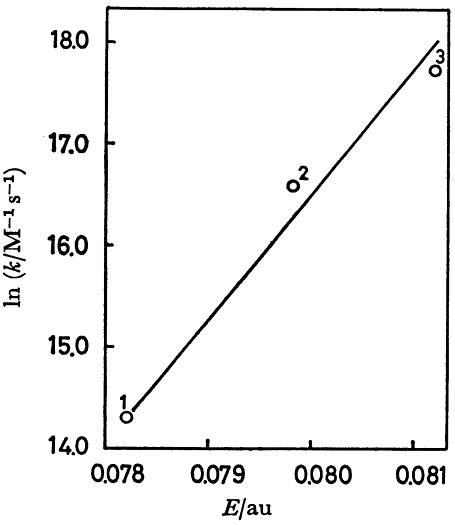

Fig. 3. The correlation of the rate constant[16] and the electrophilic energy E (in path point C) in hydrogen abstraction by the H atom from aliphatic alcohols. 1: CH_3OH, 2: C_2H_5OH, 3: i-C_3H_7OH.

TABLE 3. THE SEDE IN ALCOHOL-H SYSTEM

Path point	Substrates	Orbital[a] interaction	Total[b] energy	SEDE[b]	ET[c]
B	CH_3OH	Zero	−29.0907	0	0
		N	−29.0991	0.0084	0.0165
		E	−29.1559	0.0652	−0.1153
	C_2H_5OH	Zero	−37.7878	0	0
		N	−37.7962	0.0084	0.0165
		E	−37.8542	0.0664	−0.1222
	i-C_3H_7OH	Zero	−46.4778	0	0
		N	−46.4861	0.0083	0.0167
		E	−46.5453	0.0675	−0.1283
C	CH_3OH (1.6)[d]	Zero	−29.0431	0	0
		N	−29.0550	0.0119	0.0249
		E	−29.1213	0.0782	−0.1421
	C_2H_5OH (16)[d]	Zero	−37.7411	0	0
		N	−37.7528	0.0117	0.0249
		E	−37.8209	0.0798	−0.1504
	i-C_3H_7OH (50)[d]	Zero	−46.4319	0	0
		N	−46.4436	0.0117	0.0251
		E	−46.5131	0.0812	−0.1578
D	CH_3OH	Zero	−29.0285	0	0
		N	−29.0413	0.0128	0.0276
		E	−29.1110	0.0825	−0.1505
	C_2H_5OH	Zero	−37.7266	0	0
		N	−37.7394	0.0128	0.0276
		E	−37.8109	0.0843	−0.1593
	i-C_3H_7OH	Zero	−46.4176	0	0
		N	−46.4304	0.0128	0.0278
		E	−46.5034	0.0858	−0.1669

a)—c) See the notes in Table 2a. d) Rate constant (10^6 M^{-1} s^{-1}).[16]

Table 4. The SEDE for alcohol-Cl_2^- system

Path point	Substrates	Orbital[a] interaction	Total[b] energy	SEDE[b]	ET[c]
A	CH_3OH	Zero	−60.9592	0	0
	(0.035)[d]	*N*	−61.0001	0.0409	0.0906
		E	−61.0186	0.0594	−0.0646
	C_2H_5OH	Zero	−69.6550	0	0
	(0.45)[d]	*N*	−69.6978	0.0428	0.0967
		E	−69.7146	0.0596	−0.0656
	i-C_3H_7OH	Zero	−78.3439	0	0
	(1.2)[d]	*N*	−78.3879	0.0440	0.1028
		E	−78.4037	0.0598	−0.0666
B	CH_3OH	Zero	−60.9341	0	0
		N	−60.9894	0.0553	0.1309
		E	−60.9892	0.0551	−0.0630
	C_2H_5OH	Zero	−69.6308	0	0
		N	−69.6875	0.0567	0.1395
		E	−69.6861	0.0553	−0.0642
	i-C_3H_7OH	Zero	−78.3205	0	0
		N	−78.3788	0.0583	0.1482
		E	−78.3761	0.0556	−0.0653
C	CH_3OH	Zero	−60.8363	0	0
		N	−60.9177	0.0814	0.1951
		E	−60.9001	0.0638	−0.0769
	C_2H_5OH	Zero	−69.5339	0	0
		N	−69.6175	0.0836	0.2071
		E	−69.5981	0.0642	−0.0784
	i-C_3H_7OH	Zero	−78.2247	0	0
		N	−78.3104	0.0857	0.2189
		E	−78.2891	0.0644	−0.0797
D	CH_3OH	Zero	−60.7704	0	0
		N	−60.8751	0.1047	0.2521
		E	−60.8341	0.0637	−0.0805
	C_2H_5OH	Zero	−69.4691	0	0
		N	−69.5765	0.1074	0.2729
		E	−69.5332	0.0641	−0.0821
	i-C_3H_7OH	Zeru	−78.1609	0	0
		N	−78.2708	0.1099	0.2869
		E	−78.2254	0.0645	−0.0833

a)—c) See the notes in Table 2a. d) Rate constant (10^4 M^{-1} s^{-1}).[15]

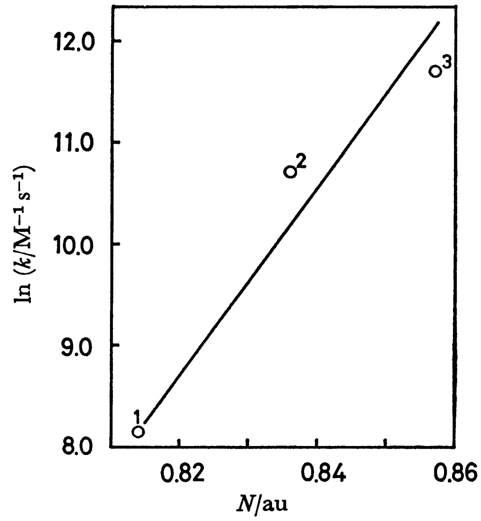

Fig. 4. The correlation of the rate constant[15] and the nucleophilic energy *N* (in path point C) in hydrogen abstraction by the Cl_2^- radical from aliphatic alcohols. 1—3, see the caption in Fig. 3.

Table 5. The correlation of the ρ values in hxdrogen abstractions and the ionization potentials

Radicals	Ionization[a] potential/eV	Electron[b] affinity/eV	ρ value[c]
t-C_4H_9	7.07		1.0
i-C_3H_7	7.90		0.8
n-C_3H_7	8.69	0.69	
C_2H_5	8.67	0.94	
CH_3	9.86	1.4	−0.1—0
C_6H_5	9.90	2.21	−0.1
H	13.16	0.80	−0.3
CCl_3	8.78	1.22	−1.46
CF_3	8.90, 10.15	1.85	
OH	13.18	1.83	−0.96[d]
Cl	13.01	3.61	−0.8—−1.9

a) Ref. 19. b) Ref 20. c) Ref 4d. d) ρ value for hydrogen abstraction with substituted methanes. Ref. 4e.

energy, but the latter increases as the C^1–H^5 bond is elongated. Thus, at the initial stage, the SEDE from the substrate to the radical is a driving force of the reaction; but as the reaction proceeds, the SEDE from the radical to the substrate is an important force in completing the reaction. It is noteworthy that although the absolute magnitude of *N* or *E* changes along the reaction path, the nucleophilic energy governs the relative reactivities of alcohols, as is shown in Fig. 4.[5c,5] Therefore the Cl_2^- radical reacts as a nucleophile.

Both frontier electron densities of HOMO (f_{HOMO}) and LUMO (f_{LUMO}) on the α hydrogen atom of alcohol[18] increase as follows: CH_3OH (f_{HOMO}: 0.234, f_{LUMO}: 0.185); C_2H_5OH (f_{HOMO}: 0.297, f_{LUMO}: 0.347); *i*-C_3H_7OH (f_{HOMO}: 0.314, f_{LUMO}: 0.592). In the case of the Cl_2^- radical, the electrophilic or the nucleophilic energy increases with an increase in f_{HOMO} or f_{LUMO}, respectively, while the nucleophilic energy does not increase in hydrogen abstractions by the H atom. The SOMO of the Cl_2^- radical (an electron occupies the LUMO of Cl_2 molecule) is high enough so that the increase of f_{LUMO} contributes largely to the increase in the nucleophilic energy, while the SOMO of the H atom is so low that the above situation is not attainable. The result obtained here leads to the conclusion that a radical having a low ionization potential is a nucleophile and one having a high potential is an electrophile. Table 5 shows the correlation of the ρ values in hydrogen abstractions by radicals[4d] and the ionization potentials. It is expected that C_2H_5 radical will react as a weak nucleophile with substituted toluenes. Although the CH_3 radical reacts as an electrophile in this case, it reacts as a nucleophile in hydrogen abstractions with chlorinated methanes.[5d] As the ionization potential of the CH_3 radical is not so high as that of the electrophilic OH radical or Cl atom, the nucleophilic energy will change largely from substrate to substrate in a nucleophilic reaction. Therefore a radical having a moderate ionization potential reacts as an electrophile or a nucleophile according to the nature of the substrate.

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