A Molecular Orbital Study of the Partial Reactivity of the Hydrogen of Aliphatic Compounds in the Hydrogen-abstraction Reaction by the Hydroxyl Radical

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The energy required to stretch a C–H bond of alkanes by 0.5 Å from an equilibrium bond length was calculated by the INDO method, and it was found that this energy has a relation with the delocalizability, D_r^R, of hydrogen atoms in alkanes, and with the activation energy for the hydrogen-abstraction reaction of the methyl radical from alkanes. The reactivities of hydrogen atoms in aliphatic alcohols and carboxylate ions, as defined by this energy were found to correlate with the partial reactivities of hydrogen atoms, just as was proposed by Anbar *et al.*, *i.e.*, the rate constants for the hydrogen-abstraction reaction of aliphatic compounds with hydroxyl radicals can be well explained by a summation of the partial reactivities assigned to primary, secondary, and tertiary hydrogen atoms bound to α- or β- (for γ-CH and δ-CH the same value as for β-CH was used) carbon atoms.

It is well established that a hydroxyl radical abstracts a hydrogen atom from C–H bonds of aliphatic alcohols and carboxylate ions. Furthermore, it is well known that the reactivity of an aliphatic compound toward the hydroxyl radical increases with an increase in the number of C–H bonds in a molecule.

Anbar *et al.*[1] determined the rate constants for the reactions of a large number of aliphatic compounds with hydroxyl radicals, and pointed out that the reactivities of long-chain compounds could be calculated by a summation of the assigned partial reactivities of the hydrogen atoms in the molecule. They proposed the following partial reactivities for the hydrogen atoms of carboxylate ions, by the best fit of simultaneous equations derived from the experimental rate constants: (a) the partial reactivities of the hydrogen atoms in the α-position to the carboxyl group are estimated to be 0.235, 2.94, and 8.90×10^8 l mol^{-1} s^{-1} per H atom for the primary ($CH_3CO_2^-$), the secondary ($RCH_2CO_2^-$), and the tertiary ($R_2CHCO_2^-$) hydrogens respectively; (b) the partial reactivities of the hydrogen atoms in the positions other than α are also estimated to be 0.606, 5.05, and 14.1×10^8 l mol^{-1} s^{-1} per H atom for the primary, secondary, and tertiary hydrogens respectively. The originally reported values are corrected by a factor of 1.68, because the rate constant for the reaction of the hydroxyl radical with ethyl alcohol, which was used as a reference substance in their determination of the rate constants, has recently been revised from 1.1×10^9 to 1.85×10^9 l mol^{-1} s^{-1}.[2]

The rate constants calculated from these partial reactivities have been proved to interpret the experimental values successfully. Therefore, it is helpful to investigate the theoretical basis of the assigned partial reactivities from the viewpoint of the molecular orbital method.

In chemical reactions, the delocalization of electrons between reactant and reagent is recognized as the major factor in determining the reactivity.[3,4] Therefore, a hydroxyl radical as well as a reactant should be included in the calculation of the reactivity of the hydrogen atom in order to take the delocalization of electrons into account. However, the total energy of the system including a hydroxyl radical and a reactant can not always be obtained because of the divergent behavior in SCF calculation. In a previous paper,[5] we showed that the reactivity of the hydrogen atom (ΔE), defined as the energy required to stretch a C–H bond by 0.5 Å from the equilibrium bond length, has a close relation with the energy for the hydrogen-abstraction reaction (ΔE_{OH}), calculated from the system including a hydroxyl radical and an amino acid. Therefore, it can be expected that ΔE gives a measure of the reactivity of the hydrogen atom in alcohols and carboxylate ions toward the hydroxyl radical in the present hydrogen-abstraction reaction.

Actually the present results show that ΔE is related to the natural logarithm of the partial reactivities of the primary, secondary, and tertiary hydrogen atoms bound to the α- and β- carbon atoms which were proposed by Anber *et al.*[1]

Method

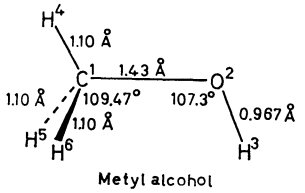
The total energies were calculated by the INDO method proposed by Pople *et al.*[6]

Results and Discussion

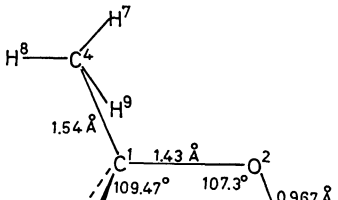
Methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, and isobutyl alcohol were taken as a series of alcohols, and acetate, propionate, butyrate, isobutyrate, and isovalerate ions were taken as a series of carboxylate ions. The geometries of these compounds used for the calculation are indicated in Fig. 1. The reactivity of the hydrogen atom expressed by ΔE is calculated by means of Eq. 1;

$$\Delta E = E(\text{C-H } 1.60) - E(\text{C-H } 1.10) \quad (1)$$

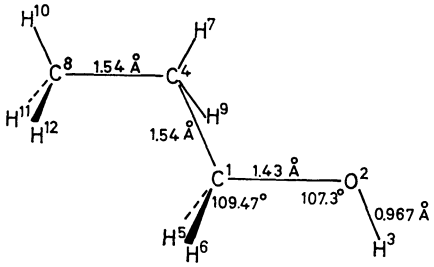
where E(C–H 1.60) is the total energy calculated by stretching the C–H bond by 0.5 Å in its singlet state, and E(C–H 1.10) is that at the equilibrium C–H distance in alcohols and carboxylate ions (assumed to be 1.10 Å). In order to examine the validity of ΔE for expressing the reactivity of the hydrogen atom in the hydrogen-abstraction reaction, we compared the ΔE of hydrogen atoms of alkanes with the activation energy for the hydrogen-abstraction reaction of the methyl radical and alkanes. As is shown in Table 1, the order of reactivity for primary, secondary, and tertiary hydrogen atoms is well explained by ΔE, and Fig. 2 shows



Metyl alcohol

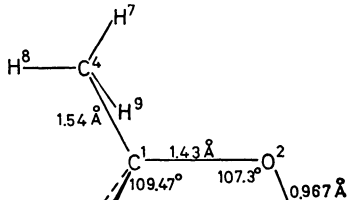


Ethyl alcohol

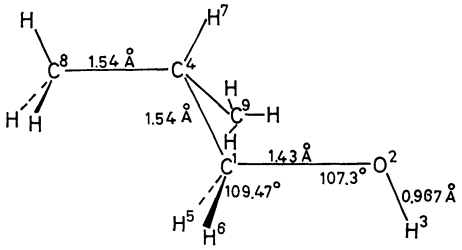


propyl alcohol

Fig. 1-1.

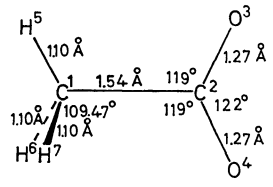


Isopropyl alcohol

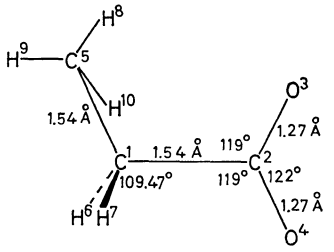


Isobutyl alcohol

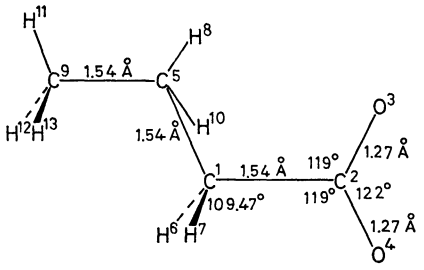
Fig. 1-2.



Acetate ion

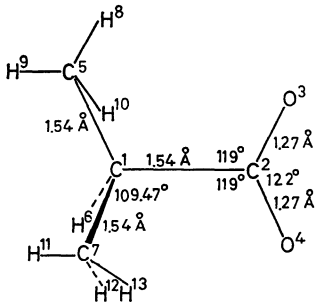


Propionate ion

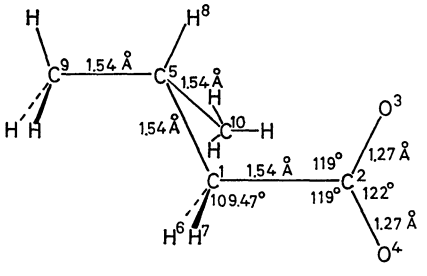


butyrate ion

Fig. 1-3.



Isobutyrate ion



Isovalerate ion

Fig. 1-4.

Fig. 1. The geometries of alcohols and carboxylate ions used for the calculation of ΔE.

TABLE 1. COMPARISON OF ΔE WITH THE EXPERIMENTALLY DETERMINED ACTIVATION ENERGY FOR THE HYDROGEN ABSTRACTION REACTION OF THE METHYL RADICAL AND ALKANES

Alkane (R-H)	ΔE (kcal/mol)	$D_r^R(H)$[a]	E (kcal/mol)[b]
CH_3-H	105.8218	0.9926	11.5
CH_3CH_2-H	101.3681	1.0029	10.0
$CH_3CH_2CH_2$-H	100.3018	1.0037	9.5
$CH_3CH_2CH_2CH_2$-H	100.0508	1.0040	9.3
$(CH_3)_2CHCH_2$-H	100.1136	1.0049	—
$(CH_3)_2CH$-H	97.2281	1.014	8.7
$CH_3CH_2CH(CH_3)$-H	97.0399	1.015	8.2
$(CH_3)_3C$-H	93.3390	1.027	7.7
$(CH_3)_2CH(CH_3)_2C$-H	92.8998	1.029	7.8

a) Ref. 8. b) N. N. Tkhomirova and V. V. Voevodskii, *Dokl. Akad. Nauk SSSR.*, **79**, 993 (1951). These values were cited in Ref. 8.

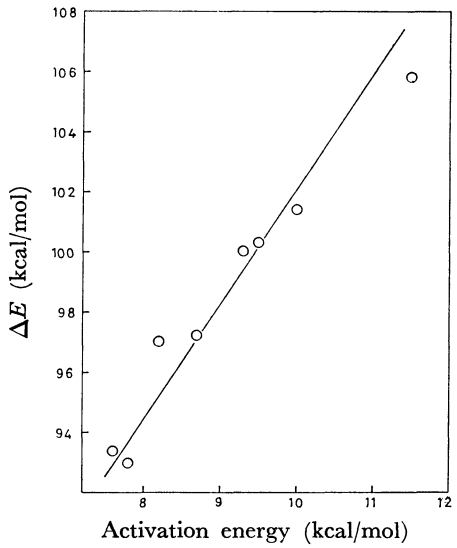


Fig. 2. The linear relationship between ΔE and activation energy for hydrogen abstraction reaction of methyl radical from alkanes.

a linear relationship between ΔE and the activation energy.

It is well known that the delocalizability, D_r^R, represented by Fukui *et al.*[7,8] has successfully been used to interpret the reactivity of saturated compounds toward several radicals.[7,8] As is shown in Table 1 and Fig. 3 for alkanes, ΔE is found to have a close relation with the D_r^R calculated by Kato *et al.*[8] Although the correlation shown in Table 1 cannot be taken as direct evidence for ΔE as a measure of the reactivity, the present result and the observed correlation between ΔE and ΔE_{OH} calculated for the partial reactivities of hydrogen atoms in amino acids[5] may support the validity of ΔE for the present purposes. The reactivities of hydrogen atoms in alcohols defined by ΔE are shown in Table 2, while Table 3 shows the result for carboxylate ions. It was suggested that hydrogen atoms bound to the identical carbon atom have different reactivities, depending on the orientation in the molecule;[9] a similar tendency is observed in the

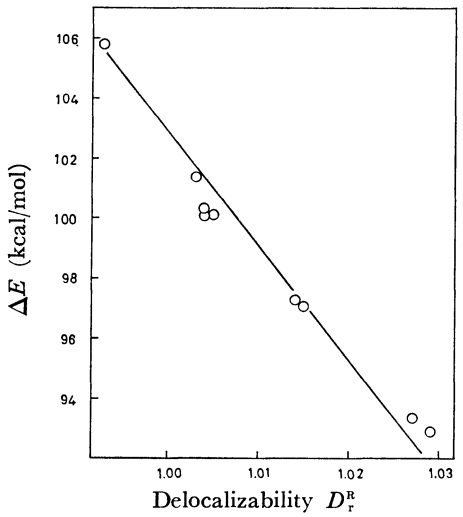


Fig. 3. The linear relationship between ΔE and Delocalizability D_r^R for alkanes.

TABLE 2. THE REACTIVITIES OF HYDROGEN ATOMS OF ALCOHOLS DEFINED BY ΔE

Alcohol		Type of C-H bond	ΔE (au)
CH_3OH	H^4	α-primary	0.1623
	H^5	α-primary	0.1584
C_2H_5OH	H^5	α-secondary	0.1516
	H^7	β-primary	0.1622
	H^8	β-primary	0.1637
$CH_3CH_2CH_2OH$	H^5	α-secondary	0.1513
	H^7	β-secondary	0.1558
	H^{10}	γ-primary	0.1605
	H^{11}	γ-primary	0.1614
$(CH_3)_2CHOH$	H^5	α-tertiary	0.1449
	H^7	β-primary	0.1605
	H^8	β-primary	0.1636
	H^9	β-primary	0.1619
	H^{10}	β-primary	0.1629
	H^{11}	β-primary	0.1599
	H^{12}	β-primary	0.1619
$(CH_3)_2CHCH_2OH$	H^5	α-secondary	0.1499
	H^6	α-secondary	0.1510
	H^7	β-tertiary	0.1498

cases of both alcohols and carboxylate ions. As the β-primary H^7 and H^8 atoms of ethyl alcohol (also the α-primary H^4 and H^5 atoms of methyl alcohol) have different reactivities, we approximate the reactivity of the β-primary hydrogen atom to the average reactivity of H^7 and H^8 atoms by the assuming Maxwell-Boltzmann distribution in order to compare ΔE with the partial reactivities; Table 4 shows the results. The same approximation was used for carboxylate ions. It is well known that, in hydrogen-abstraction reactions of radicals from alkanes, the reactivities of hydrogen atoms increase in this order; primary<secondary<tertiary, and that a similar tendency is observed for hydrogen atoms in the α-position and β-position of alcohols, as is shown in Table 4. The results for carboxylate ions are shown in Table 5 and Fig. 5. Although

Table 3. The reactivities of hydrogen atoms of carboxylate ions defined by ΔE

Carboxylate ion		Type of C-H bond	ΔE (au)
CH_3COO^-	H^5	α-primary	0.1565
	H^6	α-primary	0.1569
$CH_3CH_2COO^-$	H^6	α-secondary	0.1503
	H^8	β-primary	0.1588
	H^9	β-primary	0.1506
$CH_3CH_2CH_2COO^-$	H^6	α-secondary	0.1500
	H^8	β-secondary	0.1527
	H^{11}	γ-primary	0.1545
	H^{12}	γ-primary	0.1596
$(CH_3)_2CHCOO^-$	H^6	α-tertiary	0.1445
	H^8	β-primary	0.1572
	H^9	β-primary	0.1508
	H^{10}	β-primary	0.1588
	H^{11}	β-primary	0.1512
	H^{12}	β-primary	0.1571
	H^{13}	β-primary	0.1597
$(CH_3)_2CHCH_2COO^-$	H^6	α-secondary	0.1486
	H^7	α-secondary	0.1501
	H^8	β-tertiary	0.1467

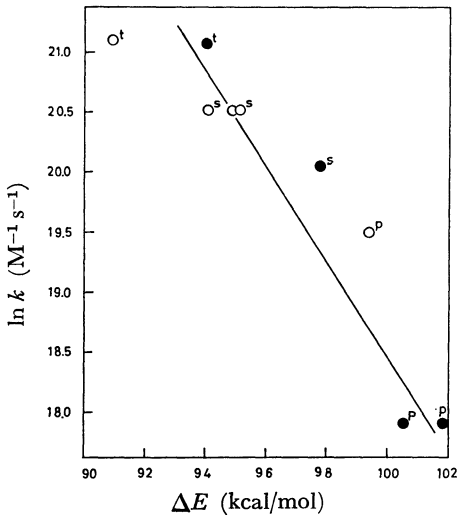


Fig. 4. The relation between ΔE and the partial reactivities of hydrogen atoms in alcohols. ○: α-, ●: β-, p: primary, s: secondary.

points are scattered, a fairly good correlation was found as a whole.

Asmus *et al.*[10] investigated the reaction site of aliphatic alcohols in the reaction with the hydroxyl radical by means of pulse radiolysis, and found that the main reaction is the abstraction of the hydrogen atom from the α-position, but hydrogen abstraction also occurs at β-, γ-, ··· positions with an increase in the number of carbon atoms. Moreover, they determined the relative probabilities of hydrogen abstraction from the α-positions of various alcohols. For example, 84.3, 53.4, 85.5, and 41.0% are obtained for C_2H_5OH, n-C_3H_5OH, $(CH_3)_2CHOH$, and n-C_4H_9OH respectively. The probabilities can be evaluated from the partial reactivities proposed by Anbar *et al.* to be 90.2, 58.5, 80.3, and 43.4% for the above alcohols respectively.

Table 4. Comparison of ΔE with the partial reactivities assigned to every C-H bond of alcohols

Type of C-H bond	Partial reactivity[a] $M^{-1}\,s^{-1}$	ΔE (kcal/mol)
α-Primary	3.02×10^8	99.3813
α-Secondary	8.40×10^8	95.0953[b]
		94.9072[c]
		94.0573[d]
α-Tertiary	1.48×10^9	90.8926
β-Primary	6.06×10^7	101.8342[e]
		100.6491[f]
β-Secondary	5.05×10^8	97.7299
β-Tertiary	1.41×10^9	93.9662
γ-Primary	6.06×10^7	100.8378

a) Ref. 1. b) Estimated from C_2H_5OH. c) From $CH_3CH_2CH_2OH$. d) From $(CH_3)_2CHCH_2OH$. e) From C_2H_5OH. f) From $(CH_3)_2CHOH$.

Table 5. Comparison of ΔE with the partial reactivities assigned to every C-H bond of carboxylate ions

Type of C-H bond	Partial reactivity[a] $M^{-1}\,s^{-1}$	ΔE (kcal/mol)
α-Primary	2.35×10^7	98.2299
α-Secondary	2.94×10^8	94.2799[b]
		94.0917[c]
		93.3752[d]
α-Tertiary	8.90×10^8	90.6417
β-Primary	6.06×10^7	94.4686[e]
		94.6931[f]
β-Secondary	5.05×10^8	95.7854
β-Tertiary	1.41×10^9	92.0217
γ-Primary	6.06×10^7	96.9299

a) Ref. 1. b) Estimated from $CH_3CH_2COO^-$. c) From $CH_3CH_2CH_2COO^-$. d) From $(CH_3)_2CHCH_2COO^-$. e) From $CH_3CH_2COO^-$. f) From $(CH_3)_2CHCOO^-$.

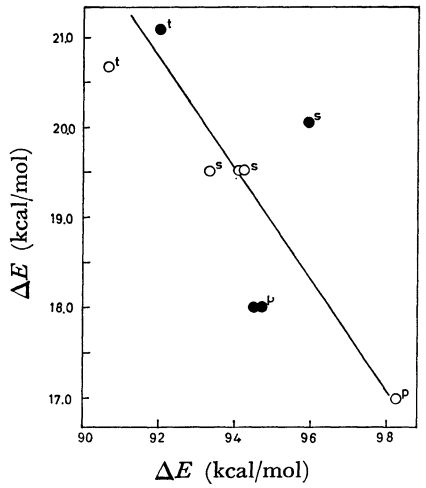


Fig. 5. The relation between ΔE and the partial reactivities of hydrogen atoms in carboxylate ions. ○: α-, ●: β-, p: primary, s: secondary.

This correlation between the observed and the estimated relative probabilities may support the idea that the reactivity of a molecule can be divided into partial reactivities. Furthermore, as is shown in Table 4, the value of ΔE calculated for the α-secondary hydrogen atom of ethyl alcohol is nearly equal to that for the α-secondary hydrogen atom of propyl alcohol or isobutyl alcohol. Similarly, the ΔE for the β-primary hydrogen atom of ethyl alcohol is approximately equal to that for the β-primary hydrogen atom of isopropyl alcohol. For hydrogen atoms in the γ-, δ-, $\cdots$ positions, the same partial reactivities as those for the β-positions are used in the paper of Anber *et al.* The values of ΔE calculated for the β-primary and γ-primary hydrogens may confirm this assignment (Table 4). A similar argument is possible for carboxylate ions (Table 5), although there remains a discrepancy between β-primary and γ-primary hydrogens.

Consequently, the present work, which takes the orientation of hydrogen atoms into consideration, supports the idea that, in hydrogen-abstraction reaction of the hydroxyl radical, the whole reactivity of a molecule can be understood in terms of the partial reactivities assigned to each site of the reaction in the molecule.

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References

1) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc., B.*, **1966**, 742.
2) R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, *Int. J. Radiat. Phys. Chem.*, **3**, 211 (1971).
3) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, and H. Shingu, *ibid.*, **22**, 1433 (1954).
4) K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **27**, 423 (1954); K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).
5) H. Shinohara, A. Imamura, T. Masuda, and M. Kondo, submitted to *Bull. Chem. Soc. Jpn.*
6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).
7) K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **34**, 442 (1961).
8) K, Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **34**, 1111 (1961).
9) K. Shimizu, K. Miyamichi, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **90**, 1206 (1969).
10) K-D. Asmus, H. Möclkel, and A. Henglein, *J. Phys. Chem.*, **77**, 1218 (1973).