Empirical Estimations of the Taft σ^*

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In the previous paper,[1] the heats of formation of gaseous carbonium ions were well estimated by the group contribution method. In the present work, the estimation of the Taft σ^*[2] is tried by means of both group contribution method and quantum-chemical calculations with simple LCAO-MO. The Taft σ^* has been used as an empirical reactivity index to understand the reactivities in the heterogeneous catalysis,[3] as well as in liquid-phase organic reactions. The additivity of the σ^* was demonstrated by Taft,[4] and Leffler and Grunwald,[4a] hence the group contribution method should be applicable also for the extended estimation of the σ^*.

The reactivities of hydrocarbons have been extensively discussed with the simple LCAO-MO by Fukui.[5] On the other hand, many works have been reported concerning relations among σ, σ°, σ^+, and quantum chemical indexes.[6] In the present work, a correlation was also investigated between the Taft σ^* and $|C_r^{\mathrm{N}}|$ determined by the simple LCAO-MO method for σ systems.[5]

Results and Discussion

Simple LCAO-MO Method. The absolute value of the coefficient, $|C_r^{\mathrm{N}}|$, of a sp^3 hybridized orbital of an unpaired electron belonging to the non-bonding molecular orbital of an alkyl radical is reported to be correlated with the bond strength of R-H by Fukui *et al.*[7]: in their paper, the bond strength was given by $\Delta H_{\mathrm{C}^+}(\mathrm{R}_1)$, the enthalpy change in the hydride abstraction reaction from a paraffin, $\mathrm{R_1H}$. The value of $\Delta H_{\mathrm{C}^+}(\mathrm{R}_1)$ has been suggested to have empirically a linear relation to σ^*.[3a] Thus, the value of σ^* may be correlated with the value of the above $|C_r^{\mathrm{N}}|$ which is calculated by the simple LCAO-MO for σ electron systems.

The calculated values of $|C_r^{\mathrm{N}}|$ are given in Table 1, where the values of Coulomb and resonance integrals were all taken from the paper by Fukui *et al.*,[7] and the calculation was carried out with a computation program named CHEMO-MO-2, which permits the chemical formula inputs.

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Table 1. Comparison of observed and calculated σ^*

		σ^* obs.[a)]	σ^* calc.[b)]	difference	$\lvert C_r^N \rvert$
1	CH_3	0	0[c)]	—	0.8965
2	CH_3CH_2	−0.100	−0.098	−0.002	0.8789
3	n-C_3H_7	−0.115	−0.121	−0.006	0.8769
4	i-C_4H_9	−0.125	−0.143	0.018	0.8746
5	n-C_4H_9	−0.130	−0.130	0	0.8767
6	t-$C_4H_9CH_2$	−0.165	−0.166	0.001	0.8720
7	i-C_3H_7	−0.190	−0.196	0.006	0.8608
8	s-C_4H_9	−0.210	−0.218	0.008	0.8588
9	$(C_2H_5)_2CH$	−0.225	−0.241	0.016	0.8568
10	t-$C_4H_9(CH_3)CH$	−0.280	−0.264	−0.014	0.8539
11	t-C_4H_9	−0.300	−0.293	−0.007	0.8422
	n-C_5H_{11}				0.8766
	n-C_6H_{13}				0.8766
12	$(C_6H_5)_2CH$	0.405	0.400	0.005	0.8445
13	$C_6H_5CH_2$	0.215	0.200	0.015	0.8711
14	$C_6H_5(CH_3)CH$	0.110	0.102	0.008	0.8524
15	$C_6H_5(C_2H_5)CH$	0.04	0.079	−0.039	0.8504
16	$C_6H_5(OH)CH$	0.765	0.760	0.005	—
17	$(OH)CH_2$	0.555	0.560	−0.005	—

a) From Ref. 2. b) By the group contribution method. c) By definition.

The correlation is very fine for alkyl groups whose σ^* values are known, as shown in Fig. 1. Thus, σ^* is empirically given by Eq. (1),

$$\sigma^* = -5.16 + 5.75\lvert C_r^N \rvert. \tag{1}$$

However, the correlation with groups containing π-electrons or heteroatoms is poor, some examples of which are also given in Fig. 1.

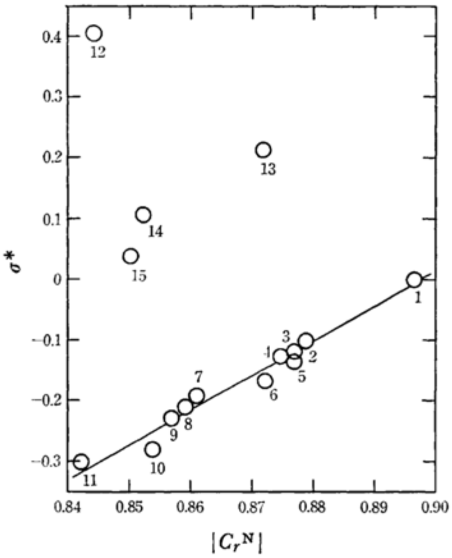

Fig. 1. A correlation between $\lvert C_r^N \rvert$ and σ^*. Numbers refer to Table 1.

Group Contribution Method. The principle of the group contribution method[1)] for the calculation of σ^* is mathematically expressed by Eq. (2) with a methyl group as the base group,

$$\sigma^*(R) = \sigma^*(CH_3) + \sum n_i Z(X_i) \tag{2}$$

where $\sigma^*(R)$ is the Taft σ^* of a group R, $\sigma^*(CH_3)$ is that of a methyl group defined to be zero, $Z(X_i)$ is the group contribution of the part-structure to σ^*, and n_i is the number of the equivalent substitutions. The values of $Z(X_i)$ for three kinds of methyl substitutions are considered: primary,[*1] next-adjacent secondary and two-next secondary.[*2] These values together with those of primary phenyl and primary hydroxyl substitutions were obtained by the method of least-squares from seventeen σ^* values in Table 1. They are shown in Table 2, where primary phenyl and hydroxyl groups substitute the primary methyl group.

Table 2. Contribution of the substituting groups

	Contribution	St. error
CH_3		
Primary	−0.098	0.004
Next-adjacent secondary	−0.023	0.004
Two-next secondary[a)]	−0.009	0.017
Primary phenyl[b)]	0.297	0.007
Primary OH[b)]	0.658	0.012

a) Calculated from $CH_3CH_2CH_2CH_2$ alone.
b) Substituting the primary methyl group.

[*1] For the estimation of the heats of formation of carbonium ions (Ref. 1), primary methyl substitutions were classified into three kinds, however, here only a kind is considered for them.

[*2] In C_4-C_3-C_2-C_1- of n-butyl group, C_1 is the base group, C_2 is primary, C_3 is next-adjacent secondary, and C_4 is two-next secondary.

The value for two-next secondary methyl group has a comparatively large standard error, which should be due to its estimation from only one value of $\sigma^*(CH_3CH_2CH_2CH_2)$. It may be, however, not so far from the true value, because the calculated σ^* of an isopentyl group agrees sufficiently with the one estimated in Fig. 1 from $|C_r^N|$ of an isopentyl radical.[*3] The contribution of the farther than two-next should be zero, which is indicated by $|C_r^N|$ of *n*-pentyl and *n*-hexyl radicals.

The agreement of the calculated σ^* with the observed ones is satisfactory, except for $C_6H_5(CH_3CH_2)CH$. Thus, the σ^* values of homologous groups can be estimated by Eq. (2). The validity of the group contribution cannot be established for other part structures because σ^* was not observed upon many groups which have equivalent substitutions.

The attenuation of the inductive effect by methylene group has been discussed.[4,8] As regards σ^*, Taft gave 1/2.8 to methylene group as the attenuation factor for some functional groups.[4] In the present paper, it will be discussed on all available data, based on the group contribution concept. Because the σ^* values of the groups having fluorine, chlorine, phenyl, propenyl, and methoxyl substituents at the various locations are known, the contribution of the substituents can be calculated by using $Z(X_i)$ already obtained. An example of the calculation is shown by the case of $CF_3CH_2CH_2$,

$$\begin{aligned}\sigma^*(CF_3CH_2CH_2) = \sigma^*(CH_3)\\ &+ Z(\text{primary } CH_3)\\ &+ Z(\text{next-adjacent secondary } CH_3)\\ &+ 3W(F)_3 \qquad (3)\end{aligned}$$

where the suffix 3 of $W(F)_3$ is the length of the carbon chain. Thus, the contribution of F attenuated by three methylenes, $W(F)_3$, can be calculated. The results of the calculations are shown in Fig. 2, where the abscissa is the carbon chain length, *m*. As for methyl groups, the *Z* values in Table 2 are used as the *W* values. In the cases of fluorine, chlorine, and methyl group, linear relations are obtained, which are formulated as following,

$$W(X_i)_m = W(X_i)_0 \exp(-2.3\, a(X_i)\cdot m)\,. \qquad (4)$$

The slopes of these linear relations, $a(X_i)$, give the attenuation effects of the one carbon chain for each functional group. The slopes are all about 0.43. Thus, the contribution of the functional group is diminished to about 1/2.7 for each carbon chain. As for phenyl group, the value for unattenuated point is out of the line and the slope is distinctly different from the others.

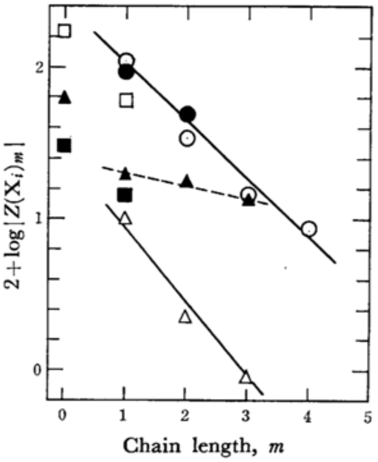

Fig. 2. The attenuation effect of methylene group for σ^*.
○: F, ●: Cl, ▲: Phenyl, △: Methyl
□: CH_3O, ■: $CH_3CH{=}CH$

TABLE 3. THE σ^* VALUES OF X_i CH=CH GROUPS

Group (X_i CH=CH)	$\sigma^{*a)}$	$W(X_i)_0$ or $\sigma^*(X_i)$
trans-$O_2NCH{=}CH$	1.70	3.73[b)]
trans-$Cl_3CCH{=}CH$	1.188	2.65
trans-$HOOCCH{=}CH$	1.012	2.84[c)]
$ClCH{=}CH$	0.900	2.84[d)]
trans-$Cl_2CHCH{=}CH$	0.882	1.94
$CH_2{=}CH$	0.653	0.490
$C_6H_5CH{=}CH$	0.420	0.600
$CH_3CH{=}CH$	0.360	0

a) From Ref. 2.
b) Calculated from $O_2NCH_2CH_2$.
c) Calculated from $HOOCCH_2$.
d) Calculated from $ClCH_2$.

An attenuation effect of the CH=CH group is studied on eight σ^* values shown in Table 3. The values of $W(X_i)_0$ are the observed or calculated $\sigma^*(X_i)$ by Eq. (4), of which $a(X_i)$ of the methylene group for various X_i is assumed to be 0.43. The calculation of the attenuation is made by the following equation,

$$\sigma^*(X_iCH{=}CH) = \text{const.} + a_{CH=CH}\ W(X_i)_0 \qquad (5)$$

where the const. is the contribution of the CH=CH group and $a_{CH=CH}$ is its attenuation effect. The value of $a_{CH=CH}$ is statistically calculated as 0.29 ± 0.05. This figure means that the attenuation effect of CH=CH is smaller in comparison with that of two methylene groups.

If the attenuation effect is generally described, the application of the group contribution method for σ^* may be extended further.

[*3] −0.132 from the $|C_r^N|$ value of 0.8764 and −0.139 by the group contribution method.

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