A Molecular Orbital Discussion of the Hammett Equation

Semi-empirical Interpretation on the Abnormality of the Benzyl Anion Type Substituent

Teiji TSURUTA, Takayuki FUENO and Junji FURUKAWA*

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This paper presents a semi-empirical consideration on the abnormality of the benzyl anion type substituent in electrophilic aromatic substitutions from the standpoint of the simple molecular orbital theory. Substituent effects in nucleophilic and radical reactions are also discussed.

Serious deviations from the Hammett equation are often observed[18] for some benzyl anion type substituents such as CH_3O or $N(CH_3)_2$, in electrophilic reactions. In the previous paper,[18] we proposed that another series of the substituent constants (σ_e) are to be used in the electrophilic reactions.

This paper presents a semi-empirical consideration on the abnormality of the benzyl anion type substituents in electrophilic reactions from the standpoint of the simple molecular orbital theory. In this connection, substituent effects in nucleophilic and radical reactions are also discussed.

The rate constant k of a chemical reaction is given by Eq. (1) or (2):

$$k=Ae^{-\Delta H^{*}/RT} \qquad (1)$$

$$k=\kappa\frac{\mathbf{k}T}{h}\, e^{\Delta S^{*}/R}\, e^{-\Delta H^{*}/RT} \qquad (2)^{5)}$$

where A is frequency factor; κ, transmission coefficient; $\mathbf{k}$, Boltzmann constant; T, the reaction temperature (°K); h, Planck constant; ΔS^{*}, activation entropy; ΔH^{*}, activation enthalpy and R denotes the universal gas constant.

The activation enthalpy may be divided into three terms:

$$\Delta H^{*}=C+\Delta E_{\sigma}+\Delta E_{\pi} \qquad (3)$$

where ΔE_{σ} and ΔE_{π} are the changes of electronic energies associated with σ- and π-bond in the activation process, respectively, and C is referred to contributions other than from the electronic energies.

Since the simple molecular orbital (MO) treatment on the substituent effect is merely concerned with the energy of the π-electron, it will easily be seen from

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* 鶴田 禎二, 笛野 高之, 古川 淳二

Eqs. (1), (2) and (3) that the method is only reasonably applicable to reaction series of the conjugated systems in which the terms $\varDelta E_\sigma$ and C can be approximated as constant.

1. CORRELATIONS OF THE SUBSTITUENT EFFECT WITH THE ELECTRON DENSITY AND WITH THE LOCALIZATION ENERGY

There are two ways[2] to interpret the substituent effect on the chemical reactivity by the molecular orbital theory. The first is the static method which deals with the effects of the substituent upon the π-electron density or free valence in the ground state. The alternative method, the localization method, calculates the difference in the π-electron energies between localized and ground states of the relevant conjugated system.

The substituent effects upon the reactivity of aromatic compounds are quantitatively expressed by the Hammett equation,[7]

$$\log k/k_0 = \rho\sigma \tag{4}$$

where k_0 is the rate constant of reaction for the unsubstituted componud, k for the substituted compound, and ρ and σ are the reaction and substituent constants.

From Eqs. (1) and (4),

$$\log k/k_0 = (\log A - \log A_0) - (\varDelta H^{\ddagger} - \varDelta H_0^{\ddagger})/2.3RT \tag{5}$$

The Hammett equation is known[18] to be valid for reactions where the following condition is satisfied,

$$\log A - \log A_0 = (a/2.3R)(\varDelta H^{\ddagger} - \varDelta H_0^{\ddagger}) \tag{6}$$

where a is the constant of the proportionality. Thus, Eq. (5) is reduced to

$$-\log k/k_0 = (1/2.3R)[(1/T) - a](\varDelta H^{\ddagger} - \varDelta H_0^{\ddagger}) = B\varDelta\varDelta H^{\ddagger} \tag{7}$$

where

$$B = (1/2.3R)[(1/T) - a]^{*}$$

and

$$\varDelta\varDelta H^{\ddagger} = \varDelta H^{\ddagger} - \varDelta H_0^{\ddagger}$$

If it is assumed[2] that $\varDelta\varDelta H^{\ddagger}$ consists largely of $\varDelta\varDelta E_\pi^{\ddagger}$, the Hammett equation may be connected with the localization energy, because $\varDelta\varDelta E_\pi^{\ddagger}$ is approximated as the difference between the localization energies of reactions for substituted and unsubstituted compounds.

From a similar assumption[2], variations of the electron density in the ground state can be related with the Hammett equation.

The Hammett substituent sigma is defined as

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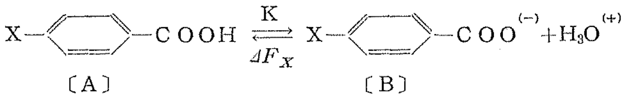
* The constant $(1/a)$ is referred to as "isokinetic temperature".[11]

$$\log K/K_0 = \sigma \tag{8}$$

where K is the equilibrium constant of dissociation for the substituted benzoic acid in water at 25°, and K_0 for the unsubstituted acid.



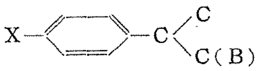
(9)

where $\varDelta F_X$ is the free energy difference between the two systems.

It has widely been recognized that the Hammett sigma constants are applicable[11] not only to a large variety of aromatic reactions, but also to various physical phenomena concerned with the electron density in the ground state.

Jaffé[10] assumed that the substituent constant for *p*-X group is proportional to the change in the electron density at *para* position (A) to X-group. The same constant of proportionality was used for *meta* isomer in his paper.

(I)



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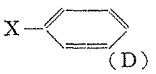

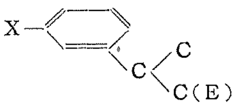

As is considered from the definition of the sigma constant, it may be more reasonable to relate the sigma value with the electron density at the position (B) rather than (A).

According to simple LCAO MO method*, the ratio of the density changes at the corresponding positions *para* to the substituent X in the two compounds (I) and (II) is given by Eq. (10),

$$(\varDelta q_B/\varDelta q_A)_p = \frac{0.033-0.039a}{0.143-0.135a} \tag{10}$$

For *meta* positions,

$$(\varDelta q_E/\varDelta q_D)_m = \frac{-0.008a}{-0.024a}\,. \tag{11}$$

From Eqs. (10) and (11), it can be seen that the ratios of the density change are different in the two pairs of derivatives.

As was pointed out in the previous paper,[18] the sigma values may vary according to the reaction mechanism. Jaffé[11] tabulated the median and mean values as well as the ranges of the sigma constant for fifteen substituents such as OH, $N(CH_3)_2$, COOR and others. The *mean* values of *m*- and *p*-sigma constant for some

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* The linear combination of the atomic orbital (molecular orbital) method in which the overlap integral is assumed zero, the exchange integral, β, and the parameter ε is 1/3.

substituents are as follows:

Group		*meta*	*para*
1	COOH	0.355	0.265
	$COOC_2H_5$	0.398	0.522
2	CHO	0.382	0.216
	$COCH_3$	0.306	0.516

These values were used in Jaffé's calculation[12] as to the molecular orbital treatment for the substituent effect. However, it is expected, on the basis of empirical organic chemistry as well as the molecular orbital theory, that the relative magnitude of sigma values for *meta* and *para* COOH groups will be parallel to that for the corresponding $COOC_2H_5$ groups. The same situation will also be true of the substituent constants for *meta* and *para* CHO and $COCH_3$ groups. However, from the table, inversions are observed in the relative magnitude of *m*- and *p*-sigma values for the two pairs of the substituents. Partial accounting for the inversion may be found in the multiplicity in the reaction mechanism and in differences in the statistical treatment* as to the substituent constants.

Furthermore, the Hammett plots of F^{19} nuclear magnetic shielding parameter, δ**, for *para* and *meta* substituted fluorobenzenes were found to lie on two separate lines.[6]

From these considerations, it seems questionable to assume the same constant of proportionality between the substituent constant and the variation in the electron density for *meta* and *para* substituents.

In this paper, discussion will be confined to the *para* substitution unless otherwise stated.

2. STANDARD REACTION

If increments of the activation energies in a standard reaction of substituted benzenes are assumed to be proportional to the changes in electron density caused by the substituents, Eqs. (12) and (13) are obtained[13] for E-*** and I-****substituted derivatives, respectively:

$$(\Delta E-\Delta E_0)_{\text{standard}}=a_0\Delta q_p=a_0(0.143-0.135\delta a) \tag{12}$$

$$(\Delta E-\Delta E_0)_{\text{standard}}=a_0\Delta q_p=a_0(-0.039\delta a) \tag{13}$$

where ΔE_0 is the activation energy for the parent compound, a_0 is a constant, and

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* The present authors are inclined to prefer the larger values as the sigma constant for *para* substituents.

** The parameter δ is considered as a measure of the electronegativity of the atom attached by fluorine.[12]

*** Benzyl anion type substituent.

**** Non-conjugating substituent.

$\delta\alpha$ is the increment of the Coulomb integral for the substituent. From Eqs. (7), (12) and (13),

$$(-\log k/k_0)_{\mathrm{standard}} = B_0\, a_0(0.143 - 0.135\delta\alpha) \tag{14}$$

$$(-\log k/k_0)_{\mathrm{standard}} = B_0\, a_0(-0.039\delta\alpha) \tag{15}$$

Since the parameter $\delta\alpha$ is a measure for the electronegativity of the heteroatom in the relevant substituent, it seems reasonable to assume the following correspondence between σ and $\delta\alpha$:

$$0.143 - 0.135\delta\alpha = b_0\sigma_e \tag{16}$$

$$-0.039\delta\alpha = b_0\sigma_i \tag{17}$$

where subscripts e and i are concerned with E- and I-substituents, and b_0 is a constant.

From Eqs. (14)-(17),

$$(-\log k/k_0)_{\mathrm{standard}} = B_0 a_0 b_0 \sigma_e = \rho_0\sigma_e \tag{18}$$

$$(-\log k/k_0)_{\mathrm{standard}} = B_0 a_0 b_0 \sigma_i = \rho_0\sigma_i \tag{19}$$

where $\rho_0(=B_0 a_0 b_0)$ may be defined as the standard reaction constant.

3. ELECTROPHILIC REACTIONS

(A) Aromatic Substitutions

If it is assumed that changes in the activation energy is equal to those in the localization energy, Eq. (20) is obtained for I-substituted benzenes :

$$\frac{-(\Delta E_i - \Delta E_0)_{\mathrm{electrophilic}}}{|\beta|} = -0.136\delta\alpha \tag{20}$$

And hence, from Eqs. (7), (17) and (20),

$$\begin{aligned}(-\log k/k_0)_{\mathrm{electrophilic}} &= B_1(-0.136)\delta\alpha \\ &= B_1(0.136/0.039)b_0\sigma_i = \rho_1\sigma_i\end{aligned} \tag{21}$$

where ρ_1 is regarded as an electrophilic reaction constant and B_1 is defined in a way similar to B_0 in Eq. (18) or (19).

In a similar way, $(\Delta E - \Delta E_0)$ for the E-substituted benzenes is given in terms of $\delta\alpha$,

$$\frac{-(\Delta E_{es} - \Delta E_0)_{\mathrm{electrophilic}}}{|\beta|} = 0.714 - 0.0603\delta\alpha \tag{22}$$

where es is concerned with the E-substituents.

And hence,

$$-\log k/k_0 = B_1(0.136/0.039)(0.205 - 0.173\delta\alpha) \tag{23}$$

For a Hammett plot of the E-substituted derivatives to fall in the line for the I-substituted ones, Eq. (24) should hold well:

$$-\log k/k_0 = B_1(0.136/0.039)(0.143-0.135\delta\alpha) \qquad (24)$$

Comparing Eq. (23) with Eq. (24), larger deviations* are expected in the relative rate constants of the E-substituted benzenes with smaller $\delta\alpha$ such as in OCH_3- and $N(CH_3)_2$-derivative. Little deviation of the Hammett plots for halogenobenzene may be attributed to a large value** of the Coulomb integral of halogen atom. It can be seen that the two straight lines for Eqs. (23) and (24) intersect with each other at a point of $\alpha=1.63$.

From Eqs. (21) and (23), a series of the substituent constants, which is regarded as equivalent to σ_e[16] or σ^{+}[15] can be obtained.

(B) Menschutkin Reaction.

It may be of interest to note that, contrary to the aromatic substitutions, the abnormality has not been found[11] in the Hammett plots for *para*-substituted dialkylanilines in the Menschutkin reaction (25) which is an electrophilic reaction in nature.

$$XC_6H_4N(CH_3)_2 + CH_3I \longrightarrow [XC_6H_4N(CH_3)_3]^{(+)}I^{(-)} \qquad (25)$$

The relative localization energy, $(\Delta\Delta E_{es})_m$, of the E-substituted aniline in the Menschutkin reaction can be calculated from a procedure similar to that for the aromatic substitution by assuming the amino group to be isolated from the conjugation in the activated state.

$$\frac{-(\Delta\Delta E_{es})_m}{|\beta|} = \frac{-(\Delta E_{es}-\Delta E_0)_m}{|\beta|} = -0.065\delta\alpha_N + 0.138 - 0.122\delta\alpha_X \qquad (26)$$

where the subscript m refers to the Menschutkin reaction.

Considering the order of magnitude*** of $\delta\alpha_N$, Eq. (26) will be reduced to Eq. (27).

$$\frac{-(\Delta\Delta E_{es})_m}{|\beta|} \fallingdotseq (0.130-0.122\delta\alpha_X) \fallingdotseq (\text{const.})(0.143-0.135\delta\alpha_X) \qquad (27)$$

A comparison of Eq. (27) with Eq. (16) will give a possible interpretation as to the applicability of the standard sigma value for the E-substituents in the Menschutkin reaction despite of its electrophilic nature.

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* Discussion may as well be confined to qualitative one, because any attempt to derive the precise σ values from the simple LCAO MO calculations seems to have little meaning.

** For example, $\delta\alpha$ of Cl atom is considered to be about 1.8.

*** About 0.1.

For I-substituted aniline, the relative localization energy, $(\Delta\Delta E_l)_m$, is given by Eq. (28),

$$\frac{-(\Delta\Delta E_l)_m}{|\beta|} = -0.058\delta\alpha_X\,. \tag{28}$$

In the actual reaction, the disaccord between Eqs. (17) and (28) was very small, which is accounted for on the basis of the small values of the Coulomb integral and of its coefficients in the Eqs. for the typical I-substituents*.

The electron density change at nitrogen atom caused by an E-substituent is given by

$$\Delta q = 0.094 - 0.065\delta\alpha_N - 0.079\delta\alpha_X \tag{29}$$

Considering the order of magnitude of the parameter $\delta\alpha_N$, the equation is reduced to

$$\Delta q \doteqdot (\text{const.})(0.143 - 0.135\delta\alpha_X) \tag{30}$$

Equation (30) suggests that the electron density change at the nitrogen atom may fit the standard Hammett sigma constant. Partial confirmation of this conclusion can be found in the substituent effect on the stretching vibration of the NH bonding of aromatic amines.[11]

4. NUCLEOPHILIC AND RADICAL SUBSTITUTIONS

The relative activation energies of nucleophilic and of radical aromatic substitutions are obtained from similar LCAO MO calculations.

(a) Nucleophilic Substitutions

i. For E-Substituted Derivatives.

$$\frac{-(\Delta E_{es} - \Delta E_0)_n}{|\beta|} = -0.321 + 0.309\delta\alpha^{**} \tag{31}$$

ii. For I-Substituted Derivatives.

$$\frac{-(\Delta E_l - \Delta E_0)_n}{|\beta|} = 0.136\delta\alpha \tag{32}$$

where the subscript n refers to the nucleophilic reactions.

(b) Radical Substitutions

i. E-Substituted Derivatives.

$$\frac{-(\Delta E_{es} - \Delta E_0)_r}{|\beta|} = 0.197 - 0.147\delta\alpha \tag{33}$$

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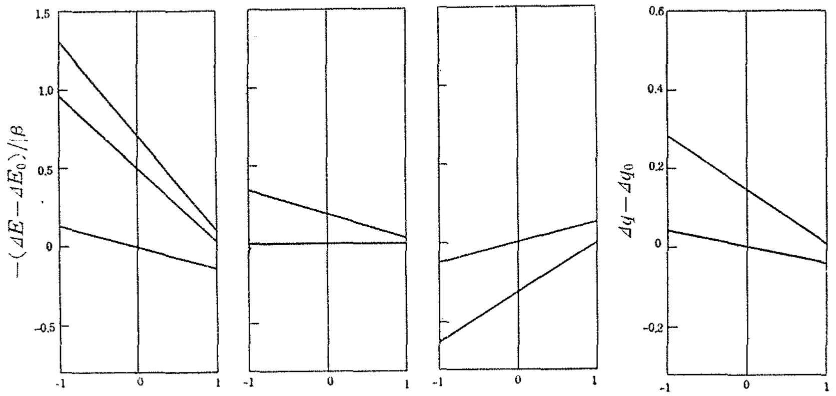
* $\delta\alpha_{CH_3} \doteqdot -0.3$.

** In Jaffé's paper[13], these figures are misprinted.

ii. I-Substituted Derivatives.

$$-\frac{(\Delta E_t-\Delta E_0)_r}{|\beta|}=0 \qquad (34)$$

where r is concerned with the radical reactions. Equations (31)-(34), together with Eqs. (20) and (22), in a range of the coulomb integral, $-1>\delta\alpha>1$, are illustrated in Fig. 1. Curves for the electron density are also added to the Figure for comparison.



δα A. Electrophilic
δα B. Radical
δα C. Nucleophilic
δα D. Density

Fig. 1. Relative activation energy for substitution reaction and relative electron density at *para* position.

From the Figure, the peculiarity of the E-substituents can be expected only in the electrophilic substitution. The relative situation of the two straight lines for the nucleophilic substitution may roughly be regarded as merely a mirror image of that of the lines for the electron density.

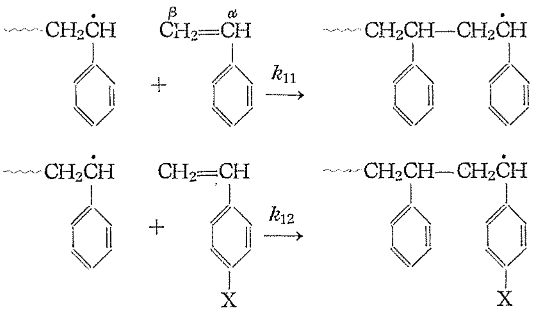
With aromatic substitution by phenyl radical, the rho value was reported as 0.675[11]. All of the substituents examined in this reaction are electron attracting ‒‒chloro-, nitro-, dichloro-, and trichloro-group ($\sigma>0$). However, since methoxy-group ($\sigma<0$) also activates[17] the *para* position towards the radical attacking, the reaction constant ρ may have a negative sign in this case. These considerations make it possible to conclude that the dependence of the rate of radical attacking upon the nature of the substituent is much smaller than in the case of the ionic substitutions, and so, factors other than the localization energy may have more serious influence upon the course of the radical reaction. Much smaller values of the reaction constant $|\rho|$ and of the correlation coefficient r in the radical substitution[11] may be considered to support the above discussion.

It is seen from the published data [1][8][9][17] that the effects of the polarity of the attacking radical on the orientation was very slight in the case of E-substituted benzenes. This seems to suggest that the relative magnitude of the activation energies in *m*- and *p*-derivatives is primarily determined by the marked difference* in the localization energies, which may account for the *o*- and *p*-orientation.

The situation, however, was found to be no longer valid with some I-substituted derivatives such as trichloromethylbenzene[4] where *m*-orientation becomes significant. A possible interpretation for this is that the difference in the localization energies of the *m*- and *p*-I-substituted isomers is so small that the relative magnitude of the activation energies may be inversed in response to minor factors other than the localization energy. It may be noted that the *mata* orientation tends to predominate with the increase in the negativity of the attacking radicals[4].

We have so far discussed the reactivity of aromatic compounds on the basis of the assumption that the position to be replaced by a reagent is isolated from the conjugated system in the activated state. However, the approximation will no longer be applicable to compare reactivities of derivatives in which difference in the localization energies is not significant.

The monomer ractivity ratio, r_1, in a radical copolymerization of vinyl compounds is the ratio of rate constants of the two propagation reactions,



According to the simple MO treament, the ratio r_1 ($=k_{11}/k_{12}$) should be determined by the energies necessary to localize the β-carbon from the π-conjugation system in the two styrenes, respectively. Contrary to this, the ratio was found to be varied with natures of the attacking radicals[3].

It was also reported that inversions in the substituent effect on the ractivity ratio might take place in the copolymerization of styrene derivatives. As an example for this it may be cited that the Hammett plot has a negative rho constant in the reaction of the substituted styrene monomer with methyl methacrylate radical but has a positive one in the corresponding reaction with styrene radical.

These phenomena may in part be attributed to the entropy term, but it will be reasonable to consider that π-conjugation between the monomer and the attacking

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* For example, the localization energies of *m*- and *p*-position in chlorobenzene were reported as 1.843 γ and 1.837 γ, respectively, where γ denotes the resonance integral with overlap integral 0.25[3].

radical should be taken into consideration in the activated state. Yonezawa and others[19] advanced a theory in which the π-conjugation energy was assumed to play an important role in the propagating process. A parallelism was observed between the relative conjugation energy and the monomer reactivity ratio with butadiene or styrene type monomers as reactants; but the situation was not true of vinyl chloride, the localization energy of which was far larger than that of the other two types of monomer.

The importance of the conjugation energy can also be seen from the fact that vinyl alkyl ether may be incorporated into a radical copolymerization with acryl ester, whereas the single polymerization of the former monomer is very difficult.

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