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Semi-empirical Treatments of the Nonlinearity of Free Energy Correlations in Aromatic Side-chain Reactions. The Multiplicity of Substituent Constants

By Takayuki FUENO, Tadashi OKUYAMA and Junji FURUKAWA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

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The nonlinearity of free energy correlations of the substituent effects in aromatic side-chain reactions has been treated by the simple LCAO MO method. The ionization equilibria of substituted phenylacetic acids, leading to the definition of "normal" substituent constants, σ^0, were taken as the basis for theoretical tests of the correlations. Thus, the integral parameters for various substituents were determined in such a way that the calculated π-electron charge densities for meta and para carbons in benzenes were proportional to the corresponding σ^0-constants. Several other typical side-chain reactions of substituted benzenes were simulated by the corresponding standard processes, and the effects of substituents on these reactions were examined by the perturbation calculations of the π-electron energy changes accompanying the reactions. It has been found that the substituent constants, σ, σ^+ and σ^-, are linearly related to the calculated energy changes. It is suggested that the treatment may be extended to other reactions to account for the sliding-scale variation in substituent constants from reaction to reaction.

It has been customary to utilize Hammett's $\rho\sigma$ equation[1] for correlating observations concerning the effects of ring substituents on the rate or equilibrium data for the reactions of benzene derivatives. The Hammett equation in its original form presumes that the standard free energy changes in certain types of reactions of substituted benzene derivatives are in a linear relation with those in the corresponding benzoic acid ionizations. This linear free energy relationship has been borne out well in many cases; indeed, there exists a voluminous literature that indicates the applicability of the Hammett equation.[2]

Several authors[3-9] have looked into the physical basis of the Hammett equation, particularly into the nature of the substituent constants, in terms of the simple molecular orbital method. These studies have been briefly reviewed in a recent article by Ehrenson.[9] Among others, Jaffé's attempts[3] to correlate the Hammett σ-constants with π-electron charge densities on the ring carbons bearing reaction sites seem to have illuminated, though with limited success, the role of mobile π-electrons in governing the relative magnitudes of σ-constants.

It is known, however, that the original Hammett relation suffers some limitations depending on the type of reaction and on the solvent conditions; thus, a number of modified sets of σ-values have been proposed by many authors.[2,10-13] The current belief that para substituents are more or less subject to multiplicity in σ-value is a conceptual outgrowth of these situations. This nonlinearity of free energy correlations, i. e., the "sliding-scale" character of sigma values, is believed to arise from the different extents of direct conjugation between substituents and reaction centers in different reactant structures and reaction types.[12,14] A molecular orbital consideration of such a multiplicity of substituent constants was first undertaken by Jaffé,[4] who was able to reproduce approximately the enhanced sigma values required for strongly electron-attracting para substituents in the ionizations of aniline and phenol.[1] The exalted electron-releasing character of some methylene anion-type para substituents in electrophilic substitutions was also accounted for by us from an examination of the effects of these substituents on the ring carbon localization energies.[7] Similar effects of this last group of substituents on the extracyclic reaction

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[1] L. P. Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, N. Y. (1940), Chapter 7.

[2] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[3] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 285, 1554 (1952); **21**, 415 (1953).

[4] H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 5843 (1954).

[5] F L. J. Sixma, *Rec. trav. chim.*, **72**, 273, 538, 543, 673 (1953); **73**, 235, 243 (1954); *J. Chem. Phys.*, **19**, 1209 (1951).

[6] D. Peters, *J. Chem. Soc.*, **1957**, 2654.

[7] T. Tsuruta, T. Fueno and J. Furukawa, *Bull. Inst. Chem. Res., Kyoto Univ.*, **34**, 214 (1956).

[8] M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3548 (1962).

[9] S. Ehrenson, " Progress in Physical Organic Chemistry," Vol. 2, Ed. by S. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience, New York (1964), p. 195.

[10] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[11] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[12] Y. Yukawa and Y. Tsuno, This Bulletin, **32**, 965, 971 (1959).

[13] C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry," Vol. 2, Ed. by S. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience, New York (1964), p. 323.

[14] H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

sites have recently been discussed by Ehrenson.⁹⁾

The purpose of the present paper is to analyze the relative magnitudes of various sets of substituent constants from a unified theoretical standpoint, and thereby clarify the cause of the above-mentioned nonlinearity of free energy correlations. To this end we will conduct second-order perturbation calculations of the energy changes of systems comprising substituted benzenes and reactive side-chains. In principle, this is a computational elaboration of the afore-mentioned treatment of Ehrenson.⁹⁾ As the basis for comparisons among different sets of substituent constants, the ionization equilibria of substituted phenylacetic acids, which lead to σ^0-values,¹¹⁾ have been selected. This is because, in these compounds, the reaction site is insulated from the aromatic π-conjugation, which otherwise may blur the standard with which one may test the departure from the linear free energy relationships. The effects of substituents on other types of benzene side-chain reactions, leading to σ, σ^+ and σ^- constants,¹,¹⁰⁾ will be examined by calculating the π-electronic energy changes accompanying the reactions. It will be shown that these calculated energy changes are closely related to the various substituent constants. It appears that extensions of the present treatment may provide a promising route to account for the sliding-scale variations of substituent constants from reaction to reaction.

The Method of Calculation

All the calculations were carried out by the simple LCAO MO method (overlap neglected). First, the π-electronic MO energies, $E_i=\alpha+m_i\beta$, and the corresponding MO coefficients, C_{it}, were calculated for various monosubstituted benzenes, XC_6H_5 (as the common unperturbed substrates). α and β have their usual meanings. Second, analogous calculations were made for isolated (unperturbed) extracyclic reaction centers, Y, whose energies and coefficients are $F_j=\alpha+n_j\beta$ and C_{ju} respectively. Third, the delocalization energies, DE, due to the linking of XC_6H_5 and Y to form disubstituted benzenes, XC_6H_4Y, were calculated from the following familiar expression,¹⁵⁾ which has been derived by the second-order perturbation method:

$$DE=2\left\{\sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}}-\sum_{j}^{\text{occ}}\sum_{i}^{\text{unocc}}\right\}\frac{(C_{ir})^2(C_{js})^2}{m_i-n_j}\left(-\frac{\gamma^2}{\beta}\right) \tag{1}$$

where the subscripts r and s denote the carbon atoms at which the components are bonded; γ is the resonance integral for such bonds. Equation 1 was used also for the system XC_6H_4Y' formed after the occurrence of the side-chain reactions. Finally, the total energy of the product, XC_6H_4Y', relative to that of the reactant, XC_6H_4Y, was obtained from

$$\Delta E_\pi=c-\Delta E \tag{2}$$

where

$$\Delta E=DE'-DE \tag{3}$$

and

$$c=2\sum_{j}^{\text{occ}}(F_j'-F_j) \tag{4}$$

The prime appearing in Eqs. 3 and 4 indicates that the quantities correspond to the product systems. Since c is independent of the substituents, X, the relative stabilities of the product systems may be expected to increase as the delocalization energy difference, ΔE, increases.

The integral parameters of heteroatoms and their bonds necessary for the calculation of the energies and coefficients of monosubstituted benzenes were determined by imposing the condition¹⁶⁾ that the charge densities on the para and meta ring carbons so obtained be proportional to the corresponding Taft σ^0-constants. The inductive effects of the substituents were roughly taken into account by assigning Coulomb integral increments to ring carbons.³⁾ Specifically, the ring carbon linked with a substituent atom, X, of the Coulomb integral parameter, k_X, was assumed to have a Coulomb integral increment, $\delta_{CX}k_X$; the inductive parameter, δ_{CX}, was taken to be 0.3 unless otherwise noted. The increments for the next-nearest ring carbons were assumed to be $\varepsilon\delta_{CX}$, with $\varepsilon=1/3$, but they were truncated for other carbon atoms.

For fixing the proportionality constant between charge densities and σ^0-values, only σ^0 meta and

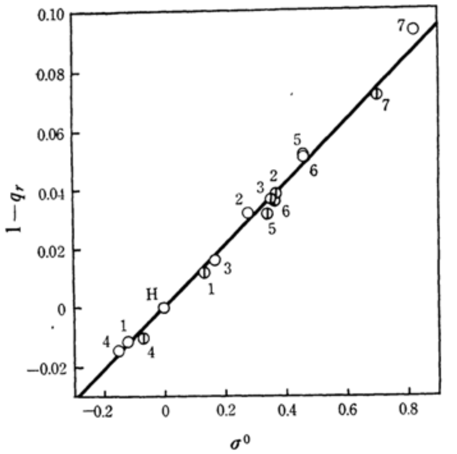

Fig. 1. The charge densities in substituted benzenes against σ^0-constants.
○, para; ⦶, meta
Numbers correspond to the substituents given in Table I. The symbol H indicates hydrogen.

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[15] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

[16] That is, $\sigma_r{}^0=\kappa(1-q_r)$, where q_r is the π-electron density calculated for a meta or para carbon, and where κ is a proportionality constant ($\kappa=9.68$).

Table I. Substituents and integral parameters

No.	Substituent	Integral parameters[a]		
1	CH_3O	$k_O=0.6$	$h_{C-O}=0.5$	$\delta_{CO}=0.3$
2	Cl	$k_{Cl}=0.9$	$h_{C-Cl}=0.45$	$\delta_{CCl}=0.6$
3	F	$k_F=1.0$	$h_{C-F}=0.6$	$\delta_{CF}=0.5$
4	CH_3	$k=-0.15$[b]		
5	$COCH_3$	$k_O=1.3$	$h_{C=O}=1.2$	
		$k_C=1.3$	$h_{C-C}=0.4$	$\delta_{CC}=0.3$
6	COOR	$k_O=1.3$	$h_{C=O}=1.2$	
		$k_{OR}=0.6$	$h_{C-OR}=0.5$	
		$k_C=1.3$	$h_{C-C}=0.4$	$\delta_{CC}=0.3$
7	NO_2	$k_N=3.0$	$h_{N=O}=1.0$	
		$k_O=1.3$	$h_{C-N}=0.3$	$\delta_{CN}=0.3$
	COOH[c]	$k_O=1.2$	$h_{C=O}=1.2$	
		$k_{OH}=0.6$	$h_{C-OH}=0.5$	
		$k_C=0.57$		
	COO^- [c]	$k_O=0.5$	$h_{C=O}=1.0$	
		$k_C=0.3$		

a) k, Coulomb integral parameter; h, resonance integral parameter; δ, inductive parameter for the ring carbon carrying substituents.

b) Inductive effect model. Ortho carbons are assigned a Coulomb integral increment 0.3 k.

c) Used for the calculations of ionization energies of benzoic acids.

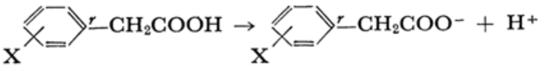
para values of the methyl group will suffice in principle, provided that the group is assumed to be a non-conjugating (inductive) substituent. In practice, however, the σ^0-values for meta and para methoxy groups were also used for the above purpose. Three unknown parameters (two Coulomb integrals, $\alpha+k\beta$, for the methoxy and methyl groups and one resonance integral, $h\beta$, for the ring carbon-methoxy bond) were so adjusted as to give the best straight-line fit of the calculated charge densities when plotted against the four σ^0-values. The slope was thus fixed. The parameters for other substituents were chosen so that the corresponding plots would fall on this straight line. The parameter values finally adopted for the various substituents investigated are listed in Table I. The proportionality of the calculated charge densities to σ^0-values is shown in Fig. 1.

Results

σ^0-Constants.—As has already been mentioned, Jaffé[3] attempted to correlate π-electron densities on meta and para carbons of substituted benzenes with the corresponding Hammett σ-constants. However, such attempts are unjustifiable, since benzoic acids, and also their conjugate bases, more or less involve resonance interactions between substituents and reaction centers.

In contrast, in the case of phenylacetic acids, the reaction site is insulated from the aromatic conjugation, so that the interactions between the ring and its substituents in these acids will remain essentially the same as in substituted benzenes. From the ionization constants of substituted phenylacetic acids, Taft[11] defined the "normal" substituent constants, σ^0. It seems, then, more reasonable to correlate the π-electron distributions in substituted benzenes with Taft's σ^0-constants than with Hammett's σ-constants.

It may be shown that the π-electron distributions in substituted benzenes are related to the dissociation energies of the corresponding phenylacetic acids. The replacement of a benzene hydrogen atom by a CH_2COOH group will introduce a perturbation to the Coulomb integral of the ring carbon, r, at which such a replacement occurs. It is to be expected that the reaction:



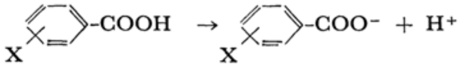
(5)

will accompany the change in this perturbation. Let us denote by $\delta\alpha_r$ and $\delta\alpha_r'$ these perturbations of the Coulomb integral before and after the reaction respectively. According to the simple LCAO MO theory, then, the total π-electronic energy change, ΔE^0, of the benzene part due to the above change in perturbation is given, to a first approximation, by

$$\Delta E^0 = q_r(\delta\alpha_r' - \delta\alpha_r) \tag{6}$$

where q_r is the π-electron density on the ring carbon, r. Since the COO^- group is less electronegative than the COOH group, it is very likely that $\delta\alpha_r' - \delta\alpha_r > 0$. Hence, the dissociation energy of phenylacetic acids will linearly increase with an increase in the q_r value.

Hammett's σ-Constants.—In the ionization of benzoic acids, the ΔE, defined by Eq. 3, is the difference in delocalization energy between benzoic acids and benzoate anions.


(7)

The integral parameters used for an isolated carboxyl group and the carboxylate anion are given in Table I. The parameter values assumed for COOH were the same as those used for COOR, except that the carbon atom in the former was assigned a smaller k value than in the latter. This assignment of a smaller k value was made in order to minimize the inductive effect of the COOH group on the ring in calculating the delocalization energies. Errors arising from such a minimization will be largely canceled by a similar disregard of the COO^- inductive effects in benzoate anions.

The values of ΔE calculated for various substituents are given in Table II. In every case the delocalization stabilization of the acid form was greater than that of the corresponding anion, i. e., $\Delta E<0$. This would mean that the smaller the ΔE in magnitude, the easier the ionization.

TABLE II. CHARGE DENSITIES IN SUBSTITUTED BENZENES AND ENERGY CHANGES FOR THE BENZOIC ACID IONIZATIONS

Substituent	σ^{0} a)	$1-q_r$	σ b)	$-\Delta E(-\gamma^2/\beta)$
p-CH_3	−0.15	−0.0145	−0.170	0.0922
p-CH_3O	−0.12	−0.0119	−0.268	0.0975
m-CH_3	−0.07	−0.0103	−0.069	0.0896
H	0	0	0	0.0860
m-CH_3O	0.13	0.0152	0.115	0.0808
p-F	0.17	0.0158	0.062	0.0841
p-Cl	0.27	0.0317	0.227	0.0771
m-$COCH_3$	0.34	0.0309	0.376	0.0755
m-F	0.35	0.0363	0.337	0.0741
m-COOR	0.36	0.0353	0.37	0.0744
m-Cl	0.37	0.0383	0.373	0.0733
p-$COCH_3$	0.46	0.0521	0.502	0.0689
p-COOR	0.46	0.0508	0.45	0.0687
m-NO_2	0.70	0.0707	0.710	0.0633
p-NO_2	0.82	0.0930	0.778	0.0569

a) Ref. 11.
b) Ref. 1.

In Fig. 2 the calculated ΔE values relative to the value for unsubstituted benzoic acid are plotted against the σ-values. It may be seen there that the relative delocalization energy difference, $\delta\Delta E$, is proportional to σ, the symbol δ indicating the energy difference with respect to the substituents. It should be noted that the points for p-CH_3O and p-F groups, whose σ-values show relatively large deviations from σ^0-values, are well fitted to the straight line.

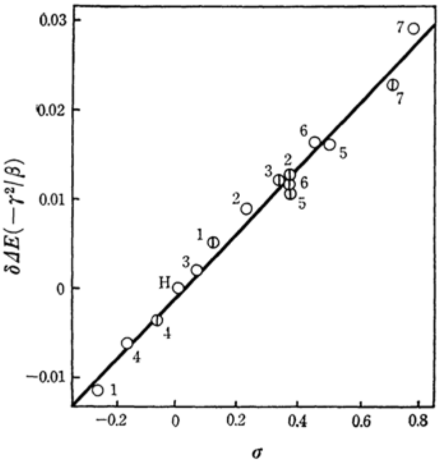
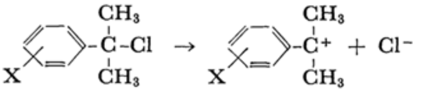


Fig. 2. The π-electronic energy changes in the ionization of substituted benzoic acids against σ-values.
○, para; ⦶, meta
Numbers correspond to the substituents given in Table I.

σ^+-Constants. — In electrophilic reactions, certain para-substituted compounds exhibit greater reactivities than would be expected from Hammett's σ-values of the substituents. From the data on the S_N1 solvolysis rates of substituted phenyldimethylcarbinyl chlorides (or, briefly, t-cumyl chlorides), Brown and Okamoto[10] defined the σ^+-values as a new set of electrophilic substituent constants.

In the present calculations, we have taken the following ionic cleavage of t-cumyl chlorides as a standard reaction:


(8)

The total π-electronic energies of the chlorides may be assumed to be equal to those of the corresponding substituted benzenes. In the resulting carbonium ions, however, the side-chain, $-\overset{+}{C}(CH_3)_2$, is incorporated in the π-conjugation. Thus, the total π-electronic energies of the cations differ substantially from those of substituted benzenes. Since the carbonium ions are recognized to be very close to the transition state of the S_N1 reactions, the above energy increment, i. e., the delocalization energy which t-cumyl chlorides would acquire upon ionic cleavage, may be regarded as a measure of the relative ease of the reaction 8.[17,18]

The delocalization energies of t-cumyl chlorides may be calculated from Eq. 1, by assuming that the $-\overset{+}{C}(CH_3)_2$ group is a single heteroatom ion with a vacant π-type atomic orbital the Coulomb integral of which is $\alpha+k\beta$. These energies obtained

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[17] N. C. Deno, "Progress in Physical Organic Chemistry," Vol. 2, Ed. by S. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience, New York (1964), p. 129.

[18] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y. (1961), Chapter 12.

TABLE III. THE DELOCALIZATION ENERGIES OF RING-SUBSTITUTED PHENYLDIMETHYLCARBINYL CHLORIDES

Substituent	σ^+ a)	$\Delta E_P{}^+(-\gamma^2/\beta)$			$\Delta E_V{}^+$ $(-\beta)$
		k c) $=0$	$k=0.2$	$k=0.3$	
p-CH_3	−0.311	0.8730	1.0790	1.2270	0.7427
p-CH_3O	−0.778	0.9397	1.2655	1.6072	0.7769
m-CH_3	−0.066	0.8561	1.0521	1.1912	0.7335
H	0	0.8333	1.0185	1.1485	0.7206
m-CH_3O	0.047	0.8021	0.9986	1.1075	0.7023
p-F	−0.073	0.8323	1.0375	1.1931	0.7216
p-Cl	0.114	0.7857	0.9635	1.0934	0.6944
m-$COCH_3$	(0.376) b)	0.7683	0.9255	1.0325	0.6819
m-F	0.352	0.7605	0.9179	1.0267	0.6772
m-COOR	0.368	0.7633	0.9185	1.0241	0.6767
m-Cl	0.399	0.7553	0.9092	1.0147	0.6739
p-$COCH_3$	(0.502) b)	0.7296	0.8713	0.9661	0.6592
p-COOR	0.489	0.7301	0.8724	0.9681	0.6582
m-NO_2	0.674	0.6944	0.8237	0.9091	0.6343
p-NO_2	0.790	0.6552	0.7698	0.8440	0.6094

a) Ref. 10.
b) Hammett's σ-values.
c) k is the Coulomb integral parameter for the side-chain carbon cation.

by the perturbation method will be denoted by $\Delta E_P{}^+$. The magnitudes of $\Delta E_P{}^+$ were calculated for various substituents, using varying k values ($k=0$, 0.2 and 0.3). The results are given in Table III, together with the corresponding σ^+-constants.

An inspection of the data listed in Table III will indicate that for each k value the $\Delta E_P{}^+$ values are larger for those substituents which have smaller σ^+-constants. This trend is compatible with the qualitative expectation that carbonium ions will be more stabilized as the charge-center carbons of the ions become less electron-deficient.[19] Also noticeable in Table III is the tendency that, in each substituent examined, the $\Delta E_P{}^+$ value increases with an increase in the k value that is, with an increasing affinity of the exocyclic carbons toward π-electrons. However, this in itself should by no means be related to observations on the relative stabilities of benzyl-type carbonium ions bearing different alkyl groups (or hydrogen atoms) on the exocyclic carbons.[20]

A rather more important feature to be noted in the $\Delta E_P{}^+-\sigma^+$ relationship is that the Coulomb parameter, k, exerts a particularly large influence on the $\Delta E_P{}^+$ values of some para-substituted compounds (p-methoxy and p-fluoro derivatives). The situations are illustrated in Fig. 3, where the relative delocalization energies, $\delta\Delta E_P{}^+$, taking the nonsubstituted t-cumyl chloride as the standard, are plotted against the σ^+-values for each assumed value of k. In each case, a straight line is seen to fit the plots for meta substituents. In order for the para points to show the best fits to the meta line, a value of $k=0.2$ would have to be assumed for the side chain.[21] If the side-chain carbon has an electronegativity different from that specified by $k=0.2$, the effects of some para substituents on reactions of the type 8 will deviate from those to be expected from their σ^+-values. The occurrence of such deviations may be taken as an indication that the relative importance of the resonance interaction between substituents and reaction sites varies according to the structure of the reactants. This view of the sliding-scale variation of substituent constants is compatible with the physical picture underlying the Yukawa-Tsuno four-parameter equation:[12]

$$\log k/k_{\mathrm{H}} = \rho\{\sigma + r(\sigma^+ - \sigma)\} \tag{9}$$

in which r is a reaction parameter which takes account of the degree of possible resonance interactions between substituents and reaction sites in the transition states. Thus, r would increase with an increase in the k value.

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[19] E. Berliner and N. Shien, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

[20] In addition to the π-electron delocalization, several other factors, such as the inductive and hyperconjugative effects of alkyl groups and the strain relief on ionization, need to be considered with regard to the carbonium ion stability. Nevertheless we feel that the $\Delta E_P{}^+$ value may be useful in comparing the relative effects of ring substituents on the stabilities of different types of carbonium ions.

[21] That the positively-charged side-chain carbon is more electronegative than the ring carbons may be confirmed by a self-consistent field treatment of the ion. The simplest test of this point may be achieved by the use of the conventional ω-technique.[22] In the case of the benzyl cation the charge density calculated for the exocyclic methylene carbon by this method is roughly 0.41.[18] The Coulomb integral parameter for the exocyclic carbon orbital of the t-cumyl cation in its ultimate self-consistency will be 0.41 times $\omega(=1.4)$ plus twice the inductive parameter (-0.15) of a methyl group. Thus, $k=0.41(1.4)+2(-0.15)=0.27$, a value which is of the correct order of magnitude.

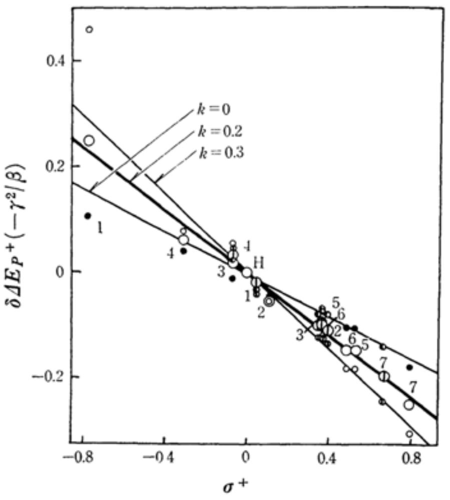


Fig. 3. The π-electronic energy changes in the dissociation of substituted *t*-cumyl chlorides against σ^+-values.

○, para; ⦶, meta for $k=0.3$
◯, para; ⦶, meta for $k=0.2$
●, para; ◐, meta for $k=0$
Numbers correspond to the substituents given in Table I.

Another significant point in Fig. 3 is its indication that the k value also affects the slope of meta lines; the slope becomes steeper as the k value increases. If this is true, the reaction constant, ρ, should increase in magnitude with the increase in the resonance parameter, r, for reactions of the type 8. This expectation is borne out by the recent experimental results gained by Yukawa and Tsuno[23] who compared the substituent effects on the S_N1 solvolysis rates of *t*-cumyl and α-phenylethyl chlorides under the same conditions. They found that α-phenylethyl chlorides gave the values $r=1.16$ and $\rho=-4.95$ while *t*-cumyl derivatives had $r=1.00$ and $\rho=-4.54$. The variation in these values observed in going from *t*-cumyl to α-phenylethyl chlorides agrees at least qualitatively with our theoretical expectation.[24]

The delocalization energies were also calculated by the variation method for the case of $k=0$. The values obtained are included in Table III. The relative energies, $\delta\Delta E_V{}^+$, are found to be proportional to the corresponding $\delta\Delta E_P{}^+$ values, as is illustrated in Fig. 4. This remarkably good linear relationship confirms the validity of our present perturbation calculations.

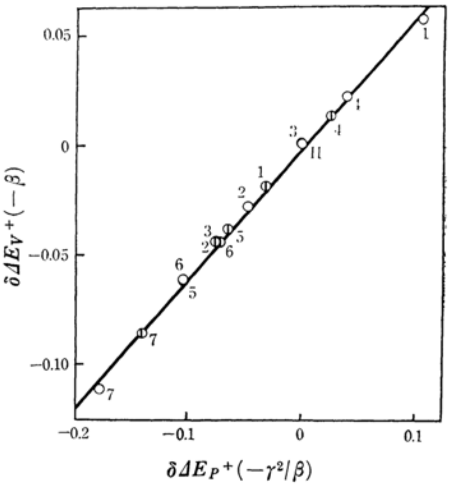
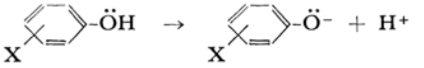


Fig. 4. Linear relationship between the π-electronic energy changes calculated by the perturbation and variation methods for the dissociation of substituted *t*-cumyl chlorides.
◯, para; ⦶, meta
Numbers correspond to the substituents given in Table I.

σ^--Constants.—Hammett first noted that, in the reactions of the derivatives of phenol and aniline, enhanced σ-values were required for such substituents as para-nitro and -cyano groups.[1] Just as the reactions whose transition states involve the electron-deficient side chains linked to an aromatic ring respond sensibly to electron-releasing para substituents, so the reactions which involve conjugating lone-pair electrons respond sensibly to electron-attracting para substituents. The special substituent constants for these substituents are designated by σ^-.

We calculated by the perturbation method the energy change, ΔE^-, accompanying the reaction:



(10)

Here the Coulomb integral parameters of the OH and O^- atomic orbitals are assumed to be $k=1$ and 0.8 respectively, and the energy change, ΔE^-, is the difference between the benzene delocalization energies, as defined by Eq. 3. The calculated energy changes are given in Table IV, together with the available data for σ^-.

In Fig. 5 the values of ΔE^- relative to the unsubstituted phenol, $\delta\Delta E^-$, are plotted against σ- or σ^--values, whichever are appropriate.

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[22] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959); A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

[23] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 873 (1965). In applying Eq. 9 to these reactions, they replaced σ by σ^0.

[24] Taking one step further, one may make a more quantitative comparison between theory and experiment. From the experimental r-values, we estimated the values of k which permitted the best linear correlationships between $\Delta E_P{}^+$ and $\sigma+r(\sigma^+-\sigma)$. The k-values thus estimated were 0.20 and 0.23 for the side chains $-\overset{+}{C}(CH_3)_2$ and $-\overset{+}{C}HCH_3$ respectively. The relative slopes of the theoretical lines corresponding to these k-values were found to be 1 and 1.07. The ratio 1 : 1.07 is in reasonable agreement with the experimental ρ ratio, 1 : 1.09, found between *t*-cumyl and α-phenylethyl chlorides.

TABLE IV. ENERGY CHANGES FOR THE PHENOL IONIZATIONS AND ANILINIUM ION DISSOCIATIONS

Substituent	σ^-	$\Delta E^-(-\gamma^2/\beta)$	$DE(-\gamma^2/\beta)$
p-CH_3		0.0430	0.4326
p-CH_3O	−0.13[a]	0.0443	0.4381
m-CH_3		0.0437	0.4366
H		0.0450	0.4444
m-CH_3O		0.0466	0.4553
p-F	0.005[a]	0.0491	0.4622
p-Cl		0.0505	0.4755
m-$COCH_3$		0.0487	0.4677
m-F		0.0496	0.4717
m-COOR		0.0492	0.4711
m-Cl		0.0499	0.4735
p-$COCH_3$	0.874[b]	0.0604	0.5028
p-COOR	0.678[b]	0.0573	0.4974
m-NO_2		0.0547	0.4999
p-NO_2	1.27[b]	0.0765	0.5480

a) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, **1961**, 388.

b) Ref. 2.

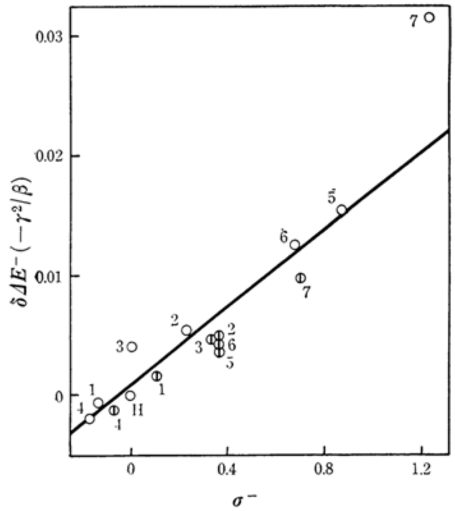

Fig. 5. The π-electronic energy changes calculated for the ionization of phenols against σ^--constants.
○, para; ⦶, meta
Numbers correspond to the substituents given in Table I.

Although the points are somewhat scattered in comparison with those in Figs. 1 to 3, it does appear that a single straight line fits the plots here also. Different choices of Coulomb parameters for the OH and O^- orbitals neither improve nor worsen the situation materially.

As an alternative to the above theoretical quantity, $\delta\Delta E^-$, the benzene delocalization energy itself could be used as a measure of the σ^--constants. This would be particularly valid when the ionizations of anilinium salts are to be considered. The delocalization energies calculated for the case of $k=1$ are listed in Table IV and are plotted against σ- and σ^--values in Fig. 6. It may be seen in Fig. 6 that the plots corresponding to the σ^--values fall on the meta line, in agreement with Jaffé's previous conclusion reached by the use of a different set of integral parameters.[4]

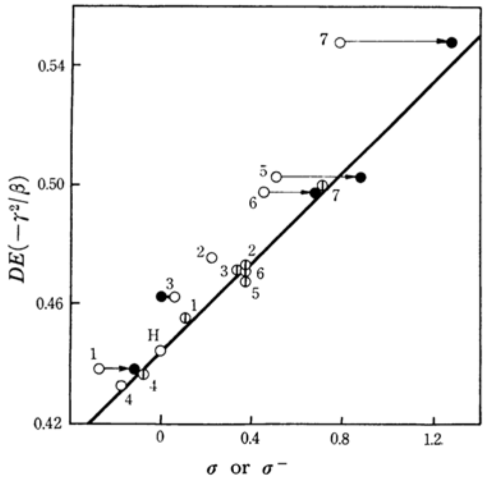

Fig. 6. Delocalization energies calculated for the acid dissociations of anilinium ions against σ and σ^-.
○, σ para; ⦶, σ meta; ●, σ^-
Numbers correspond to the substituents given in Table I.

Discussion

Although it is definite that π-electrons make dominant contributions to the properties of conjugated compounds, any attempt to establish correlations between the distribution of such electrons and their role in controlling molecular reactivities must be judged with due caution. So far as the substituent effects on aromatic side-chain reactions are concerned, only those reactions which are governed by the normal substituent constants, σ^0, will respond directly to the electronic charge distributions effected by substituents. In other reactions, these two modes of substituent effects (on reactions and charge distributions) are more or less biased to the extent that they may permit discrimination. This is the basis of our present treatment of the nonlinearity of free energy correlations in aromatic side-chain reactions.

Our treatment is based on the assumption that the potential energy changes in the transition states caused by substituents would parallel the relative free energy changes for reactions. Although this assumption is a usual and irreplaceable starting point for the present sort of treatment, it is not always fulfilled in given reaction series.[13,25]

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[25] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, New York, N. Y. (1963), Chapter 9.

Nevertheless, we feel that imperfections arising from such difficulties will be minimized in the present treatment, inasmuch as our primary interest has been in the free energy correlations among different types of side-chain reactions. The integral parameters, which are used so as to mediate between substituent effects on different types of reactions, may partly absorb the uncertainties concerning the role of kinetic energy and entropy terms.

One major question which might be raised with regard to our treatment concerns the disregarding of the effects of factors other than π-conjugation. For instance, we have not considered explicitly the role of σ-inductive effects, which are definitely operative in reactions. Further, Dewar and Grisdale⁸⁾ have suggested that direct-field effects of substituents are even more important than σ-inductive effects and that the Hammett σ-constants may be related primarily to such effects and mesomeric effects. However, since there exists no justified way of separating σ-inductive (or, perhaps, direct-field) effects from mesomeric effects, we have avoided attempting to estimate these two contributions separately. Rather, in the interests of methodological simplicity, we have implicitly assumed that the inductive and field effects may at least be partly embodied in Hückel-type treatments by assigning relatively large inductive parameters to the ring carbons neighboring substituents.[26)]

Finally, a word should be said about the inductive parameters, δ_{CX}, assumed for the C–Cl and C–F bonds. The adherence to the assignment $\delta_{CX}=0.3$ for these bonds has always resulted in anomalously large deviations of the *p*-chloro and *p*-fluoro points from the straight lines shown in Figs. 2, 3, 5 and 6. Since it turned out, from the calculations, that the choice of the values of 0.6 and 0.5 for the C–Cl and C–F bonds respectively greatly improved the corresponding plots in the ΔE-σ relationships, these values were used for testing the correlations of σ^0 with other substituent constants. It is conceivable that the parameters δ_{CX} are not constant over different bonds.

The authors wish to thank Professor Yasuhide Yukawa and Dr. Yuho Tsuno of Osaka University for their valuable suggestions and discussions.

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26) It is agreed that relatively large inductive parameters are required in order to predict the reasonable magnitudes for meta electron densities.[3)] Peters[6)] has demonstrated that even equal π-electron densities can be predicted for para and meta carbons when the inductive parameters are assumed to propagate gradually along the bonds, diminishing by as large a constant factor as $\varepsilon=0.53$. Thus, the disregard of the π-inductive and field effects is largely counterbalanced by the choice of the parameters $\delta_{CX}=0.3$ and $\varepsilon=1/3$.