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Resonance Effect in Hammett Relationship. IV. Linear Free Energy Relationship based on the Normal Substituent Constants*

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A set of normal substituent constants, σ^0, was derived from the rates of alkaline hydrolysis of *m*- and *p*-substituted ethyl phenylacetates in 60% (v/v) aqeuous acetone at 25.0°C. The obtained values of σ^0-constants were generally identical with Taft's values within experimental uncertainty. On the basis of the derived σ^0, substituent effects on the general electrophilic reactions were correlated excellently by the equation, $\log k/k_0=\rho(\sigma^0+r\Delta\bar{\sigma}_R^+)$, where $\Delta\bar{\sigma}_R^+$ corresponds to the exaltation of Brown and Okamoto's σ^+ from σ^0. The similar treatment could be applied also to the nucleophilic reactions. The utility of this equation for the estimation of resonance contribution and for the consideration of reaction mechanisms are discussed.

The general failure of the Hammett equation[1] to correlate electrophilic reactivities led to the suggestion of the use of alternate substituent constants, denoted by σ^+, derived from the substituent effect in an electrophilic reaction.[2-5] Various authors proposed their own set of σ^+ values from the individual reference reaction.[3-5] Later, Brown and Okamoto have proposed the familiar σ^+ constants, defined by the substituent effects on the solvolysis rates of phenyldimethylcarbinyl chlorides, and demonstrated the utility of their σ^+ to the prediction of electrophilic reactivities.[5] The exalted contribution of electron releasing *para* substituents can be attributed to the additional delocalization by resonance of the positive charge produced at the reaction site. The σ^+ treatment stands on an assumption that the substituent constant in electrophilic reactions remains a constant relative to the marked change in ρ. However, the degree of the resonance delocalization must depend on the amount of charge produced or the electron deficiency of the reaction site. Accordingly, the σ^+ of respective *para* substituents should be subject to variation with reactions. It should be inevitably required for *para* substituents to add a second term, taking into account such an exalted resonance contribution.[3,6]

At this point of view, the relationship (1) was proposed[6] for the correlation of substituent effects on general electrophilic reactions,

$$\log k/k_0 = \rho(\sigma + r\Delta\sigma_R^+) \tag{1}$$

where r is a constant depending on the resonance effect in the reaction, and $\Delta\sigma_R^+$ measures the capacities of substituents to supply electrons by resonance. $\Delta\sigma_R^+$ values were defined by the increments of Brown and Okamoto's σ^+ from σ. The applicability of Eq. 1 was demonstrated in the original paper[6] with the excellent results for 35 representative electrophilic reactivities. Thereafter, Eq. 1 has been utilized in order to correlate various reactivities and elucidate the reaction mechanism by a number of investigators.[7,8] These are reviewed entirely in several recent articles.[9-11] Analogous equations have been proposed[7a,12,13] in these few years, but none of them appears more useful practically or more

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[1] L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); "Physical Organic Chemistry," McGraw-Hill, New York (1940), Chapt. 7, p. 184.

[2] For the review, see, P. R. Wells, *Chem. Revs.*, **63**, 171 (1963).

[3] Y. Tsuno, T. Ibata and Y. Yukawa, This Bulletin, **32**, 960 (1959); Y. Yukawa and Y. Tsuno, ibid., **32**, 965 (1959).

[4] D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1151 (1952); J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953); N. C. Deno and A. Schriesheim, ibid., **77**, 3051 (1955); N. C. Deno and W. L. Evans, ibid., **79**, 5804 (1957); J. Miller, *Austral. J. Chem.*, **9**, 61 (1956).

[5] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); ibid., **80**, 4979 (1958); H. C. Brown, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, New York (1963), Chapt. 2, p. 34.

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

[7] a) J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, **1959**, 3036. b) C. Eaborn and J. A. Waters, ibid., **1961**, 542; C. Eaborn and R. Taylor, ibid., **1961**, 1012; R. Baker, R. W. Bott, C. Eaborn and P. P. M. Greasley, ibid.,, **1964**, 627; R. W. Bott, C. Eaborn D. R. M. Walton, ibid., **1965**, 384.

[8] R. Taylor, G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, **84**, 4817 (1962); R. Taylor and G. G. Smith, *Tetrahedron*, **19**, 937 (1963); T. Inukai, This Bulletin, **35**, 400 (1962); L. A. Singer, and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963); T. I. Crowell, C. E. Bell, Jr., and D. H. O'Brien, ibid., **86**, 4973 (1964); W. P. Jencks, "Progress in Physical Organic Chemistry," Vol. II, Interscience, New York (1964), p. 110.

general to cover a wide variety of reactions.

While the relationship (1) is conventionally based on the σ-standard and the resonance parameter $\Delta\sigma_R^+$ was defined originally by $\sigma^+-\sigma$, it is evidently known that the Hammett σ-constant involves in itself the σ^+-type exalted resonance contribution to a considerable extent. Taft[14,15] and Wepster[16] have proposed independently that the unexalted or normal substituent constants, σ^0 or σ^n, should be taken as the standard of the benzene subtituent contribution instead of σ. Of course, for the practical purpose, it is believable that the original definition of the relationship (1) must be the best choice of the standard.[17] However, in view of further development of this type of approach and performing the theoretical analysis of the substituent effect, the additional resonance contribution to the unexalted effect, σ^0, should be fully included into the additional resonance term corresponding to $r\Delta\sigma_R^+$. It was therefore attempted to develop an alternate treatment of substituent effects based on the σ^0-standard.

In this connection, σ and σ^+ on which our original treatment is based are the most familiar to the organic chemist and well established sets of substituent constants. While the σ^0-constant was derived by Taft[14,15] statistically from the reactions free from the mutual conjugative interaction between substituent and the reaction site, the numerical values do not appear to be so precise because of the lack of sufficient data available at that time. As similar to the pK_a of benzoic acids for σ, the σ^0 should be defined by the substituent effect on the dissociation of phenylacetic acids. In practice, however, the effects are so small relative to the experimental uncertainty to evaluate the precise constants. Accordingly, first of all, the more reliable experimental σ^0-values have been determined on the basis of the substituent effects on alkaline hydrolysis of ethyl phenylacetates. In the present paper are reported and discussed the determination of σ^0-constants and the development and generality of the alternate treatment based on the σ^0-constants obtained.

Experimental

Most of phenylacetic acids were prepared by the Willgerodt reaction of the appropriate acetophenones.[18] The modified procedure using sulfur and morpholine was employed; the morpholides were separated, washed and hydrolyzed with concentrated potassium hydroxide solution. This method was generally successful except for *p*-chloro and *p*-bromo derivatives. Another method generally employed was the hydrolysis of the nitriles prepared from the correspondingly substituted benzyl halides. *m*-Fluoro and *m*-chloro derivatives were obtained from the corresponding benzoic acids by the Arndt-Eistert reaction.[19] The other substituted derivatives were prepared by the convenient method in the literature (see Table I). The acids were purified by the recrystallization or the distillation of the esters, followed by the recrystallizations of regenerated acids. The acids were esterified by the standard method and finally the esters were fractionated or recrystallized immediately before the rates of their hydrolysis were measured. Any impurities or undesirable isomers were not detected by vapor phase chromatography. The physical constants of these materials were listed in Table I.

Acetone which had been treated with potassium permanganate was distilled, dried over potassium carbonate and fractionated. It was diluted with freshly boiled, deionized water to give a 60% (v/v) aqueous acetone.

Kinetic Measurement.—The rates of the hydrolysis of all these phenylacetic esters were determined in 60% aqueous acetone solution at 25.00±0.01°C by following the decrease of conductance of the solution. The procedure employed for this measurement was essentially the same as that described by Hancock.[20] The initial concentrations of alkali and the ester were precisely equal (0.01—0.005 M) and the reaction was followed up to the extent of 90% reaction. The initial conductance was determined by the reading of conductance of alkaline solution alone. All runs showed strictly second order kinetics, while in some cases slight deviations from the kinetic plot was observed in the initial 5—10% reaction period. The rate constants from different runs agreed within 1% except for *p*-bromo derivative, which did not give a precise second order rate constant and the average deviation of repeated runs was about 3% for this derivative. The rate constants obtained are listed in Table II.

Of the slow reacting derivatives, the rates were determined also by means of the titration method under the same condition as the above. The procedure employed was essentially the same as that described in

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[9] R. O. C. Norman, "Electrophilic Substitution in Benzene Compounds," Elsevier (1965).

[10] J.E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley, New York (1963), Chapt. 6, p. 128.

[11] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 873 (1965).

[12] J. R. Knowles, R. O. Norman and G. K. Radda, *J. Chem. Soc.*, **1960**, 4885.

[13] R. E. Dessy and J. Y. Kim, *J. Am. Chem. Soc.*, **82**, 686 (1960); J. Hine, ibid., **82**, 4877 (1960).

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

[15] R. W. Taft, Jr., I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); ibid., **81**, 5343 (1959); R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, ibid., **81**, 5354 (1959).

[16] H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

[17] In the original paper (Ref. 6), we used the σ-values from Jaffé's compilation (H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953)), but it should be better to utilize the σ-values from the pK_a values of benzoic acids. Thus a little change in the original parameters has to be necessary for some substituents.

[18] E. Schwenk and E. Bloch, *J. Am. Chem. Soc.*, **64**, 3051 (1942); M. Carmack and D. F. DeTar, ibid., **68**, 2029 (1946).

[19] W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley, New York (1942), Chapt. 2, p. 38.

[20] C. K. Hancock, E. A. Meyers and B. J. Yager, *J. Am. Chem. Soc.*, **83**, 4211 (1961).

TABLE I. PHENYLACETIC ACIDS AND ETHYL PHENYLACETATES

Substituent	Acid		Ethyl ester	
	M. p., °C	Method$^{a)}$	B. p., °C/mmHg	M. p., °C
p-CH_3O	88—88.5$^{d,e)}$	W	117.5/3.5$^{i)}$	
p-CH_3S	99—100$^{f)}$	W		57—57.5$^{n)}$
p-C_6H_5O	79.5	W	150/0.7$^{o)}$	
p-C_6H_5	161—161.5$^{d)}$	W	167—168/3.5	Solid
p-CH_3	92—93$^{e,f)}$	W	112—112.5/9.5$^{e)}$	
p-C_2H_5	91.5—92$^{g)}$	W	143/22$^{p)}$	
p-i-C_3H_7	51.5—52.5$^{h)}$	W	144.5—145/19$^{q)}$	
p-t-C_4H_9	82—83$^{i)}$	W	126.5/6$^{j)}$	
p-F	84.5$^{f,i)}$	A	103—104/10$^{e)}$	34.5—35.5$^{e)}$
p-Cl	105$^{e,i)}$	N(W)	110—111/4	33—34$^{j)}$
p-Br	114—114.5$^{d)}$	N(W)	143.5—144/11	27—29$^{e)}$
p-CH_3CO		b		61—62$^{b,e)}$
p-NO_2	153$^{c,i)}$	c		64.5—65$^{e)}$
β-Napht.	140.5—141$^{j,k)}$	W	148.5/3.5	32—33$^{j)}$
Unsubst.	77—77.5		83.5—84/4	
m-CH_3	63.5—64$^{e,f)}$	N	119—119.3/13$^{e)}$	
m-F		A	98—98.5/10$^{j)}$	
m-Cl		A	118—118.5/7.5$^{i)}$	
m-Br	101—101.5$^{l)}$	W	145.5/14$^{r)}$	
m-CH_3CO	104—104.5$^{b)}$	b	138/3.5	
m-NO_2	118.5—119$^{e,m)}$	N	142—142.5/3$^{e)}$	

a) The method of preparation: W, Willgerodt reaction (Ref. 18); A, Arndt-Eistert reaction (Ref. 19); N, nitrile synthesis. b) Preparation by acetylation of ethyl phenylacetates; D. Papa, E. Schwenk and A. Klingsberg, *J. Am. Chem. Soc.*, **68**, 2133 (1946). c) Nitration of phenylacetonitrile; " Org. Synthesis," Coll. Vol. I, 396 (1956). d) E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 798 (1946). e) Ref. 22. f) R. C. Elderfield and K. L. Burgess, *J. Am. Chem. Soc.*, **82**, 1975 (1960). g) *Anal.*, Found: C, 73.10; H, 7.33. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. h) *Anal.*, Found: C, 74.23; H, 8.06. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%. i) Ref. 24. j) Ref. 23. k) E. Schwenk and E. Bloch, *J. Am. Chem. Soc.*, **64**, 305 (1942). l) C. D. DePuy and D. H. Froemsdorf, ibid., **79**, 3710 (1957). m) D. L. Yabroff and C. W. Porter, ibid., **54**, 1199 (1932). n) *Anal.*, Found: C, 62.76; H, 6.71; S, 15.12. Calcd. for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25%. o) *Anal.*, Found: C, 75.25; H, 6.49. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%. p) *Anal.*, Found: C, 75.18; H, 8.61. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%. q) *Anal.*, Found: C, 75.75; H, 8.92. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. r) *Anal.*, Found: C, 49.58; H, 4.72; Br, 32.53. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.41; H, 4.56; Br, 32.87%.

TABLE II. RATE CONSTANTS OF HYDROLYSIS OF SUBSTITUTED ETHYL PHENYLACETATES IN 60% AQUEOUS ACETONE AT 25°C

Subst.	$10^2\times k_2$	Subst.	$10^2\times k_2$
p-CH_3O	3.50	β-Napt.	5.03
p-CH_3	3.30	Unsubst.	4.36
p-C_2H_5	3.26	m-CH_3	3.71
p-i-C_3H_7	3.80	m-F	9.67
p-t-C_4H_9	2.96	m-Cl	9.33
p-C_6H_5	4.78	m-Br	9.64
p-F	7.07	m-CH_3CO	10.50
p-Cl	8.23	p-CH_3CO	13.2
p-Br	8.7	m-NO_2	21.8
p-C_6H_5O	5.17	p-NO_2	27.0
p-CH_3S	5.27		

the literature.[21] The equal initial concentration of round 0.01 M for alkali and ester was employed for all runs. The aqueous acetone solution of sodium hydroxide was frequently prepared and standardized. More than triplicated runs were carried out for respective esters. The respective run, which involved more than 12 measurements convering two half-lives, followed the second order kinetic law, with slight fluctuation of few points. The average deviation of a run was estimated to be within 2%, and the reproducibility of repeated runs to be ±3%. The aveaged rate constants obtained were identical within experimental uncertainty with those by means of the conductivity measurement.

Results and Discussion

The Standard σ^0-Constnat.—A difficulty in the determination of precise σ^0-constants arises from the low susceptibility to the substituent change of the insulated reactivity, the reactivity free from the mutual conjugative interaction between substituent and reaction site. In view of comparatively large substituent effects, alkaline hydrolysis of substituted phenylacetic esters is

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[21] D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, **1937**, 1430.

the most appropriate reference reaction of σ^0-constants. While the rates of alkaline hydrolysis of ethyl phenylacetates were available in the literature[22] for several derivatives in 60% aqueous acetone solution, data were not enough to determine precise σ^0-constants. Thus the more extensive study of this reaction was carried out for a variety of substituted derivatives in order to derive a reliable set of σ^0-constants. According to the preliminary experiments, the reaction proceeded rather too fast in this solvent at 25°C to follow by the usual titration method. This might cause the large experimental error in the results. Therefore the rates were determined by following the change in electric conductivity of the solution during reaction. The results were satisfactory in all the case. When we had finished the series of experiments, additional data for the same reaction by means of titration method were published.[23] They agreed to our results for most of derivatives but did not for several derivatives, such as *p-t*-butyl and *m*-nitro derivatives. Accordingly, the re-examination was undertaken for slow reacting derivatives by means of titration method, while this confirmed our results from the conductivity measurement, which appeared to give more accurate results in comparison with the other method. The disagreement of highly reactive derivatives, especially a large deviation of *m*-nitro derivative,[22] might be responsible to the experimental difficulty in titration measurement. The recent data on the alkaline hydrolysis of the same esters in aqueous alcohol,[24] in which the reaction proceeds considerably slow (ca. 5 times), are much closely related to the present results in spite of different solvents. For the other derivatives, the excellent reproducibility of data from the repeated runs evidently estimates the high reliability of our results due to conductivity measurements. The further support of our results is the fact that the effects of substituents, log k/k_0,

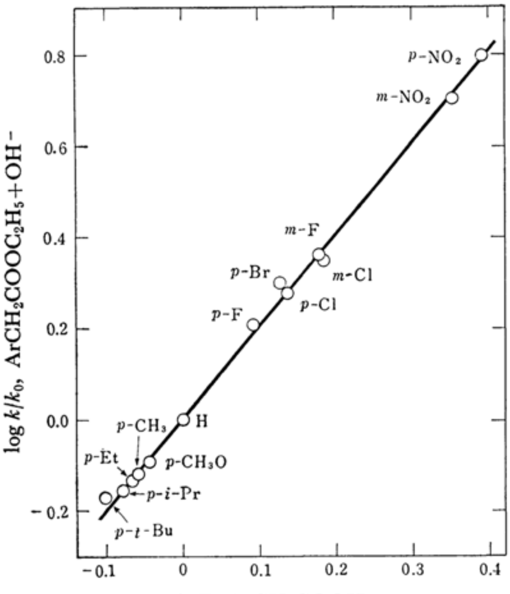

Fig. 1. Linear free energy relation between dissociation of phenylacetic acids and hydrolysis of ethyl phenylacetates.

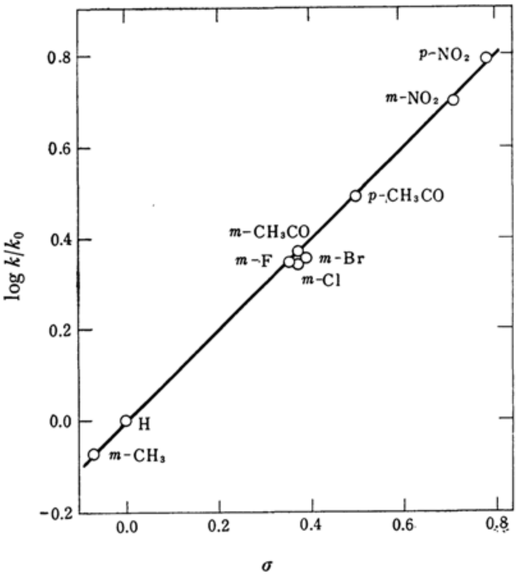

Fig. 2. Hammett plot of the alkaline hydrolysis of ethyl phenylacetates.

TABLE III. SUBSTITUENT PARAMETERS

p-Substituent	σ^0	$\Delta\bar{\sigma}_R^+$
CH_3O	−0.100	−0.678
CH_3	−0.124	−0.187
C_2H_5	−0.131	−0.164
i-C_3H_7	−0.156	−0.124
t-C_4H_9	−0.174	−0.082
C_6H_5	0.039	−0.218
F	0.212	−0.285
Cl	0.281	−0.167
Br	0.30	−0.15
β-Napht.	0.062	−0.197
CH_3S	0.083	−0.68
C_6H_5O	0.076	
HO	−0.16*	−0.82
NH_2	−0.36*	−1.00
$N(CH_3)_2$	−0.48*	−1.30

* Derived from other reactivities statistically.

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[22] R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph and E. M. Smith, ibid., **1961**, 3247.

[23] R. O. C. Norman and P. D. Ralph, ibid., **1963**, 5431.

[24] J. G. Watkinson, W. Watson and B. L. Yates, ibid., **1963**, 5437.

TABLE IV. SUMMARY OF CORRELATIONS OF σ^0-TYPE REACTIVITIES[a)]

Reaction	ρ	s[b)]	R[c)]	n[d)]
pK_a, Phenylacetic acids, water, 25°C[e)]	0.502	0.013	0.998	12
Phenylacetic acids with diphenyldiazomethane, ethanol, 35.6°C[f)]	0.347	0.011	0.997	8
Saponification, ethyl arylacetates, 85.4% aq. ethanol, 24.8°C[g)]	1.092	0.031	0.998	9
Saponification, ethyl arylacetates, 87.8% aq. ethanol, 30°C[h)]	1.020	0.022	0.999	7
Saponification, ethyl arylpropionates, 87.8% aq. ethanol, 30°C[i)]	0.639	0.013	0.999	7
Saponification, substituted-benzyl benzoates, 70% aq. acetone, 25.0°C[j)]	0.990	0.017	0.999	14
Saponification, benzyl acetates, 60% aq. acetone, 25°C[k)]	0.793	0.017	0.998	9
pK_a, Benzylammonium ions, water, 25°C[l)]	1.087	0.031	0.996	12
Benzoic acids with diphenylguanidine, benzene, 25°C[m)]	2.10	0.086	0.993	17
pK_a, Ar-PO_3H^-, water, 25°C[n)]	1.104	0.038	0.997	11
Alkaline hydrolysis, ArO-$Si(C_2H_5)_3$, 51.4% aq. ethanol, 25°C[o)]	1.976	0.019	0.999	6
pK_a, *trans*-Arylcyclopropylcarboxylic acids, 50% aq. ethanol, 25°C[p)]	0.515	0.045	0.996	8
Saponification, ethyl arylcyclopropylcarboxylates, 87.8% aq. ethanol, 30°C[i)]	0.873	0.030	0.996	8

a) The Hammett type correlation based on σ^0 values obtained in the present investigation. b) Standard deviation. c) Correlation coefficient. d) The number of substituents involved in the calculation. e) Ref. 25. f) R. M. O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963). g) Ref. 24. h) K. Kindler, *Ann.*, **452**, 90 (1927); A. Fischer, J. Packer, J. Vaughan, A. F. Wilson and E. Wong, *J. Org. Chem.*, **24**, 155 (1959): For the rate of the unsubstituted derivative, 12.2×10^{-3} reported by the latter was used. i) R. Fucks and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963). j) Y. Yukawa, Y. Tsuno and M. Sawada, Unpublished. k) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, **1938**, 1801; E. Tommila, *Ann. Acad. Sci. Fennicae*, **59**, No. 4 (1942): The unsubstituted derivative was omitted from the correlation. l) L. F. Blackwell, A. Fischer, R. D. Topsom and J. Vaughan, *J. Chem. Soc.*, **1964**, 3588: *p*-Fluoro group was not included in the calculation. m) M. M. Davis and H. H. Hetzer. *J. Res. Natl. Bur. Standards*, **60**, 569 (1958). n) H. H. Jaffé, L. D. Freedman and G. O. Doack, *J. Am. Chem. Soc.*, **75**, 2209 (1953). o) E. Aekerman, *Acta Chem. Scand.*, **11**, 373 (1957). p) R. Fucks, C. A. Kaplan, J. J. Bloomfield and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

obtained can be correlated linearly with those on the dissociation of phenylacetic acids[25)] as illustrated in Fig. 1. This can be compared with the linear free energy correlation between hydrolysis of benzoic esters and the pK_a of benzoic acids.

As would be anticipated, for all *meta* substituents and conjugatively electron attracting *para* substituents, a precisely linear Hammett correlation was obtained (Fig. 2). The ρ value is equal to 0.978 with standard deviation of $+0.010$ and the correlation coefficient 0.999. On the basis of this correlation, the apparent substituent constants of this reaction were calculated. The resulted constants are generally identical with Taft's σ^0 values within usual uncertainty, and expected to be more reliable than the latter. This set of substituent constants in Table III can correlate precisely the substituent effects on the hydrolysis of substituted benzyl benzoates.[26)] The unexalted reactivities which recently have become available in the literature can be also correlated excellently with the above set, as summarized in Table IV. The excellent results in the table indicate that the present set can be generally utilized as the standard σ^0-constant. In the following treatment therefore the values in Table III will be used as the standard σ^0-constants.

It is of interest to note that the effects of alkyl groups in the present reaction follow clearly the inductive order, while they appear to follow the Baker-Nathan order in aqueous alcohol.[24)] The analogous behavior of alkyl groups was also noted in the saponification of benzoic esters,[27)] and also in the other reactions.[23,28)] The substituent effect is sensitive to conditions of reaction.[15,16)] Taft has suggested the solvent dependency of σ^0-constants of particular substituents, such as *p*-methoxy group,[14)] but this was not distinctly significant in the reactivities sited. The further investigation of the dependency of σ^0-constants upon reactions, solvents and the other conditions is under progress in this laboratory[26)] and will be published in near furure.

Correlations of Reactivities.—In view of the general utility of Eq. 1 using $\Delta\sigma_R^+$ as the resonance substituent constants, the increment of Brown and Okamoto's σ^+ to the σ^0 is expected

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25) J. F. J. Dippy and R. H. Lewis, ibid., **1936**, 644; J. F. J. Dippy and F. R. Williams, ibid., **1934**, 161; J. F. J. Dippy and J. E. Page, ibid., **1938**, 357; A. Fischer, B. R. Mann and J. Vaughan, ibid., **1961**, 1093.

26) Y. Yukawa, Y. Tsuno and M. Sawada, Unpublished.

27) E. Berliner, M. C. Beckett, E. A. Blommers and B. Newman, *J. Am. Chem. Soc.*, **74**, 4940 (1952).

28) V. J. Shiner, Jr., and C. J. Verbanic, ibid., **79**, 369 (1957).

TABLE V. CORRELATIONS OF ELECTROPHILIC REACTIVITIES

A. Side Chain Reaction

No.	Reaction	ρ	r	s[1)	R[2)	Ref.[3)
1	Brown and Okamoto's σ^+	(1.000)	(1.000)			
2	Pinacol rearrangement, tetraphenylpinacols	−2.83	1.24	0.15	0.991	5
3	Solvolysis, phenylethyl chlorides, in 80% aq. acetone, 45°C	−4.95	1.161	0.044	1.000	6
4	Solvolysis, anisylarylcarbinyl chlorides, in 85% aq. ethanol, 0°C	−2.643 −3.02	1.176 1.043	0.105 0.058	0.998 0.999	7 7a
5	Solvolysis, benzhydryl chlorides, in 70% aq. acetone, 0°C	−4.583	1.140	0.102	0.997	8
6a	Solvolysis, benzhydryl chlorides, in ethanol, 25°C	−3.806	1.172	0.22	0.989	9
6b	Solvolysis, benzhydryl chlorides, in ethanol, 25°C	−4.126	1.172	0.125	0.998	10
7	Solvolysis, 9-arylfluorenyl chlorides, in 90% methanol - acetone, 25°C	−3.420	1.016	0.103	0.997	11
8	Pyrolysis, α-arylethyl acetates, 600°K	−0.643	0.998	0.022	0.997	12
9	Ion pair formation, triphenylmethyl chlorides, in SO_2, 0°C	−4.043	0.885	0.048	0.998	13
10	Hydration, arylacetylenes, 50.2°C	−4.453	0.867	0.094	0.998	14
11	Protodegermylation, arylethynyltriethylgermanes, perchloric acid, 29°C	−3.294	0.755	0.067	0.999	15
12	*t*-Stilbenes with perbenzoic acid	−1.095	0.718	0.043	0.999	16
13	Acetolysis, ω-diazoacetophenones, 40°C	−0.818	0.667	0.011	1.000	17
14	Rearrangement, arylpropenylcarbinols	−3.705	0.650	0.023	1.000	18
15	Acetolysis, neophyl brosylates, 70°C	−3.745	0.612	0.025	1.000	19
16	Rearrangement, acetophenone oximes, in sulfuric acid, 51°C	−1.938 −1.930	0.658 0.632	0.110 0.116	0.995 0.996	20 20a
17	Rearrangement, acetophenone-oxime-picrates, in dichlorobutane, 70°C	−4.116	0.600	0.150	0.995	21
18	Solvolysis, biphenylyl dimethylcarbinyl chlorides, in 90% aq. acetone, 25°C	−1.526	0.589	0.089	0.991	22
19	Benzoic acids with diphenyldiazomethane, in ethanol, 30°C	−0.908 −0.913	0.289 0.280	0.026 0.022	0.998 0.999	23 23a

B. Aromatic Substitution

No.	Reaction	ρ	r	s	R	Ref.
20	Molecular bromination	−9.49	1.418	0.194	0.999	24
21	Molecular chlorination	−7.79 −7.95	1.239 1.221	0.110 0.100	0.993 0.994	24 24a
22	Protodeboronation	−4.94	1.091	0.163	0.998	25
23	Mercuration	−3.974	1.050	0.120	0.997	26
24	Acetylation	−9.52	0.813	0.336	0.992	27
25	Bromodesilylation	−6.62	0.808	0.21	0.991	28
26	Ethylation, ethyl bromide - gallium bromide, in ethylene dichloride	−2.647	0.774	0.090	0.991	29
27a	Protodesilylation, sulfuric acid	−4.942	0.761	0.021	1.000	30
27b	Protodesilylation, perchloric acid	−5.318 −5.283	0.734 0.732	0.045 0.058	0.999 1.000	31 31a
28a	Protodegermylation, sulfuric acid	−4.333	0.744	0.052	1.000	32
28b	Protodegermylation, perchloric acid	−4.629	0.727	0.039	1.000	33
29	Protodeplumbylation	−2.419	0.664	0.059	0.999	34
30	Protodemercuration	−2.87	0.61	0.29	0.981	35
31	Protodestannylation	−3.723	0.561	0.015	0.999	36
32	Protodesilylation, biphenyls	−1.325	0.424	0.024	0.999	37

C. Equilibrium

No.	Reaction	ρ	r	s	R	Ref.
33	pK_R^+, Benzhydrols	−9.37 −9.59	1.078 1.143	0.44 0.49	0.995 0.999	38 38a
34	pK_{BH^+}, Benzaldehydes	−1.764	1.164	0.099	0.996	39

No.	Reaction	ρ	r	s	R	Ref.
35	pK_{BH^+}, Benzalacetophenones	−1.339	0.872	0.024	1.000	40
36	pK_{BH^+}, Azobenzenes	2.238	0.849	0.27	0.998	41
37	pK_{R^+}, Triarylcarbinols	−11.39	0.787	0.49	0.999	38
		−11.50	0.768	0.73	0.997	42a
		−11.37	0.742	0.51	0.998	42b
38	pK_{BH^+}, Acetophenones	2.200	0.760	0.070	0.998	43
39	pK_{BH^+}, Benzoic acids	1.167	0.558	0.057	0.992	44
		1.146	0.553	0.053	0.993	44a
40	pK_{BH^+}, Pyridine oxides	2.684	0.550	0.14	0.996	45
41	Aryltropylium ions	2.055	0.464	0.083	0.993	46
42	pK_{BH^+}, Benzamides	1.243	0.364	0.058	0.992	47
43	pK_a, Benzoic acids, in water, 25°C	1.000	0.272	0.012	1.000	48
44	pK_a, Benzoic acids, in methanol	1.415	0.274	0.029	0.999	49
45	pK_a, Benzoic acids, in ethanol	1.515	0.253	0.043	0.997	50
46	pK_a, Benzoic acids, in *n*-propanol	1.569	0.237	0.025	0.999	51
47	pK_a, Benzeneboronic acids, in water	2.141	0.222	0.036	0.999	52

D. Non-reactivity Data

No.	Reaction	ρ	r	s	R	Ref.
48	F^{19} chemical shift, *p*-fluorobenzophenones in sulfuric acid	7.469	1.068	0.019	0.998	53
49	Ionization potential, benzyl radicals	1.140	1.015	0.082	0.999	54
50a	F^{19} chemical shift, *p*-fluorobenzophenone - BCl_3 complexes, dichloromethane	7.410	0.797	0.18	0.999	55
50b	F^{19} chemical shift, *p*-fluorobenzophenone - BF_3 complexes, dichloromethane	6.592	0.797	0.18	0.998	55
51	F^{19} NMR chemical shift, *p*-fluorobenzophenones, dichloromethane	2.398	0.325	0.064	0.998	55
52	UV $1/\lambda_{max}$, malachite green, in acetic acid	6.13	0.752	0.3	0.997	56

a) The summary of the results of the least squares application of Eq. 2. Substituents generally included were the selected groups; *p*-methoxy, *p*-alkyl, *p*-phenyl, *p*-halogens, well behaving *metas* substituents and *para*+R substituents, otherwise noted.

b) Reference numbers in the last column refer to those bellow the table rather than those in the text.

1) Standard deviation. 2) Correlation coefficient. 3) Literatures and remarks; reference numbers refer to the following rather than those cited in the text. 4) Ref. 5 in the text. 5) W. E. Bachmann and E. H. Mosher, *J. Am. Chem. Soc.*, **54**, 1124 (1932); W. E. Bachmann and J. W. Ferguson, ibid., **56**, 2081 (1934). 6) Y. Yukawa, Y. Tsuno and Y. Kusuyama, Unpublished. 7) J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964). 7a) *p*-Nitro group was excluded from the calculation. 8) G. Kohnstam, **1960**, 2066; V. J. Shiner, Jr. and C. J. Verbanic, *J. Am. Chem. Soc.*, **79**, 369 (1957). 9) J. F. Norris and C. Banta, ibid., **50**, 1804 (1928); J. F. Norris and J. T. Blake, ibid., **50**, 1808 (1928). *p*-Methoxy group was not included into the calculation. 10) S. Nishida, privte communication; J. Packer, J. Vaughan and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958). 11) R. Bolton, N. B. Chapman and J. Shorter, *J. Chem. Soc.*, **1964**, 1895. 12) Ref. 38 in the text. 13) N. N. Lichtin and M. J. Vignale, *J. Am. Chem. Soc.*, **79**, 579 (1957); N. N. Lichtin and P. D. Bartlett, ibid., **73**, 5530 (1951); N. N. Lichtin and H. Glanzer, ibid., **73**, 5537 (1951); N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 164 (1956). 14) R. W. Bott, C. Eaborn and D. R. M. Walton, *J. Chem. Soc.*, **1965**, 384. 15) R. W. Bott, C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.*, **1**, 420 (1964). 16) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525. 17) Ref. 3 in the text. 18) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, **1947**, 1096. 19) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957). 20) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1151 (1952); D. E. Pearson and J. D. Burton, ibid., **19**, 957 (1954). 20a) Based on the data reported in, P. J. McNulty and D. E. Pearson, *J. Am. Chem. Soc.*, **81**, 612 (1959). 21) R. Huisgen, J. Witte, H. Walz and W. Jira, *Ann.*, **604**, 191 (1957). 22) T. Inukai, This Bulletin, **35**, 400 (1962). 23) J. D. Roberts, E. A. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949); R. A. Benkeser, G. E. Deboer, R. E. Robinson and D. H. Sauve, ibid., **78**, 682 (1956); N. B. Chapman, J. Shorter and J. H. P. Utley, *J. Chem. Soc.*, **1962**, 182. 23a) Correlation with the exclusion of *p*-fluoro group. 24) Data taken from, L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1661 (1962). 24a) The correlation excluding *m*-bromo group. 25) H. G. Kuivila, *J. Am. Chem. Soc.*, **83**, 2167 (1961). 26) H. C. Brown and G. Goldman, ibid., **84**, 1650 (1962). 27) H. C. Brown and G. Marino, ibid., **84**, 1658 (1962). 28) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, **1957**, 4449. 29) H. C. Brown and A. H. Neyens, *J. Am. Chem. Soc.*, **84**, 1655 (1962). 30) F. B. Deans and C. Eaborn, *J. Chem. Soc.*, **1959**, 2299. 31) C. Eaborn, ibid., **1956**, 4858. 31a) *p*-Dimethyamino-, *p*-hydroxy- and β-naphthyl-groups were included into the calculation. 32) C.

Eaborn and K. C. Pande, *J. Chem. Soc.*, **1961**, 5082. 33) C. Eaborn and K. C. Pande, ibid., **1961**, 297. 34) C. Eaborn and K. C. Pande, ibid., **1961**, 3715. 35) R. E. Dessy and J. Y. Kim, *J. Am. Chem. Soc.*, **82**, 686 (1960). 36) C. Eaborn and J. A. Waters, *J. Chem. Soc.*, **1961**, 542. 37) R. Baker, R. W. Bott, C. Eaborn and P. M. Greasley, ibid., **1964**, 627. 38) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955); N. C. Deno and W. L. Evans, ibid., **79**, 5804 (1957). 38a) *p*-Dimethylamino group was included. 39) K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959). 40) D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **84**, 4312 (1962). 41) H. H. Jaffé and R. W. Gardner, ibid., **80**, 319 (1958). 42a) The correlation including *p*-dimethylamino, *p*-amino and *p*-hydroxy groups. 42b) The correlation including *p*-dimethylamino and *p*-hydroxy groups. 43) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **80**, 6355 (1958). 44) R. Stewart and K. Yates, ibid., **82**, 4059 (1960). 44a) *m*-Chloro group was excluded. 45) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955); J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, **1957**, 4375; C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shaker and A. M. White, *Tetrahedron*, **21**, 1055 (1965). 46) C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964). 47) J. T. Edward, H. S. Chang, K. Yates and R. Stewart, *Can. J. Chem.* **38**, 1518 (1960). 48) Data taken from, D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); *p*-Dimethylamino, *p*-amino and *p*-hydroxy groups were included. 49) J. H. Elliot and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454 (1941). 50) J. H. Elliott and M. Kilpatrick, ibid., **45**, 466 (1961). 51) J. H. Elliott, ibid., **46**, 221 (1942). 52) G. E. K. Branch, D. L. Yabroff and B. Bettman, *J. Am. Chem. Soc.*, **56**, 937 (1934); ibid., **56**, 1865 (1934); ibid., **56**, 1850 (1934). 53) R. W. Taft and Y. Tsuno, unpublished. 54) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961). 55) R. W. Taft, unpublished. 56) C. C. Barker, M. H. Bride, G. Hallas and A. Stamp, *J. Chem. Soc.*, **1961**, 1285.

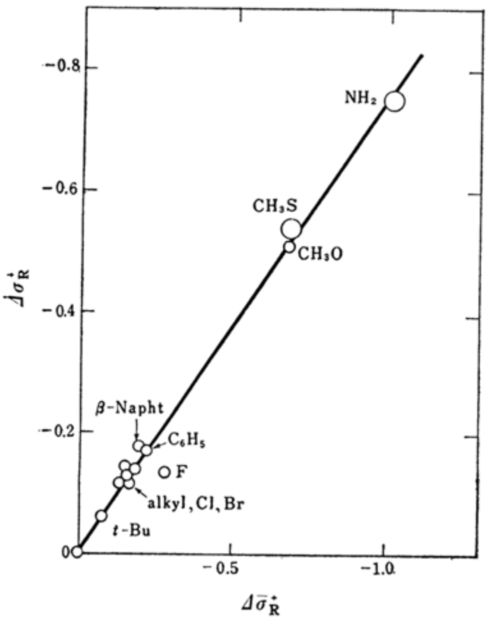

Fig. 3. Relation between $\varDelta\sigma_R^+$ and $\varDelta\bar{\sigma}_R^+$.

to be capable of being the resonance substituent constant. The increment $\sigma^+ - \sigma^0$ in fact runs precisely parallel to $\varDelta\sigma_R^+$ for corresponding substituents, as shown in Fig. 3. The correlation can be given by :

$$\varDelta\sigma_R^+ = 0.74(\sigma^+ - \sigma^0).$$

The quantity, $\sigma^+ - \sigma^0$, can correlate also linearly the exalted resonance contribution involved in Hammett σ-values, $\sigma - \sigma^0$, with a proportionality constant of 0.26.[29] These facts evidently suggest that the individual set of these increments is measuring in the different scale the identical quantities capable of being the resonance substituent parameter. The replacement of the standard from σ to σ^0 does not result the change in the form of the equation. Thus the alternate relationship can be represented by Eq. 2,

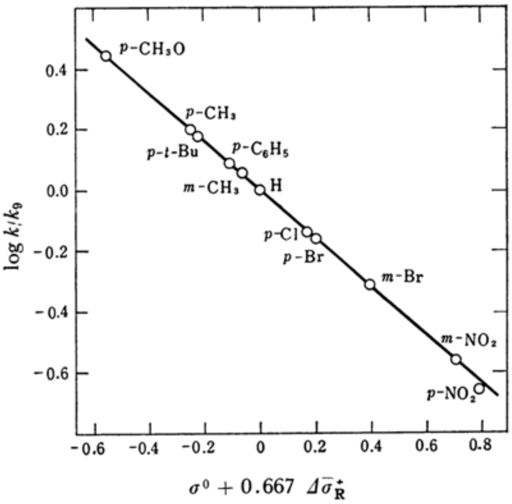

Fig. 4. Application of Eq. 2 to the decomposition of ω-diazoacetophenones in acetic acid at 40°C.

$$\log k/k_0 = \rho(\sigma_0 + r\varDelta\bar{\sigma}_R^+) \qquad (2)$$

where a new set of resonance substituent parameters, $\varDelta\bar{\sigma}_R^+$, was defined by $\sigma^+ - \sigma^0$ in Brown and Okamoto's scale.

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[29] An anomaly arises in *p*-fluoro group in this correlation; only fluoro group deviates measurably from the correlation line. A satisfactory explanation of the deviation is not immediately available, but the deviation of this group is not significant in the other benzoic reactivities, such as hydrolysis of benzoic esters or the reaction of benzoic acids with diphenyldiazomethane. Therefore, the deviation does not deny the applicability of the present treatment for fluoro group.

Equation 2 has been applied successfully to correlate representative electrophilic reactivities including the benzoic reactivities, by using the method of least squares. The results are summarized in Table V and several examples are illustrated in figures. Our previous result on the decomposition of diazoacetophenones in acetic acid[3] was correlated excellently with an r-value of 0.667 as shown in Fig. 4. For our recent data of the hydrolysis of m- and p-substituted α-phenylethyl chlorides in 80% aqueous acetone at 45°C,[30] Hammett equation resulted a scattered plot but Eq. 2 gave an excellent straight line for the same data using an r of 1.16. This can be compared in Figs. 5 and 6. The precision of the correlations can be easily estimated by standard deviations and correlation coefficients in Table V. The excellent result covering a wide variation of ρ and a variety of reactions evidently confirms the generality of this empirical relationship (2).

Most of the correlations in Table V were obtained primarily on the basis of reactivities of selected substituents. Dimethylamino-, amino, hydroxy-, and some others were not included into the calculations of correlations, because σ^0 and $\Delta\sigma_R^+$ values for these groups are not equivalently reliable as those for the other well-behaving substituents. Whereas the inclusion of these groups into calculations usually did not result the significant change in the correlation.

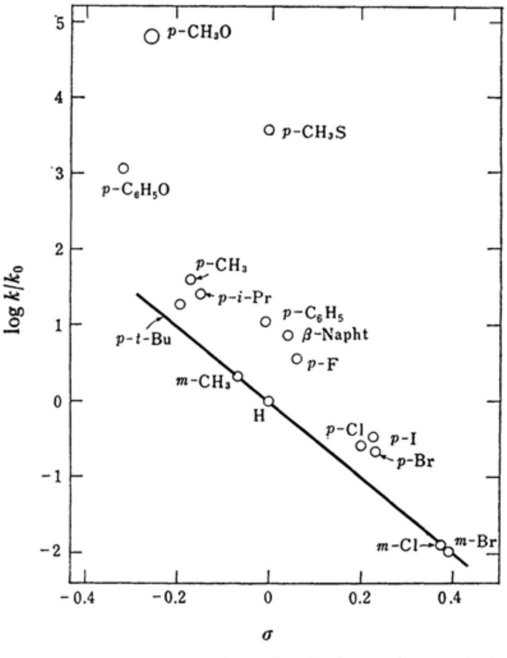

Fig. 5. Hammett plot of solvolysis of α-arylethyl chlorides.

ρ and r in Eq. 2 might be practically covariant and compensate for variations of each other. Our treatment is essentially based as the standard

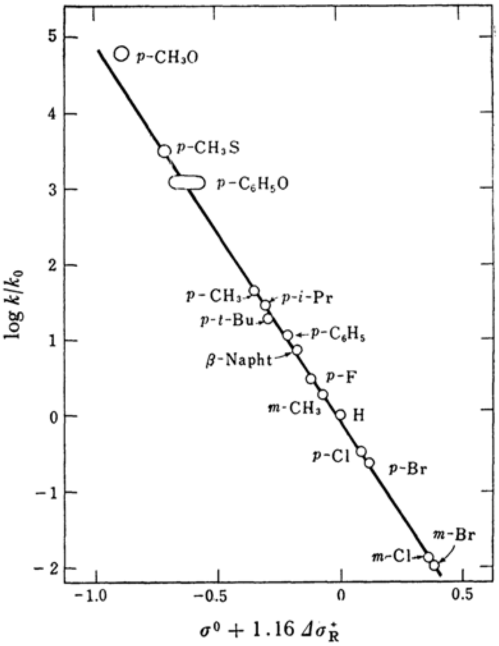

Fig. 6. Application of Eq. 2 to the solvolysis of α-arylethyl chlorides.

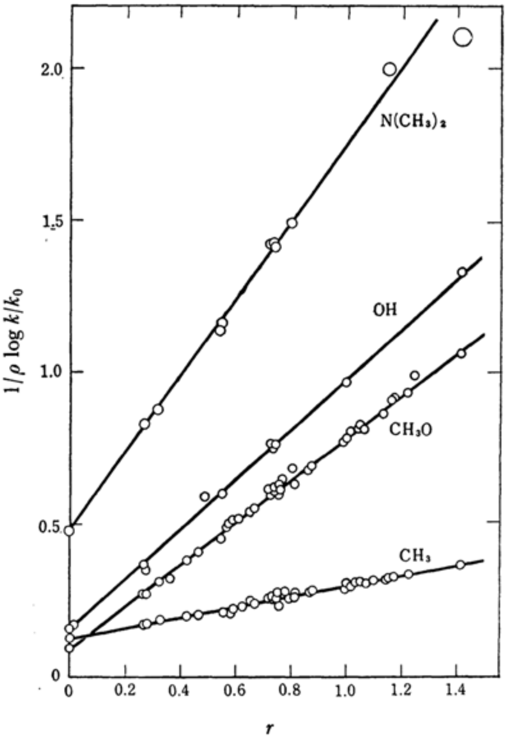

Fig. 7. Dependency of the effects of *para* substituents on r.

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[30] Y. Yukawa, Y. Tsuno and Y. Kusuyama, to be published.

on the ρ_m value, which should be the general basis of the Hammett type linear free energy correlations.[3,15,16] Certainty of the resulted correlation or r must depend on the reliability of ρ-value, and accordingly depend on the number of *meta* substituents involved in the series. ρ values obtained by the least squares application of Eq. 2 were generally found to agree with values calculated from *meta* reactivities alone. This should be an important fact to support our treatment, and thus r-value is not merely a mathematical compensating parameter but appears to be a parameter characteristic of the reaction practically independent of ρ-value.

Figure 7 illustrates the variation of apparent substituent constants, $1/\rho \log k/k_0$, of respective groups as a function of r for varied reactions. The respective substituents indicates clearly the first order dependence upon r. Since the gradient corresponds to $\Delta\bar{\sigma}_{\rm R}^{+}$ and the intercept to σ^0 of respective substituents, the linear dependency is an evidence for the constancy of $\Delta\bar{\sigma}_{\rm R}^{+}$ parmameters of these groups independent of reactions. Dimethylamino and hydroxy groups also indicate clearly the linear dependency covering over a remarkable variation of reactivities. Here again it should be mentioned that these groups were not included in the calculation of r values. Thus this should be the strong support to the certainty of the present relationship for a wide variety of substituents including these strongly conjugative substituents. Unfortunately, data are not sufficiently available in the literature for *p*-amino, *p*-methylmercapto and *p*-phenoxy groups to examine the validity of parameters. Additional data must be awaited.

The present type equation is expected to be applied for the correlation of conjugatively electron attracting *para* substituents in the nucleophilic reactions.[31] This can be realized by Eq. 3,

$$\log k/k_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_{\rm R}^{-}) \qquad (3)$$

using the difference, $\sigma^- - \sigma^0$, as the resonance substituent constant, $\Delta\bar{\sigma}_{\rm R}^{-}$. The dissociation of phenols or anilines will be perhaps the extreme case of this equation; these were referred to $r=1$. The linear correlation in Fig. 8 is illustrating the application of Eq. 3 to the dissociation of substituted thiophenols[32] which requires $r=0.52$. NMR chemical shifts of the acetylenic proton of substituted phenylacetylenes[33] resulted an excellent correlation in terms of r of 0.63 for *para* electron attracting groups. Yoshioka et al.[34] reported that the dissociations of several series of sulfonanilides were correlated linearly, giving r's close to 0.5. Although further examination may have to be required for Eq. 3, few other data of this reactivity class are available in the literature. However, these results may be sufficient to suggest that the present type treatment can be applicable not only to electrophilic but nucleophilic reactions.

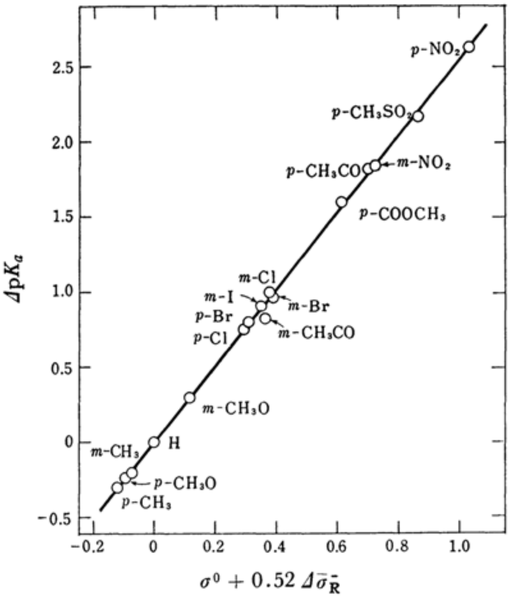

Fig. 8. Application of Eq. 3 to the dissociation of substituted thiophenols.

From the general success of the present type and original treatments, and also from a precise proportionality between $\Delta\sigma_{\rm R}^{+}$ and $\Delta\bar{\sigma}_{\rm R}^{+}$, it can be conclusive that there should exist a general measure of the resonance capacity of substituents. The substituent effect on reactivities can be represented by the generalized form,

$$\log k/k_0 = \rho(\sigma^0 + \psi) \qquad (4)$$

where ψ represents the exalted contribution of *para* substituents, exclusively attributable to the resonance contribution. The present result shows that ψ can be given by

$$\psi = r\Delta\bar{\sigma}_{\rm R}^{+} \quad \text{and/or} \quad = r\Delta\bar{\sigma}_{\rm R}^{-} \qquad (4')$$

for conjugatively electron releasing *para* substituents in electrophilic reactions and electron attracting *para* substituents in nucleophilic reactions, respectively. This is an actual establishment of the linear free energy relationship for the exalted resonance contribution. Equation 4 associated with 4′ is in the other view the separation of substituent effect into the substituted phenyl polarity and the polarizability effects.

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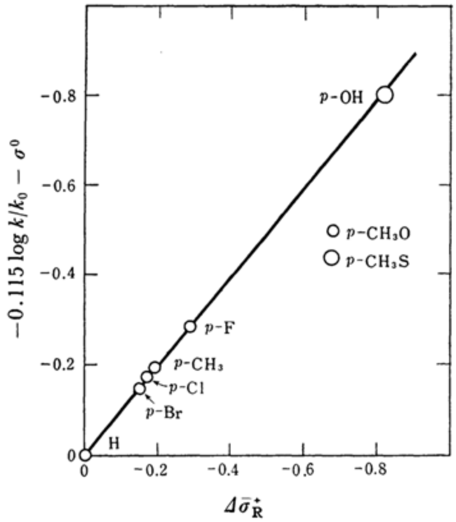
31) Y. Yukawa, *J. Soc. Org. Synth. Chem. Japan, sp. ed.*, 69 (1962).

32) F. G. Bordwell and H. H. Andersen, *J. Am. Chem. Soc.*, **75**, 6019 (1953); G. Schwarzenbach and H. A. Egli, *Helv. Chim. Acta*, **17**, 1176 (1934).

33) Y. Yukawa and H. Yamada, *J. Chem. Soc. Japan, Pure Chem. Sect., (Nippon Kagaku Zasshi)*, **85**, 501 (1964).

34) M. Yoshioka, K. Hamamoto and T. Kubota, This Bulletin, **35**, 1723 (1962); A. Willi, *Helv. Chim. Acta.* **39**, 49 (1956).

As pointed out frequently,[11,14,15,35] ϕ term is susceptible to various factors such as the loss of resonance due to steric inhibition, specific solvation, and beyond the question experimental errors. An excellent result with the present treatment should be an evidence supporting that only the polar contribution, inductive and resonance contributions, is the dominant factor of the given reactivity. The ordinary effects, such as the dependency of resonance upon solvation or desolvation, will be included in r and also in ρ as a common factor. On the other hand, the deviation from the correlation should be taken as an evidence for the existence of some specific effects of particular substituents. An illustrative example of the case is the bromination of polymethylbenzenes. Illuminati reported the substituent effect on the nuclear bromination of substituted durenes, isodurenes and mesitylenes, where only the desired attacking nuclear position is opened.[36] On the basis of Eq. 2, the additional resonance contribution, ϕ, to this reaction is separated using $\rho = -8.69$. Figure 9 shows the plot of ϕ-values against $\Delta\bar{\sigma}_R^+$. The points for alkyl- and halo-groups fall on a line giving an r of 1.00 whereas methoxy and methylmercapto groups deviate from the line. The deviation might be attributed to the steric loss of resonance interaction with the ring due to the twisting from the coplanarity by adjacent methyl groups. The resonance contribution of the other groups may not be affected sterically, so that they satisfy the linear relation with $\Delta\bar{\sigma}_R^+$. p-Hydroxy groups, of which the rate is estimated from that of the 2, 6-dimethyl derivative,[12] is also usually free from such an effect and thus satisfies the correlation. Illuminati has pointed out the inhibition of resonance only for p-nitro group on the basis of the Hammett correlation, while he did not verify that of methoxy or methylmercapto group, simply because the lack of any reliable standard correlation. The considerably lower r than that of the bromination of monosubstituted benzenes can be explained reasonably in terms of the incorporated stabilization of the transition state by the electron releasing methyl groups in the polymethylbenzene case. The slightly low ρ value is referred to the same reason and also to the steric contribution of methyl groups to the reaction center.



Eig. 9. Resonance contribution in the bromination of polymethylbenzenes.

One of the characteristic features of our treatment is the introduction of the variable r for variations of resonance from reaction to reaction. In our concept, r must be a measure of the degree of resonance interaction between substituent and reaction site. As mentioned previously,[6,11] r remains approximately a constant for reactions which have the closely similar structure of the transition state. In the case of dissociations of substituted benzoic acids, ρ-parameter varies considerably with respect to the change in the condition such as solvent change, whereas r remains so constant as to give a constant σ-value for respective substituents. In the carbonium ion reactions, trityl derivatives gave an approximately constant r of 0.8, and the benzhydryl provided r-value close to 1.1.

In the series of solvolysis reactions, cumyl chlorides have an r-value of unity by the definition, α-phenylethyl chlorides provide a precise r value of 1.16, and benzyl derivatives r-value round 1.5.[37] The changes of r can be attributed to variations of the degree of aryl participation in competition with electron donation by the adjacent methyl group. The variation in ρ does not provide any useful indication.

In the case of Beckmann rearrangement of acetophenone oximes (16 and 17), the change of the leaving group resulted the distinctly different ρ values but comparable r values. Closeness of r might be a suggestion of the close similarity of the transition state. Change in ρ provides few information about the mechanism. On the contrary, the solvolysis of cumyl and neophyl

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[36] G. Illuminati, *J. Am. Chem. Soc.*, **80**, 4941 (1958); ibid., **80**, 4945 (1958); E. Baciocchi and G. Illuminati, ibid., **86**, 2677 (1964).

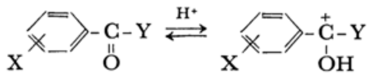
[35] C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry," Vol. II, Interscience, New York (1964), Chapt. 6, p. 323.

[37] The definite r-value can not be determined for this reactivity; as for example, the solvolysis of benzyl tosylates appears to involve the change in the reaction mechanism due to substituent changes. Accordingly, even ρ_m value can not be accurately determined for this reaction. (J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953); F. T. Fang, J. K. Kochi and G. S. Hammond, ibid., **80**, 563 1958).

derivatives (1 and 15) resulted comparable ρ-values but different r-values, suggesting the different structures of transition states.

The gas phase pyrolysis of substituted α-phenylethyl acetates, studied by Smith et al.,38) can be compared interestingly with the solvolysis of phenylethyl chlorides in an aqueous acetone.30) The pyrolysis of acetates gave a remarkably small ρ but a comparable r value with that for the solvolysis of the chlorides indicating the resemblance of the transition states of both reactions.

In the series of the protonation equilibria of the benzoyl derivatives (No. 34, 38, 39 and 42),



where Y's are H, CH_3, OH and NH_2, r-value decreases from 1.16 to 0.36 in the increasing order of electron donating capacities of Y-substituents. This can be explained reasonably in terms of the competitive participation of aryl and Y-substituent groups. ρ parameter appears to be a complicated resultant of the pertinent factors, while the condition of reactions is nearly the same. From these facts, r-parameter can be discernible as the more appropriate measure of the electronic requirement of the transition state than ρ-parameter.

A theoretical approach to the present-type linear free energy relationship (2 and 3) has been recently carried out by Fueno and Furukawa.39) Hammett σ and various σ^+-type substituent constants were calculated as the delocalization energy changes of substituted benzyl-type carbonium ions by the perturbation and also variation methods.40) The results suggested that the variation of estimated Coulomb parameter k in $\alpha+k\beta$ for the reaction site, assumed as a heteroatom ion, was proportional to the change in r of the present study. Thus the experimental r, the degree of resonance contribution, appears to be compatible with the degree of delocalization estimated from M. O. approximation.

Theoretically both r and ρ should be responsible to the variation of electron density at the reaction site, accordingly, both parameters might be correlated in some way with each other. Norman12) has proposed recently Eq. 5 for the correlation of aromatic electrophilic reactions,

$$1/\phi \log k/k_0 = \sigma_G + \phi\sigma_P \qquad (5)$$

where ϕ is the electron demand constant, σ_G is a measure of the ground state polarization and σ_P the polarizability constant of a substituent. In view of the formal similarity to our relationship, he has attempted to rationalize his Eq. 5 in terms of our parameters.41) σ_G can be equated to σ^0. σ_P might correspond to our resonance parameter in its concept and reasonably be expected to be proportional to the latter. Further correspondence requires that r value has to be parallel to ρ values of various reactions, provided ϕ being equal to ρ. In view of the nature of ρ, such a parallelism will be observable only in the closely limited reaction series. Norman has demonstrated the existence of linearity between both parameters for 6 aromatic electrophilic substitution reactions. Whereas, Eaborn has indicated the other examples against this.42) In Fig. 10 are figured out both parameters for aromatic substitutions obtained in the present investigation. The resulted correlation is clearly far out of the accuracy of usual linear free energy correlations, even if a linearity may exist. Generally the present result does not necessarily agree with Norman's assumption. Norman equation appears to be describing the limited theoretical model of the ideal aromatic substitution reaction, while such an ideal series of reactions can not easily be observed experimentally.

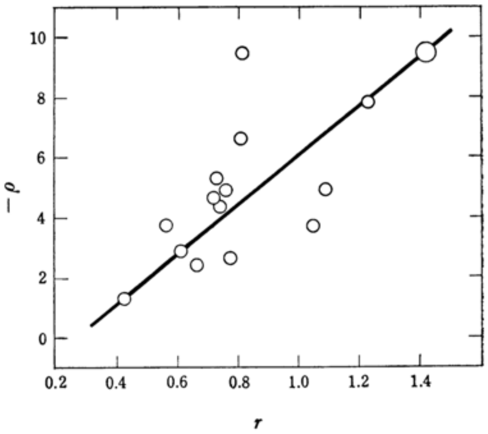


Fig. 10. Relation between ρ and r of aromatic electrophilic substitutions.

Of the empirical treatments of the substituent effect, Taft equation14,15) has been most generally accepted.2) The separation of the substituent effect into inductive and resonance effects appears to be most likely and physically meaningful. His equation is often employed in the literature

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38) R. Taylor, G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, **84**, 4817 (1962).

39) T. Fueno and J. Furukawa, private communication. Authors are indebted to their invaluable advices and discussions.

40) The integral parameters for substituents were determined in such a way as to give the calculated pi-electron change densities being proportional to the corresponding σ^0-constants, and these fixed parameters were employed for the calculation of other sets of substituent constants.

41) R. O. C. Norman and G. K. Radda, *Tetrahedron Letters*, **1962**, 125.

42) R. W. Bott and C. Eaborn, *J. Chem. Soc.*, **1963**, 2130.

to electrophilic reactivities as the form,[43]

$$\log k/k_0 = \rho_I\sigma_I + \rho_R\sigma_R^0 \quad (6)$$

where σ_R^0 may be replaced by σ_R or σ_R^+. The precision of the fit is usually comparable with that of the present treatment. According to Taft's definition,[14] σ_I is a constant of respective substituents independent of reactions, and ρ_I has to be equal to ρ_m value. However, on applying Eq. 6 to -R *para* substituents in the electrophilic reaction, it is found that the best ρ_I value obtained is not always equal to ρ_m value.[44] The statistically most probable ρ_I of a given reaction significantly varies depending on the choice of his resonance parameters. For instance, the application of Eq. 6 to Brown's reference reaction of σ^{+}[5] results the ratios of σ_I/σ_m of 1.00 (by definition), 1.35 and 1.50, dependent on the use of σ_R^+, σ_R and σ_R^0, respectively. These variations exceed distinctly the limit of the common uncertainty; more interestingly, they are rather systematic. The similar difficulties are not rarely observed in Taft's treatment, and are inevitable from the mutual nonlinearity of his resonance parameters for respective substituent. Thus, any set of his resonance parameters can not accomplish generally the linear resonance free energy relationship. These treatments might be perhaps the overextension or a kind of incorrect use of Taft equation. As Taft mentioned by himself,[14,15] individual set of his resonance parameters should be employed limitedly for its appropriate reactivity class, otherwise, the correlation obtained means merely a mathematically best result and either ρ_I or ρ_R resulted will lend little help to the elucidation of the mechanism of a given reaction. While Taft equation is conceptually reasonable and meaningful, the present treatment (4) togehter with (4') has the advantage of Taft's one in the view point of the linear resonance free energy relationship.

The insulated aryl reactivities can be separated conceptually into mesomeric and inductive effects. Accordingly, Eq. 4 for general reactivities can be rewritten in the form,

$$\log k/k_0 = \boldsymbol{I} + \boldsymbol{R}_0 + \boldsymbol{\Psi} \quad (7)$$

where $\boldsymbol{I}$ and $\boldsymbol{R}_0$ represent the inductive and mesomeric effects in the insulated reactivities. Either $\boldsymbol{R}_0$ or $\boldsymbol{\Psi}$ is essentially responsible to the inherent resonance capacity of respective substituents. Hence it might be plausible to expect that both $\boldsymbol{R}_0$ and $\boldsymbol{\Psi}$ terms can be described by a common resonance parameter inherent in the individual substituent. As usual, $\boldsymbol{R}_0$ could be replaced by Taft's σ_R^0, whereas, σ_R^0 is not exactly proportional to $\Delta\bar{\sigma}_R^+$ and is incapable of being linear free energy description of $\boldsymbol{\Psi}$ contributions. The general applicability of our $\Delta\bar{\sigma}_R^+$ for the $\boldsymbol{\Psi}$ contribution would lead to the expectation that a measure of the conceptual $\boldsymbol{R}_0$ will be practically realizable from our resonance parameters. The estimated $\boldsymbol{R}_0$-parameter might not be exactly equal to Taft's σ_R^0 parameter, and as a sequence, this might estimate a different scale of the inductive effect for the aryl-residue from Taft's σ_I scale. Such an analysis of the substituent effect should be of great importance and interest, to obtain some informations about the essential implication of the present treatment and also the nature of the substituent effect. The analysis along this line has been recently carried out in this laboratory and will be the subject of a forthcoming publication.

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[43] A. Bryson, *J. Am. Chem. Soc.*, **82**, 4862 (1960); *Austral. J. Chem.*, **16**, 401 (1963); I. R. Fox, P. L. Levins and R. W. Taft, Jr., *Tetrahedron Letters*, **1961**, 249; R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).

[44] To be discussed in the forthcoming paper.