Resonance Effect in Hammett Relationship. III. The Modified Hammett Relationship for Electrophilic Reactions

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As shown in Part II[1] of this series, the substituent constants in Brown and Okamoto's scale were derived for a number of electron releasing para substituents by correlating various sets of σ^+[2-8]. These values will possibly extend the utility of the Brown and Okamoto's equation[2,10] over a wider range of substituent changes[1,5,10,11]. However, it is clear that the unique set of σ^+ does not always describe the best situation of substituent contributions in various reactions, even though Brown and Okamoto's σ^+ may have an apparent generality. It would be attributed to the changes in availability of the *transition state resonance* in various reactions. The resonance con-

tribution of respective para substituents as well as the magnitude of σ^+ would not be maintained constant but varied from reaction to reaction[1]. Then, the Brown and Okamoto's and also other authors' sets of σ^+[3-9] should be utilized respectively in the limited extent of reaction series[1,3].

Our success in correlating various sets of σ^+ by Eq. 1[1] appears to imply some suggestions in regard to the Hammett type treatment[12] of electrophilic reactions.

$$(\sigma^+_A - \sigma) = r(\sigma^+_B - \sigma) \qquad (1)$$

Here r is a proportionality constant, and σ^+_A represents one of various sets of σ^+ and σ^+_B another set of σ^+. In a given para substituent, the increments of various σ^+ values relative to the usual σ constant[12]

1) Y. Yukawa and Y. Tsuno, This Bulletin, **32**, 965 (1959).

2) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

3) Y. Tsuno, T. Ibata and Y. Yukawa, This Bulletin, **32**, 960 (1959).

4) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955).

5) N. C. Deno and W. L. Evans, ibid., **79**, 5804 (1957).

6) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); D. E. Pearson and J. D. Burton, ibid., **19**, 957 (1954).

7) J. Miller, *Australian J. Chem.*, **9**, 61 (1956).

8) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953); G. S. Hammond et al., ibid., **80**, 653, 568, 573 (1958).

9) J. Packer, J. Vaughan and A. F. Wilson, *J. Org. Chem.*, **23**, 1215 (1958).

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

11) Brown has derived recently the averaged σ^+ values for p-NHe$_2$, p-NH$_2$ and p-OH, etc., from σ^+ values of other electrophilic reactions, while the agreement is by no means within satisfactory precision (Ref. 10). Deno's expansion of σ^+ in Brown and Okamoto's scale appears also to be unsuccessful (Ref. 5).

12) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); "Physical Organic Chemistry", McGraw-Hill Book Co., New York (1940), p. 194; H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

are possibly considered to be a function of its resonance ability. Then, the equation may be a linear resonance energy relationship. Therefore, it appears logical to extend this relationship to general electrophilic reactions combining with Hammett equation[12]. If the above relationship would hold in a variety of electrophilic reactions, the Hammett relationship for electrophilic reactions may be represented empirically according to Eq. 2,

$$\log k/k_0 = \rho(\sigma + r\Delta\sigma_R^+) \qquad (2)$$

where r is a reaction constant describing the degree of the transition state resonance or measuring the magnitude of positive charge to be necessarily stabilized at the transition state, and $\Delta\sigma_R^+$ which corresponds to a proper set of $\sigma^+ - \sigma$ is a substituent constant suggesting the resonating capacity of substituent. From the foregoing point of view, we are free to take one of various sets of the quantities $\sigma^+ - \sigma$ as a proper set of the $\Delta\sigma_R^+$.

The *resonance substituent constant*, $\Delta\sigma_R^+$, is now defined conveniently using the set of quantities $\sigma^+ - \sigma$ in Brown and Okamoto's scale[13]; i. e., the r is taken as unity in Brown and Okamoto's reference reaction, the solvolysis of aryldimethylcarbinyl chlorides in 90% aqueous acetone at 25°C,

$$\Delta\sigma_R^+ \equiv \sigma^+{}_{\text{Brown and Okamoto}} - \sigma \qquad (3)$$

Eq. 2 is undoubtedly to be satisfied by the reactions to which the Brown and Okamoto's equation was applicable, because the latter equation corresponds to the present Eq. 2 when r is equal to unity. The same is also certain in the electrophilic reactions which are correlated linearly with other sets of σ^+. The second term of Eq. 2 would vanish in the correlation of meta substituents, evidently because the Hammett relationship would hold in general electrophilic reactions as far as the mata substituents are concerned. Accordingly, ρ in Eq. 2 can be replaced by the ρ_{meta} value and the equation may be usually solved on the basis of ρ_{meta} value[14].

An empirical relationship should be required to examine critically the general applicability. Fortunately, in an enormous

number of electrophilic reactions, satisfactory results have been realized in terms of this relationship. In the present paper, then, the results of application and generality of this relationship are described.

Correlation of Reactivities

In view of the origin of this relationship, it is a matter of course that the relationship should describe satisfactorily the substituent effect in the respective reference reactions, from which various sets of σ^+ were derived. These are clear in Figs. 1 and 2. The rates of decomposition of ω-diazoacetophenones both in acetic acid at 40.00°C[3] and in 75% aqueous acetic acid at 25.20°C[1] are reproduced strictly in terms of Eq. 2, setting r to be 0.556 and nearly the same value 0.60, respectively.
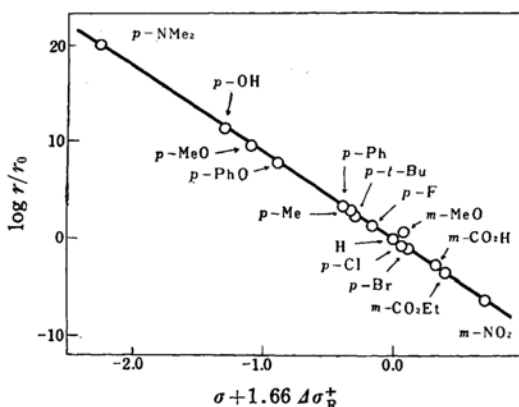

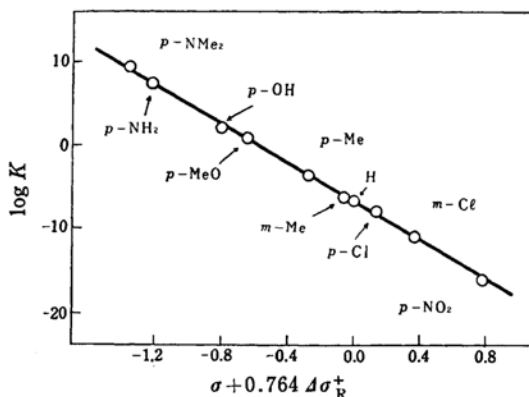Fig. 1. Relative reactivities in halogenation of monosubstituted benzenes at 25°C (*3*).

Fig. 2. Dissociation of triphenylcarbinols in sulfuric acid at 25°C (*22*).

13) A tentative set of $\Delta\sigma_R^+$ has been derived on the basis of Deno's reference reaction and applied preliminarily for several electrophilic reactions. [Y. Yukawa and Y. Tsuno, "Yûki Hannōkikō no Shimpo—Recent Advances in the Mechanism of Organic Reactions", (in Japanese) Vol. I, (1958), p. 1.]. However, the present definition of $\Delta\sigma_R^+$ in Brown and Okamoto's scale appears to be more available, in view of its frequent employment encountered in recent literatures.

14) Although various values of σ_{meta}^+ have been given by Brown and others (Refs. 2 and 10), the differences between $\sigma^+{}_{\text{meta}}$ and σ_{meta} are of magnitude comparable to experimental error. Even if they were significant, the situation of the relationship is unaltered but ρ value must be calculated by solving the regression Eq. 4.
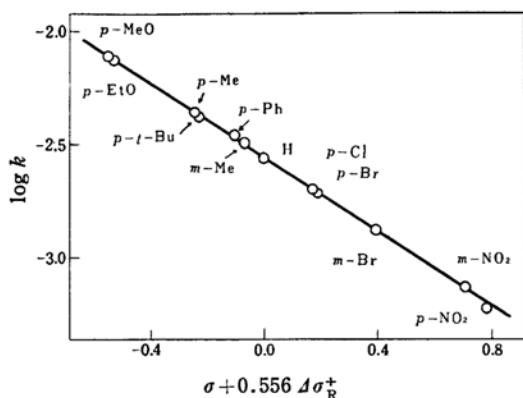
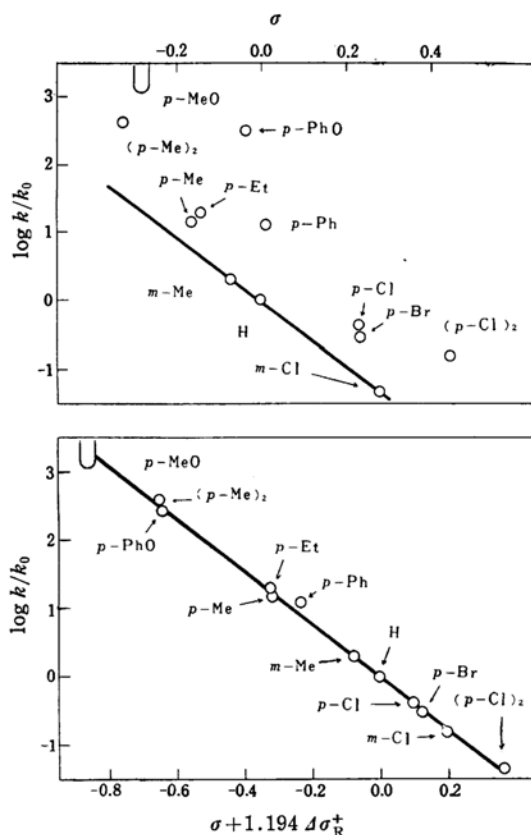Fig. 3. Decomposition of ω-diazoacetophenones in acetic acid at 40.00°C (25).

Fig. 4. Ethanolysis of benzhydryl chlorides at 25°C (10).

The Pearson's rate data of the Beckmann rearrangement[6] are also correlated in terms of $r = 0.434$. The numerical values of $\Delta\sigma_R^+$ used are the one given in Table III of the foregoing paper.

A typical example of electrophilic reactions is the solvolysis of arylalkyl halides. Norris and coworkers[15] reported the ethanolysis rates of benzhydryl chlorides.

The Hammett plots of para electron releasing substituents deviate markedly in the upper side of the meta correlation line. With regard to meta substituents, a linear Hammett relationship is obtained, and the slope, ρ_{meta}, is -3.72.

$$\log(k/k_0)_m = -3.72\,\sigma_{meta}$$

Using this ρ value, r is calculated to be 1.194. Then, the rates of the ethanolysis can be expressed by an equation

$$\log k/k_0 = -3.72(\sigma + 1.194\,\Delta\sigma_R^+)$$

In Fig. 4 is demonstrated the fine correlation of $\log k/k_0$ vs. $\sigma + 1.194\,\Delta\sigma_R^+$. In the same manner, the rates of ionization of triarylcarbinyl chlorides to form the ion pairs

$$(C_6H_5)_3C\text{–}Cl \rightarrow (C_6H_5)_3C^+//Cl^-$$
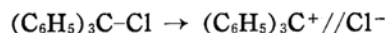
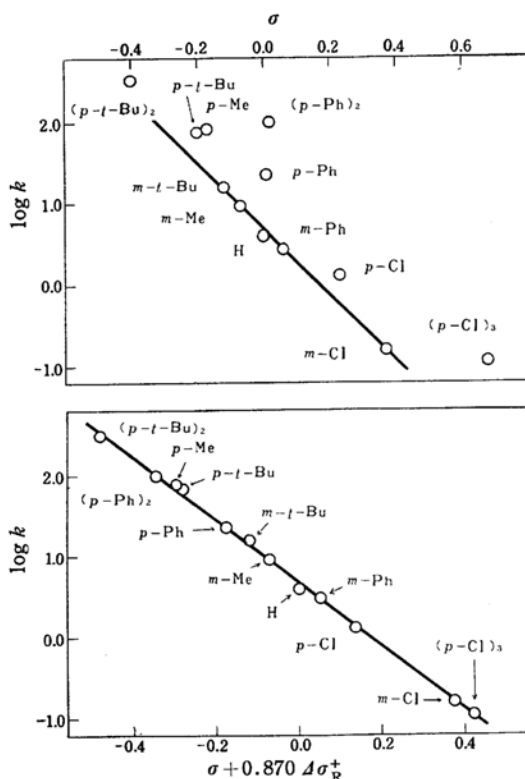in liquid sulfur dioxide[16] are correlated linearly. As is clear in Fig. 5, the correla-

Fig. 5. Dissociations of triphenylcarbinyl chlorides in liquid sulfur dioxide at 0°C (20).

15) J. F. Norris and C. Benta, *J. Am. Chem. Soc.*, **50**, 1804 (1928); J. F. Norris and J. T. Blake, ibid., **50**, 1808 (1928).

16) N. N. Lichtin and M. J. Vignale, ibid., **79**, 579 (1957); N. N. Lichtin and P. D. Bartlett, ibid., **73**, 5530 (1951); N. N. Lichtin and H. Glazer, ibid., **73**, 5537 (1951); N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 164 (1956).

tion is fully satisfactory; $\rho = -4.046$ and $r = 0.870$.

At the theoretical ground, the standard of correlation should be based on the meta correlation line, while there are relatively few adequate data which involve the rates of many meta derivatives. For the data involving a few rates of meta derivatives, the correlation is realized by solving the Eq. 4 for a and b on the basis of the method of least squares[17],

$$\log k = a\sigma + b\Delta\sigma_R^+ + \log k_0 \qquad (4)$$

where a and b correspond to ρ and $r\rho$, respectively. In this manner, the solvolysis rates of benzhydryl chlorides in methanol and in isopropanol[18] provide excellent correlations giving $r = 1.234$ and 1.350, respectively. Similarly, the dissociation of identically substituted benzhydrols in sulfuric acid at $25°C$[5] is correlated linearly in terms of $\rho = -9.112$ and $r = 1.175$.
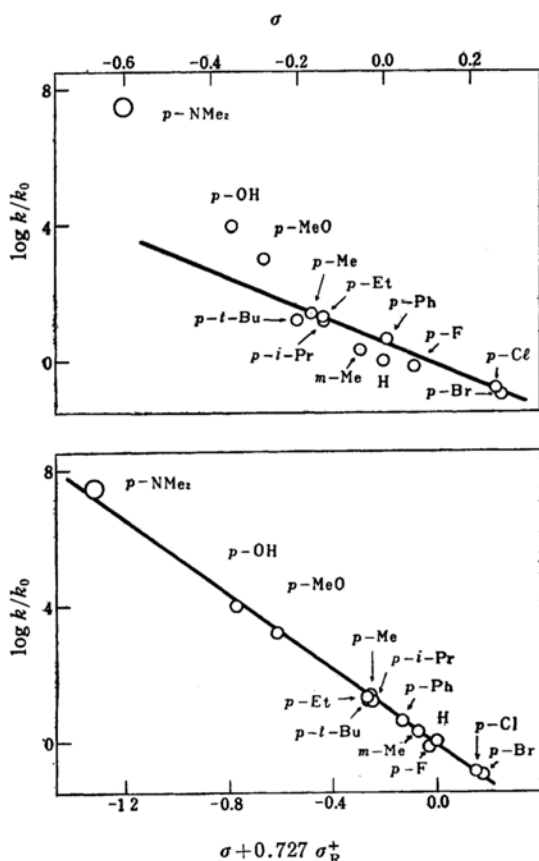
The present treatment is successful not only in the solvolysis but in other types of electrophilic reactions, such as aromatic electrophilic substitutions. Recent data of the nitration[19] and the halogenation[6,20] of substituted benzenes, and protonolysis
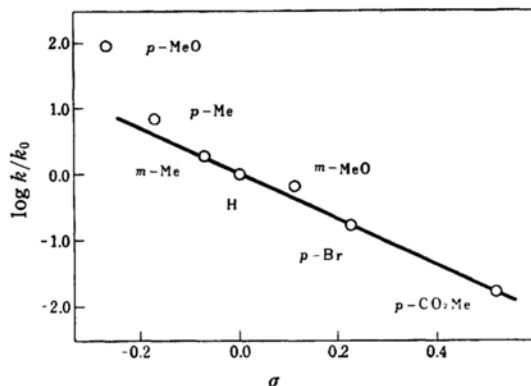
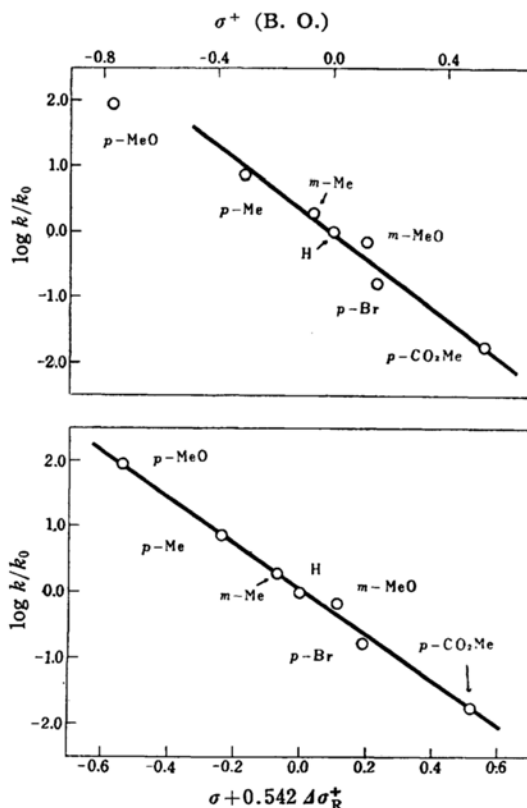Fig. 7—a.　Acetolysis of neophyl brosylates at $70°C$ (27).

Fig. 6.　Protodesilylation of phenyltrimethyl-silanes (23).

羃 Fig. 7—b.　Acetolysis of neophyl brosylates at $70°C$ (27).

17)　C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry", John Wiley & Sons, Inc., New York (1954), p. 245.
18)　S. Altscher, R. Baltzly and S. W. Blackman, *J. Am. Chem. Soc.*, **74**, 3649 (1952).

19)　J. D. Roberts et al., ibid., **76**, 4525 (1954).
20)　a)　P. B. D. de la Mare, *J. Chem. Soc.*, **1954**, 4450;
　　b)　P. B. D. de la Mare and J. T. Harvey, ibid., **1956**, 36; ibid., **1957**, 131; P. B. D. de la Mare and M. Hassan, ibid., **1957**, 3004.
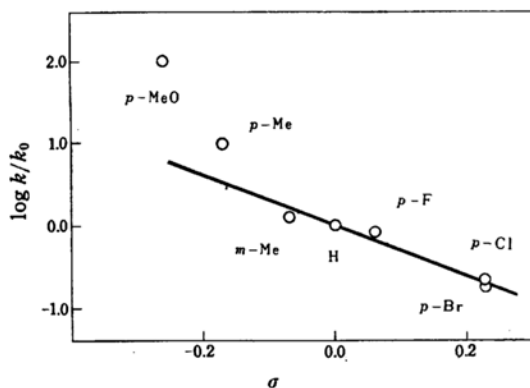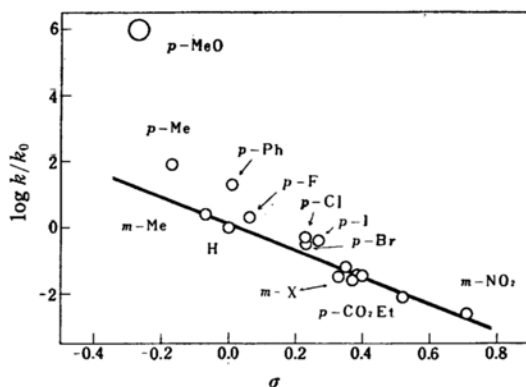
Fig. 8—a. Rearrangement of phenylpropenyl-carbinols (32).
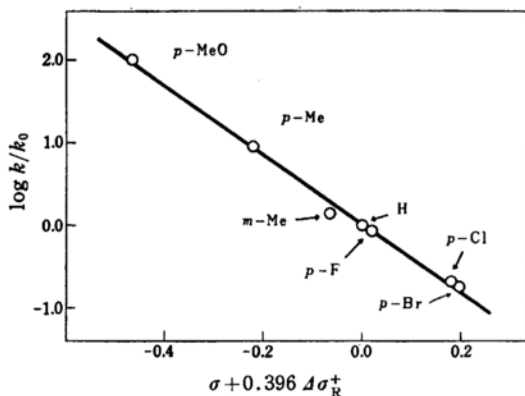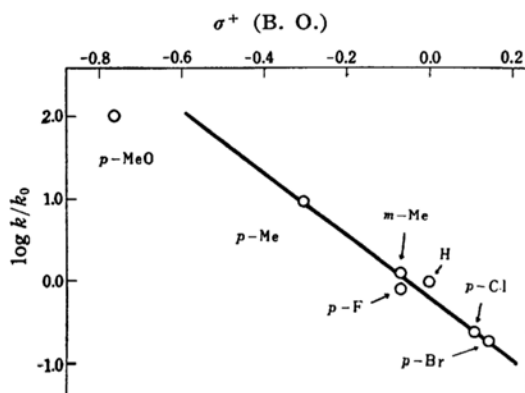

Fig. 9—a. Brominolysis of benzeneboronic acids (2).

Fig. 8—b. Rearrangement of phenylpropenyl-carbinols (32).
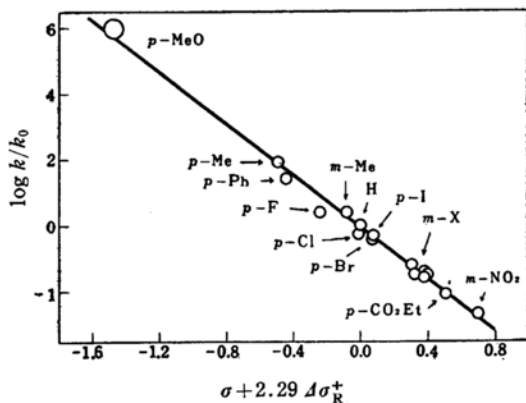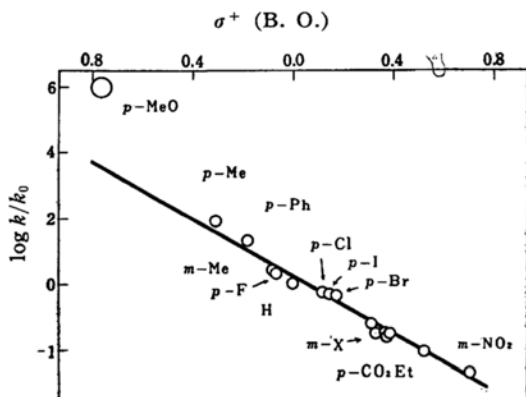
Fig. 9—b. Brominolysis of benzeneboronic acids (2).

of phenyltrimethylsilanes[21] (Fig. 6) are described satisfactorily. In the reactions quoted above, the Brown and Okamoto's relationship also results apparently but not strictly linear figures. This may be in accord with the fact that the r factors of these are considerably close to unity (see, Table I).

Recently, Winstein and coworkers[22]

reported that the rates of acetolysis of neophyl brosylates failed to give a good result by the Hammett treatment, and also that the correlation was slightly improved by the Brown and Okamoto's. According to the latter treatment, para electron releasing groups fall below the meta line, contrary to the results of the

21) C. Eaborn, ibid., 1956, 4858.

22) R. Heck and S. Winstein, J. Am. Chem. Soc., 79, 3432 (1957).
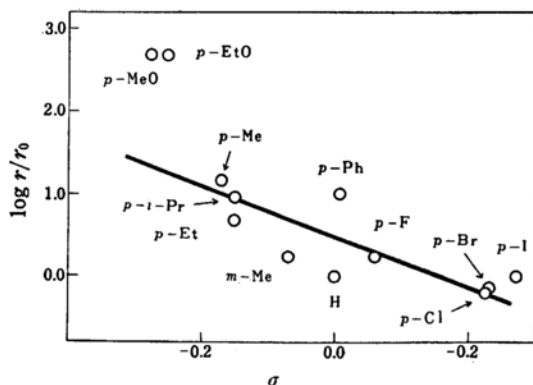
Fig. 10—a, Migratory aptitudes in the pinacol rearrangement (4).

Fig. 11—a. Epoxidation of cis-dimethylstilbenes at 30°C (33).

Fig. 10—b. Migratory aptitudes in the pinacol rearrangement (4).
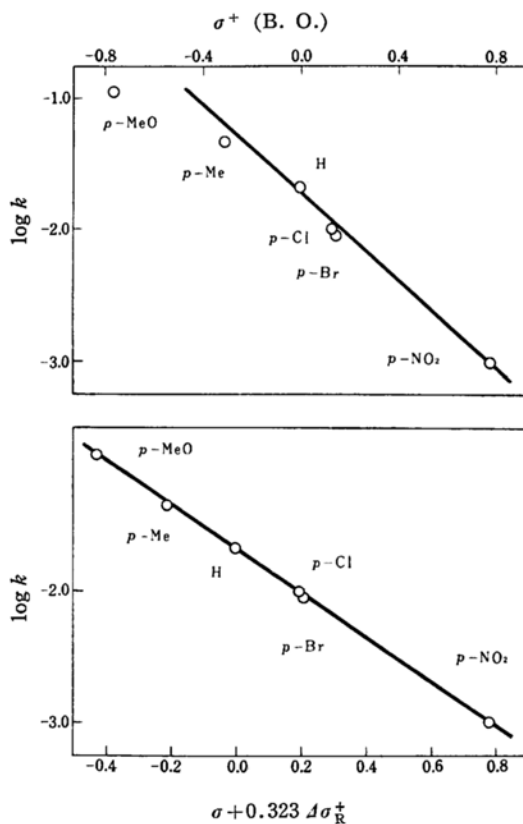
Fig. 11—b. Epoxidation of cis-dimethylstilbenes at 30°C (33).

Hammett one. However, the present treatment produces a successful figure (Fig. 7) of this reaction, in terms of $r = 0.542$. The Beckmann rearrangement of acetophenonoxime picrylethers[23] is correlated with Eq. 2, giving r to be 0.469, although the plot against Brown and Okamoto's σ^+ concaves downward. The

rates of the rearrangement of phenylpropenylcarbinols[24] are of the same kind ($r = 0.396$), as seen in Fig. 8. The resonance contribution of substituents in these reactions is estimated to be only a half of that in Brown and Okamoto's reference reaction. Therefore, it is natural that Brown and Okamoto's treatment overestimates the

23) R. Huisgen, J. Witte, H. Walz and W. Jira, *Ann.*, **604**, 191 (1957).

24) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, **1947**, 1096.

TABLE I. RESULTS OF APPLICATION OF THE PRESENT RELATIONSHIP

No.	Reaction	ρ	r	$s^{a)}$	$n^{b)}$	Reference
1	Solvolysis of phenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25°C	−4.518	1.000	0.093	21	2, d, e
2	Brominolysis of the benzeneboronic acids in 20% acetic acid and 0.40 M sodium bromide at 25°C	−3.84	2.29	0.313	16	25, c, f
3	Halogenation of substituted benzenes at 25°C	−8.82	1.660	0.414	15	7, c
4	Migratory aptitudes in the pinacol rearrangement of symmetrically substituted tetraarylpinacols	−2.523	1.602	0.120	12	26, d, g
5	Dissociation of monosubstituted benzhydrols in sulfuric acid at 25°C	−5.236	1.492	0.023	7	4, 5, d
6	Epoxidation of stilbenes with phthaloyl peroxide in tetrachloromethane at 80°C	−1.630	1.388	0.034	7	27, c, h
7	Solvolysis of benzhydryl chlorides in isopropyl alcohol at 25°C	−4.004	1.350	0.070	6	18, d
8	Solvolysis of benzhydryl chlorides in methanol at 25°C	−4.022	1.234	0.110	6	18, d
9	Solvolysis of benzhydryl chlorides in ethanol at 25°C	−4.140	1.198	0.095	10	9, 30, c, j
10	Solvolysis of benzhydryl chlorides in ethanol at 25°C	−3.721	1.194	0.087	12	15, c, i
11	Dissociation of identically disubstituted benzhydrols in sulfuric acid at 25°C	−9.112	1.175	0.335	8	4, 5, d, k
12	Rearrangement of α-phenylethyl chlorocarbonates in dioxane at 70°C	−3.060	1.166	0.048	5	31, d
13	Bromination of benzenes by hypobromous acid and perchloric acid in 50% aqueous dioxane at 25°C	−5.276	1.145	0.080	7	20b, d, l
14	Rearrangement of α-phenylethyl chlorocarbonates in toluene at 80°C	−2.808	1.138	0.117	5	31, d
15	Chlorination of benzalacetophenones	−3.413	1.128	0.033	4	32, c
16	Solvolysis of monohalobenzhydryl chlorides in 70% aqueous acetone at 25°C	−4.118	1.007	0.023	5	33, d
17	Migratory aptitudes in the Schmidt rearrangement of diphenylethylenes	−2.77	0.90	0.10	6	34, c
18	Reactivities of substituted benzenes toward nitration in nitromethane or acetic acid at 25°C	−6.377	0.897	0.327	12	19, c, m
19	Solvolysis of triphenylcarbinyl chlorides in 40% ethanol/60% ethyl ether at 0°C	−2.52	0.88	0.132	8	35, c, n
20	Dissociation of triphenylcarbinyl chlorides in liquid sulfur dioxide at 0°C	−4.046	0.870	0.101	12	15, c, o
21	Basicities of monosubstituted azobenzenes	−2.293	0.853	0.100	11	36, c
22	Equilibrium constants for carbonium ions from triphenylcarbinols in sulfuric acid at 25°C	−11.73	0.764	0.335	10	4, 5, d
23	Phenyltrimethylsilanes with perchloric acid in 72% aqueous methanol at 50°C	−5.597	0.727	0.125	13	21, d, p
24	Epoxidation of trans-stilbenes by perbenzoic acid at 30°C	−1.055	0.713	0.029	9	28, c
25	Acid catalyzed decomposition of ω-diazoacetophenones in acetic acid at 40°C	−0.823	0.556	0.008	12	1, 3, d, q
26	Acid catalyzed decomposition of ω-diazoacetophenones in 75% aqueous acetic acid at 25.20°C	−1.222	0.603	0.025	10	1, d, r
27	Acetolysis of neophyl brosylates at 70°C	−3.384	0.542	0.077	7	22, c
28	Diels-Alder reactions of phenylbutadienes with maleic anhydride in dioxane at 45°C	−0.711	0.475	0.038	5	37, c
29	The Beckmann rearrangement of acetophenone oxime picrylethers in dichlorbutane at 70°C	−4.243	0.464	0.233	12	1, 23, d
30	The Beckmann rearrangement of acetophenone oximes in 94.5% sulfuric acid at 50.9°C	−1.983	0.434	0.044	9	6, c
31	Decomposition of diphenylmethylcarbinyl azides in acetic acid/sulfuric acid at 25°C	−2.092	0.436	0.072	7	38, d
32	Rearrangement of phenylpropenylcarbinols in 60% aqueous dioxane at 30°C	−4.056	0.396	0.080	7	24, d
33	Epoxidation of cis-dimethylstilbenes in benzene at 30°C	−1.692	0.323	0.020	6	29, c

| 34 | Epoxidation of *trans*-dimethylstilbenes in benzene at 30°C | −1.554 | 0.249 | 0.035 | 6 | 29, c |
| 35 | Diphenyldiazomethanes with benzoic acid in toluene at 25°C | −1.570 | 0.190 | 0.036 | 12 | 39, c |

a) The standard deviation of experimental points from the regression line.

b) The number of points involved in the calculation.

c) The correlation obtained on the basis of ρ_{meta} value which were derived from the rates for meta substituted and nonconjugating para substituted derivatives.

d) The correlation obtained in aid of Eq. 4.

e) The correlation obtained by setting a priori $r = 1.000$.

f) The correlation of $r = 2.05$ and $\rho = -4.31$ was resulted on the basis of Eq. 4.

g) *m*-Methoxy group was omitted from the correlation.

h) The point of *p*-carbethoxy group deviates considerably from meta line and was not included in the calculation of ρ_{meta} value.

i) The point for *p-t*-butyl group deviates seriously and was omitted from the calculation of r value.

j) *p*-Phenyl group supplies a greater driving force than that expected from this correlation.

k) *p*-Dimethylamino and *p*-phenyl groups were not included in the calculation.

l) *m-t*-Butyl group was not included in the calculation and experimental value of −0.078 was resulted for σ_{meta} of this group.

m) Points for meta derivatives deviate from the ρ_{meta} line.

n) *p*-Fluoro group deviates significantly.

o) σ value of +0.06 was employed for *m*-phenyl group. Trisubstituted derivatives were omitted from the calculation, since the cross conjugation effect appeared to be possibly involved.

p) Excepting *p*-dimethylamino and *p*-hydroxy groups, was obtained the partial correlation; $r = 0.622$, $\rho = -5.535$ and $s = \pm 0.026$. $\varDelta\sigma_R^+$ values for these groups were calculated on the basis of this correlation; −1.20 for *p*-dimethylamino and −0.60 for *p*-hydroxy groups.

q) On the basis of ρ_{meta} value of −0.830, r value of 0.539 was obtained.

r) *p*-Phenyl group was not included in the calculation.

situation in these reactions. The same is true in the case of the decomposition of diazoacetophenones, as mentioned in the foregoing papers[1,3].

Conversely, the plots against Brown and Okamoto's σ^+ remain to be concaved upward in the brominolysis rates of benzeneboronic acids[25] and the migratory aptitudes of tetraphenyl pinacols[26], to the contrary, the present treatment exhibits fine correlations, whose r values are 2.29 and 1.60, respectively. These are the reverse of that mentioned above.

The curved correlation with Brown and Okamoto's σ^+ is fairly often observed in other reaction series, in accordance with the view that the availability of resonance contribution of para substituents is varied to a considerable extent by the changes of reaction series. Recently, Greene pointed out[27] that the rates of epoxidation of *trans*-stilbenes with phthaloyl peroxide satisfied the Brown and Okamoto's relation-ship. According to the present treatment, this reaction provides a fine figure of $r = 1.388$. Similarly, the oxidation with perbenzoic acid is successful in terms of $r = 0.713$[28]. Furthermore, the perbenzoic acid oxidation of *cis*- and *trans*-dimethyl-stilbenes[29] exhibits excellent correlations giving r of only 0.2~0.3, in contrast with the failure of the Brown and Okamoto's. Fig. 11 demonstrates the correlation of

25) H. G. Kuivila and A. R. Hendrikson, *J. Am. Chem. Soc.*, **74**, 5068 (1952); H. G. Kuivila and C. E. Benjamin, ibid., **77**, 4834 (1955).

26) W. E. Bachmann and F. H. Mosher, ibid., **54**, 1124 (1932); W. E. Bachmann and J. W. Ferguson, ibid., **56**, 2081 (1934).

27) F. D. Greene and W. W. Rees, ibid., **80**, 3432 (1958).

28) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525.

29) O. Simamura, Private communication. The authors are indebted to Professor O. Simamura who kindly made his data available to us prior to publication.

30) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **1940**, 949.

31) K. B. Wiberg and T. M. Skryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

32) H. P. Rothbaum, I. Ting and P. W. Robertson, *J. Chem. Soc.*, **1948**, 980.

33) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y. (1953), p. 332.

34) S. N. Ege and K. W. Sherk, *J. Am. Chem. Soc.*, **75**, 354 (1953).

35) A. C. Nixon and G. E. K. Branch, ibid., **58**, 492 (1936).

36) H. H. Jaffé and R. W. Gardner, ibid., **80**, 319 (1958).

37) E. J. DeWitt, C. T. Lester and G. A. Ropp, ibid., **78**, 2101 (1956).

38) C. H. Gudmunsen and W. E. McEwen, ibid., **79**, 329 (1957).

39) C. K. Hancook, R. F. Gilby, Jr. and J. S. Westmoreland, ibid., **79**, 1917 (1957).

oxidation of the *cis*-dimethylstilbenes in benzene at 30°C, with Brown's and the present equations.

Discussion

As measured by the standard deviations, the fit is as excellent as that seen in the representative Hammett correlation[12]. It is also clear that the present relationship describes rather precisely or is applicable to a greater extent of electrophilic reactions than the Brown and Okamoto's.

According to the results, r varies over a wide range from 0.2 to 2.3 with respect to the change in reaction, and ρ also from -12 to -0.6. Furthermore, it is significant that the magnitudes of $\Delta\sigma_R^+$ are maintained precisely constant with large variation of ρ and r values. The r and ρ values obtained through Eq. 4 are usually equal within experimental uncertainty to those obtained on the basis of meta correlation line.

In comparison with Brown and Okamoto's results[2,10], the following facts may be pointed out. Brown and Okamoto's ρ^+ values appear to be somewhat more negative than ρ of the present paper, in the reactions giving r values greater than unity. Conversely, they are less negative than the present one when $r < 1$. Considering that the present ρ values are identified with the corresponding ρ_{meta} values, it is clear that Brown and Okamoto's equation over- or under-corrects the validity of resonance contribution in these reactions. Only in the reactions having r within $0.7\sim1.3$, the Brown and Okamoto's equation would be apparently successful. This indicates the limitation of the application of Brown and Okamoto's relationship[40]. The application for the reactions far out of the limitation would involve the possibility to lead to some erroneous conclusion. However, a relatively large number of reaction series in the literature appears to be involved in the region of r within $0.7\sim1.3$. Then, the Brown and Okamoto's relationship would be applicable to a considerable extent of reaction series at the practical ground[2,10].

The modified Hammett relationship proposed in this paper involves an additional parameter and variable. The former is defined as a resonance parameter for a given substituent, but the latter is merely a proportionality constant in view of the origin of this equation. Accordingly, it is of interest and necessary to know the character of the latter quantity. Although both ρ and r are varied significantly with respect to the change in reaction series, the variation of r value does not appear to be dependent upon the change in ρ value. In the Beckmann rearrangement of acetophenonoximes in sulfuric acid (30)[6] and that of oxime picrylethers in dichlorobutane (29)[23], ρ differs greatly but r exhibits an identical value. The identical r value may give a good account of the close similarity of both transition states regardless of the different leaving groups and reaction conditions, while, little is described on the transition state model by the different ρ values. In the solvolysis of aryldimethylcarbinyl chlorides[2] and neophyl brosylates[22], the change in r is significant relative to the change in ρ. This may interpret plausibly the different modes of the resonance stabilizations of both transition states.
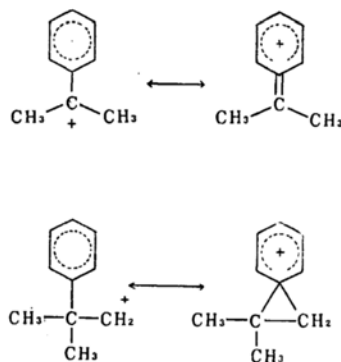
Therefore, it might be acceptable to say that the r would be a parameter characteristic of the structure of the possible transition state model as well as a parameter measuring the availability of the transition state resonance. As seen in Table I, approximately constant r of 1.2 is given for the reaction series to produce benzhydryl carbonium ions, and r of about 0.8 for those to produce trityl carbonium ions. The relatively small fluctuation would be presumably within experimental uncertainty. Unfortunately, few data are available in the literature to examine this concept more precisely.

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40) The reactions quoted by Brown and Okamoto contains the reactions giving r less than 0.6 or more than 1.5. The standard deviations of these are slightly large, but the significant trend of curvature would not always parallel the standard deviation. It is evidently suggested by the difference between ρ^+ resulted and ρ_{meta} values.

The remaining subject of interest will be the theoretical consideration of the present relationship 2, and then the resonance substituent constant, $\Delta\sigma_R^+$.

The substituent effect would be considered to consist of inductive and resonance components[41,42], and the σ constant defined by Hammett is usually expressed by Eq. 5 [2,41,42],

$$\sigma = \sigma_I + \sigma_R \qquad (5)$$

where σ_I is the inductive effect and σ_R is the resonance polar effect[42] of the substituent. Recently, Taft has evaluated the σ_I values by modifying his σ^* values for aliphatic series[42,43] on the basis of the Roberts' σ' scale[44], and the σ_R values by subtracting the σ_I values from the corresponding Hammett σ constants. It is well known that the substituent constant would not always be independent of the reaction nature. This would be referred to differing contributions of the resonance component of substituent effect[41], independently of the inductive component.

Furthermore, Taft has suggested that the linear free energy relationship would hold as far as the inductive component of reactivity is concerned[45].

Consequently, the Hammett equation may be expressed by Eq. 6,

$$\log k/k_0 = \rho_I\sigma_I + R \qquad (6)$$

In theory, the linear free energy relationship should suffice for the respective one of several components of substituent contribution[46]. If the residual R, $\log k/k_0 - \rho_I\sigma_I$, consists of only the resonance contribution, the linear resonance energy relationship may be predictable in regard to the quantity, $\log k/k_0 - \rho_I\sigma_I$.

$$\log k/k_0 - \rho_I\sigma_I = R = \rho_R\bar\sigma_R \qquad (7)$$

where ρ_R is a reaction constant and $\bar\sigma_R$ is a proper parameter representing the resonating capacity of the substituent. Eq. 7 can be rewritten as Eq. 8,

$$\log k/k_0 = \rho(\sigma_I + q\bar\sigma_R) \qquad (8)$$

where $\rho=\rho_I$ and $q=\rho_R/\rho_I$.

Here, $\bar\sigma_R$ should be essentially identical with σ_R in Eq. 5 since the $\bar\sigma_R$ corresponds to σ_R in the representative Hammett correlations. This relationship may be reasonably adopted also to electrophilic reactions.

On the other hand, the present equation can be formulated as Eq. 9,

$$\log k/k_0 = \rho(\sigma_I + \sigma_R + r\Delta\sigma_R^+) \qquad (9)$$

Combining Eqs. 8 and 9, Eq. 10 is derived.

$$q\bar\sigma_R = \sigma_R + r\Delta\sigma_R^+ \qquad (10)$$

Then, the linear relationship 11 must be derived, considering $\bar\sigma_R$ is identical with σ_R in Eq. 5,

$$\Delta\sigma_R^+ = q'\sigma_R \qquad (11)$$

where q' is equal to $(q-1)/r$

The exact value of σ_R is difficult to evaluate, but it is logical to replace conveniently the theoretical values by the corresponding Taft's one. In practice, using the Taft's values instead of the σ_R, an apparently linear plot of $\Delta\sigma_R^+$ is provided, as shown in Fig. 12; given q' is equal to 0.962, the standard deviation of the fit being 0.121. If the Taft's σ_R value could describe suitably the σ_R component, it might be possible to realize generally the linear resonance energy relationship
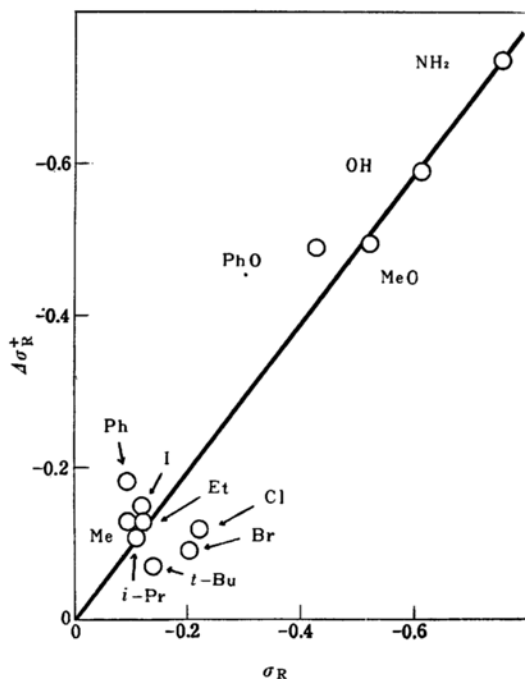

Fig. 12. Correlation of $\Delta\sigma_R^+$ with Taft's σ_R values.

41) The contributions of other specific effects such as solvation and bond energy effects are also involved but they are usually small relative to the above components.
42) R. W. Taft, Jr., in Newman's "Steric Effect in Organic Chemistry", Chapt. 13, John Wiley & Sons, Inc., New York (1956).
43) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729 (1952); ibid., **74**, 3120 (1952); ibid., **74**, 4231 (1953).
44) J. D. Roberts and W. T. Moreland, Jr., ibid., **75**, 2167 (1953).
45) R. W. Taft, Jr., ibid., **80**, 2436 (1958).
46) Y. Yukawa and Y. Tsuno, see the *refrence* under Ref. 13; G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry", Prentice-Hall, Inc., New York (1941), p. 192.

7, therefore, the general Hammett relationship 8. Then, it might be also possible to derive the unique set of σ_R and σ_I on the basis of the present results. However, Taft's σ_R value is by no means excluded from discussion, even though it may be acceptable from a theoretical standpoint. It is a question, at first, whether the Roberts' σ' scale may correspond strictly to that of the inductive effect in benzene system or not. The uncertainty of σ^* increasingly remains in his σ_I value, and must be accumulated in his σ_R value. Furthermore, the actual correlation of electrophilic reactions with his parameters is of considerably poorer precision[47]. On the other hand, $\Delta\sigma_R^+$ stands on a reasonable assumption that the increment of σ^+ relative to σ constant is attributed only to the resonance contribution. The uncertainty derived into this parameter may be entirely referred to only the experimental error of Brown and Okamoto's σ^+.

From these viewpoints, the general Hammett relationship with the parameters derived from $\Delta\sigma_R^+$, if possible, appears to be far more reliable than that with Taft's σ_I and σ_R values. However, it is the generality of Eq. 2, then the $\Delta\sigma_R^+$, that must be settled first. Unfortunately, further examination of the generality is limited by the lack of adequate data in literatures. The adequate literature data which contain rates of many meta derivatives constitute only one third of the data quoted in Table I. Without these reactions, the correlation obtained on the basis of Eq. 4 can not be referred to any standard of correlation such as meta line, although these are believed to be the best descriptions of their respective situations. Moreover, the utilities of $\Delta\sigma_R^+$ values for substituents more negative than p-methoxyl group have been scarcely examined at all. Then, the adequate data are highly desirable.

However, the excellent fit of the present relationship for 35 reaction series may be taken to be sufficient support for regarding this as a general relationship. Further investigations now in progress will be reported in forthcoming papers.

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47) This conclusion is independent of Taft's results (Ref. 45). According to his result in the latest paper on the correlation of Brown and Okamoto's reference reaction, remarkable deviations are observed for p-CH$_3$O and p-F derivatives. Full discussion will be made in a proceeding paper, although his treatment disagrees with our concept.