Resonance Effect in Hammett Relationship. II. Sigma Constants in Electrophilic Reactions and their Intercorrelation

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Recently, Brown and Okamoto have demonstrated a practical success in correlating various electrophilic reactions by a single set of σ^{+} [1,2], obtained from the substituent effects in solvolysis of phenyldimethylcarbinyl chlorides. Their treatment should involve the assumption that the substituent effects in electrophilic reactions remain constant relative to marked variation in the ρ value. This is inconsistent with our view[3] that the reasonance interactions by a para substituent would depend greatly on the nature of the reactions, so that the effects

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[1] 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).

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

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

in electrophilic reactions could not possibly be correlated with a unique set of σ^+. The present view may be reasonable and perhaps the general one[4,5]. Brown and Okamoto's view could be confirmed by the identity of σ^+ values independently derived from other reactions. However, the various sets of σ^+ are varied significantly with respect to changes in the reference reaction[3,6–11]. The reported fact that the σ^+ constant derived from the decomposition of ω-diazoacetophenones differed from the corresponding Brown and Okamoto's[3] constant may afford evidence in favor of the present view.

The variations of σ^+ value for a given para substituent are generally referred to different availabilities of the resonance in various reference reactions, if other factors are maintained constant. On the other hand, failure of the linear $\rho\sigma^+$ relationship could be attributable also to the change in mechanism in a reaction series[12]. Brown has quoted[1], as an example, the solvolysis of benzyl tosylates[5,7], in which the change from S_N1 to S_N2 mechanisms occurred through changes of substituent. In the decomposition of diazoacetophenones, it may be possible to consider that the dissociation of nitrogen molecule competes with the attack of acetate ion in the driving force of the reaction[3]. If this was true, both mechanisms should indicate different responses to the ionizing power of the medium possibly because the stabilization of the carbonium ion produced will be important only in the former mechanism. Therefore, the substituent effects may be sensitive to the changes of solvent. Accordingly, kinetic study of the decomposition of diazoacetophenones was carried out in 75% aqueous acetic acid solution at 25.20°C, in order to confirm the reliability of our σ^+ values.

To the completion of this study, the foregoing view has been concreted and our attention has been directed to correlate empirically these independent sets of σ^+ according to a simple but reasonable relationship. In this paper, the results of the kinetics and of an approach to the correlation of σ^+ are presented.

Experimental

All diazoacetophenones were prepared by the procedure described in the preceding paper[3]. The stock solvent was made up by mixing 75 parts by volume of acetic acid with 25 parts by volume of distilled water. Acetic acid was purified by the usual method[13] and carefully fractionated, b. p. 117.5~118.0°C.

Rate Measurements. — The rates of the decomposition were determined by following the rate of evolution of nitrogen. The apparatus and the procedures were similar to those described in previous papers[3,14]. The temperature of the reaction bath was controlled to 25.20°C within an accuracy of ±0.01°C. Measurements were carried out in 75 ml. of aqueous acetic acid. The quantitative amount of nitrogen was obtained by the decomposition of respective derivatives of diazoacetophenone in aqueous acetic acid at 25.20°C. The rate of evolution of nitrogen followed strictly the first order kinetic law. Individual runs showed average deviations of far less than 1%, and duplicate runs gave rate constants agreeing within 2% or better. *p*-Phenyl-, *p*-bromo- and *m*- and *p*-nitro derivatives are soluble with greater difficulty in this solvent at this reaction temperature than in anhydrous acetic acid. Nitro derivatives were warmed with vigorous shaking at about 40°C to complete dissolution, prior to measurement. But this could not be applied to other derivatives, because of their high reactivities. *p*-Phenyl derivative is far less soluble in this solvent and deviation from the first order kinetic law was observed. The calculated rate constant increased gradually as the reaction proceeded and reached a constant value at 60% completion of the reaction. The rate constants obtained are summarized in Table I.

TABLE I. RATES OF THE DECOMPOSITION OF ω-DIAZOACETOPHENONES IN 75% AQUEOUS ACETIC ACID AT 25.20°C

Subst.	$k_1\times10^3$ [a]	Subst.	$k_1\times10^3$ [a]
p-CH_3O	28.3 ±0.2	H	5.86 ±0.04
p-C_2H_5O	26.9 ±0.3	*p*-Cl	3.71 ±0.03
p-CH_3	12.07±0.08	*p*-Br	2.94 ±0.07
p-*t*-C_4H_9	10.6 ±0.1	*m*-NO_2	0.816±0.005
m-CH_3	7.43±0.06	*p*-NO_2	0.638±0.004
p-C_6H_5	6.97±0.15		

a) The average rate constant in reciprocal min. and the average deviation.

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[4] P. B. D. de la Mare, *J. Chem. Soc.*, **1954**, 4450.

[5] F. T. Fang, J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **80**, 563 (1958); G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, ibid., **80**, 568 (1958); G. S. Hammond and C. E. Reeder, ibid., **80**, 573 (1958).

[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. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

[8] N. C. Deno and A. Schriesheim, ibid., **77**, 3051 (1955).

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

[10] J. Miller, *Australian J. Chem.*, **9**, 61 (1956).

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

[12] C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951).

[13] A. Weissberger, "Technique of Organic Chemistry", Vol. VII; "Organic Solvents", 2nd Ed., Interscience Publishers, Inc., New York (1955).

[14] Y. Yukawa and Y. Tsuno, *J. Am. Chem. Soc.*, **79**, 5530 (1957); J. F. Lane and R. L. Feller, ibid., **73**, 4230 (1951).

Results

As listed in Table I, rates of the decomposition of diazoacetophenones are significantly increased in aqueous acetic acid relative to those in anhydrous acetic acid. Parallel to this, the sensitivity of the reaction to substituent effects appears to be considerably increased. Whereas the failure of the linear Hammett relationship is also observed in the aqueous medium just as in the case of an anhydrous medium³⁾. Electron releasing para substituents supply higher acceleration than would be anticipated by the normal Hammett relationship (Fig. 1). Such a result has been discussed by us³⁾ and a number of other authors¹,²,⁴⁻¹²⁾ and needs no further elucidation.

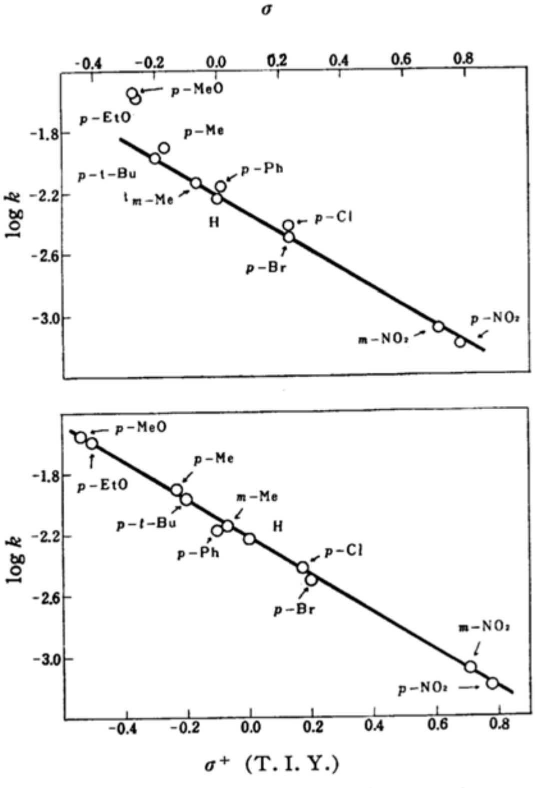

Fig. 1. Plot of the present data against the ordinary σ and our σ^+ constants.

In both reactions, the substituent effects would presumably be invariant, if the transition state remains approximately constant through changes of solvent. An evidence for the identity of substituent effects would generally be provided by a linear relationship between the corresponding $\log k/k_0$ of the two reactions. In fact, all the experimental points of $\log k/k_0$ in aqueous acetic acid fall just on the line expected from the $\log k/k_0$ in anhydrous medium. The correlation is given by an equation

$$\log (k/k_0)_{\mathrm{aq}} = 1.510 \log (k/k_0)_{\mathrm{anhyd}}$$

This indicates that the changes of medium reflect only ρ value and the substituent effect is not varied in either medium. The above correlation can of course be rewritten in terms of our σ^+ values³⁾ (Fig. 1). Statistical treatment¹⁵⁾ gives a correlation 1,

$$\log (k/k_0) = (-1.253 \pm 0.020)\,\sigma^+ \qquad (1)$$

The standard deviation of experimental $\log k$ from the best line is 0.027 and the correlation coefficient is 0.999. The ρ^+ value is closely equal to the ρ_{meta} value, 1.237±0.018, which was obtained from points for m-CH_3, m-nitro, p-nitro and unsubstituted derivatives. On the basis of this ρ^+ value (1), a new set of σ^+ values can be derived from the rates in aqueous acetic acid. They are given in Table II. The present values agree with the previous one. p-Phenyl and p-bromo groups differ considerably in magnitude from the foregoing ones³⁾. These are of no doubt attributable to the lower solubilities in aqueous acetic acid (see, *Experimental*). The discrepancies of others are substantially contained within experimental uncertainty. As a result, it may be conclusively suggested that the σ^+ derived from the previous result describes the best situation of the substituent effect in this reaction. Then, it appears to be evidently confirmed that the changes in mechanism as suggested by Brown and Okamoto might not occur through substituent changes in this reaction, and also that the rise in reactivities

TABLE II. σ^+ CONSTANTS

Subst.	σ^+_{aq} a)	$\sigma^+_{\mathrm{anhyd}}$ b)	$\sigma^+_{\mathrm{B.O.}}$ c)
p-CH_3O	−0.537	−0.537	−0.764
p-C_2H_5O	−0.519	−0.512	
p-CH_3	−0.241	−0.234	−0.306
p-t-C_4H_9	−0.196	−0.209	−0.250
p-C_6H_5	(−0.051)	−0.103	−0.179 d)
p-Cl	+0.168	+0.175	+0.112
p-Br	(+0.249)	+0.202	+0.148

a) The present study.
b) The set derived from the decomposition in anhydrous acetic acid (Ref. 3).
c) Brown and Okamoto's set of σ^+, taken from Ref. 1.
d) The value quoted from Ref. 2.

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15) H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953).

of electron releasing para substituents could be attributable entirely to the increase of the resonance contribution.

These facts appear evidently to support the present view in preference to Brown and Okamoto's[1,2].

The linear free energy relationship would essentially hold in more or less limited reaction series in which the substituent effects are close to each other[3]. With the above considerations in mind, a given electrophilic reaction should be correlated with one of these sets of σ^+ most suitable to the resonance effects of substituents in it. However, it appears to be inconvenient practically. Therefore, it is necessary and desirable to correlate these independent sets of σ^+ with a relationship of practical use.

Discussion

The substituent effect can generally be treated as the sum of independent contributions of inductive and resonance components[16]. The former contribution refers to the electron distribution through the *sigma* bonds of a benzene nucleus and the latter to the electron delocalization through the resonance interaction of a substituent with the benzene *pi* electron system. An ordinary Hammett σ constant could be represented according to Eq. 2,

$$\sigma = \sigma_I + \sigma_R \qquad (2)$$

where σ_I is an inductive effect and σ_R is a so-called *resonance polar effect*[16]; σ_R represents the substituent contribution through resonance with the benzene *pi* bonds to the electron density on the nuclear carbon atom at which the functional group is attached.

The substituent effect should be essentially independent of the reaction, whereas it is not always invariant, causing failure of the Hammett linear free energy relationship. The variation of substituent effect would be attributed only to the changes in contribution of the resonance component. The inductive component, the electron distribution through *sigma* bond, should essentially remain constant. The *resonance polar effect* may also be independent of the nature of reactions. However, the resonance component will no longer remain constant in the case of electrophilic reactions. The large electron demand produced at the reaction center of transition state must be delocalized[1-9]. This could be dissipated by the aid of the resonance interactions with electron releasing para substiuents through benzene *pi* orbitals. Then, the resonance effect becomes far greater than the ordinary *resonance polar effect*, σ_R, and σ^+ values result from this reason.

Brown and Okamoto's set of σ^+ may be represented[1]

$$\sigma^+ = \sigma_I + \sigma_R^+ \qquad (3)$$

where σ_R^+ is a resonance effect in the Brown and Okamoto's reference reaction[1,2]. Other authors' sets of σ^+ are also treated in the same manner, although the σ_R^+ are by no means invariant of reactions. In general, the quantity σ_R^+ should be a variable and a function of the resonating capacity of substituent with the electron deficient reaction center through the benzene *pi* electron system. Since σ_I may undoubtedly remain constant through the changes of reaction type[16], the attention could be centered on the changes of σ_R^+. Inductive effect can be eliminated, combining Eqs. 2 and 3

$$\sigma^+ - \sigma = \sigma_R^+ - \sigma_R \equiv G(\mathrm{R}) \qquad (4)$$

Here, the quantity $\sigma^+ - \sigma$ should be a function of the resonance effect only, and this quantity just describes the magnitude of respective deviations of para substituents from the meta correlation line. Consequently, it may be anticipated that the analysis of the function $G(\mathrm{R})$ could provide a key to correlate the various sets of σ^+. The formulation of $G(\mathrm{R})$ will be realized practically by tracing changes of the quantity $\sigma^+ - \sigma$.

In actual practice, Brown and Okamoto's and Miller's quantities are plotted linearly against the corresponding quantities of the decomposition of diazoacetophenones, as illustrated in Figs. 2 and 3. These correlations are given by the following equations:

$$(\sigma^+ - \sigma)_{\mathrm{Brown,\ Okamoto}} = 1.847(\sigma^+ - \sigma)$$

and

$$(\sigma^+ - \sigma)_{\mathrm{Miller}} = 3.185(\sigma^+ - \sigma)$$

The standard deviations of the fits are ±0.015 and ±0.007, respectively. Then, the substituent effects in the decomposition of diazoacetophenones can be reproduced

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[16] R. W. Taft, Jr., in Newman's "Steric Effect in Organic Chemistry", Chapt. 13, John Wiley & Sons, Inc., New York (1956). R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729 (1952); ibid., **74**, 3120 (1952); ibid., **75**, 4231 (1953); ibid., **79**, 1045 (1957); R. W. Taft, Jr. and I. C. Lewis, ibid., **80**, 2436 (1958). Y. Yukawa and Y. Tsuno, "Yuki Hannokiko no Shimpo (Recent Advances in the Mechanism of Organic Reactions)", Vol. I, Maki Publishers, Inc., Tokyo (1958), p. 1.

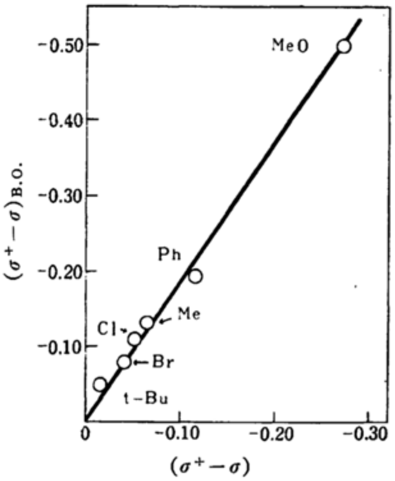

Fig. 2. Plot of Brown and Okamoto's quantity, $\sigma^+-\sigma$, against our quantity.

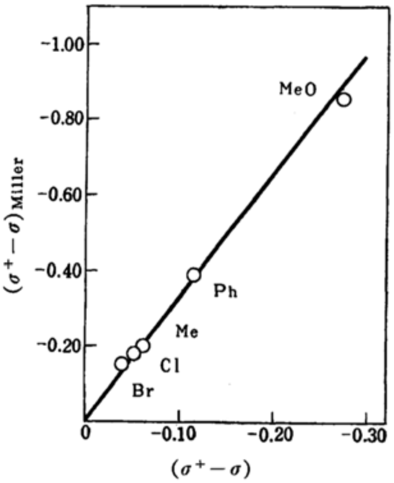

Fig. 3. The correlation between Miller's and our quantities, $\sigma^+-\sigma$.

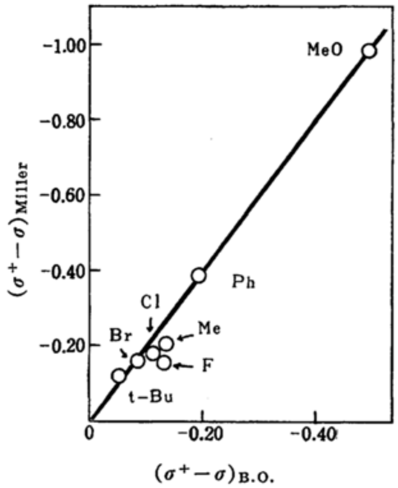

Fig. 4. Correlation of Miller's quantity, $\sigma^+-\sigma$, with Brown and Okamoto's one.

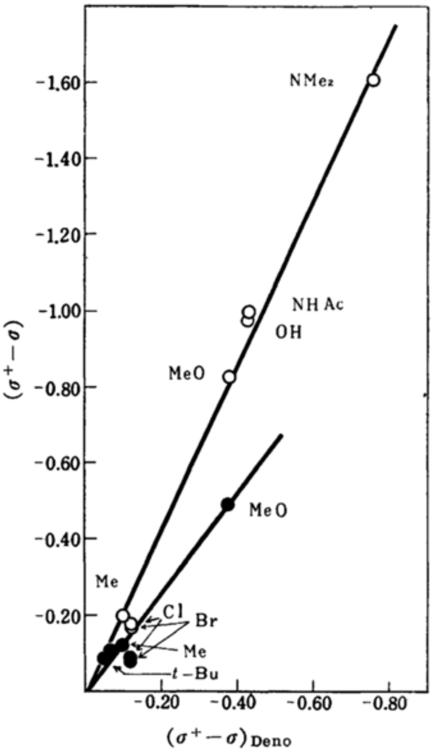

Fig. 5. Correlations of Miller's and Brown and Okamoto's quantities, $\sigma^+-\sigma$, with Deno's one: Open circles, Miller's and closed, Brown and Okamoto's.

precisely from various sets of σ^+. This may afford an indirect bit of evidence of our previous discussion of this reaction[3].

Furthermore, strictly linear correlations are observed in respective pairs of other sets of σ^+, as shown clearly in Figs. 4 and 5. These are represented as follows:

$$(\sigma^+-\sigma)_{\text{Brown, Okamoto}}=0.576(\sigma^+-\sigma)_{\text{Miller}}$$

$$(\sigma^+-\sigma)_{\text{Brown, Okamoto}}=1.347(\sigma^+-\sigma)_{\text{Deno}}$$

and

$$(\sigma^+-\sigma)_{\text{Deno}}=0.456(\sigma^+-\sigma)_{\text{Miller}}$$

The standard deviations are 0.015, 0.002 and 0.025, respectively. Then, these correlations can be held covering a wide range of substituent changes, especially, the last one covers the range from *p*-alkyl to *p*-dimethylamino groups. The same is true in the case of other sets, such as Packer's[11] and Pearson's[6].

As a conclusion, the function *G*(R) can be regarded, to a first approximation, as a linear function of the quantity, $\sigma^+-\sigma$. Consequently, the general relationship 5 may be established empirically

TABLE III. CALCULATED VALUE OF BROWN AND OKAMOTO'S σ^+

p-Subst.	Calculated σ^+ value A[a] 1.847[g]	 B[b] 0.576[g]	 C[c] 1.347[g]	 D[d] 0.820[g]	 E[e] 0.838[g]	Exptl.[f] value (1.000)	Average value	$\sigma^+-\sigma$[h]
NMe_2		−1.53	−1.62				−1.60	−1.00
NH_2			−1.40				−1.40	−0.74
NHAc		−0.61	−0.59				−0.60	−0.58
OH		−0.92	−0.91				−0.92	−0.56
CH_3O	−0.765	−0.754	−0.766		−0.729	−0.764	−0.756±0.014[l]	−0.496
C_2H_5O	−0.744						−0.744	−0.494
C_6H_5O		−0.528			−0.559		−0.543	−0.51
CH_3	−0.301[i]	−0.288	−0.305	−0.299	−0.306	−0.306	−0.301±0.006[l]	−0.131
C_2H_5				−0.293	(−0.315)[k]	−0.291	−0.292	−0.141
i-C_3H_7				−0.282		−0.276	−0.279	−0.125
t-C_4H_9	(−0.217)[j]	−0.267	−0.251			−0.250	−0.256±0.010[l]	−0.053
C_6H_5	−0.200	−0.219		−0.177	(−0.240)[k]	−0.179	−0.194±0.020[l]	−0.200
F						−0.071	−0.071	−0.130
Cl	+0.118[i]	+0.122			+0.130	+0.112	+0.121±0.007[l]	−0.106
Br	+0.162	+0.138			+0.154	+0.148	+0.151±0.010[l]	−0.081
I						+0.132	+0.132	−0.144

a) The value calculated on the basis of our σ^+ value (Ref. 3).

b) Calculated from Miller's set of σ^+ (Ref. 10).

c) The value obtained from Deno's set of σ^+ (Refs. 7 and 8).

d) The value on the basis of σ^+ given by Packer et al. (Ref. 11) from the ethanolysis rates of benzhydryl chlorides (E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **1940**, 949).

e) Calculated from Norris and coworkers' data on the solvolysis of benzhydryl chlorides in absolute ethanol (J. F. Norris and C. Benta, *J. Am. Chem. Soc.*, **50**, 1804 (1928); J. F. Norris and J. T. Blake, ibid., **50**, 1808 (1928): see, the forthcoming paper, (Y. Yukawa and Y. Tsuno, This Bulletin, **32**, 971 (1959).).

f) Brown and Okamoto's σ^+ value (Ref. 1).

g) The r value in the relationship 5; the proportionality constant of the quantity, $\sigma^+-\sigma$, to the corresponding one of Brown and Okamoto.

h) This value should essentially be equal to the difference of Brown and Okamoto's σ^+ from the ordinary Hammett σ constant. This could be regarded as a measure of the resonating power of respective substituents. This has been utilized successfully in regard to the resonance substituent constant, $\Delta\sigma^+_R$, and will be reported in a subsequent paper.

i) The value based on σ^+ obtained in the present study.

j) This group showed deviation from the correlation 5 setting $r=1.847$, and was omitted from the calculation. Such a deviation was observed in the Pearson's correlation of σ^+ (Ref. 6).

k) This group deviates seriously and was not included in the calculation.

l) Standard deviation.

$$(\sigma^+{}_A-\sigma)=r(\sigma^+{}_B-\sigma) \tag{5}$$

where r is a parameter which remains constant in a reaction series but is a variable of reactions. This parameter may arise without doubt from differing contributions of the resonance effect in reference reactions.

The reliability of the approximation can be substantiated by the close agreement of calculated values on the basis of this relationship with an experimental one. This is clearly exhibited in the comparison of calculated with the experimental values of Brown and Okamoto's σ^+, as shown in Table III. Computed values for respective substituents are in accord with the experimental one, without serious exceptions. The averaged standard deviations of calculated values are estimated to be ±0.009. This is excellent as compared with the agreement of the comparision given by Deno[9], and by Brown and Okamoto[2]. Then, the results in Table III will possibly extend the utility of Brown and Okamoto's set to the substituents having no experimental σ^+ value in their scale.

Through these results, the particular

features of interest have arisen. As mentioned in the above discussion, the quantities $\sigma^+ - \sigma$ may be regarded as a function of the resonance capacity of substituents. Therefore, the relationship 5 is in itself a linear resonance energy relationship. The σ^+ values, in turn, could be represented by the following relationship, using a proper set of the quantities $\sigma^+ - \sigma$ in a single scale

$$\sigma^+ = \sigma + r(\bar{\sigma}^+ - \sigma) = \sigma + r\varDelta\sigma_R^+$$

where $\bar{\sigma}^+$ is a correct set of σ^+ and $\varDelta\sigma_R^+$ represents the standard set of the quantities $\sigma^+ - \sigma$. Consequently, electrophilic reactions in general will possibly be correlated by a modified Hammett equation,

$$\log (k/k_0) = \rho(\sigma + r\varDelta\sigma_R^+)$$

This has been realized by using the numerical values of $\varDelta\sigma_R^+$ in Brown and Okamoto's scale. The utility of this relationship will be described in Part III.

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