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A Critical Examination of the Applicability of A Linear Free Energy Relationship to Aromatic Substitution Reactions[1,2]

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The applicability of a linear free energy relationship to the electrophilic substitution reactions of monosubstituted benzenes has been re-examined. It has been found that the σ^+-constants determined from the slopes of linear relationships between log (k/k_H) and S_f or ρ are in excellent agreement with the σ^+-values devised by the independent study of the solvolysis of substituted *t*-cumyl chlorides. Diagrams of log (k/k_H) *versus* the ρ-values determined by examination of 10 representative electrophilic substitution reactions yield satisfactory linear relationships for *p*-methoxy, 2-fluorenyl, *p*-methyl, *p*-*t*-butyl, *m*-methyl, *p*-chloro, *p*-bromo, *m*-fluoro, *m*-chloro and *m*-bromo. The comparison of the results for electrophilic substitution and Hammett side-chain reactions indicates the applicability of the Selectivity Treatment is fully as general and equally as precise as the Hammett relationship. In the first-order Selectivity Treatment, the highly activating substituents, exhibiting important resonance interactions in the transition state, are as satisfactorily accommodated as the deactivating groups where such interactions are absent or unimportant. Serious discrepancies have been detected in only three cases. The steric inhibition of resonance in biphenyl leads to deviations for the *p*-phenyl substituent. The *m*-*t*-butyl and *p*-fluoro groups also exhibit more scatter than may be attributed to experimental errors. These completely random deviations are ascribed to the multiplicity of factors attendent to the determination of the precise nature of the transition state for the substitution reactions. Solvation influences and variations in the π-complex character of the activated complex appear to be most important. In spite of these deviations, it is significant that the available data for electrophilic substitutions are correlated with a precision which is comparable with that realized in the usual Hammett treatment of side-chain reactions.

The applicability of a simple first-order linear free energy relationship for substitution in the aromatic nucleus has been under investigation in our laboratories for approximately ten years. It appears desirable to subject the results realized to date to critical scrutiny.

It was originally observed that the substitution data for toluene could be correlated by the empirical expression[3] 1.

$$\log p_f^{Me} = b \log (p_f^{Me}/m_f^{Me}) \qquad (1)$$

It was suggested that a relationship of this type might be general for the substitution of various benzene derivatives.[3]

Exception was taken to this suggestion. It was argued that resonance contributions of the substituent must be enhanced in an unpredictable manner in the transition state, so that the contribution of the substituent could not be represented by a constant.[4-6]

Hammett's original suggestion concerning the possible correlation of the logarithms of the rate and equilibrium constants of *meta* and *para* substituted benzene derivatives was greeted with similar skepticism.[7] Fortunately, many data for the reactions of these derivatives were available and Hammett was able to present convincing evidence that linear correlations existed between the logarithms observed for the rate or equilibrium constants of one reaction and the corresponding quantities of another reaction.[8]

Ideally, the proposal that a similar linear free energy treatment existed for aromatic substitution should have been subjected to test by the same approach. Unfortunately, only very limited data for the substitution reactions of monosubstituted benzenes were available in 1953. Consequently, it was not possible to adopt the technique employed by Hammett.

In testing the applicability of a reaction to the Hammett treatment (2)

$$\log (k/k_H) = \rho\sigma \qquad (2)$$

it is customary to plot log k or log K *versus* the σ-values. The realization of a linear correlation establishes that the reaction in question adheres to the treatment. The slope of the correlation line defines the value of the reaction constant, ρ, for the process under examination.

The application of this procedure to the results for aromatic nitration and halogenation indicated these substitution data could not be accommodated by the Hammett substituent constants.[4,5] However, this observation did not eliminate the possibility that the results might be correlated by a different set of constants derived for electrophilic reactions. Unfortunately, no simple route to the necessary constants was evident.

In the Hammett treatment, it has been a basic assumption that the electronic effect of the substituents could be represented as a constant.[9] In view of the argument for a variable resonance contribution of a substituent in electrophilic reactions,[4-6] it was not possible to extend this assumption to the electrophilic area. Therefore, the first problem for consideration was the possibility of representing the influence of a given substituent by a constant in substitution reactions.

In 1955, the empirical relationship 1, which correlated satisfactorily the available data for the electrophilic substitution of toluene, was shown to be derivable by algebraic manipulation of

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(1) Directive Effects in Aromatic Substitution. LV.

(2) Supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the said Fund.

(3) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6295 (1953).

(4) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(5) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Am. Chem. Soc.*, **76**, 4525 (1954).

(6) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1956).

(7) At that time the conflict centered on the theoretical problems involved in the correlation of rate data with equilibrium results; L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935).

(8) L. P. Hammett, "Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 6.

(9) This view has recently been challenged: (a) H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959); (b) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

the Hammett equation 2.[10] This approach yielded the empirical constant b as a function of the substituent constants $\sigma_{m-\mathrm{Me}}$ and $\sigma_{m-\mathrm{Me}}$(3).[10]

$$b = \sigma_{p-\mathrm{Me}}/(\sigma_{p-\mathrm{Me}} - \sigma_{m-\mathrm{Me}}) \qquad (3)$$

However, the value of b calculated in this way, utilizing the Hammett substituents $\sigma_{p-\mathrm{Me}}$ and $\sigma_{m-\mathrm{Me}}$, deviated seriously from the value of b determined experimentally.[10]

This result confirmed the observations of de la Mare, Roberts and their associates[4,5] regarding the unsuitability of the Hammett substituent constants for aromatic substitution reactions. However, the excellence of the correlation indicated that the electronic contributions of the methyl substituent could be represented by a constant. A new series of constants, σ^+, were suggested for application to the substitution reactions 4,5.

$$\log (k/k_{\mathrm{H}}) = \rho\sigma^+ \qquad (4)$$

$$b = \sigma^+_{p-\mathrm{Me}}/(\sigma^+_{p-\mathrm{Me}} - \sigma^+_{m-\mathrm{Me}}) \qquad (5)$$

It was possible to calculate the value of $\sigma^+_{p-\mathrm{Me}}$ by assuming $\sigma^+_{m-\mathrm{Me}} = \sigma_{m-\mathrm{Me}}$. (This assumption is justified theoretically on the basis of the view that no important resonance interactions are possible for *meta* substituents in the transition states for the substitution processes. It is also justified experimentally on the basis of the observation that the Hammett σ_m-values were found suitable for the correlation of the data for nitration in the *meta* position.[5])

The next problem for consideration was the extension of the investigation to other substituents. In the well-known Hammett treatment, the applicability of a given reaction to the equation 3 is examined by a plot of log (k/k_{H}) *versus* σ. It is evident that an alternative approach would be to examine the validity of the application of a linear free energy treatment by maintaining the group constant while plotting log (k/k_{H}) *versus* the value of ρ for different reactions. The realization of a satisfactory linear relationship would indicate that the electronic contribution of the substituent group could be represented by a constant. Moreover, the slope of the line would provide the σ^+-value for the substituent in question.

Unfortunately, this treatment could not be applied in the absence of values for the reaction constants for representative substitution reactions. This difficulty was circumvented by the adoption of log $(p_f^{\mathrm{Me}}/m_f^{\mathrm{Me}})$ as a substitute for the reaction constant. This quantity was termed the Selectivity Factor, S_f (6,7).

$$S_f \equiv \log (p_f^{\mathrm{Me}}/m_f^{\mathrm{Me}}) \qquad (6)$$

$$\equiv \log (2 \times \%\ para/\%\ meta) \qquad (7)$$

In the form 8

$$\log (k/k_{\mathrm{H}}) = bS_f \qquad (8)$$

this approach was termed the Selectivity Relationship. The quantity S_f is clearly proportional to the reaction constant (9).

$$S_f = \rho(\sigma^+_{p-\mathrm{Me}} - \sigma^+_{m-\mathrm{Me}}) \qquad (9)$$

In effect, the selectivity approach employes a value for the reaction constant based on substitution data for a single substituent, the methyl group. The slope of the correlation line observed for each substituent group allows the estimation of the σ^+_{R}-constants (10).

$$\log (k_{\mathrm{R}}/k_{\mathrm{H}}) = \sigma_{\mathrm{R}}^+/(\sigma^+_{p-\mathrm{Me}} - \sigma^+_{m-\mathrm{Me}})\, S_f \qquad (10)$$

In recent years the applicability of the Selectivity Relationship to a number of benzene derivatives has been examined: toluene,[11-13] *t*-butylbenzene,[14] anisole,[15] biphenyl,[16] fluorene[16] and the halobenzenes.[17] With one exception, biphenyl, the results support the original thesis that the data for electrophilic substitution of benzene derivations can be correlated with reasonable precision by a simple first-order linear free energy treatment, such as the Selectivity Relationship.

Partial Rate Data for Substitution.—It is our purpose here to re-examine the correlation of data for substitution reactions by the more customary Hammett approach to a linear free energy treatment. The renewed interest in aromatic substitution has prompted considerable experimental work. New data have been provided for a wide range of substituent groups and many reactions have been examined. However, certain substituents and reactions, typical of the others, have received somewhat greater attention. Our survey has been restricted to 13 substituent groups and 10 reactions. The choice of reactions has been dictated largely by the inclusion of data for several substituents to permit a reliable calculation of ρ.

Six reactions involving the replacement of hydrogen and four carefully studied model reactions involving the cleavage of other bonds are considered. The ρ-values extend from -2.4 for Friedel–Crafts ethylation to -12.1 for non-catalytic bromination. The experimental observations for the solvolysis of substituted *t*-cumyl chlorides which yield another basis for the definition of the σ-values are included for comparison. The logarithms of the partial rate factors are summarized in Table I.

Linear Relationships for Electrophilic Reactions.—With the data now available it is possible to revert to a more conventional order for the examination of the applicability of a linear free energy treatment to substitution reactions. A satisfactory relationship requires, as a first condition, the existence of a linear correlation between the log (k/k_{H}) values exhibited in one reaction with those exhibited by any other reaction.[7] That this requirement is fulfilled for the electrophilic reactions is illustrated in Fig. 1.

In Fig. 1, the log (k/k_{H}) values for mercuration are plotted against the log (k/k_{H}) values for the solvolysis reaction. The correlation achieved for this electrophilic substitution is typical of the diagrams for other substitution reactions. The adherence of these data to linear relationships is

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(10) C. W. McGary, Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 3037 (1955).

(11) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300, 2306 (1955).

(12) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(13) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(14) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5615 (1959).

(15) L. M. Stock and H. C. Brown, *ibid.*, **82**, 1942 (1960).

(16) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1242 (1962).

(17) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1668 (1962).

TABLE I

SUMMARY OF RESULTS FOR ELECTROPHILIC SUBSTITUTION REACTIONS

Reaction	Logarithms of partial rate factor[a]													
	ρ[b]	*p*-OMe	2-Fl	*p*-Me	*p*-*t*-Bu	*p*-Ph	*m*-*t*-Bu	*m*-Me	*p*-F	*p*-Cl	*p*-Br	*m*-F	*m*-Cl	*m*-Br
Solvolysis[c]	−4.5	3.53	2.24	1.41	1.16	0.81	0.27	0.29	0.33	−0.52	−0.68	−1.60	−1.81	−1.84
Ethylation[d]	−2.4			0.76		.35		.17	− .13	− .27	− .36	−0.94	−0.99	−1.06
Mercuration[e]	−4.0	3.36	2.09	1.37	1.24	.81	0.53	.35	.47	− .44	− .57	−1.40	−1.22	−1.27
Bromodeboronation[c]	−4.3			1.88		1.34		.52	.50	− .27	− .38	−1.41	−1.46	−1.36
Protodesilylation[f]	−4.6	3.18	1.69	1.33	1.19	0.55		.36	− .12	− .87	−1.00		−1.92	
Bromodesilylation[g]	−6.2			1.69	1.47	1.10		.46	− .17	−1.04	−1.15		−2.52	
Nitration[e]	−6.5		3.32	1.69	1.76	1.27	0.58	.32	− .11	−0.89	−0.99		−3.08	−3.01
Bromination (P)[h]	−8.7			2.74				.67	.66	− .84	−1.21	−3.04	−3.25	−3.28
Acetylation[i]	−9.1	6.25	4.58	2.87	2.82	2.39	1.11	.68	.18	− .90	−1.08		−3.52	
Chlorination[h]	−10.0	7.67	5.53	2.91	2.60	2.78	0.73	.69	.64	− .42	−0.54	−2.44	−2.85	−2.73
Bromination[h]	−12.1	10.0	6.80	3.38	2.91	3.47	0.78	.74						

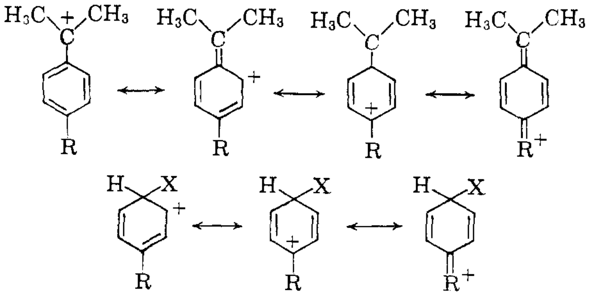
[a] The data are presented in summary in the references appended to the table. The original literature citations are presented in these references. [b] Based on the correlation observed for log (k/k_H) with the *t*-cumyl chloride solvolysis data: see Discussion. [c] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958). [d] H. C. Brown and A. Neyens, *ibid.*, **84,** 1665 (1962). [e] H. C. Brown and G. Goldman, *ibid.*, **84,** 1650 (1962). [f] C. Eaborn, *J. Chem. Soc.*, 4858 (1956). [g] C. Eaborn and D. E. Webster, *ibid.*, 4449 (1957). [h] L. M. Stock and F. W. Baker, *J. Am. Chem. Soc.*, **84,** 1661 (1962). [i] H. C. Brown and G. Marino, *ibid.*, **84,** 1658 (1962).

comparable to the agreement found for Hammett side-chain reactions.

An earlier examination of the results for the solvolysis of the *t*-cumyl chlorides indicated the values for log (k/k_H) for the *meta* substituents were correlated by the Hammett σ_m-values.[18] The data for *para* substituents deviated seriously. The observation for the adherence of the *meta* results, however, provided a direct method for the definition of ρ for the solvolysis reaction as −4.54.[18] The slope of the line in the linear correlation illustrated in Fig. 1 is $\rho/-4.54$. Accordingly, the approach permits the reliable calculation of ρ-values for the substitution reactions based on the inclusion of data for all of the substituents examined in each reaction. These values are summarized in Table I.

Evaluation of the σ^+-Constants.—There are three essentially equivalent procedures which allow the establishment of parameters for the description of the influence of substituent groups. One approach is to select one reaction as a standard and to define the constants in terms of that reaction. This is the approach adopted by Hammett as discussed.[2]

The precision achievable in the determination of rate constants for *t*-cumyl solvolysis made its selection as a model highly attractive. Inspection of the intermediates involved in solvolysis and substitution processes reveals several important similarities and differences.



In the *t*-cumyl carbonium ion, the electron deficiency is stabilized by interaction with both the side-chain and the aromatic ring. In the σ-complex, this deficiency is associated only with the disrupted aromatic nucleus. Although this feature of the model could, in principle, introduce serious difficulties, none are observed. Utilizing the experimental values of log (k/k_H) and the value of ρ as −4.54 based on the correlation of the *meta* reactivities provide the data necessary for the evaluation of σ^+. These constants are summarized in Table II.

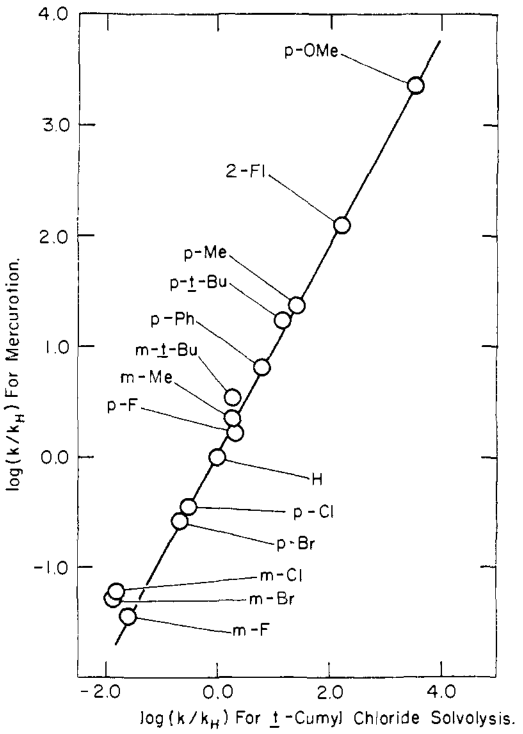


Fig. 1.—The relationship between log (k/k_H) for mercuration and log (k/k_H) for *t*-cumyl chloride solvolysis.

A second procedure for the evaluation of the σ^+-constants is provided by the direct examination of substitution data. The empirical relationships (11) between log(k/k_H) and S_f, the Selectivity Factor, for the correlation of substitution reactions have been shown to be derivable from the Hammett equation. The slopes of these Selectivity Relation-

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

TABLE II

SUBSTITUENT CONSTANTS FOR SUBSTITUTION REACTIONS

Substituent	Method of evaluation		
	Solvolysis	S_t method[a]	ρ method[b]
p-Methoxy	−0.764	−0.74 ± 0.02	−0.78
2-Fluorenyl	− .49	− .47 ± .05	− .54
p-Methyl	− .311	− .280 ± .004	− .30
p-*t*-Butyl	− .256	− .260 ± .02	− .25
m-Methyl	− .059	− .069[c]	− .069[c]
m-*t*-Butyl	− .069	− .090 ± .02	− .08
p-Fluoro	− .073	− .02 ± .05	..
p-Chloro	.114	.13 ± .05	0.10
p-Iodo	.135	.13 ± .08	..
p-Bromo	.150	.15 ± .05	.14
m-Fluoro	.352	.30 ± .04	.35
m-Chloro	.399	.38 ± .08	.37
m-Bromo	.405	.35 ± .08	.39

[a] Selectivity relationship. [b] Extended Selectivity Relationship. [c] Adopted Hammett value.

ship lines are dependent on the σ^+-substituent constants (11). The assignment of $\sigma_{m-\mathrm{Me}}$ as −0.069 allows the calculation of the other constants from the statistical analyses for each substituent group. The results are summarized in Table II.

A third procedure also utilizing the substitution data is described in the following section. The values for σ^+ obtained by this approach are also presented in Table II.

It is evident that the three different approaches yield values in consistent good agreement.

Application of the Extended Selectivity Treatment to Representative Hammett Reactions.—As pointed out in the Introduction, the most direct method for the evaluation of the constancy of an electronic contribution of a given substituent is by a plot of the relative rate data against ρ. A linear relationship would indicate the validity of the assumption of constancy. The slope of the line would then yield the σ-value. It was desirable to evaluate this approach by first examining its application to typical substituents in typical Hammett side-chain reactions before extending the treatment to aromatic substitution reactions. Another advantage of this technique is the comparison achieved between data fitting the Hammett equation and data correlated by the Extended Selectivity treatment.[19]

Accordingly, the literature was searched and data assembled for a randomly selected series of Hammett side-chain reactions. All side-chain reactions which exhibit electron-deficient transition states were excluded. A major requirement for inclusion was that the reaction data included results for a significant number of representative substituent groups.[20]

The results of the Extended Selectivity treatment applied to these representative Hammett reactions for four representative substituents are represented graphically in Fig. 2–5. These diagrams illustrate two important factors. First, the substituent groups *p*-OMe, *p*-Me, *p*-F and *p*-Cl all exhibit deviations from a correlation line based on the Hammett σ-constants. The discrepancies are perhaps somewhat greater for

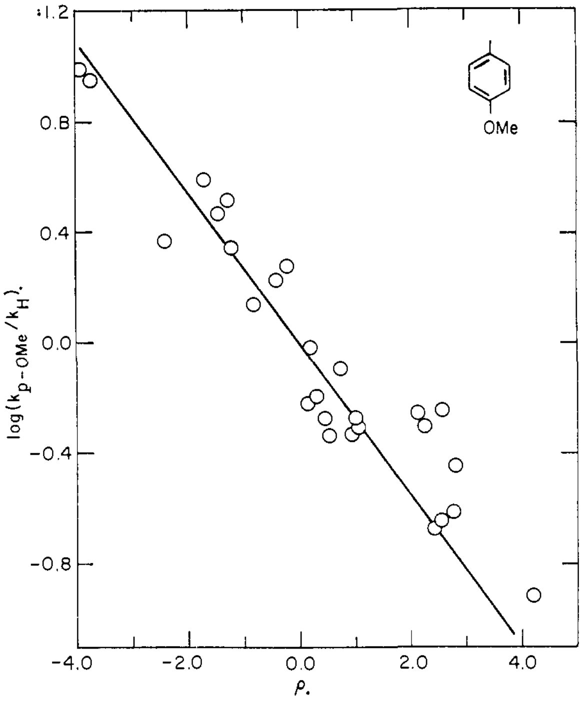

Fig. 2.—The relationship between $\log(k/k_H)$ for the Hammett side-chain reactions of *p*-methoxy substituted benzenes and the reaction constant.

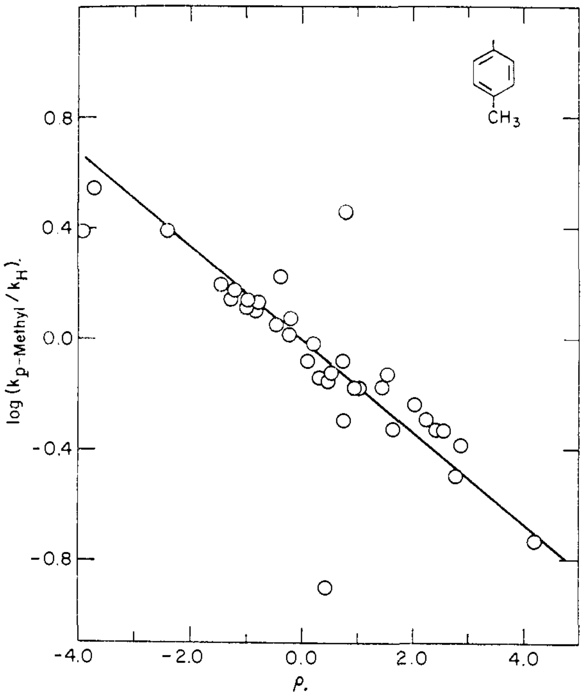

Fig. 3.—The relationship between $\log(k/k_H)$ for the Hammett side-chain reactions of *p*-methyl substituted benzenes and the reaction constant.

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[19] This approach involving ρ is termed the Extended Selectivity Treatment to distinguish it from the Selectivity Treatment involving S_f, a quantity proportional to the reaction constant (9). This procedure has the obvious advantage of a soundly based ρ-value rather than one based on a single reaction.

[20] A related compilation is summarized in ref. 13. The data will be published in a detailed review now under preparation by the authors.

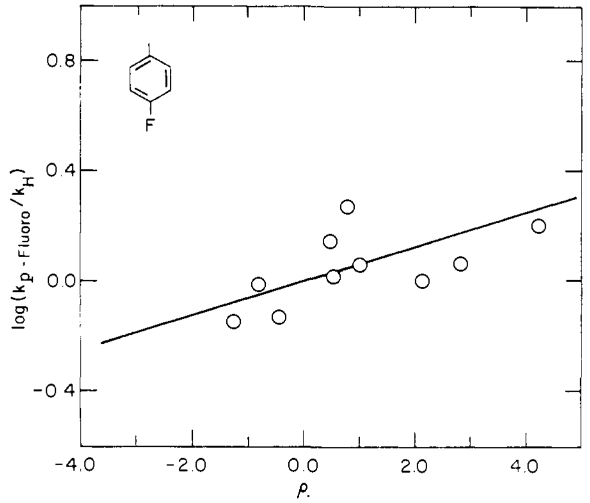

Fig. 4.—The relationship between log (k/k_H) for the Hammett side-chain reactions of *p*-fluoro substituted benzenes and the reaction constant.

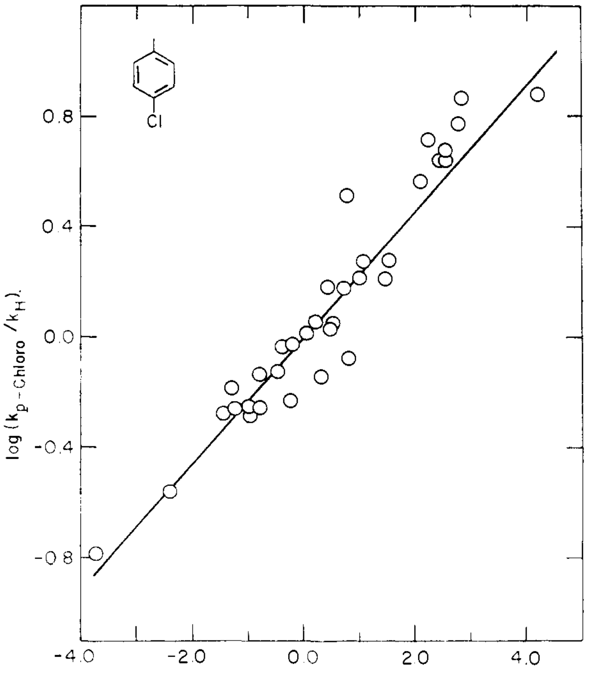

Fig. 5.—The relationship between log (k/k_H) for the Hammett side-chain reactions of *p*-chloro substituted benzenes and the reaction constant.

the *p*-F group, but the paucity of data for this substituent obscures the significance of the conclusion. The second significant observation is the lack of a correlation between the magnitude of the displacement from the correlation line and ρ.

The view that serious deviations from the Hammett equation originated in resonance interaction was reiterated in 1959.[9a] Wepster and his associates observed serious discrepancies in the σ-values for certain side-chain reactions. It is clear from their report and from our own work[13] that electrophilic side-chain reactions are poorly accommodated by linear free energy treatments.

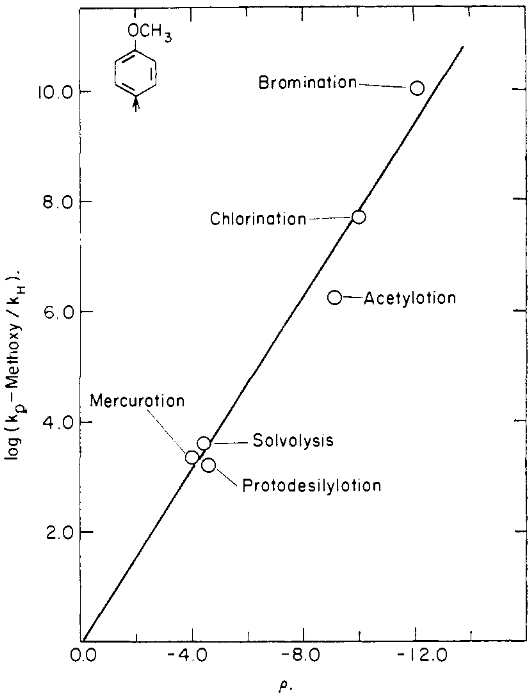

Fig. 6.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of anisole and the reaction constant.

This result, however, does not negate the precise application of σ^+-constants to electrophilic substitution.

Application of the Extended Selectivity Treatment to Representative Substitution Reactions.—A similar examination of the data for 13 representative substituent groups provides the means for evaluating the applicability of a linear free energy relationship for various aromatic substituents. It is now possible to apply the Extended Selectivity Treatment to the available results to test the validity of a simple σ^+-correlation and to test the merits of the description of the substituent parameter σ^+ as a constant.

The most highly activating substituent examined in the course of these studies was the *p*-methoxy group.[15] Studies of electrophilic substitution in the *para* position of anisole provide the data presented in Fig. 6. The corresponding Hammett side-chain reactions of *p*-anisyl derivatives are illustrated in Fig. 2. Certain random variations are detectable in both cases. However, the adherence to a linear treatment is most satisfactory. For the electrophilic substitution reactions, large variations in the reaction constants do not introduce an unexpected alteration of reactivity. Accordingly, for the anisole molecule with large reasonance contributions in the transition state a linear relationship provides a satisfactory correlation. In our opinion, this observation requires a revision of the notion that resonance stabilization will necessarily alter as the electrophilic properties, *i.e.*, selectivity, of the reagent are modified.

Further support for this conclusion is obtained through an examination of the data for substitution in the 2-position of fluorene,[16] Fig. 7. A linear

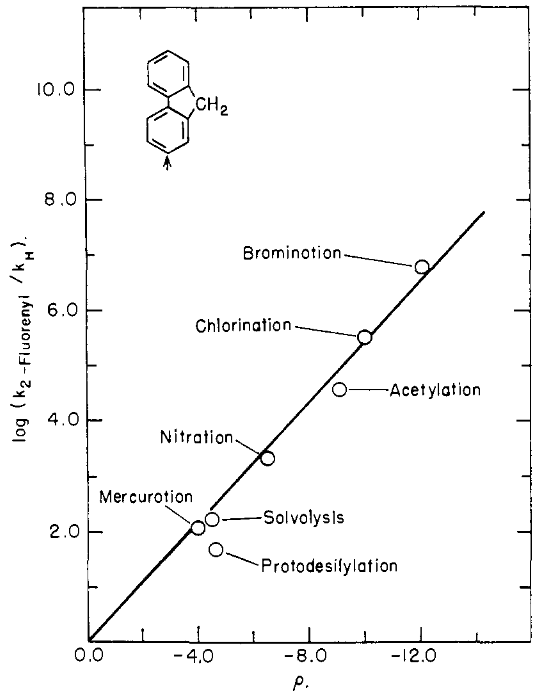

Fig. 7.—The relationship between log (k/k_H) for electrophilic substitution in the 2-position of fluorene and the reaction constant.

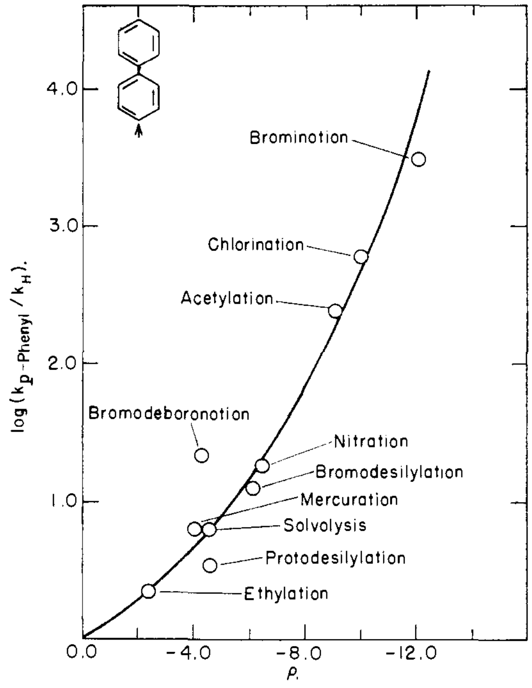

Fig. 8.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of biphenyl and the reaction constant.

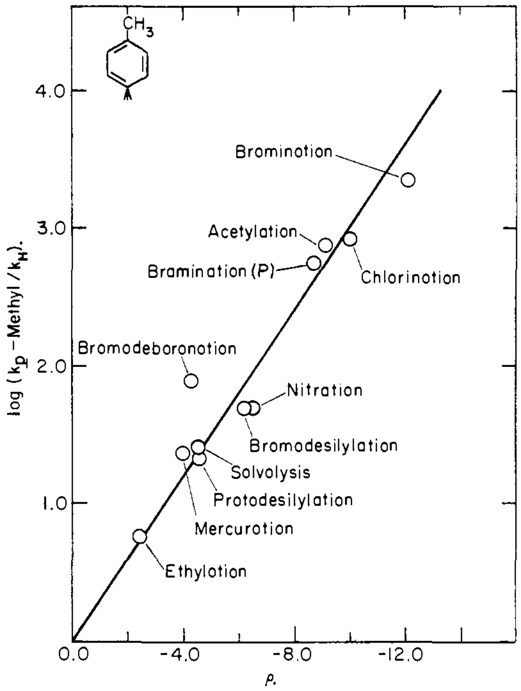

Fig. 9.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of toluene and the reaction constant.

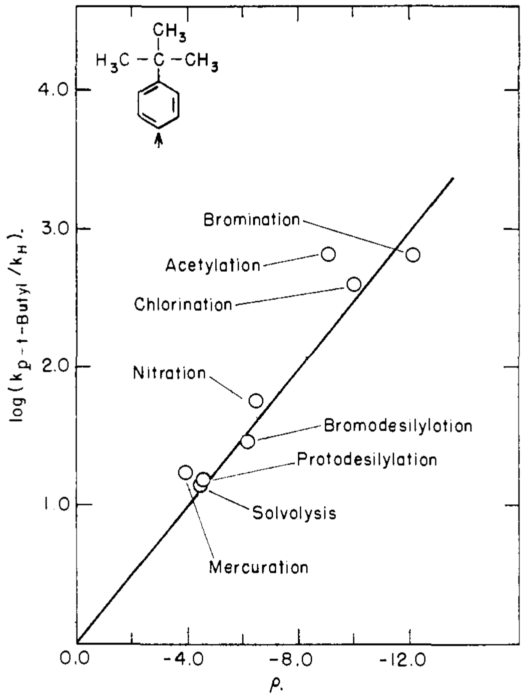

Fig. 10.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of *t*-butylbenzene and the reaction constant.

correlation is found for this hydrocarbon which is also greatly activated toward electrophilic substitution because of the important resonance interactions of the fused, planar phenyl substituent.

On the other hand, the substitution reactions of biphenyl,[16] Fig. 8, exhibit a real deviation from a treatment based on the linear free energy hypothesis. As pointed out, highly activating substituents do not exhibit important deviations from linearity. This result and the far greater reactivity of the 2-position in planar fluorene prompted an explanation for the deviation for biphenyl on the basis of a steric effect. Specifically, it was proposed that the *ortho* hydrogens intro-

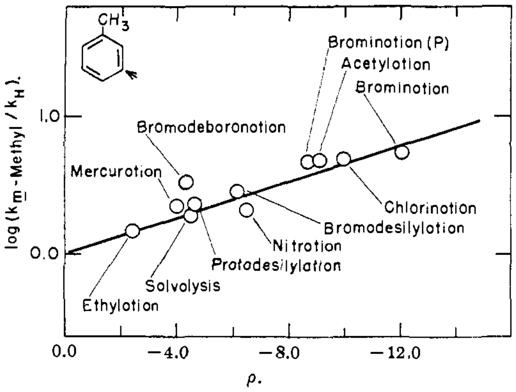

Fig. 11.—The relationship between log (k/k_H) for electrophilic substitution in the *meta* position of toluene and the reaction constant.

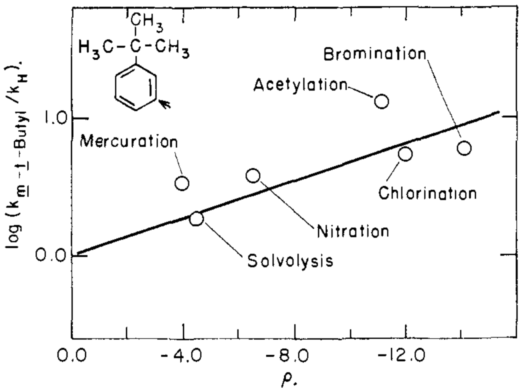

Fig. 12.—The relationship between log (k/k_H) for electrophilic substitution in the *meta* position of *t*-butylbenzene and the reaction constant.

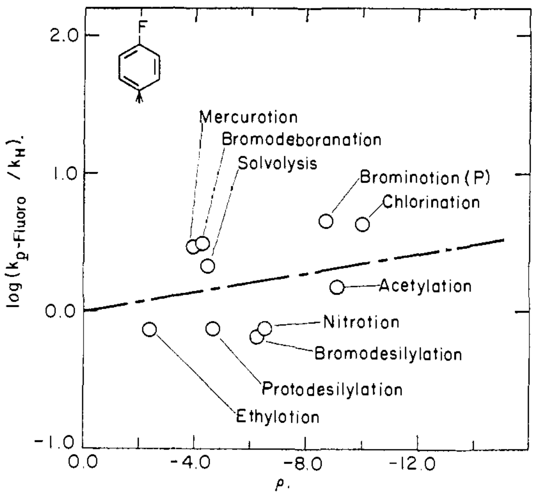

Fig. 13.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of fluorobenzene and the reaction constant.

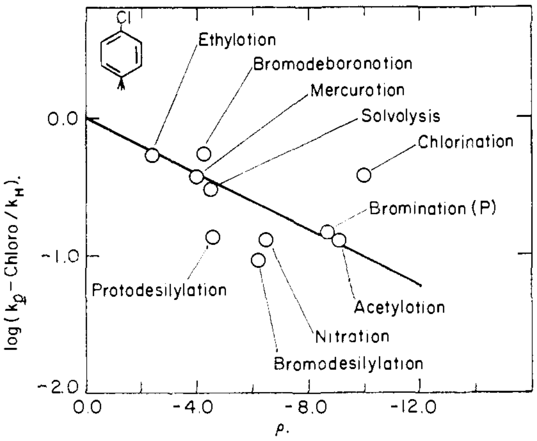

Fig. 14.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of chlorobenzene and the reaction constant.

duced an energy barrier to the achievement of coplanarity resulting in diminished and variable resonance stabilization.[16]

The diagram for *p*-methyl, Fig. 9, is apparently typical of the behavior of other *p*-alkyl substituents as indicated by the analysis for *p*-*t*-butyl, Fig. 10. An examination of a series of side-chain reactions of *p*-tolyl derivatives, Fig. 3, indicates the deviations from the correlation lines are similar in both treatments. Indeed, a more detailed evaluation of these results revealed the electrophilic substitution reactions were, in fact, correlated with superior precision.[13]

The reactivity in positions *meta* to methyl and *t*-butyl substituents is examined in Figs. 11 and 12. Only insignificant experimental variations are observed for *m*-methyl. For *m*-*t*-butyl, on the other hand, the deviations from linearity are large. Unfortunately, these variations, although probably real, are not much greater than the experimental uncertainties involved in the measurements.[14] The variation observed in this case is discussed more fully in the following section.

The substitution data for *p*-fluoro are presented in Fig. 13. Considerable scatter from a line defined by the average value of σ^+_{p-F} is evident. The variations are not appreciably greater than observed for *m*-*t*-butyl, Fig. 12. Moreover, the absence of a relationship between the log p_f^F values and the reaction constants is also certain.[21,22] Although it is not apparent from the data summarized in Table I and presented graphically in Fig. 13, there is not a relationship between the value of the partial rate factor and the charge (+1 or 0) of the electrophile.[23] It has been argued[23] that uncharged reagents would evoke a greater resonance stabilization in the transition state than charged electrophiles. The reduced activation of *p*-F in ethylation, protodesilylation, nitration and acetylation suggest that this viewpoint is reasonable. However, other data not presented in this summary reveal that other positive reagents, as those involved in protodeboronation and tritium exchange, yield p_f^F values of the same magnitude as neutral reagents. Certain

[21] The treatment based on an interaction between ρ and σ devised by Norman and his associates has been discussed previously, ref. 17.

[22] J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

[23] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 240 and references cited.

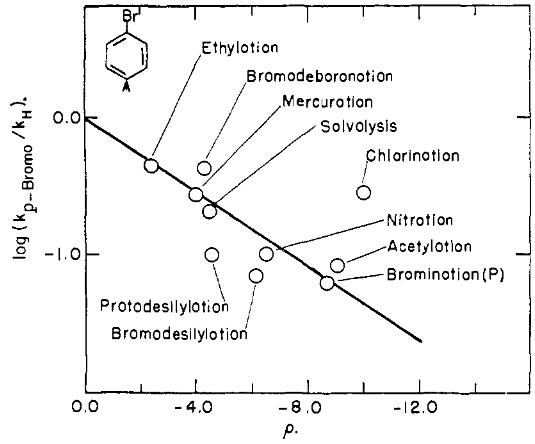

Fig. 15.—The relationship between log (k/k_H) for electrophilic substitution in the *para* position of bromobenzene and the reaction constant.

neutral reagents, as in bromodesilylation, also provide inverse behavior to that expected on the basis of the polarization argument.[24] Accordingly, the charge-type of the electrophile involved in the reaction does not offer an attractive explanation for the deviations.

To explore this aspect of the problem in greater detail, the results for the Hammett side-chain reactions of *p*-fluorinated derivatives were examined, Fig. 4. It is apparent that the deviations from the Hammett equation are equally as large as for the Selectivity Relationship. For both treatments the deviations are independent of the magnitude of ρ. The problems involved in the determination of reactive reactivity are further discussed in the following sections.

The electrophilic substitution reactions of *p*-chloro and *p*-bromo substituted aromatics are illustrated in Figs. 14 and 15. These substituent groups yield only a tenfold (maximum) decrease in the reactivity of the benzene nucleus. As discussed, the variations are not excessive. This point is illustrated by an inspection of the data available for side-chain reactions of *p*-chloro derivatives Fig. 5. As in the other cases, already treated, the random scatter detectable in the Hammett equation is not significantly smaller than found for the electrophilic reactions. The two treatments are equally precise.

The extension of the discussion to the reactions of the *meta* position in fluoro-, chloro- and bromobenzene,[17] Figs. 16–18, reveals the existence of a satisfactory relationship in each case.

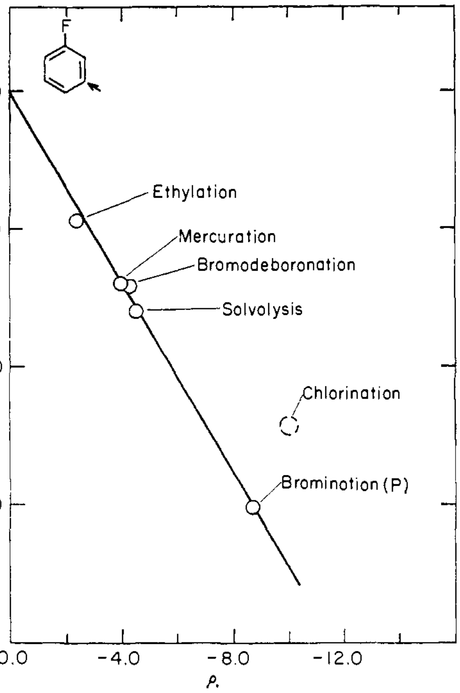

Fig. 16.—The relationship between log (k/k_H) for electrophilic substitution in the *meta* position of fluorobenzene and the reaction constant.

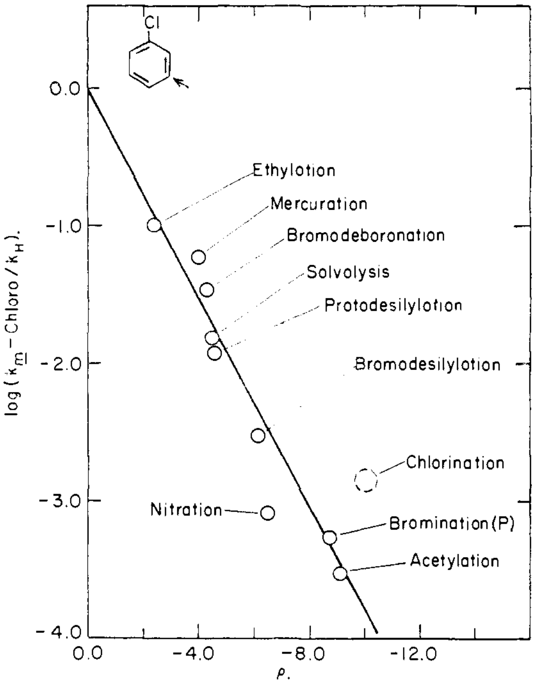

Fig. 17.—The relationship between log (k/k_H) for electrophilic substitution in the *meta* position of chlorobenzene and the reaction constant.

Origin of Deviation.—In the preceding discussion it has been possible to assess critically three important suggestions concerning the origin of deviations from the treatment. The resultant correlations for anisole and fluorene require the abandonment of the view that resonance contributions are widely variable. The randomness of the deviations in all of the diagrams presented provided a sound indication of the absence of a relationship between the electrical influences of the substituent groups and the reaction constant. Further, the accumulation of new data for a spectrum of substitution processes suggests correlations of relative reactivity on the basis of the charge-type of the electrophile are also inappropriate.

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[24] This point has also been discussed by C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 179 (1960).

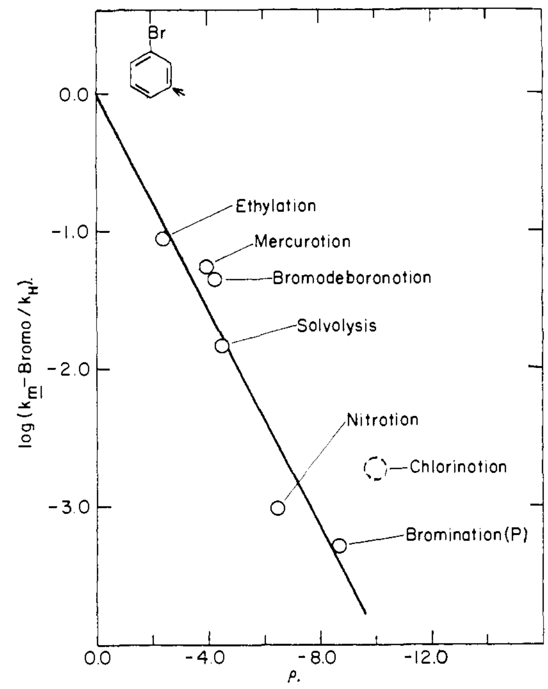

Fig. 18.—The relationship between log (k/k_H) for electrophilic substitution in the *meta* position of bromobenzene and the reaction constant.

It is our view that the discrepancies observed for these substitution reactions are largely the consequences of a multiplicity of minor influence operative in the transition state. These influences are particularly apparent for substituent groups which introduce only minor variations in the rate relative to benzene. The four most important factors appear to be complexation of the substituent with the electrophilic reagent or catalyst, the involvement of π-complex character in the transition state for the reaction, rate effects originating in the rupture of the carbon–hydrogen bond and differential solvation of the electron-deficient transition states. Recent experimental investigations have demonstrated the importance of each of these factors in the determination of rate ratios. The difficulties encountered in the correlation of the observations for the chlorination of the halobenzenes led to the proposal of an interaction between the electrophilic reagent and halobenzenes.[17] Pearson and his associates have recently demonstrated the utility of swamping catalysts to alter the electrical properties and reactivity of aromatics.[25] The extent of involvement of π-complex character in the transition state has been demonstrated to introduce remarkable variations in the relative reactivities observed in the nitration reaction.[26] In this extreme case the observations appear to require that the rate of formation of the π-complex is the slow step. A third problem involved in these reactions is the significance of carbon–hydrogen bond rupture as a factor leading to a determination of relative rate.[27] Clearly the influence of the substituent group on the rate of formation of the σ-complex and its rate of decomposition are frequently opposed. Accordingly, it would not be surprising to discover variations in relative reactivity because of this cause. The fourth factor is related to the differential solvation energy of apparently similar transition states. For non-catalytic chlorination, this influence is capable of introducing significant variations in the relative rates of reaction of the *para* position of toluene and *t*-butylbenzene.[28]

Conclusion.—In summary, the facts obtained for 13 substituent groups in 10 characteristic substitution reactions have been shown to adhere with reasonable precision both to the Selectivity Relationship and to the Extended Selectivity Relationship. The random deviations from the correlation lines impose only minor limitations on the scope and utility of this treatment. Clearly, the Hammett equation, equally susceptible to random variations as shown by comparison of common substituent groups, has proved to be a most powerful tool for the examination of mechanisms and concepts in organic chemistry. The discrepancies observed in the correlations for electrophilic substitution reactions do not appear to be associated with the more apparent properties of these reactions, *i.e.*, charge of the electrophilic reagent or variations in resonance interaction as a consequence of the modification of selectivity. Rather the principal limitations are imposed by the variation in the location of the transition state along the reaction coördinate by other more subtle factors. To attempt to accommodate these influences in a meaningful free energy treatment would appear to require very elegant techniques for the dissection of multiparameter equations. It is, indeed, misleading to believe that such treatments will necessarily be more precise or more accurate.

The conclusion of this research is then that the Selectivity Relationship, or better, the Extended Selectivity Relationship provide a reasonable and simple technique for the correlation of data for the substitution in the benzene ring. The important corollaries attendant to this conclusion reflecting the structure and reactivity relationships involved have already been presented.

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(25) D. E. Pearson, H. W. Pope, W. W. Hargrove and W. E. Stamper, *J. Org. Chem.*, **23**, 1412 (1958).

(26) G. A. Olah, S. J. Kuhn and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

(27) G. Goldman, Thesis, Purdue University Libraries, 1959.

(28) L. M. Stock and A. Himoe, unpublished results.