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An Examination of the Applicability of the Selectivity Relationship to the Electrophilic Substitution Reactions of the Halobenzenes[1,2]

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The applicability of the Selectivity Relationship to the electrophilic substitution reactions of the halobenzenes has been examined. For substitution *meta* to the halogens, the ratios log m_f^X/log p_f^{Me} are *m*-F, −0.96 ± 0.14; *m*-Cl, −1.22 ± 0.26; and *m*-Br, −1.14 ± 0.25. The σ^+-constants calculated from these ratios are in good agreement with the values based on *t*-cumyl chloride solvolysis. Graphical analysis of the data for *meta* substitution indicates substantial agreement with the expectations of the Selectivity treatment. For substitution *para* to the halogens, the ratios log p_f^X/log p_f^{Me} are *p*-F, 0.07 ± 0.14; *p*-Cl, −0.41 ± 0.17; *p*-Br, −0.48 ± 0.18 and *p*-I, −0.43 ± 0.27. The σ^+-constants calculated from these ratios are also in agreement with the predictions of the solvolysis studies. Graphical analysis of these data for *p*-Cl, *p*-Br and *p*-I indicates the substitution reactions involving the replacement of hydrogen adhere to the relationship satisfactorily. On the other hand, substitution reactions involving the rupture of a carbon–metal bond exhibit more serious deviations from the correlation line. The results, however, provide reasonable agreement with the expectations of a first-order free energy correlation. For *p*-F, the situation is less certain. The large variations found in the logarithmic ratio are revealed as random deviations by the graphical analysis. The magnitude of these deviations is not greater than that found for the *p*-Cl substituent in Hammett side-chain reactions. Moreover, the application of second-order treatments does not provide a better correlation of the data or an understanding of the deviations. It is suggested that the observations are compatible with the expectations of the Selectivity Relationship. The random discrepancies are considered to be the consequence of the operation of other factors, *e.g.*, association of reagent and substrate, which introduce variations in reactivity but cannot be introduced into free energy treatments.

Introduction

The original proposal that the electrophilic substitution reactions of the monosubstituted benzenes might be correlated satisfactorily by a modified Hammett treatment was made in 1953.[3] In the past few years data have been obtained providing a test of this suggestion by an examination of the adherence of the results to the Selectivity Relationship.[4] The partial rate factors have been examined for the substitution reactions of toluene,[5] *t*-butylbenzene,[6] anisole,[7] biphenyl[8] and fluorene.[8]

Investigations in this and other laboratories have shown the treatment to apply satisfactorily to *m*-methyl,[5f] *p*-methyl[5f] and *p*-*t*-butyl[6d] substituents. For the *m*-*t*-butyl[6d] and *p*-methoxy[7b] groups, the limited experimental results indicated the applicability of the Selectivity treatment to be somewhat less precise but no less satisfactory than for the other substituents. On the other hand, the electrophilic substitution reactions for biphenyl did not yield a satisfactory correlation.[8e] The utility of the treatment for 2-substitution in planar fluorene[8e] suggested the intrusion of a steric effect in biphenyl causing serious variations in the electronic contributions of the *p*-phenyl group.[8e]

Other interpretations have been advanced concerning the discrepancies exhibited by the phenyl substituent. The opposing resonance and inductive roles of the *p*-phenyl group have been argued to interfere with the achievement of a correlation based on the simple first-order Hammett equation.[9] A discussion of certain electrophilic substitution reactions of biphenyl and the halobenzenes led Norman and his associates to this conclusion.[10] Similar views had been expressed earlier by de la Mare and Hassan.[11] Indeed, this viewpoint has been made the basis of second-order, three-parameter correlation equations for electrophilic reactions.[10,12]

The detailed investigations of selected substituent groups[5-8] have not included a substituent group with large and opposing electronic influences. Clearly, the halobenzenes were ideally suited for this purpose. Accordingly, the mercuration,[13a] ethylation,[13b] acetylation[13c] and chlorination[13d] reactions have been studied. The experimental results of these investigations and other studies are summarized and examined for adherence to the Selectivity Relationship in this paper.

Discussion

Summary of Data for Substitution Reactions of the Halobenzenes.—The partial rate factors and associated quantities for the substitution of fluoro-, chloro-, bromo- and iodobenzene are summarized

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(1) Directive Effects in Aromatic Substitution. LIV.

(2) This research supported in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(3) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

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

(5) (a) F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959); (c) H. C. Brown, G. Marino and L. M. Stock, *ibid.*, **81**, 3310 (1959); (d) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959); (e) H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959); (f) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

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(7) (a) H. C. Brown and M. Dubeck, *ibid.*, **82**, 1939 (1960); (b) L. M. Stock and H. C. Brown, *ibid.*, **82**, 1942 (1960).

(8) (a) H. C. Brown, M. Dubeck and G. Goldman, *ibid.*, **84**, 1229 (1962); (b) H. C. Brown and A. Neyens, *ibid.*, **84**, 1233 (1962); (c) H. C. Brown and G. Marino, *ibid.*, **84**, 1236 (1962); (d) H. C. Brown and L. M. Stock, *ibid.*, **84**, 1238 (1962); (e) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1242 (1962).

(9) In view of the rapidly expanding literature concerning multiparameter $\rho\sigma$ treatments it appears desirable to refer to the proposed Selectivity Relationship and the original Hammett equation as first-order treatments.

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

(11) P. B. D. de la Mare and M. Hassan, *ibid.*, 3004 (1957).

(12) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

(13) (a) H. C. Brown and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1650 (1962); (b) H. C. Brown and A. Neyens, *ibid.*, **84**, 1655 (1962); (c) H. C. Brown and G. Marino, *ibid.*, **84**, 1658 (1962); (d) L. M. Stock and F. W. Baker, *ibid.*, **84**, 1661 (1962).

TABLE I

PARTIAL RATE FACTORS FOR *meta* AND *para* SUBSTITUTION IN THE HALOBENZENES

		Fluoro		Chloro		Bromo		Iodo		
Reaction, conditions[a]	S_f	m_f	p_f	m_f	p_f	m_f	p_f	m_f	p_f	Ref.
Bromination(P), Br_2, HOAc–CH_3NO_2, 25°	2.05	0.0010[b]	4.62	0.00057[b]	0.145	0.00053[b]	0.0618	0.0022[b]	0.0802	14
Chlorination, Cl_2, 60% HOAc, 25°	2.10	.0056[b,c]	3.93	.0023[bc]	.406	.0032[b,c]	.310	.....	....	13d
Acetylation, AcCl, $AlCl_3$, $C_2H_4Cl_2$, 25°	2.19	....	1.51	.0003	.125	....	.084	.....	....	13c
T exchange, ArT, H^+, H_2O–CF_3CO_2H, 25°	1.88	.002[d]	1.79	.0015	.161	.001[d]	.090	.003[d]	.112	15
Nitration, HNO_3, CH_3NO_2, 25°	1.36[e]	....	0.77	.00084	.130	.00098	.103	.0112	.776	16
Bromodeboronation, $ArB(OH)_2$, Br_2, 20% HOAc, 25°	1.37	.039	2.81	.0349	.539	.044	.413	.072	.498	17
Bromodesilylation, $ArSiMe_3$, Br_2, 98.5% HOAc, 25°	1.23	....	0.68	.0030	.092	....	.071	.....	.088	18
Mercuration, $Hg(OAc_2)_2$, HOAc, 25°	1.01	.04	2.98	.060	.36	.054	.27	.....	....	13a
Protodeboronation, $ArB(OH)_2$, H_2SO_4–H_2O, 25°	1.38	.032	2.1	.025	...	....	.30	.....	....	19
Protodesilylation, $ArSiMe_3$, $HClO_4$, MeOH–H_2O, 51.2°	0.96	....	0.75	.012	.13	....	.10	.....	.10	20
Destannylation, $ArSnMe_3$, $HClO_4$, EtOH–H_2O, 50°	.47	....	.62	.039	.187	....	.145	.....	....	21
Degermanylation, $ArGeEt_3$, $HClO_4$, MeOH–H_2O, 50°	.86	....	.92	.017	.167	....	.127	.....	.13	22
Ethylation, EtBr, $GaBr_3$, $C_2H_4Cl_2$, 25°	.58	.116	.738	.102	.538	.087	.433	.....	....	13b
Solvolysis, $ArCMe_2Cl$, 90% Acetone, 25°	1.114	.025	2.14	.016	.305	.014	.208	.023	.244	23

[a] Electrophilic reagent, catalyst, solvent and temperature. [b] Average value of two approximate methods; see ref. 14. [c] Based on kinetic data for *p*-halotoluenes; see ref. 13d. [d] Approximate values; see ref. 15. [e] Value for S_f in doubt; see text.

in Table I. For convenience the *ortho* partial rate factors are not included in the table.

The partial rate factors assembled in Table I are not devoid of errors or uncertainties. The bromination data are based on the polymethylbenzene approach[14] and are subject to the limitations imposed by the possible failure of simple additivity in the influences of substituent groups. Similarily, the m_f-values for chlorination are based on rate data for disubstituted compounds.[13d] The tritium exchange, acetylation, mercuration and ethylation studies appear to be free of significant error.

Unfortunately, the results for the nitration reaction are subject to rather large uncertainties. At the present it is not possible to compare the influence of substituents under similar conditions. Values for S_f in the range 1.22 to 1.66 have been reported for the nitration reaction. These variations reflect the real change in selectivity of nitration reagents and the experimental uncertainty in the analyses for small concentrations of *meta* isomer in the presence of large concentrations of the other products. A recent study revealed S_f for nitration with acetyl nitrate in acetic anhydride at 25° to be 1.36.[16c] These conditions are very similar to those employed by Bird and Ingold to measure the relative rates of nitration of the halobenzenes.[16a] The isomer distributions obtained by Roberts and his associates, however, are for reaction with fuming nitric acid in nitromethane.[16b] Indications that acetyl nitrate is possibly a more selective reagent than pure nitric acid are provided by the variations in relative rate observed for these reactions. The iodobenzene to benzene rate ratio was found to be 0.13 for the reaction of the ester in acetic anhydride and only 0.22 by reaction of the acid in nitromethane.[16b] The large uncertainty in this reaction is indicated in the diagrams.

The model reactions studied by Eaborn and Kuivila and their associates also appear to have been carefully examined. However, an examination of the experimental results for the bromodeboronation reaction indicated the existence of uncertainties of 10–15% in the rate constants.[24] Moreover, the large changes in relative rate involved in these studies required the adoption of different conditions for the comparison of diverse substituents. The variations in relative rate introduced by this procedure appear to be small. However, caution appears advisable in discussions centering on minor variations in reactivity in these series. As pointed out by Eaborn and Waters,[21] the destannylation reaction does not adhere to the treatment and these data are not considered in the discussion.

Electrical Influences of Halogen Substituents.— As has been pointed out, the halogen substituents exhibit a remarkable sequence of reactivity. The results summarized in Table I indicate the *p*-F and H substituents have approximately the same effect on the rate of electrophilic reactions. The other *p*-halogens deactivate the aromatic ring with *p*-chloro less deactivating than *p*-bromo. The influence of the *p*-iodo substituent is quite variable but apparently intermediate between the *p*-chloro and *p*-bromo groups.

All the *m*-halogens decrease the reactivity of the benzene nucleus. For this position, the reactivity sequence is very similar to that found for *para* substitution. The observations indicate H >> *m*-F > *m*-Cl = *m*-Br. This order is reflected in the Hammett σ-constants for the halogens, σ_{m-F}

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(14) G. Illuminati and G. Marino, *J. Am. Chem. Soc.*, **78**, 4975 (1956).

(15) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 2388 (1961).

(16) (a) M. L. Bird and C. K. Ingold, *ibid.*, 918 (1938); (b) J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **76**, 4527 (1954); (c) L. M. Stock, *J. Org. Chem.*, **26**, 4120 (1961); also ref. 10.

(17) H. G. Kuivila and A. R. Hendrickson, *J. Am. Chem. Soc.*, **74**, 5068 (1952).

(18) C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 179 (1960); 4449 (1957).

(19) K. V. Nahabedian and H. G. Kuivila, *J. Am. Chem. Soc.*, **83**, 2167 (1961).

(20) C. Eaborn, *J. Chem. Soc.*, 4858 (1956); F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959).

(21) C. Eaborn and J. A. Waters, *ibid.*, 542 (1961).

(22) C. Eaborn and K. C. Pande, *ibid.*, 297 (1961).

(23) H. C. Brown, Y. Okamoto and G. Ham, *J. Am. Chem. Soc.*, **79**, 1906 (1957).

(24) We are indebted to Professor Kuivila for providing us with the original observations.

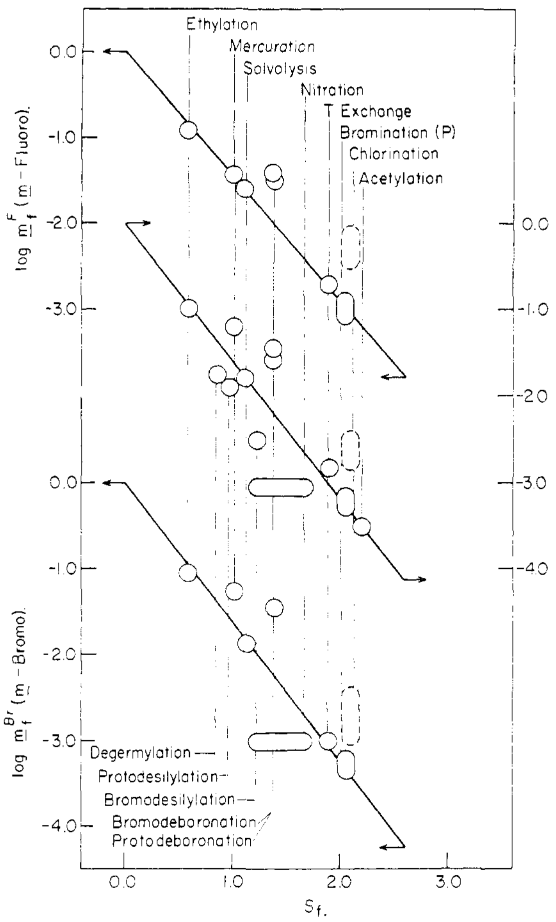
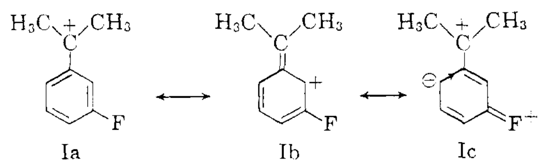


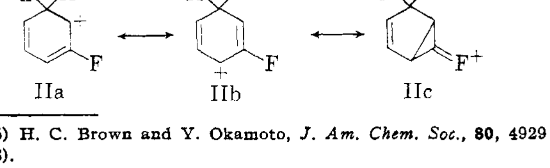
Fig. 1.—Relationship between log m_f^X for *m*-F, *m*-Cl and *m*-Br and the Selectivity factor, S_f. Arrows on the correlation lines indicate the proper ordinate. The guide lines are defined by the S_f value for each reaction.

0.337, σ_{m-Cl} 0.373, σ_{m-Br} 0.391 and the σ^+-constants based on the solvolysis reaction,[25] σ^+_{m-F} 0.352, σ^+_{m-Cl} 0.399 and σ^+_{m-Br} 0.405. In each case the *m*-fluoro group deactivates less than the other halogens. For the solvolysis of *t*-cumyl chlorides, it was suggested that the *m*-fluoro group was capable of electron release by conjugation coupled with inductive relay as shown in structure Ic.

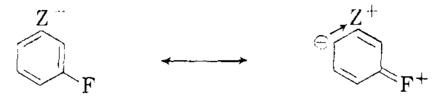


Ia Ib Ic

The finding that a similar order of reactivity exists for electrophilic substitution requires a modification of this interpretation. Structures of the type Ic are not possible in the σ-complex. In the transition state for direct substitution reactions, as approximated by the σ-complex, resonance interaction is permissible only through structure IIc. Another interpretation for the *meta* sequence is based on the polarization of the aromatic by an electrophilic reagent (Z+). In this situation, the latent resonance effects of the *m*-fluoro substituent are induced as in IIIb.



IIa IIb IIc



IIIa IIIb

The role of *p*-halogen substituents on reactivity has already been the subject of much qualitative discussion in the literature. For emphasis, however, it is pertinent to remark that the resonance interaction in the *para* position is large. Using Taft's σ'-values as an estimate of the inductive component for each halogen yields the resonance factors as: $\sigma^+_{p-F} - \sigma_F' = -0.57$; $\sigma^+_{p-Cl} - \sigma_{Cl}' = -0.36$; $\sigma^+_{p-Br} - \sigma_{Br}' = -0.30$; $\sigma^+_{p-I} - \sigma_I' = -0.24$. The resonance stabilization of the *p*-fluoro group is comparable with that available from *p*-acetylamino or *p*-phenoxy.

Applicability of the Selectivity Relationship to *m*-Halogens.—The experimental results for the electrophilic substitution reactions of the highly deactivated *meta* position are tested for adherence to the treatment by eq. 1 and 2

$$\log m_f^X = \frac{\sigma^+_{m-X}}{\sigma^+_{p-Me} - \sigma^+_{m-Me}} S_f \qquad (1)$$

$$\log m_f^X = \frac{\sigma^+_{m-X}}{\sigma^+_{p-Me}} \log p_f^{Me} \qquad (2)$$

Graphical analysis of the data for the *m*-fluoro *m*-chloro and *m*-bromo substituents is provided in Fig. 1. The log m_f^X values, excluding the three observations for *m*-I, are plotted against S_f.

Inspection of the diagram reveals substitution *meta* to the halogens appears to follow the predictions of the Selectivity Relationship. Certain serious deviations are detected. However, these discrepancies are small in view of the difficulties in obtaining accurate estimates of the extent of substitution at the deactivated *meta* position. In particular, the deviations for non-catalytic chlorination are large. This observation is presumably the consequence of the failure of the additivity principle in the evaluation of the m_f-values.[13d]

It should be noted, however, that these deviations are considerably less than an order of magnitude. Other random variation is observed in the reactions involving the cleavage of carbon–metalloid bonds The reactions involving the replacement of hydrogen yield an excellent correlation with the predictions of the relationship.

A more detailed examination of the m_f results is obtained by a test of the adherence of the data to eq. 2. The logarithmic ratios, log m_f^X/log p_f^{Me}, are summarized in Table II. The σ^+_{m-X} constants obtained from these ratios are presented and compared with the values based on *t*-cumyl chloride solvolyses.[25]

The logarithmic ratios, Table II, are sensibly constant exhibiting a standard deviation of approximately 20%. Notwithstanding the experi-

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[25] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4929 (1958).

TABLE II

LOGARITHMIC RATIOS AND SIGMA CONSTANTS FOR *meta* SUBSTITUTION IN THE HALOBENZENES

Substituent	n^a	$\left[\frac{\log m_f^X}{\log p_f^{Me}}\right]^b$	σ^+_{m-X} Subst.[c]	σ^+_{m-X} Solv.[d]
m-F	7	-0.96 ± 0.14	0.30 ± 0.04	0.352
m-Cl	12	$-1.22 \pm .26$	$.38 \pm .08$	.399
m-Br	7	$-1.14 \pm .25$	$.35 \pm .08$	.405
m-I	3	$-0.87 \pm .18$	$.27 \pm .05$	.359

[a] Number of reactions studied. [b] Based on eq. 2. [c] Based on eq. 2 with σ^+_{p-Me} -0.31, ref. 25. [d] Ref. 25.

mental limitations of these data, the variations in the ratio are probably real. The randomness observed for these reactions is not greater than found for the simple Hammett equation (see following discussion). Importantly, the σ^+_{m-X} constants calculated from the substitution data are in agreement with the predictions of the solvolysis experiments.[25]

Applicability of the Selectivity Relationship to *p*-Halogens.—The experimental results for electrophilic substitution *para* to the halogens are examined in terms of eq. 3 and 4.

$$\log p_f^X = \frac{\sigma^+_{p-X}}{\sigma^+_{p-Me} - \sigma^+_{m-Me}} S_f \qquad (3)$$

$$\log p_f^X = \frac{\sigma^+_{p-X}}{\sigma^+_{p-Me}} \log p_f^{Me} \qquad (4)$$

The results are presented graphically in Fig. 2 by a diagram of the log p_f^X values against S_f. A more complete analysis of the data is provided through an examination of the observations by eq. 4, Table III.

TABLE III

LOGARITHMIC RATIOS AND SIGMA CONSTANTS FOR *para* SUBSTITUTION IN THE HALOBENZENES

Substituent	n^a	$\left[\frac{\log p_f^+}{\log p_f^{Me}}\right]^b$	σ^+_{m-X} Subst.[c]	σ^+_{m-X} Solv.[d]
p-F	13	0.069 ± 0.139	-0.021 ± 0.048	-0.073
p-Cl	12	$-.409 \pm .166$	$.126 \pm .052$	.114
p-Br	13	$-.481 \pm .179$	$.149 \pm .055$	.150
p-I	6	$-.432 \pm .274$	$.134 \pm .084$	.135

[a] Number of reactions. [b] Based on eq. 4. [c] Based on eq. 4 with σ^+_{p-Me} -0.31, ref. 25. [d] Ref. 25.

Consideration of the results for *p*-Cl and *p*-Br indicates the agreement of the data with the predictions of the Selectivity Relationship (3) is equivalent to that obtained for the *m*-halogens. The graphical evaluation of the results, Fig. 2, reveals the reactions involving the replacement of hydrogen are correlated with good precision by the relationship. The reactions involving the rupture of carbon–metalloid bonds exhibit serious, but apparently random, variations. For *p*-Cl the ratio, log p_f^{Cl}/log p_f^{Me}, is -0.319 ± 0.065 for seven hydrogen replacements but increased to -0.534 ± 0.157 for five cleavage studies. The results are, as yet, too meager to yield a final test of this point. As has been pointed out by Eaborn and Pande,[22] the nature of the transition state for the breaking of carbon–hydrogen and carbon–metal bonds may prove to be fundamentally different.

The results for the *p*-iodo substituent yield an even greater scatter than observed for *p*-Cl and *p*-Br groups. The limited data now available do not allow a test of the Selectivity treatment. Even more unfortunate has been the failure to examine the consequences of the observation that the cleavage of the carbon–iodine bond is competitive with the substitution reactions.[26]

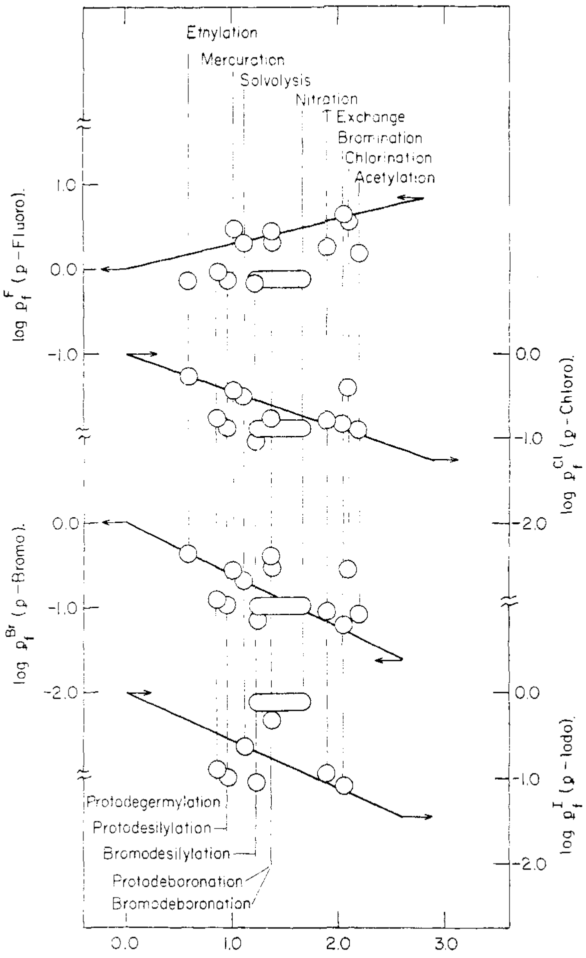

Fig. 2.—Relationship between log p_f^X for *p*-F, *p*-Cl, *p*-Br and *p*-I and the Selectivity factor, S_f. Arrows on the correlation lines indicate the proper ordinate. The guide lines are defined by the S_f-value for each reaction.

The analysis of the data on the basis of eq. 4, Table III, reveals the values of σ^+_{p-Cl}, σ^+_{p-Br} and σ^+_{p-I} obtained on the basis of substitution data to be in agreement with the predictions of the solvolysis of *t*-cumyl chloride.[25]

In contrast to the results for the other halogens, the *p*-fluoro substituent yields relative rate data exhibiting serious deviations from a linear treatment. At first glance, the discrepancies appear far greater than should be tolerated in a simple first-order treatment, Fig. 2. More careful inspection indicates that the absolute magnitude of the average discrepancy is no greater than for the other halogens. It is only the fact that the partial rate factor for *p*-fluoro is so close to unity (log $p_f^F \approx 0$) that causes these discrepancies to appear to be so large in comparison with the data for other substituents.

The situation may be clarified by a slightly different treatment of the data, based on eq. 5.

[26] Several examples of the replacement of I in the course of nitration are discussed by A. F. Holleman, *Chem. Revs.*, **1**, 186 (1924).

$$\log (p_f^{Me}/p_f^{F}) = \frac{\sigma^+_{p-Me} - \sigma^+_{p-F}}{\sigma^+_{p-Me} - \sigma^+_{m-Me}} S_f \qquad (5)$$

Although the data still exhibit considerable scatter (Fig. 3), it is evident that the discrepancies are of the same order of magnitude as those of the other halogens (Fig. 2). A point of particular interest is the randomness of the variations. The electrophilic reactions involving the replacement of hydrogen fall on either side of the line. A similar randomness is found for model substitution reactions in which groups other than hydrogen undergo displacement. There does not appear to be any dependence on rho. In this situation the first-order Selectivity treatment, although subject to the limitations indicated, is as satisfactory as other more complicated analyses.

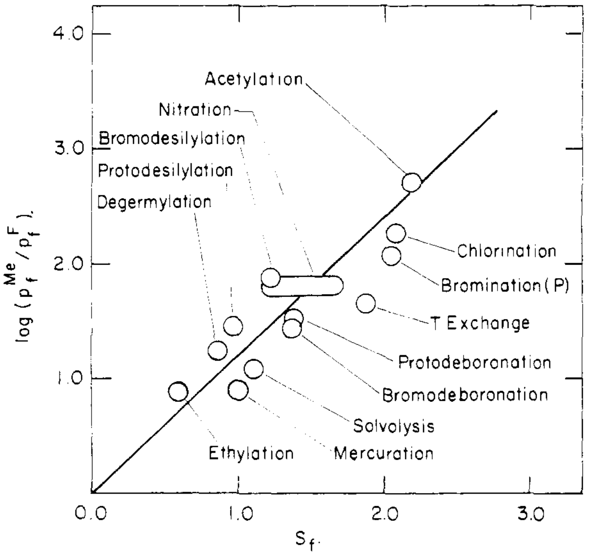

Fig. 3.—Relationship between log (p_f^F/p_f^{Me}) and the Selectivity factor, S_f.

Applicability of First-order Treatments to Aromatic Substitution.—Relevant to the behavior of the halogen substituents is the precision to be expected from a first-order treatment. A previous examination of the utility of the Selectivity Relationship and Hammett equation for the correlation of the data for substitution and side-chain reactions of toluene and tolyl derivatives, respectively, revealed the greater precision of the S_f procedure.[5f] It appeared desirable to re-examine this problem for the halogen substituents. Fortunately, the *p*-chloro substituent had been studied in almost all the reactions which had been employed for the examination of *m*- and *p*-tolyl. The log p_f^{Cl} values obtained for these reactions are plotted against log (p_f^{Me}/m_f^{Me}) in Fig. 4.

From this diagram it is apparent that the deviations encountered in the Selectivity treatment are not significantly different from the observations for the Hammett relationship. Indeed, the deviations from the diagram for *p*-F, Fig. 3, are not substantially greater than observed for *p*-Cl in the side-chain reactions. The limitations of the Hammett equation have recently been pointed out by Wepster and his associates.[27] These investigators have also concluded that the *p*-halogens were subject to considerable variation in their influences on side-chain reactions.

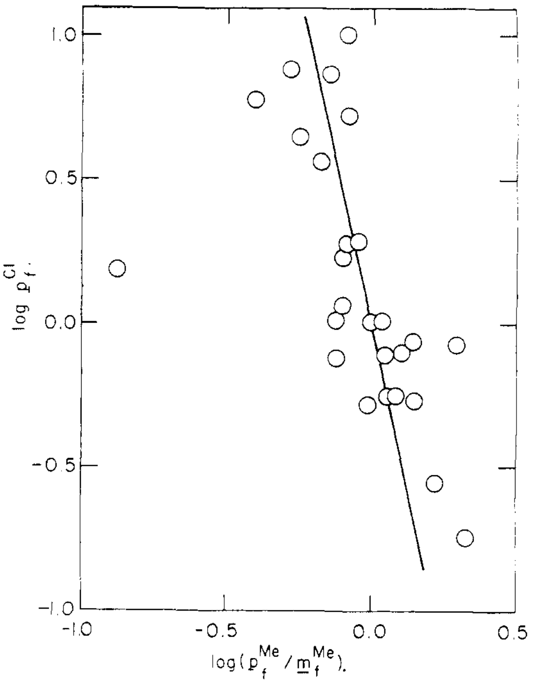

Fig. 4.—Relationship between log p_f^{Cl} and log (p_f^{Me}/m_f^{Me}) for Hammett side-chain reactions.

Two recent attempts have been made to devise a better correlation for the treatment of reactions involving electron-deficient intermediates.[10,12] One theory argues that additional parameters should be added to the $\rho\sigma$ relationship to accommodate greater stabilization by the donor groups.[12] Superior correlations are reported. It is possible that the interpretation presented by Yakawa and Tsuno is meaningful. It is equally possible that the superior correlations achieved are the result of the introduction of two additional parameters.

Norman and his associates have attempted to account for the reactivities of monosubstituted benzenes in terms of a three-parameter equation (6).[10] This relationship was devised as a means

$$\log p_f^X = \sigma_G^X \phi + \sigma_P^X \phi^2 \qquad (6)$$

to relate the reactivity of a substituent to its ground state electron density, σ_G, and polarization properties, σ_P, with ϕ a measure of the electron demand in the transition state. Data are now available which allow a more complete test of this equation. Adoption of the σ_G and σ_P values reported[10] permits the calculation of ϕ for several reactions not available to Norman and his co-workers. The results for p_f^{Cl} are typical, Fig. 5.

Although this treatment introduces an additional parameter, the deviations from the predicted correlation line appear to be even greater than observed in the first-order $\rho\sigma^+$ approach. The failure of the Norman equation to yield a better correlation is presumably the consequence of an incorrect assumption. The view that ρ(ϕ in the Norman treatment) is indicative of electron demand is not entirely correct. We had shown previously that

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

the contribution of a *p*-Me group in electrophilic side-chain reactions was variable.[5f] For example, in several solvolytic reactions the ρ-values deduced for *m*-substituents were of similar magnitude. The $\sigma^{+}_{p\text{-Me}}$ values, however, exhibited almost 2-fold variation.[28] Behavior of this nature is not considered in the Norman approach. Yukawa and Tsuno, on the other hand, specifically provide for this effect and introduce their third and fourth parameters to account for it.

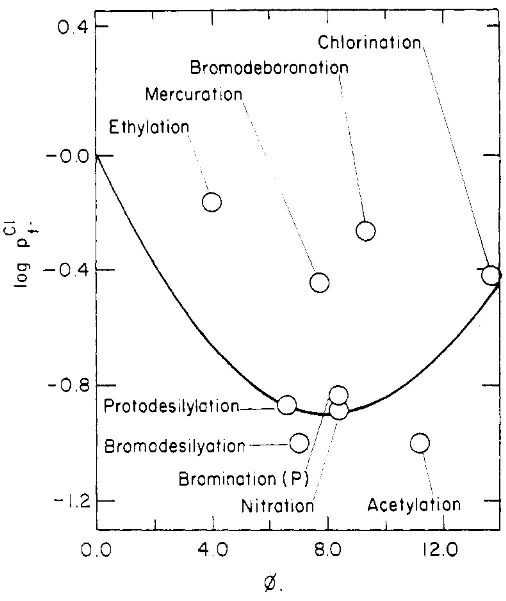

Fig. 5.—Relationship between log p_f^{Cl} for substitution reactions and ϕ, the electron-demand constant. The solid line is predicted by the σ_G- and σ_P-constants assigned to the *p*-chloro substituent, ref. 10.

Apparently, there are limitations in the utility of a first-order treatment for electrophilic side-chain reactions which are not encountered in substitution reactions. Although random deviations from the Selectivity Relationship are found, this treatment yields reasonably satisfactory correlations. Several suggestions have been made concerning the origin of the deviations. For example, the consequences of changes in the nature of the transition state for carbon–metal bond rupture apparently lead to real deviations for certain substituents. The involvement of the properties and stabilizing factors important in π-complexes in the activated complex for the substitution process has been suggested previously. In addition to these influences, specific interactions between substituent groups in the aromatic nucleus and electrophilic reagents are also frequently significant.[29] The rather large deviations exhibited in the non-catalytic chlorination reaction are probably the result of such interactions. For iodobenzene, the association is sufficiently important to lead to bond rupture and the formation of iodobenzene dichloride. The halo substituents interact with acceptor molecules in the order I > Br > Cl > F.[29] It is pertinent that the chlorination reaction exhibits a larger deviation for bromobenzene than for chlorobenzene and no deviation for fluorobenzene. The increase in reactivity detected for *p*-Br and *p*-Cl is presumably the consequence of a mild polarization of the reagent and the aromatic. In contrast to the results for the chlorination reaction, study of the bromination of the polymethylbenzenes yields partial rate factors in good agreement with the predictions of the Selectivity treatment. The apparent unimportance of an association between bromine and the substituent halogens in the polymethylbenzenes[14] is considered to originate in the well-known sensitivity of charge transfer complexes to steric effects. It is our suggestion that the importance of the association is considerably reduced by the methyl groups flanking each halo substituent. This interruption of the association provides results in fine agreement with expectations of the relationship.

In conclusion, the application of a first-order linear free energy treatment to substitution reactions appears to be reasonably satisfactory for a variety of substituent groups. For the *p*-halogens, the scatter is somewhat greater than encountered for other substituents. We suggest these observations are largely the consequence of molecular interactions leading to variations in the energy of the transition state. Clearly these factors which are important in the detailed understanding of reactivity cannot be incorporated into any free energy treatment. This reservation does not detract significantly from the utility of the simple first-order Selectivity Relationship.

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(28) This problem has been examined for several α-substituted benzyl halides; Y. Okamoto, Ph.D. Thesis, Purdue University, 1957.

(29) L. J. Andrews, *Chem. Revs.*, **54**, 750 (1954).