regarding the hydration of isobutylene. There are several kinds of information which are not parallel in the two systems. These are: the difference in the Gross–Butler correlation, the difference in entropies of activation, and the difference in the solvent isotope effect. It appears to the present authors that these differences may possible be explicable in terms of the differences in structure and stability of the reacting organic molecule and the resulting unstable intermediates, rather than in terms of different mechanisms. These points will need further study.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Rate Data and Isomer Distribution in the Reactions of the Halobenzenes with Mercuric Acetate in Acetic Acid. Partial Rate Factors for the Mercuration Reaction[1–3]

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The rate constants and isomer distributions for the mercuration of fluorobenzene with mercuric acetate have been determined at 90, 70 and 50°. The product distribution at 90° is 59.4% *p*-, 6.9% *m*- and 33.7% *o*-; at 70°, 62.7% *p*-, 4.8% *m*- and 32.5% *o*-; at 50°, 66.7% *p*, 3.3% *m*- and 30.0% *o*-fluorophenylmercuric acetate, respectively. Utilizing earlier data for the mercuration of benzene under these conditions, the partial rate factors at 25° are calculated: p_f^F 2.98, m_f^F 0.040, o_f^F 0.63. These results indicate a small activation of the *para* position and a strong deactivation of the *meta* position. Because of the major side-reaction of mercuric acetate with the solvent, it was necessary to determine the reactivities of chlorobenzene and bromobenzene relative to benzene by a competitive procedure. At 90° the relative rates, $k_{ClC_6H_5}/k_{C_6H_6}$ and $k_{BrC_6H_5}/k_{C_6H_6}$ are 0.090 and 0.080, respectively. The isomer distribution for the mercuration of chlorobenzene at 90° is 48.4% *p*-, 21.5% *m*- and 30.1% *o*-; whereas bromobenzene yields 46.0% *p*-, 25.8% *m*- and 28.2% *o*-. The data were utilized to calculate the partial rate factors at 25°: chlorobenzene, p_f^{Cl} 0.36, m_f^{Cl} 0.060 and o_f^{Cl} 0.075; bromobenzene, p_f^{Br} 0.27, m_f^{Br} 0.054, o_f^{Br} 0.070. The results reveal a deactivation of all positions, least in the *para*. The order of reactivity in the *para* position is F > H > Cl > Br. In the *meta* position a different order is observed, H > Cl $\simeq$ Br > F. The available data on the mercuration of monosubstituted benzene derivatives are assembled and examined. An excellent linear free energy correlation is obtained for the substitution data with the electrophilic substituent constants, σ^+, based on the solvolysis of the *t*-cumyl chlorides.

Introduction

The utility of the Selectivity Relationship[4] in correlating the available data for the substitution of aromatics has now been examined for a number of systems containing activating groups: toluene,[5] *t*-butylbenzene,[6] anisole,[7] biphenyl[8] and fluorene.[8]

Satisfactory correlations were achieved with toluene,[5f] *t*-butylbenzene[6d] and anisole.[7b] However, biphenyl exhibited a serious deviation.[8e] This deviation was attributed to a unique consequence of the biphenyl ring system. It was postulated that a steric energy barrier to coplanarity in the transition state was an important factor in the reactivity of biphenyl. It was argued that this energy barrier was, in part, overcome in electron-demanding reactions resulting in decreased and variable contributions by the *p*-phenyl substituent. In support of this interpretation, the limited data for the planar fluorene system appeared to give a reasonably good correlation with the Selectivity Relationship.[8e]

Alternative interpretations have been suggested. Thus the failure to achieve a satisfactory linear relationship with biphenyl has been attributed to the conflicting inductive and electromeric influences of the phenyl substituent.[9] Consequently, it appeared desirable to extend these investigations and to examine the substituent effects of groups exhibiting large electron-withdrawing inductive effects and equally important electromeric contributions. The halobenzenes are ideally suited for this purpose.

The results for the mercuration of the halobenzenes are summarized in the present paper. Data for the ethylation,[10a] acylation,[10b] and halogenation[10c] are presented in the following papers of this group. In the final paper,[10d] the applicability of the Selectivity Treatment to the available substitution data for the halobenzenes is examined.

Results

Fluorobenzene.—The rate of mercuration of fluorobenzene by mercuric acetate in glacial acetic acid was determined by following the decrease in mercuric acetate concentration titrimetrically with standard thiocyanate solution. A large excess of

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(1) Directive Effects in Aromatic Substitution. L.

(2) This research was supported 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) Based upon a thesis submitted by Gordon Goldman in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) (a) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953); (b) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955); (c) 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. Bolton, *ibid.*, **81**, 3320 (1959); (f) L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(6) (a) H. C. Brown and M. Dubeck, *ibid.*, **81**, 5608 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959); (c) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5613 (1959); (d) **81**, 5621 (1959).

(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. H. 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) For a discussion and leading references, J. R. Knowles, R. O. C Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(10) (a) H. C. Brown and A. Neyens, *J. Am. Chem. Soc.*, **84**, 1655 (1962); (b) H. C. Brown and G. Marino, *ibid.*, **84**, 1658 (1962); (c) L. M. Stock and F. W. Baker, *ibid.*, **84**, 1661 (1962); (d) L. M. Stock and H. C. Brown, *ibid.*, **84**, 1668 (1962).

aromatic, 1.0 *M*, was utilized to avoid significant incursion of polymercuration by the mercuric acetate, 0.10 *M*. The data yielded a first-order rate constant, which was the sum of the first-order rate constants for the reaction of mercuric acetate with the fluorobenzene and with the solvent. In contrast to the case for the more reactive aromatics, this side-reaction was quite important in kinetic runs with fluorobenzene. It represented approximately 40% of the total mercuric acetate consumed. Accordingly, the known first-order rate constant for the reaction of mercuric acetate with acetic acid was subtracted from the observed first-order constant to obtain the true first-order rate constant for the mercuration of fluorobenzene. Division of this quantity by the average value of the fluorobenzene concentration over the reaction period provided the second-order rate constant for the mercuration of fluorobenzene.

At 25° the rate of the reaction is too slow to be followed conveniently. Therefore the rates were measured at 90, 70 and 50°. The rate data are summarized in Table I.

TABLE I

RATES OF REACTION OF BENZENE AND FLUOROBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	Rate constant, $10^5 k_2$, l. mole^{-1} sec.$^{-1}$		Relative rate
	Fluorobenzene	Benzene[a]	
90.0	1.80	3.42	0.526
70.0	0.303	0.565	.536
50.0	.0470	.075	.627
25.0	.00290[b]	.00413[b]	.702

[a] Ref. 11. [b] Calculated from data at other temperatures.

The isomer distribution was determined for reaction conditions similar in all respects to those employed for the kinetic measurements. The reaction mixtures were quenched at appropriate time intervals in an equal volume of water. The isomeric fluorophenylmercuric acetates were precipitated quantitatively as the insoluble bromides and converted to the corresponding isomeric bromofluorobenzenes by treatment with bromine. The proportions of the isomeric bromofluorobenzenes present in the reaction products were established by means of gas chromatography. The results are summarized in Table II.

TABLE II

ISOMER DISTRIBUTIONS IN THE MERCURATION OF FLUOROBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	Isomer distribution, %		
	ortho-	*meta-*	*para-*
90.0	33.7	6.9	59.4
70.0	32.5	4.8	62.7
50.0	30.0	3.3	66.7
25.0	28.7[a]	1.8[a]	69.5[a]

[a] Calculated from rate constants and isomer distributions at higher temperatures.

The observed rate data, Table I, and the isomer distributions, Table II, were employed to calculate the partial rate constants for each temperature. These partial rate constants were utilized to evaluate the energies, heats and entropies of activation. Knowledge of the activation parameters permitted the evaluation of the partial rate constants and the total rate constant at 25°. These data are summarized in Table III. The partial rate constants were also utilized to calculate the isomer distribution at 25°, reported in Table II.

Chlorobenzene.—In the mercuration of fluorobenzene, the side reaction between mercuric acetate and acetic acid represented only 40% of the total reaction (see Table VIII, Experimental Part). In the slower mercuration of chlorobenzene the side-reaction with solvent represented 80% of the total reaction. The rate constant observed at 90° was 0.37×10^{-5} l. mole^{-1} sec.$^{-1}$ providing the relative rate, chlorobenzene to benzene, as 0.108. However, little confidence could be placed in this result because of the very large side reaction. Accordingly, it was decided to determine the reactivity of chlorobenzene relative to benzene by a competitive method. Chlorobenzene, 0.80 *M*, and benzene, 0.20 *M*, in acetic acid were mercurated, the arylmercuric bromides precipitated as in the determination of the isomer distributions, and the product treated with bromine to form bromobenzene and a mixture of the three isomeric bromochlorobenzenes.

Gas chromatographic analysis provided both the relative rate of reaction and the isomer distribution. The relative rate, chlorobenzene to benzene, obtained in this manner was 0.090. The agreement with the less precise relative rate, 0.108, obtained by the direct measurement is reasonable. The isomer distribution observed was 30.1% *o*-, 21.5% *m*- and 48.4% *p*-chlorophenylmercuric acetate.

In order to obtain the relative rate and the isomer distribution at 25°, we decided to rely on our observation that the entropies of activation for the mercuration reaction have exhibited a remarkable constancy.[12] Accordingly, an average value $\Delta S^{\ddagger}$ -24.0 e.u. was adopted and both the rate at 25° and the partial rate constants at that temperature were calculated. The relative rate and isomer distribution at 25° obtained on the basis of these approximations are summarized in Table IV.

Bromobenzene.—The mercuration of bromobenzene proceeded at a rate even slower than that of chlorobenzene. Accordingly, here also the reactivity was established at 90° by means of the competitive technique. The relative rate and isomer distribution at 25° were calculated by assuming a constant entropy of activation of -24.0 e.u.[12] The results are summarized in Table IV.

Discussion

Effect of the Halogen Substituents.—The halogen substituents in aromatic systems have long constituted a difficult problem for quantitative treatment.[13,14] On the one hand, the relative electronegativities of the halogens[15] predict that they should exhibit an electron-withdrawing effect which would decrease with increasing atomic weight

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(11) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2306, 2310 (1955).

(12) See ref. 8a for a discussion of this point.

(13) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); J. W. Baker and H. B. Hopkins, *ibid.*, 1089 (1948).

(14) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 733 ff.

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

TABLE III

PARTIAL RATE CONSTANTS AND DERIVED KINETIC DATA FOR THE MERCURATION OF BENZENE AND FLUOROBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Compound	Partial rate constant k_2, l. mole^{-1} sec.$^{-1}$ × 10^6 25.0°	50.0°	70.0°	90.0°	$\Delta E_{act.}$, kcal. mole^{-1}	log A	$\Delta H^{\ddagger}$, kcal. mole^{-1}	$\Delta S^{\ddagger}$, cal. deg.$^{-1}$
Benzene[a]	0.00688	0.125	0.943	5.70	22.2	8.12	21.6	−23.6
Fluorobenzene								
ortho[a]	.00423	.070	.493	3.03	22.0	7.72	21.3	−25.5
meta[a]	.00026	.0078	.073	0.60	25.2	8.95	24.6	−19.8
para	.0205	.315	1.90	10.7	20.6	7.65	20.0	−26.0
Benzene[b]	.0413	.750	5.65	34.2	22.2	8.91	21.6	−19.6
Fluorobenzene[c]	.0290	.470	3.03	18.0	21.3	8.06	20.6	−24.0

[a] One position. [b] For all six positions. [c] For all positions—total rate constant.

TABLE IV

RELATIVE RATE AND ISOMER DISTRIBUTION FOR THE MERCURATION OF CHLOROBENZENE AND BROMOBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Benzene	Temp. °C.	Relative rate	Isomer distribution, % *ortho*-	*meta*-	*para*-
Chloro-	90.0	0.090[a]	30.1	21.5	48.4
	25.0	.100[b]	25.1[b]	17.9[b]	57.0[b]
Bromo-	90.0	.080	28.2	25.8	46.0
	25.0	.090[b]	26.6[b]	22.4[b]	51.0[b]

[a] A value of 0.108 was realized in a direct determination of the second-order rate constant. [b] Calculated from the data at 90.0° and assuming $\Delta S^{\ddagger}$ −24.0 e.u.; see ref. 8a.

TABLE V

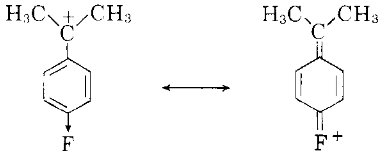
PARTIAL RATE FACTORS FOR THE HALOGEN SUBSTITUENTS FOR THE MERCURATION REACTION AND THE *t*-CUMYL SOLVOLYSIS

	Partial rate factors					
	Mercuration (25°)			*t*-Cumyl solvolysis (25°)		
Halogen	o_f	m_f	p_f	o_f	m_f	p_f
Fluoro	0.63	0.040	2.98	0.0502	0.0251	2.14
Chloro	.075	.060	0.36	.00786	.0156	0.305
Bromo	.070	.054	.27	.00607	.0144	.208
Iodo				.0100	.0233	.244

F > Cl > Br > I. However, this order is rarely observed. Presumably, the conjugative capacity is greatest for fluorine and decreases with increasing atomic weight. It was pointed out by Dippy and Lewis that any order, from F > Cl > Br > I, to the opposite order, F < Cl < Br < I, could be realized by a judicious combination of these two opposing effects.[16]

To facilitate the discussion, the partial rate factors for the mercuration of the halobenzenes and for the solvolysis of the halo-*t*-cumyl chlorides[17] are summarized in Table V.

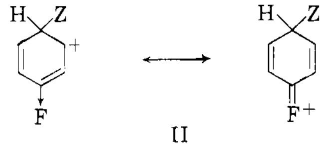
With one exception, *p*-fluoro, the halogen substituents deactivate the ring toward mercuration and depress the rate of solvolysis of the *t*-cumyl chlorides. In the solvolysis reaction, *p*-fluoro exhibits a slight activating effect (p_f 2.14). This had been attributed to resonance stabilization of the electron-deficient transition state, approximated in I by the carbonium ion.



I

Similarly, in the mercuration reaction *p*-fluoro exhibits a slight activating effect (p_f^{F} 2.98). Here also the electron-deficient transition state, represented by the intermediate σ- complex, is stabilized by electron-density provided by the *p*-fluoro substituent (II).

The effects of *p*-chloro and *p*-bromo parallel each other in the two reactions under discussion. Although there is a modest deactivation observed, the effect is much less than for the *meta* position. The results are consistent with the proposal that the conjugative contributions of both *p*-chloro and *p*-bromo substituents in these reactions are significant, but fail to overcome their greater inductive contributions.



II

In the *meta* positions the inductive contributions are larger and the opposing conjugative contributions are much smaller.[18] Consequently, all of the halogens exhibit a strong deactivating effect in the *meta* position, with only minor variations among the individual substituents.

Interesting differences are revealed between the two reactions in the *ortho* position. It is evident that *t*-cumyl solvolysis is much more sensitive to the steric requirements of the substituent in the *ortho* position than is the mercuration reaction. However, the topic is not pertinent to the objectives of the present investigation and a detailed discussion of the phenomena will be deferred.

Correlation of the Mercuration Data.—With completion of the present study, partial rate data for mercuration by mercuric acetate in glacial acetic acid have been obtained for 16 different *meta* and *para* substituents. It appears appropriate at this time to examine the utility of the electrophilic substituent constants, largely derived from the solvolysis of *t*-cumyl chlorides[19] for the correlation of the data. The partial rate factors are summarized in Table VI.

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(16) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 649 (1936).

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

(18) Such conjugative contributions are believed to operate by increasing the electron-density in the *ortho* positions, where the effect is then relayed to the reaction center by induction. See discussion, ref. 17, and the following paper.

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

TABLE VI

PARTIAL RATE DATA FOR THE MERCURATION OF SUBSTITUTED BENZENES WITH MERCURIC ACETATE IN GLACIAL ACETATE ACID AT 25.0°

Substituent	Relative rate	Isomer distribution, %			Partial rate factors			Ref.
		ortho	*meta*	*para*	o_f	m_f	p_f	
Methoxy	448	14.0	0	86.0	188		2310	[a]
Acetamido	46.1			(100)[f]			277	[a]
Phenoxy	64.8			(100)[f]			194	[a]
(Fluorene)[g]	51.1			80			122	[b]
Methyl	6.54	29.4	11.5	59.1	5.77	2.26	23.2	[c]
t-Butyl	4.00	0.0	28.4	71.6	0.0	3.41	17.2	[d]
Phenyl	2.71	2.0	19	79	0.08	0.77	6.42	[b]
Hydrogen[h]	1.00				1.00	1.00	1.00	[c]
Fluoro	0.702	28.7	1.8	69.5	6.30	0.040	2.98	[e]
Chloro	.100	25.1	25.8	46.0	0.075	.060	0.36	[e]
Bromo	.090	26.6	22.4	51.0	0.070	.054	0.27	[e]

[a] Ref. 7a. [b] Ref. 8a. [c] Ref. 11. [d] Ref. 6*a*. [e] Present study. [f] Assumed 100% substitution in *para* position. [g] Substitution of fluorene in 2-position. [h] Rate constant for benzene at 25.0°: 0.0413×10^{-6} l. mole^{-1} sec.$^{-1}$.

It is evident from Fig. 1 that an excellent correlation is realized for the relative rate data with the electrophilic substituent constant, σ^+. The reaction constant, ρ, for mercuration is calculated to be −4.00. Mercuration appears to yield data which are correlated with excellent precision by the σ^+-constants. The utility of these constants in correlating the available data for the ethylation,[10a] acetylation,[10b] bromination[10c] and chlorination[10c] reactions will be examined in the following papers of this group.

Experimental Part

Materials.—The halobenzenes were commercial products, purified by distillation through a packed column rated at 60 theoretical plates. They exhibited the following properties: fluorobenzene, b.p. 85.0° at 740 mm., $n^{20}\text{D}$ 1.4670; chlorobenzene, b.p. 131° at 745 mm., $n^{20}\text{D}$ 1.5246; bromobenzene, b.p. 155° at 745 mm., $n^{20}\text{D}$ 1.5597. The absence of significant impurity was indicated by gas chromatography.

Mercuric acetate (Mallinckrodt analytical reagent) was used as the mercurating agent. Glacial acetic acid (Baker and Adamson reagent grade) was employed as the solvent medium. It had been previously demonstrated that minor variations in the water content did not influence the rates significantly.[6a]

The isomeric bromohalobenzenes used in the isomer distribution and relative rate measurements were commercial samples purified in a similar fashion to the halobenzenes. They possessed the following physical properties: *o*-bromofluorobenzene, b.p. 149° at 746 mm., $n^{20}\text{D}$ 1.5345; *m*-bromofluorobenzene, b.p. 57° at 22 mm., $n^{20}\text{D}$ 1.5280; *p*-bromofluorobenzene, b.p. 150° at 750 mm., $n^{20}\text{D}$ 1.5275; *o*-bromochlorobenzene, b.p. 197° at 750 mm., $n^{20}\text{D}$ 1.5810; *m*-bromochlorobenzene, b.p. 196° at 750 mm., $n^{20}\text{D}$ 1.5760; *p*-bromochlorobenzene, m.p. 67.0°; *o*-dibromobenzene, b.p. 97° at 8 mm., $n^{20}\text{D}$ 1.6107; *m*-dibromobenzene, b.p. 66° at 5 mm., $n^{20}\text{D}$ 1.6072; *p*-dibromobenzene, m.p. 89.5°. The purity of these compounds was checked by gas chromatography on a tricresyl phosphate column employing the conditions used in the determination of the isomer distributions. The data on the conditions utilized for the analyses and the observed retention times are summarized in Table VII.

TABLE VII

RETENTION TIMES OF BROMOHALOBENZENES[a]

Benzene	Temp., °C.	Retention times, min.		
		ortho	*meta*	*para*
Bromofluoro-	102[b]	16.0	10.9	13.0
Bromochloro-	135[c]	21.4	16.0	17.4
Dibromo-	149[d]	26.4	20.2	21.6

[a] Column: 2-meter tricresyl phosphate on Chromosorb. [b] Flow rate: 160 cc. of helium per min. [c] Flow rate: 125 cc. of helium per min.

Rate Measurements for the Mercuration of Fluorobenzene.—Stock solutions of mercuric acetate, 0.150 *M*, and fluorobenzene, 3.00 *M*, were prepared and utilized for the kinetic measurements. In preparing a reaction mixture for the rate measurement, 50.00 ml. of the mercuric acetate solution and 25.00 ml. of the aromatic solution was introduced *via* pipets into the reaction flask, yielding a solution which was 0.100 *M* in mercuric acetate and 1.000 *M* in the aromatic at 25.0°. Ten-ml. samples of the solution were transfered to thin-walled glass bulbs and sealed. The bulbs were placed in a constant temperature bath maintained at the appropriate temperature. Ten minutes was allowed for the solution in the bulb to come to reaction temperature. One bulb was then removed, quickly crushed in ice-water, and the mercuric ion content was determined titrimetrically by means of standard potassium thiocyanate solution. This analysis was taken as the initial mercuric acetate concentration. The rate of reaction was then followed by removing the bulbs at appropriate time intervals and measuring the loss of mercuric ion.

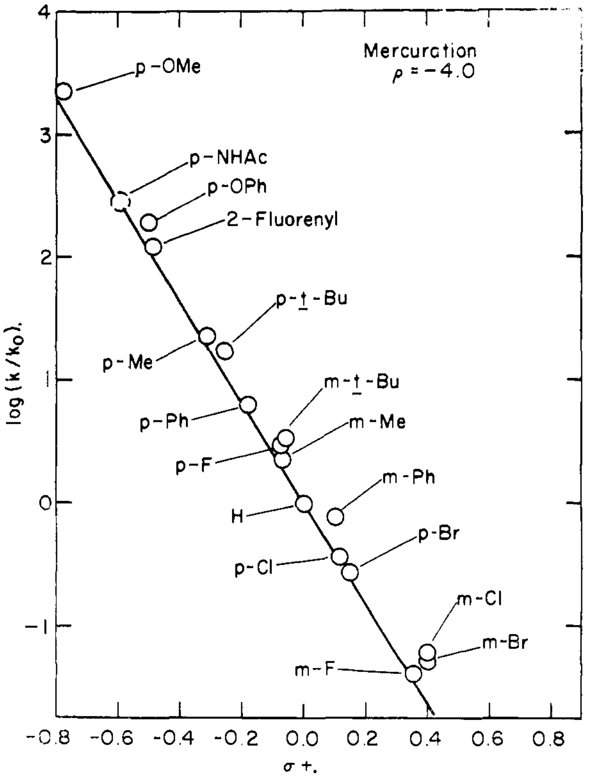

Fig. 1.—Relationship between $\log(k/k_0)$ for mercuration and the σ^+-constants.

First-order rate constants were calculated on the basis of the rate of disappearance of the mercuric acetate. These constants were corrected for the first-order side reaction between mercuric acetate and acetic acid. In the reaction of fluorobenzene with mercuric acetate, the side reaction represented 40% of the total reaction.

Typical data for the reaction of mercuric acetate with fluorobenzene and the solvent are summarized in Tables VIII and IX.

TABLE VIII

TYPICAL DATA FOR THE RATE OF MERCURATION OF FLUOROBENZENE AT 90.0°

Time, min.	Vol. KSCN (0.102 M),^{a} ml.	x^b	$k_1 \times 10^5$,^{c} sec.$^{-1}$
0	19.70	0.000	
90	18.40	.013	2.62
180	17.45	.023	2.40
248	16.80	.030	2.36
306	16.10	.037	2.58
361	15.65	.041	2.45
408	15.20	.046	2.49

[a] Original concentration: [ArH] 1.00 M and [Hg(OAc)$_2$] 0.100 M. [b] Mercuric acetate consumed. [c] Average value of rate constant is $2.47 \pm 0.06 \times 10^{-5}$ sec.$^{-1}$.

Taking the first-order rate constant for reaction with solvent to be 0.90×10^{-5} sec.$^{-1}$,[20] the first-order rate constant for the mercuration of fluorobenzene becomes $2.470 - .90 = 1.57 \times 10^{-5}$ sec.$^{-1}$. Correcting the concentration for the expansion of the solvent at 90° (concentration at 25.0° × 1.04/0.957) and dividing by the average concentration of the aromatic, 0.951 M, the second-order rate constant, 1.80×10^{-5} l. mole^{-1} sec.$^{-1}$, is obtained.

The rate data are summarized in Tables I and III.

Isomer Distribution Measurements on Fluorobenzene.—The reaction mixtures utilized for the isomer distributions were identical in all respects to those employed in the kinetic measurements. The reactions were quenched after approximately 25% of the mercuric acetate was consumed.

In a typical experiment, 25.0 ml. of 3.00 M fluorobenzene in glacial acetic acid and 50.0 ml. of 0.1500 M mercuric acetate were allowed to come to thermal equilibrium and then were quickly mixed. When the reaction had reached approximately 25% completion as calculated from the rate constants, the mixture was quickly cooled and quenched in an equal volume of water. Excess unreacted fluorobenzene was removed by aspiration under vacuum at room temperature and the soluble fluorophenylmercuric acetates were converted into the insoluble bromides by addition of a 2-fold excess of lithium bromide. The bromides were isolated in yields of 95% of the calculated quantity.

TABLE IX

RATE OF MERCURATION OF ACETIC ACID AT 90.0°

Time, min.	Vol. KSCN (0.102 M),^{a} ml.	x^b	$k_1 \times 10^5$,^{c} sec.$^{-1}$
0	19.70	0.000	
220	18.60	.011	0.90
391	17.75	.019	.94
511	17.25	.024	.93
631	16.85	.029	.90
751	16.05	.037	1.03
858	15.55	.043	1.06

[a] Original concentration: [Hg(OAc)$_2$] 1.00 M. [b] Mercuric acetate consumed. [c] Average value of rate constant is 0.96×10^{-5} sec.$^{-1}$.

A sample of the isomeric fluorophenylmercuric bromides, 0.900 g., was suspended in carbon tetrachloride and converted to the isomeric bromofluorobenzenes by careful treatment with a minute excess of bromine. After several hours, the slight excess of bromine was removed by washing with sodium bisulfite solution, followed by water. The carbon tetrachloride solutions were dried and analyzed by gas chromatography (Table VII). The conversion to the isomeric bromofluorobenzenes was quantitative. The experimental results are summarized in Table II.

The Mercuration of Chlorobenzene and Bromobenzene at 90.0°.—The determinations were performed in an identical manner to that described previously for the isomer distribution in fluorobenzene, with one exception. The reaction mixtures were composed of two aromatics: 0.800 M in halobenzene and 0.200 M in benzene. The reactions were determined by the analysis of the residual mercuric acetate.

The arylmercuric acetates were converted to the bromides and then treated with bromine. The relative rate was based upon the analysis of the relative amounts of bromobenzene and bromohalobenzene present in the reaction mixture. External standards were employed to establish the concentrations of the haloaromatics. The same reaction mixtures were utilized for the isomer distribution. The experimental results are summarized in Table IV.

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[20] This value is an average of a number of determinations by C. W. McGary, Jr., M. Dubeck and G. Goldman.