influence of the *p*-fluoro substituent in ethylation.[7b] A more detailed discussion is reserved for the final paper.[7d]

Correlation of the Acetylation Data.—Data have now been obtained for 11 *para* substituents and 5 additional *meta* groups covering a broad range of reactivity. It is of interest at this time to test a correlation of these data against the set of electrophilic substituent constants, σ^+, based upon the solvolysis of substituted *t*-cumyl chlorides.[23] The data are summarized in Table III.

The linear relationship between $\log(k/k_0)$ and σ^+ is illustrated in Fig. 1.

Experimental Part

Materials.—Aluminum chloride, acetyl chloride and ethylene dichloride were purified as described previously.[3,24,25] The halobenzenes were commercial products distilled through an efficient column: fluorobenzene, b.p. 83.9–84.2° at 751 mm., n^{20}_D 1.4666; chlorobenzene, b.p. 130.7–130.8° at 745 mm., n^{20}_D 1.5244; bromobenzene, b.p. 154° at 748 mm., n^{20}_D 1.5595.

p-Chloroacetophenone was synthesized in 85% yield,[26] converted to the semicarbazone, and the latter was recrystallized to constant m.p. 200–200.5°.[27] The ketone was regenerated by heating with hydrochloric acid.[28] The product exhibited the constants: b.p. 84–85.5° at 3 mm., n^{20}_D 1.5555, m.p. 19°.[27] *m*-Chloroacetophenone was a sample available from an earlier synthesis by Mr. T. Kawanami (methylcadmium chloride and *m*-chlorobenzoyl chloride): b. p. 102.5–103.5° at 10 mm. Similarly, *p*-bromo- and *p*-fluoroacetophenone were available from earlier studies.

Relative Rates.—The procedure utilized for the relative rate studies was essentially that developed earlier for determining the toluene to benzene reactivity ratio.[3] After the reaction mixture had been quenched, *p*-nitroanisole was added as an internal standard. Calibration curves were constructed for synthetic mixtures of *p*-nitroanisole and the acetophenones. The concentrations of the ketones were determined by comparison of the area of the product peaks with the area of the internal standard peak. The results are summarized in Table I.

---

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

(24) H. C. Brown and F. R. Jensen, *ibid.*, **80**, 2291, 2296 (1958).

(25) F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959).

(26) R. Adams and C. R. Noller, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 109–111.

(27) A. Wahl and J. Rolland, *Ann. chim.*, [10] **10**, 27 (1928), reported m.p. 200–201°, m.p. *p*-chloroacetophenone 20–21°.

(28) L. I. Smith and J. E. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Rates and Isomer Distributions in the Non-catalytic Chlorination of the Halobenzenes and Certain Halotoluenes in Aqueous Acetic Acid. Partial Rate Factors for the Halogenation of the Halobenzenes[1]

BY LEON M. STOCK AND FRANK W. BAKER[2]

RECEIVED NOVEMBER 10, 1961

The non-catalytic chlorination of the halobenzenes and certain halotoluenes has been examined in an acetic acid solvent containing 20.8 *M* H_2O and 1.2 *M* HCl at 25°. The relative rates of chlorination established are benzene, 1.00; fluorobenzene, 0.74; chlorobenzene, 0.10; bromobenzene, 0.072. The isomer distributions found for reaction under kinetic conditions were 10.9% *o*- and 89.1% *p*-chlorofluorobenzene; 32.4% *o*- and 67.6% *p*-dichlorobenzene; 38.6% *o*- and 61.4% *p*-chlorobromobenzene. These observations provide the partial rate factors: o_f^F 0.22, p_f^F 4.0; o_f^{Cl} 0.097, p_f^{Cl} 0.41; o_f^{Br} 0.084, p_f^{Br} 0.31. *meta* Partial rate factors were estimated by an examination of the relative rates and product distributions for the chlorination of *p*-fluoro-, *p*-chloro- and *p*-bromotoluene. The rates relative to benzene adopted as 1.00 were *p*-fluorotoluene, 1.94; *p*-chlorotoluene, 0.51; *p*-bromotoluene, 0.49. The product distributions were found to be 64.2% 2- and 35.8% 3-chloro-4-fluorotoluene; 76.8% 2,4- and 24.2% 3,4-dichlorotoluene; 86.3% 2- and 13.7% 3-chloro-4-bromotoluene. The m_f-values estimated from rate data were not fully consistent with those predicted from the product ratios. The average m_f-values are m_f^F $5.6 \pm 1.9 \times 10^{-3}$, m_f^{Cl} $2.3 \pm 0.6 \times 10^{-3}$, m_f^{Br} $3.2 \pm 1.6 \times 10^{-3}$. A study of the chlorination of *o*- and *m*-chlorotoluene revealed the rates exhibited a 30% deviation from calculated values. Apparently the additivity principle is not entirely satisfactory for these aromatics. The results for non-catalytic halogenation and bromination by hypobromous acid are summarized and examined for adherence to a first-order $\rho\sigma^+$ treatment. The correlations obtained are indicative of the utility of the σ^+-constants.

Introduction

The influences of the halogens on reactivity have presented a difficult test of theory. A most salient observation was made by Dippy and Lewis[3] who pointed out the combination of the electron-withdrawing inductive effect with the electron-donating resonance effect could lead to any order of reactivity of the four halogens. The information available in the literature suggested the inductive effect was dominant in aliphatic compounds.[4] On the other hand, reactions involving the development of an electron-deficient transition state revealed the resonance contributions of the halogens to be considerable.[5]

Few quantitative studies of the electrophilic substitution reactions of the halobenzenes have been reported. An examination of the data for the halogenation indicated several deficiencies. The most pertinent study, an investigation of the chlorination in 80% acetic acid, was carried out in 1948.[6] Unfortunately, the relative rates for the halobenzenes compared to benzene in the chlorination reaction were based on an estimated rate constant for benzene under the conditions adopted. Further, the product ratios for non-catalytic chlorination

---

(1) Directive Effects in Aromatic Substitution. LIII. In view of the similar objectives of this study and the efforts of Professor Herbert C. Brown in this area, this report is presented together with the other studies of the substitution reactions of the halobenzenes.

(2) National Science Foundation Summer Fellow, 1961.

(3) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936).

(4) See R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, editor, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 586 ff.

(5) A summary is available for solvolytic reactions; G. Kohnstam, *J. Chem. Soc.*, 2066 (1960).

(6) P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948).

were unestablished.[7] More recently, the influence of the halogen substituents on the bromination reaction has been examined by Illuminati and Marino.[8] Their polymethylbenzene approach yielded relative rates for the *m*- and *p*- halogens which were correlated with excellent precision by the σ^+-constants.[8,9]

In previous work in this Laboratory it had been established that the nuclear chlorination reaction was greatly accelerated in aqueous acetic acid.[10] Under these conditions no major changes in the selectivity of the chlorine molecule were detected. Accordingly, this observation made possible an investigation of the deactivated halobenzenes by selective non-catalytic chlorination. The extent of *meta* substitution in the halobenzenes was small. An estimate of the *meta* partial rate factors was obtained by the determination of the rates and products of the chlorination of the *p*-halotoluenes.

Results

The experimental conditions were selected as representing a balance between a convenient reaction rate and reasonable solubility of the aromatic substrate. Acetic acid containing 20.8 *M* water and 1.20 *M* hydrogen chloride (about 60% acetic acid by volume) was adopted as the reaction solvent. Batches of this solvent could be prepared with reasonable precision. However, the reproducibility of the rate for benzene was checked in each new preparation as a special control.

The reaction of chlorine with the halobenzenes, halotoluenes, benzene and *p*-xylene was followed by iodometric procedures.[10] An attempt to extend the study to iodobenzene was unsuccessful. The addition of chlorine to iodobenzene in solution precipitated iodobenzene dichloride quantitatively.[11]

The second-order rate constants are summarized in Table I. The chlorination reaction obeyed second-order kinetics. However, the rate constants for the chlorination of *p*-bromotoluene exhibited a small acceleration over the course of the reaction. The effect was just beyond the limit of experimental error and appeared to be associated with the exposure of the reaction mixture to air. The rate constants reported in Table I for *p*-bromotoluene are based on the first 40% of the reaction where this influence was negligible.

Variation in the concentration of the aromatic substrate has been shown often to introduce significant change in the determined rate constant. Since concentration changed from 0.005 *M* for reactive *p*-xylene to 0.2 *M* for benzene, it appeared desirable to evaluate the possible intrusion of an important error by this route. In dilute solution, the rate of reaction of chlorine with *p*-chloro- or *p*-bromotoluene was not measurably altered by a 2-fold change in aromatic concentration. For chlorobenzene, however, a 2-fold change from 0.1 to 0.2 *M* reduced the rate by 20%. Competitive studies of the chlorination of fluorobenzene and bromobenzene were undertaken to more fully evaluate the validity of the kinetic relative rates. The findings of three experiments confirming the results of the kinetic approach are summarized in Table II.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR CHLORINATION IN 60% ACETIC ACID[a] AT 24.90°

Compound	Concentration, *M* [ArH]	Concentration, *M* [Cl$_2$]	$10^3 k_2$, l. mole^{-1} sec.$^{-1}$	Relative rate[b]
p-Xylene	0.00402	0.00295	10,500 ± 200	2.3×10^3
	.00402	.00337	12,400 ± 600	
Benzene	.225	.0127	4.82 ± 0.15	1.00
	.225	.0145	5.00 ± .14	
	.225	.0099	5.13 ± .04	
Fluorobenzene	.235	.0141	3.68 ± .09	0.736
	.235	.0359	3.68 ± .06	
Chlorobenzene	.0983	.0200	0.506 ± .045	0.100
	.0983	.0206	.512 ± .044	
	.0979	.0408	.507 ± .013	
	.0991	.0425	.504 ± .002	
	.121	.0574	.482 ± .009	
	.0845	.0372	.503 ± .026	
	.235	.0397	.415 ± .004	
Bromobenzene	.0942	.0322	.319 ± .008	0.0724
	.0942	.0213	.358 ± .005	
	.0756	.0283	.397 ± .007	
	.0757	.0102	.375 ± .008	
o-Chlorotoluene	.0481	.0258	3.36 ± .05	0.686
	.0481	.0182	3.41 ± .20	
	.0481	.0362	3.46 ± .15	
	.0481	.0347	3.50 ± .29	
m-Chlorotoluene	.0728	.0471	194 ± 2.00	38.2
	.0728	.0361	189 ± 5.0	
	.0750	.0400	191 ± 6.0	
p-Chlorotoluene	.0836	.0222	2.25 ± 0.13	0.508
	.0493	.0185	2.49 ± .05	
	.0493	.0217	2.58 ± .07	
	.0493	.0196	2.55 ± .05	
p-Fluorotoluene	.0477	.0224	10.3 ± .02	1.94
	.0535	.0258	9.49 ± .03	
	.0535	.0247	9.31 ± .03	
p-Bromotoluene	.0260	.0159	2.57 ± .02	0.494
	.0260	.0139	2.64 ± .02	
	.0458	.0318	2.32 ± .07	
	.0420	.0297	2.34 ± .09	

[a] Solvent composition: 20.8 *M* H_2O, 1.2 *M* HCl. [b] Based on average second-order rate constant. Not all rate measurements included in average are reported in the table.

TABLE II

COMPETITIVE CHLORINATION OF FLUOROBENZENE AND BROMOBENZENE IN 60% ACETIC ACID[a] AT 25°

Concentration, *M* Initial [C_6H_5F]	Concentration, *M* Initial [C_6H_5Br]	Concentration, *M* Final [ClC_6H_4F]	Concentration, *M* Final [ClC_6H_4Br]	Relative rate[b] k_F/k_{Br}
0.0192	0.0509	0.0119	0.0036	13.5 ± 1.6
.0291	.0271	.0141	.0016	10.6 ± 0.8
.0160	.0843	.0085	.0044	13.2 ± 1.3
			Mean value	12.4 ± 1.2

[a] Solvent composition, 20.8 *M* H_2O, 1.2 *M* HCl. [b] Fluorobenzene to bromobenzene, average of three analyses by vapor phase chromatography.

The product ratios were examined in order to ascertain the positional rates. Kinetic conditions were adopted with the further provision that the aromatic to chlorine ratio was maintained sufficiently high to obviate disubstitution. Gas chromatographic analysis indicated that products of disubstitution were not present. Yields about 95% of theory were obtained as indicated by the use of an internal standard. The products of the chlorination of chloro- and bromobenzene were determined by chromatography on tricresyl phosphate liquid phase. The *ortho* and *para* isomers were easily re-

---

[7] The isomer distribution for the chlorination of fluorobenzene in acetic acid is reported to be 10% *o*- and 90% *p*-chlorofluorobenzene in a footnote; P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

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

[9] H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

[10] L. M. Stock and A. Himoe, *ibid.*, **83**, 1937 (1961).

[11] R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 277 (1958).

solved. No *meta* isomer was detected. The conditions used for these analyses were not completely satisfactory for fluorobenzene. A more expedient method was selected. The isomeric chlorofluorobenzenes were separated from the reaction mixture by gas chromatography and analyzed by infrared spectroscopy.

The isomer distributions established for the halobenzenes are summarized in Table III.

TABLE III

ISOMER DISTRIBUTIONS FOR THE NON-CATALYTIC CHLORINATION OF THE HALOBENZENES IN 60% ACETIC ACID AT 25°

Compound	Isomer distribution, %	
	ortho	*para*
Fluorobenzene	9.8	90.2
	11.9	88.1
Mean value	10.9 ± 1.8	89.1 ± 1.8
Chlorobenzene	31.8	68.2
	33.0	67.0
Mean value	32.4 ± 0.6	67.6 ± 0.6
Bromobenzene	38.5	61.5
	40.5	59.5
	37.3	62.7
	38.2	61.8
Mean value	38.6 ± 0.9	61.4 ± 0.9

The difficult analysis for the *meta* isomer in the presence of large amounts of the *ortho* and *para* products led us to attempt to estimate the *meta* partial rate factor indirectly. For this purpose, the relative rates and product distributions for the chlorination of 4-substituted toluenes were examined. The kinetic observations are presented in Table I. The product distributions for monochlorination as assessed by gas chromatography are summarized in Table IV.

TABLE IV

PRODUCT DISTRIBUTION FOR THE NON-CATALYTIC CHLORINATION OF 4-HALOTOLUENES IN 60% ACETIC ACID AT 25°

Toluene	Product distribution		
	2-Chloro-	3-Chloro-	Tri-[a]
4-Fluoro	63.9	36.1	3.2
	64.5	35.5	3.8
	64.3	35.7	0.0
Mean value	64.2 ± 0.2	35.8 ± 0.2	
4-Chloro-	78.1	21.9	2.2
	79.5	20.5	..
	75.8	24.2	2.4
	73.9	26.1	0.0
Mean value	76.8 ± 1.8	24.2 ± 1.8	
4-Bromo-	85.4	14.6	0.0
	87.2	12.8	0.0
Mean value	86.3 ± 0.8	13.7 ± 0.8	

[a] Trisubstituted toluene resulting from the further chlorination of the 2- and 3-chlorohalotoluenes; reported as % area observed relative to disubstituted toluenes.

In preliminary experiments employing halotoluenes to chlorine ratios of near unity, the reaction products were found to contain a small, 2–4%, amount of less volatile materials. These substances, presumably dichlorinated aromatics, were not detected in subsequent experiments performed with the aromatic in 2-fold or greater excess.

A more serious problem is the assignment of structure to the products of monochlorination. For each *p*-halotoluene, the elution chromatographs revealed a large peak followed by a smaller band. In the chlorination of *p*-chlorotoluene, the products were readily identified by comparison with available authentic materials. For the chlorination of *p*-bromotoluene, the second peak was positively identified as 3-chloro-4-bromotoluene by comparison of the infrared spectra and retention time with an authentic sample. The first eluted substance was then assigned the 2-chloro-4-bromotoluene structure. For the chlorination of *p*-fluorotoluene, the first peak was assigned the structure of 2-chloro-4-fluorotoluene based on an examination of the infrared spectra and the published Raman spectra.[12] The other product was concluded to be 3-chloro-4-fluorotoluene. These assignments were examined by the chromatographic isolation of additional material and analysis of the n.m.r. spectrum as presented in the Experimental Part.

Discussion

Partial Rate Factors.—The isomer distributions and kinetic relative rates provide the partial rate factors for the *ortho* and *para* positions of the halobenzenes. The *meta* partial rate factors for these compounds are based on rate data and product ratios for substitution of the 4-halotoluenes. These results are summarized in Table V.

TABLE V

PARTIAL RATE FACTORS FOR NON-CATALYTIC CHLORINATION IN 60% ACETIC ACID AT 25°

Compound	Partial rate factors		
	ortho	*meta*[a]	*para*
Toluene	608.	5.6 ± 0.6	705
Fluorobenzene	0.223	0.0056 ± .0019	3.93
Chlorobenzene	.0972	.0023 ± .0006	0.406
Bromobenzene	.0838	.0032 ± .0016	0.310

[a] Based on indirect measurements; see text.

The *ortho* and *para* partial rate factors determined by direct analysis of the major products of chlorination together with the kinetically evaluated relative rates appear to be on a firm experimental basis. Although the rates of chlorination of the aromatics are slightly altered by changes in concentration, this influence is not sufficiently great to introduce major uncertainties. The competitive rate established for fluorobenzene relative to bromobenzene is 12.4 compared to the kinetic result, 10.2. Further, the kinetic relative rates established for reaction in 60% acetic acid are in essential agreement with the observations of de la Mare and Robertson for reaction in 80% acetic acid.[6] Accordingly, the partial rate factors for *ortho* and *para* substitution may be employed with some confidence.

The *meta* partial rate factors are less certain. The values reported as an average in Table V were obtained by independent methods. The application of the additivity principle to the product distribution among the 2- and 3-positions of a 4-halotoluene yields the relationship

---

[12] E. Pendl and R. Radinger, *Montash.*, **72**, 378 (1939). The similarities and differences in the infrared spectra of 2,4- and 3,4-dihalotoluenes are further discussed in the Experimental Part.

TABLE VI

RELATIVE RATES, ISOMER DISTRIBUTIONS AND PARTIAL RATE FACTORS FOR NON-CATALYTIC HALOGENATION OF MONO-SUBSTITUTED BENZENES

Substituent	Rel. rate, k_R/k_B	Isomer distribution, %			Partial rate factors			Ref.
		ortho	*meta*	*para*	o_f	m_f	p_f	
A. Bromination in acetic acid at 25°								
Hydroxy-[a]	6.1×10^{11}			(100)[b]			3.7×10^{12}	c
Methoxy-[a]	1.8×10^{9}	1.6		98.4	8.6×10^{7}	(2.0)[d]	1.0×10^{10}	e
Phenoxy-[a]	1.7×10^{7}			(100)[b]			1.0×10^{8}	f
Acetylamino-[a]	2.1×10^{8}			(100)[b]			1.2×10^{9}	g
Naphthalene[a]	1.4×10^{5}	1.0[h]		99.0[i]	2.1×10^{3}[h]		2.08×10^{5}[i]	j,k
Fluorene[a]	2.1×10^{6}			100[h]			6.33×10^{6}[h]	l
Phenyl-[m]	1.0×10^{3}	2.5		97.5	3.75×10	(0.3)[d]	2.92×10^{3}	l
Methyl-[m]	6.0×10^{2}	32.9	0.3	66.8	6.00×10^{2}	5.5	2.42×10^{3}	n
Ethyl-[m]	4.6×10^{2}	33.8		66.2	4.65×10^{2}		1.8×10^{3}	o,p
i-Propyl-[m]	2.6×10^{2}	23		77	1.8×10^{2}		1.2×10^{3}	o,q
t-Butyl-[m]	1.4×10^{2}	1.20	1.47	97.5	4.7	6.1	8.06×10^{2}	
B. Chlorination in acetic acid at 25°								
N-Acetylamino-[a]	6.2×10^{5}	32.5		67.5	6.1×10^{5}		2.52×10^{6}	s,t
Methoxy-[a]	9.7×10^{6}	21		79	6.1×10^{6}		4.6×10^{7}	u,v
Fluorene[a]	1.1×10^{5}			(100)[b]			3.39×10^{5}	w
Phenyl-[a]	4.2×10^{2}	53		47	3.35×10^{2}	(0.74)[d]	6.00×10^{2}	w
Methyl-[a]	3.4×10^{2}	59.8	0.48	39.7	6.17×10^{2}	4.95	8.20×10^{2}	x
Ethyl-[a]	2.9×10^{2}	51.5		48.5	4.50×10^{2}		8.40×10^{2}	o,p
i-Propyl-[a]	1.8×10^{2}	(40)[b]		(60)[b]	2.18×10^{2}		6.50×10^{2}	o
t-Butyl-[a]	8.8×10	21.5	2.29	76.2	5.66×10	6.0	4.01×10^{2}	r
Fluoro-[y]	7.4×10^{-1}	10.1		89.1	2.23×10^{-1}	5.6×10^{-3}	3.93	y
Chloro-[y]	1.0×10^{-1}	32.4		67.6	9.72×10^{-2}	2.3×10^{-3}	4.06×10^{-1}	y
Bromo-[y]	7.2×10^{-2}	38.6		61.4	8.38×10^{-2}	3.2×10^{-3}	3.10×10^{-1}	y
C. Bromination by HOBr, $HClO_4$ in 50% dioxane at 25°								
Phenyl-	12.6	56.8	1.5	41.7	10.7	0.28	15.6	z
Methyl-	36.2	70.3	2.3	27.4	76	2.5	59	aa
t-Butyl-	12.0	37.7	7.2	53.2	13.6	2.6	38.5	bb
D. Bromination of substituted polymethylbenzenes in acetic acid–nitromethane at 30°								
Methyl-						4.72	534	cc
Fluoro-						10.4×10^{-4}	4.62	dd
Chloro-						5.7×10^{-4}	14.5×10^{-2}	dd
Bromo-						5.3×10^{-4}	6.18×10^{-2}	dd
Iodo-						22.2×10^{-4}	8.02×10^{-2}	dd
Cyano-						8.7×10^{-7}	3.10×10^{-6}	ee

[a] In dry acetic acid. [b] Estimated from qualitative observations. [c] Rate: see ref. 17. [d] Estimated value based on kinetic results. [e] Rate and isomer distribution: L. M. Stock and H. C. Brown, *J. Am. Chem., Soc.*, **82**, 1942 (1960). [f] Rate: P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951); see also ref. *c*. [g] Rate: P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *ibid.*, 276 (1943). [h] 2-Position. [i] 1-Position. [j] Rate: S. F. Mason, *J. Chem. Soc.*, 4329 (1958). [k] Isomer distribution: E. Berliner, F. J. Ochs and G. L. Zimmerman, *J. Org. Chem.* **23**, 495 (1958), for reaction in 50% acetic acid. [l] Rate and isomer distribution: H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **84**, 1238 (1962). [m] In 85% acetic acid. [n] Rate and isomer distribution: H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957). [o] Rate: P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943), see also E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949). [p] Isomer distribution: H. C. Brown and A. Neyens, *ibid.*, **84**, 1655 (1962). [q] Isomer distribution: J. H. Lamneck, *ibid.*, **76**, 1106 (1954). [r] Rate and isomer distribution: L. M. Stock and H. C. Brown, *ibid.*, **81**, 5615 (1959). [s] Rate: P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1519 (1958). [t] Isomer distribution: K. J. P. Orton and A. E. Bradfield, *ibid.*, 986 (1927). [u] Rate: B. Jones, *ibid.*, 430 (1943). [v] Isomer distribution: B. Jones and E. N. Richardson, *ibid.*, 3939 (1956), and L. M. Stock and A. Himoe, unpublished results. [w] Rate and isomer distribution: P. B. D. de la Mare, *et al.*, *Chemistry & Industry*, 1086 (1958). [x] Rate and isomer distribution: H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957). [y] This study, in 60% acetic acid. [z] P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 3004 (1957). [aa] P. B. D. de la Mare and J. T. Harvey, *ibid.*, 36 (1956). [bb] P. B. D. de la Mare and J. T. Harvey, *ibid.*, 131 (1957). [cc] G. Illuminati, *Ric. Sci.*, **26**, 2752 (1956). [dd] G. Illuminati and G. Marino, *J. Am. Chem. Soc.*, **78**, 4975 (1956). [ee] G. Illuminati, *ibid.*, **80**, 4941 (1958).

$$\% \text{ 2-substn.}/\% \text{ 3-substn.} = o_f^{Me} m_f^{X} / o_f^{X} m_f^{Me} \quad (1)$$

The *ortho* partial rate factors determined by direct methods are available. An estimate of the required m_f^{Me} was provided by an analysis of the rate for *p*-xylene in terms of eq. 2. Unfortunately, the rate

$$k_{p\text{-xylene}}/k_{\text{benzene}} = 4 o_f^{Me} m_f^{Me}/6 \quad (2)$$

of chlorination of *p*-xylene in 60% acetic acid is somewhat uncertain because of its high reactivity. Solution of eq. 2, however, yields m_f^{Me} as 5.6 ± 0.6, a result in good agreement with the m_f^{Me} value 5.0 established for reaction in dry acetic acid.[13] Adoption of the estimated value together with the *ortho* partial rate factors provides m_f^{F} 3.75 ± 0.37 × 10^{-3}, m_f^{Cl} 2.96 ± 0.32 × 10^{-3}, m_f^{Br} 4.82 ± 0.52 × 10^{-3} on the basis of eq. 1.

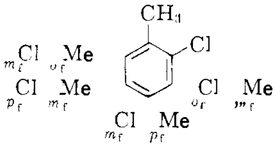
Another approach similarly assuming additivity of the substituent effects allows an independent analysis for m_f^{X} from the kinetic results by eq. 3.

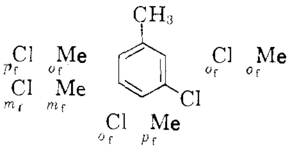
$$k_{p\text{-halotoluene}}/k_{\text{benzene}} = (2o_f^{\text{Me}}m_f^{\text{X}} + 2o_f^{\text{X}}m_f^{\text{Me}})/6 \quad (3)$$

As discussed, the partial rate factors necessary to the calculation are known. Solution of eq. 3 in terms of the relative rates observed for the 4-halotoluenes (Table I) yields m_f^{F} 7.50 $\pm$ 0.25 $\times$ 10^{-3}, m_f^{Cl} 1.60 $\pm$ 0.10 $\times$ 10^{-3}, m_f^{Br} 1.66 $\pm$ 0.10 $\times$ 10^{-3}. The estimated uncertainty is introduced by the error in m_f^{Me} as already discussed.

Although the disagreement between the m_f-values is not large, the discrepancy is almost certainly greater than the experimental error. The deviations are not ordered. Thus, a comparison of the m_f-values obtained from the relative rates with those deduced from the product ratios indicates a higher value for m_f^{F} by the rate method, but lower values for m_f^{Cl} and m_f^{Br}.

To examine the origin of the discrepancy in more detail, it was desirable to evaluate the utility of the *ortho* and *para* partial rate factors for the prediction of relative rates. To this end, we measured the rate of chlorination of *o*- and *m*-chlorotoluene.

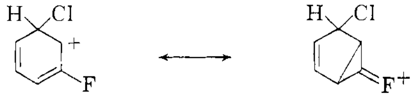




Observed k/k_B	0.69	Observed k/k_B	38.2
Predicted k/k_B	0.97	Predicted k/k_B	59.0

The relative rates are predicted on the basis of the partial rate factors reported in Table V. For both substances the observed rates are only 70% of the predicted value. The prediction for *m*-chlorotoluene is independent of the values for m_f. Accordingly, it appears that the problem may arise from concurrent deviations in the *ortho* and *para* partial rate factors rather than originating entirely in m_f itself. This finding suggests that the application of the additivity principle to variously substituted compounds will not be as satisfactory as found for substitution of the polymethylbenzenes.[13,14]

The *para* partial rate factors for chlorination are in the order F $\simeq$ H $>$ Cl $\simeq$ Br. The *meta* factors are in the order H $>>$ F $>$ Br $\simeq$ Cl. This sequence for each position is quite similar to the behavior of these substituents in the mercuration reaction.[15] The resonance component operative with the halogens apparently provides substantial stabilization in the electron-deficient transition state. The reactivity in the *para* position is clearly far greater than could be anticipated on the basis of the inductive influences of these groups. An even more curious situation prevails for substitution in the less active *m*-position. The *m*-F substituent is more activating than *m*-Cl or *m*-Br. More importantly, the *m*-F substituent is more activating than expected on the basis of its inductive influence. To account for this behavior in terms of resonance and induction in the activated state requires the contribution of an unusual resonance form (Ib). The view that the reaction is assisted by a resonance influence relayed from an adjacent position provides an alternative explanation but must be invoked in the ground state of the molecules, IIb. These choices are discussed in more detail in the following manuscript.[16]



Ia Ib

IIa IIb

Correlation of Halogenation Data with Electrophilic Substituent Constants.—The results reported for the non-catalytic halogenation of monosubstituted benzenes are summarized in Table VI. In addition to the observations presented in the table, data are available in the literature for other substituent groups[17] for which σ^+-constants are as yet unestablished. The partial rate factors established by the polymethylbenzene approach are also presented in the table. Finally, the few observations for the bromination of monosubstituted benzenes with hypobromous acid catalyzed by mineral acid are included for convenient comparison. The adherence of these results to a linear free energy relationship is examined in Figs. 1–4.

Inspection of these diagrams reveals that there can be but little doubt concerning the utility of the σ^+-constants. Certain of the data define points which are approximate in the sense that either the σ^+-constant is estimated (p-NHCOCH$_3$ or p-OH) or the partial rate factors were obtained by the analysis of kinetic results (as for *meta* chlorination of the halobenzenes as discussed previously). Nevertheless the correlations covering a wide range of relative reactivity for each reaction are fully satisfactory. Deviations from the relationships are not absent. For biphenyl, the deviations are expected and have been discussed in detail.[18] The only other serious discrepancy exists for the *p*-chloro and *p*-bromo substituents in the chlorination reaction reported here. The *p*-fluoro substituent correlates quite precisely. The well-known association between molecular chlorine and iodobenzene suggests the possible importance of similar association between the substituents in chloro- and bromobenzene and the halogen. Although the interaction is clearly considerably weaker in these halobenzenes it may prove significant in the determination of reactivity.

The results summarized graphically yield a significant conclusion regarding the importance of polari-

---

[13] H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

[14] The results for the nitration of a variety of disubstituted benzenes are discussed by P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, pp. 59 ff.

[15] H. C. Brown and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1650 (1962).

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

[17] See P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953), for a partial summary of these results.

[18] L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1242 (1962).

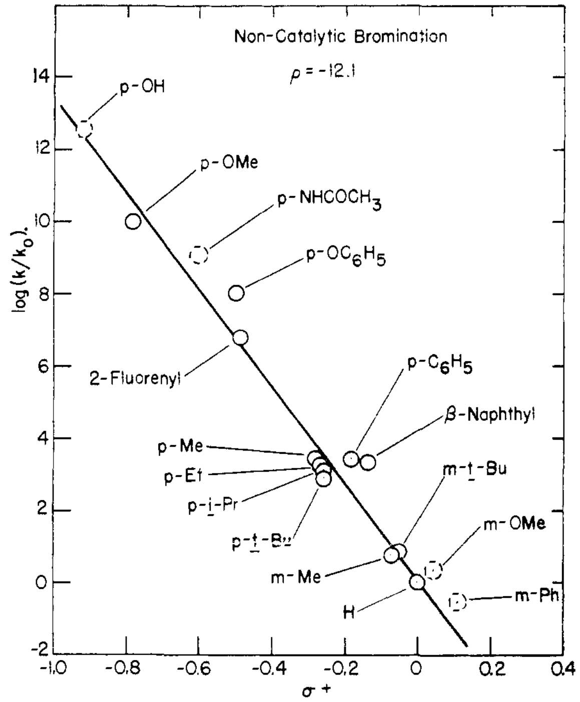


Fig. 1.—Relationship between log(k/k_0) for non-catalytic bromination and the σ^+-constants.

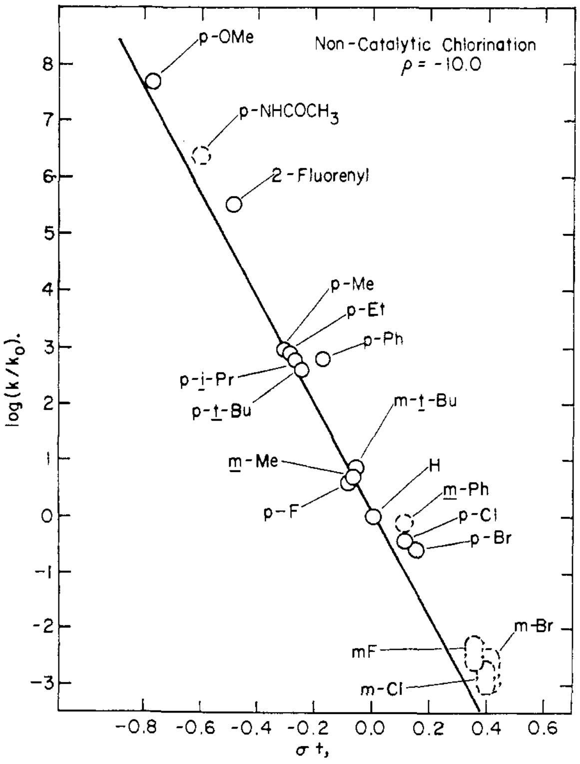


Fig. 2.—Relationship between log(k/k_0) for non-catalytic chlorination and the σ^+-constants.

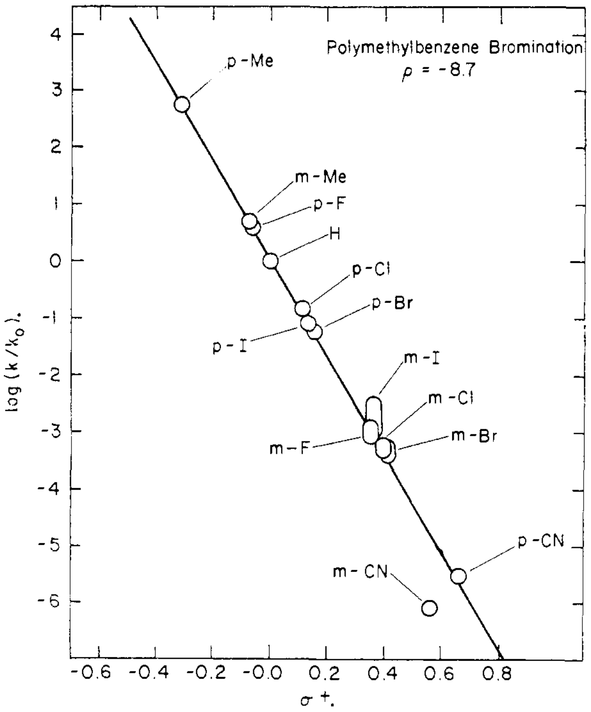


Fig. 3.—Relationship between log(k/k_0) for the bromination of substituted polymethylbenzenes and the σ^+-constants.

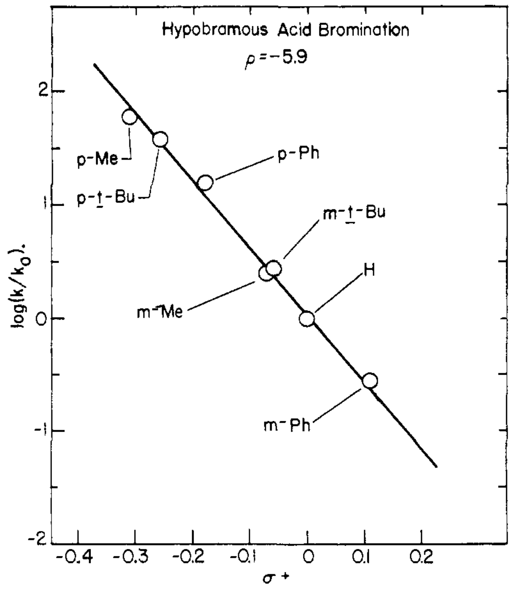


Fig. 4.—Relationship between log(k/k_0) for acid-catalyzed hypobromous acid bromination and the σ^+-constants.

zation as a factor in the determination of the electrical influences of substituent groups. The reactivities of monosubstituted benzenes in bromination by molecular bromine and by hypobromous acid are correlated equally satisfactorily by the σ^+-constants. In the first case the reagent is an unchanged molecular bromine. In the second instance, the reagent apparently is best described as a bromonium cation or as a hydrated bromonium cation. These reagents do not appear to cause a significant alteration in the electrical effects of substituents. Polarization of the aromatic substrate by positive reagents, accordingly, appears to be of little importance in the cases thus far subjected to study.

Experimental Part

Materials.—Acetic acid and concentrated hydrochloric acid (Baker and Adamson) were used without further purification. The solvent prepared from these materials and distilled water did not consume halogen. *p*-Xylene was Phillips Research Grade rated at 99.88% purity. Chlorine (99.5%) was used as obtained from the Matheson Co. The halobenzenes and halotoluenes were commercial materials further purified by fractionation or crystallization from melts. These materials exhibited the following refractive indices: fluorobenzene, $n^{20}\mathrm{D}$ 1.4652; chlorobenzene, $n^{20}\mathrm{D}$ 1.5246; bromobenzene, $n^{20}\mathrm{D}$ 1.5595; *o*-chlorofluorobenzene, $n^{26}\mathrm{D}$ 1.4922; *p*-chlorofluorobenzene, $n^{26}\mathrm{D}$ 1.4910; *o*-dichlorobenzene, $n^{26}\mathrm{D}$ 1.5479; *o*-bromochlorobenzene, $n^{26}\mathrm{D}$ 1.5780; *o*-chlorotoluene, $n^{26}\mathrm{D}$ 1.5215; *m*-chlorotoluene, $n^{26}\mathrm{D}$ 1.5180; *p*-chlorotoluene, $n^{26}\mathrm{D}$ 1.5181; *p*-fluorotoluene, $n^{26}\mathrm{D}$ 1.4679; *p*-bromotoluene, $n^{25}\mathrm{D}$ 1.5480. These values are in good agreement with the literature. The purity was further checked by infrared spectra, vapor phase chromatography or kinetically. Rate data were obtained from different samples of aromatic. Customarily these results were within experimental error.

The 2,4- and 3,4-dichlorotoluenes and 3-chloro-4-bromotoluene were obtained as commercially available samples contaminated with small concentrations of their isomers. The purification was effected by vapor phase chromatography. Only amounts sufficient for infrared analyses were obtained.

Kinetic Measurements.—The solvent was prepared from 600 ml. of distilled water, 200 ml. of concentrated hydrochloric acid and brought to volume in a 2-l. flask with glacial acetic acid. Batches of this solvent could be prepared reproducibly as established by the constancy of the rate of chlorination of benzene, k_2 0.500×10^{-2} and 0.510×10^{2} l. mole^{-1} sec.$^{-1}$, respectively, for two preparations. These solvents consumed less than 6% of the available chlorine in 24 hours. All kinetic experiments were complete in 10 hours or less. The kinetic experiments were carried out in the dark (aluminum foil) in a constant temperature bath at 24.88 ± 0.01°. Conventional iodometric procedures were employed.[6,10]

Product Distributions.—The isomer ratios were established by gas chromatography on a tricresyl phosphate column.[10] For the halobenzenes no difficulties were encountered in the separation of the isomeric dichlorobenzenes and chlorobromobenzenes. The chlorofluorobenzenes, unfortunately, were not fully resolved. We took advantage of the availability of a Beckman IR 7 spectrophotometer for this analysis.[19] The product chlorofluorobenzenes were isolated by gas chromatography and analyzed in carbon disulfide solution. Known samples of the isomers were used to standardize the method. The frequencies employed were 755 cm.$^{-1}$ for the *ortho* isomer and 828 cm.$^{-1}$ for the *para* isomer. Representative results for the examination of known mixtures are summarized in Table VII.

TABLE VII

TYPICAL RESULTS FOR THE ANALYSIS OF KNOWN MIXTURES OF ISOMERIC DIHALOBENZENES

	Composition, %			
	Known		Found	
Benzene	*ortho*	*para*	*ortho*	*para*
Chlorofluoro-[a]	9.9	90.1	10.0	90.0
Dichloro-[b]	31.8	68.2	31.9	68.1
Chlorobromo-[b]	39.6	60.4	37.9	62.1
	39.6	60.4	38.0	62.0

[a] By infrared spectroscopy. [b] By vapor phase chromatography.

The monochlorination products of the *p*-halotoluenes were separated and analyzed without difficulty by chromatography at 150° on a 5-foot column of tricresyl phosphate on Chromosorb. The products of the chlorination of *p*-chlorotoluene were identified by comparison of retention times and by examination of the infrared spectra of materials eluted from the column. There is no uncertainty in the assignment of the chromatographic bands. Both isomeric chloro-4-bromotoluenes were not available. The second elution band of this reaction mixture, however, was shown to be 3-chloro-4-bromotoluene on the basis of the identical retention time and infrared spectra of an authentic sample. The first material emerging from the column is presumed to be 2-chloro-4-bromotoluene. Its infrared spectra was similar to that of 2,4-dichlorotoluene as discussed below. The chlorination of *p*-fluorotoluene also yielded two products with retention times compatible with monochlorinated product. The materials were trapped as they emerged from the column and the infrared spectrum examined. The first isomer exhibited a spectrum virtually identical with the reported Raman spectrum of 2-chloro-4-fluorotoluene. Further information for the structural assignment was obtained by n.m.r. spectroscopy.

The infrared spectra of the two chlorofluorotoluenes were compared with those of 2,4- and 3,4-dichlorotoluene and 2-chloro- and 3-chloro-4-bromotoluene. All spectra were obtained in dilute carbon disulfide solution. Certain characteristic absorptions appeared in the 1400–700 cm.$^{-1}$ region which were useful to distinguish between the 2,4- and 3,4-dihalotoluenes. It was found that the 3,4-dihalotoluenes exhibited a weak band at 1210 cm.$^{-1}$ which was absent in the 2,4-isomers. The 2,4-compounds, on the other hand, had a strong absorption in the region 1055–1040 cm.$^{-1}$ and a weaker absorption in the range 995–990 cm.$^{-1}$. These bands were absent from the spectra of the 3,4-dihalotoluenes. Further, the 2,4-isomers exhibited three strong peaks in the 900–800 cm.$^{-1}$ region in contrast to only two strong bands for the 3,4-compounds. The greater multiplicity observed in this region for the 2,4-isomers was characteristic of the entire region examined.

The n.m.r. spectra of the isomeric chloro-4-fluorotoluenes was also examined and compared with that of 4-fluorotoluene. The methyl resonances occurred at 82.8 ± 0.3, 88.5 ± 0.5 and 93.7 ± 2.7 c.p.s. down field from tetramethylsilane at 40 Mc. for 4-fluorotoluene, 3-chloro- and 2-chloro-4-fluorotoluene, respectively. The shift toward lower field absorption for 2-chloro-4-fluorotoluene is compatible with a decrease in the shielding of the methyl group by an adjacent *o*-chloro substituent. The multiplets observed for ring hydrogen and ring fluorine were not useful for the assignment of structure because of the similarities in coupling constants and chemical shifts. The F^{19} spectrum of *p*-fluorotoluene, for example, was found to be a nicely resolved quintet. Quartets were observed for the F^{19} resonance in both 2-chloro- and 3-chloro-4-fluorotoluene.

Acknowledgment.—This work was supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

---

[19] It is a pleasure to acknowledge the contribution of the National Science Foundation toward the purchase of this instrument (Grant No. NSF-G-17854).