187. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XIII.*[1] *Bromination by Hypobromous Acid in Concentrated Mineral Acids.*

By P. B. D. DE LA MARE and I. C. HILTON.

Correlations between the rates of bromination of relatively unreactive aromatic compounds by acidified solutions of hypobromous acid in aqueous solvents, and acidity as measured by stoicheiometric acidity, by the h_0 function, and by the j_0 function, have been investigated. Distinction between the possible brominating species, bromine cation (Br^+) and hypobromous acidium ion ($BrOH_2^+$), cannot be made with certainty, though the latter seems the more probable. For some substrates in aqueous sulphuric acid, $BrHSO_4$ may be an effective electrophile. Partial rate factors for bromination *meta* to deactivating groups have been estimated from the results and are compared with those for other substituents. The results accord well with H. C. Brown's electrophilic substituent constants (σ^+), except for the *m*-NMe_3^+-group. For this substituent, rates of aromatic substitutions would be predicted better by $\sigma^+ = 0{\cdot}67$.

FOR acid-catalysed chlorination by hypochlorous acid, evidence has been presented[2] that in the rate-equation a kinetic term $-d[ClOH]/dt = k[ArH][ClOH][H^+]$ can characterise chlorination by two independent chlorinating species which are interconverted at a

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[1] Part XII, Beaven, de la Mare, Johnson, and Klassen, *J.*, 1962, 988.

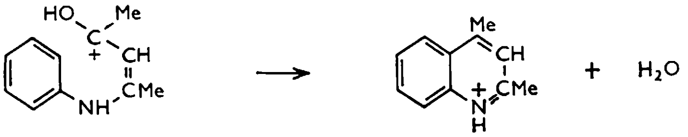
[2] de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 192; de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

measurably slow rate. These must both be positively charged, so they must both be forms of positive chlorine, and they must be so differently solvated that they can be treated as separate chemical entities separated by an energy-barrier; we formulated them [2] as the chlorine cation, Cl^+, and the hypochlorous acidium ion, $ClOH_2^+$.

Although the same kinetic form has long been established for acid-catalysed bromination by hypobromous acid,[3-6] no similar kinetic distinction between the bromine cation, Br^+, and the hypobromous acidium ion, $BrOH_2^+$, has been achieved, perhaps because the interconversion is too rapid. It has been suggested by Gold and Hawes [7] that a distinction could be obtained for a case, such as this, where proton-loss from the aromatic compound is not important in the rate-determining stage,[8] by measuring the variation of rate with acidity in the concentration region in which the stoicheiometric acidity, the acidity function h_0, and the acidity function j_0 are all different.

Several applications of acidity functions to problems of aromatic substitution seem to have provided useful information. The rate of nitration in mixtures of sulphuric acid and water [9] can be shown to follow * the acidity function J_0 rather then H_0. For several aromatic substrates, including neutral molecules as well as arylammonium ions, the slope of the graph of $\log_{10} k_2$ against $-J_0$ is greater than unity. Since nitration under these conditions is known from independent evidence to involve the nitronium ion,[10] this result might be taken [7] as indicating that other electrophilic substitutions in which the electrophile is produced by a similar acid-catalysed heterolysis would also follow J_0, perhaps with a high slope. Accordingly, several acid-catalysed arylalkylations [11] of which the rates follow J_0, have been interpreted as reactions involving carbonium ions as the electrophiles.

The rate of acid-catalysed cyclodehydration of certain anils [12] is, on the other hand, more directly related to the acidity function H_0; and hence this reaction has been regarded as an internal electrophilic attack by the carbonium centre derived from a protonated carbonyl group:



For a similar reason,[13] nitrosation of phenol catalysed by perchloric acid may involve the nitrous acidium ion, $H_2NO_2^+$.

Accordingly, we have determined the dependence on acidity of the bromination of benzoic acid, phthalic acid, nitrobenzene, trimethylanilinium perchlorate, and *o*-nitrobenzoic acid by hypobromous acid. The results are not clearly diagnostic of the nature of the electrophilic species; they do, however, provide some interesting information concerning acid-catalysis of these reactions, and concerning the effects of deactivating substituents on reactivity.

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* We shall use this form of words to imply that a plot of $\log_{10} k$ (where k is the rate-coefficient) against $-J_0$ is linear with a slope of nearer to 1 than for the corresponding plot against $-H_0$.

[3] Shilov and Kaniev, *Compt. rend. Acad. Sci. U.S.S.R.*, 1939, **24**, 890.
[4] Derbyshire and Waters, *J.*, 1950, 564, 571.
[5] Branch and Jones, *J.*, 1954, 2317.
[6] de la Mare and Harvey, *J.*, 1956, 36.
[7] Gold and Hawes, *J.*, 1951, 2102.
[8] de la Mare, Dunn, and Harvey, *J.*, 1957, 923.
[9] (*a*) Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871; Lowen, Murray, and Williams, *J.*, 1950, 3318; Bonner, Bowyer, and Williams, *J.*, 1952, 3274; (*b*) Deno and Stein, *J. Amer. Chem. Soc.*, 1956, **78**, 578.
[10] Cf. Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.
[11] Bethell and Gold, *J.*, 1958, 1905; Bonner, Clayton, and Williams, *J.*, 1957, 2867.
[12] Bonner, Thorne, and Wilkins, *J.*, 1955, 2351.
[13] Morrison and Turney, *J.*, 1960, 4827.

EXPERIMENTAL

Some of the materials and methods have been described in earlier papers in this series.[6,8] The following materials were obtained by fractional distillation or recrystallisation of commercial specimens: benzene, b. p. 79·9°/752 mm.; nitrobenzene, b. p. 73°/4 mm.; benzoic acid, m. p. 122°; phthalic acid, m. p. 200—205° (decomp.); *o*-nitrobenzoic acid, m. p. 146°. Trimethylanilinium perchlorate was prepared from the iodide, m. p. 217°, to a solution of which in water was added a solution of sodium perchlorate. The precipitate, recrystallised from methanol, had m. p. 182—183° [lit.,[14] 175° (decomp.)].

Reagents were obtained and standardised by conventional methods. Kinetic measurements were made in the usual way, and with the usual precautions. Rate-coefficients have been calculated by conventional formulæ. Allowance was made for the finite infinity-titres, amounting to about 5% of the total concentration of hypobromous acid; these result [5,15] from bromate and other decomposition products of hypobromous acid. All the experiments were carried out with *ca.* 0·01M-concentrations of aromatic compound and *ca.* 0·003M-BrOH at 25°. Tables (*a*)—(*d*) give examples of typical kinetic runs.

(*a*) Benzene, 0·0099M; BrOH, *ca.* 0·004M; $HClO_4$, 0·1465M; 10 ml. samples titrated with 0·005N-$Na_2S_2O_3$.

Time (sec.)	10·2	17·0	23·7	31·5	40·8	49·5	900	∞
Titre (ml.)	14·40	12·60	10·49	9·01	7·79	6·77	0·51	0·50
k_2 (l. mole^{-1} sec.$^{-1}$)	—	2·3	2·8	2·7	2·5	2·5	—	—

(*b*) Phthalic acid, 0·01035M; BrOH, *ca.* 0·003M; $HClO_4$, 4·07M; 25 ml. samples titrated with 0·002N-$Na_2S_2O_3$.

Time (sec.)	175	360	557	885	1260	1890	2710	5280
Titre (ml.)	70·40	57·85	47·04	33·10	22·40	12·15	6·28	2·02
k_2 (l. mole^{-1} sec.$^{-1}$)	—	0·12	0·12	0·13	0·13	0·14	0·14	—

(*c*) Trimethylanilinium perchlorate, 0·01125M; BrOH, 0·0038M; $HClO_4$, 4·04M; 25 ml. samples titrated with 0·002N-$Na_2S_2O_3$.

Time (sec.)	43	256	440	780	1165	1960	3790	7260	12,060	∞
Titre (ml.)	101·80	91·40	82·05	68·45	56·50	39·20	19·78	9·77	7·05	7·00
k_2 (l. mole^{-1} sec.$^{-1}$)	—	0·050	0·054	0·056	0·057	0·058	0·059	0·058	—	—

(*d*) Nitrobenzene, 0·00959M; BrOH, 0·00369M; $HClO_4$, 4·00M; 10 ml. samples titrated with 0·005N-$Na_2S_2O_3$.

Time (sec.)	60	150	240	480	960	1565	2400	5460	∞
Titre (ml.)	14·80	14·20	13·54	12·16	10·15	7·60	5·50	1·95	0·50
k_2 (l. mole^{-1} sec.$^{-1}$)	—	0·0048	0·0053	0·0054	0·0050	0·0055	0·0056	0·0059	—

The results are summarised in the Tables (A)—(E).

(A) *Benzoic acid.*	In $HClO_4$			In H_2SO_4				
Acid (M)	0·492	0·946	1·930	0·547	1·040	1·532	2·024	2·517
$-H_0$	−0·14	0·20	0·73	−0·09	0·26	0·56	0·85	1·13
$-J_0$	0·20	0·91	2·07	0·10	0·66	1·16	1·64	2·11
k_2 (l. mole^{-1} sec.$^{-1}$)	0·11	0·27	$1{\cdot}1_5$	0·13	0·41	1·1	4·3	6·2

(B) *Phthalic acid.*

$HClO_4$ (M)	2·54	3·07	3·57	4·07	4·58	5·08	5·33	5·58	5·84
$-H_0$	1·03	1·26	1·50	1·75	2·01	2·29	2·42	2·58	2·74
$-J_0$	2·74	3·26	3·76	4·29	4·87	5·45	5·75	6·05	6·35
k_2 (l. mole^{-1} sec.$^{-1}$)	0·016	0·031	0·061	0·13	0·25	0·46	0·75	0·79	1·22

(C) o-*Nitrobenzoic acid.*

$HClO_4$ (M)	4·99	7·00	8·06	9·02
$-H_0$	2·24	3·61	4·41	5·11
$-J_0$	5·34	7·85	9·38	10·80
k_2 (l. mole^{-1} sec.$^{-1}$)	0·0030	0·074	1·0	12·0

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[14] Hofmann, Höbold, and Quoos, *Annalen*, 1912, **386**, 304.

[15] Wilson and Soper, *J.*, 1949. 3376,

(D) *Trimethylanilinium perchlorate.*

(i)

$HClO_4$ (M)	2·52	3·04	3·54	4·04	4·54	5·04	5·54	6·00
$-H_0$	1·02	1·26	1·50	1·73	2·00	2·26	2·55	2·85
$-J_0$	2·71	3·24	3·73	4·23	4·80	5·40	6·00	6·55
k_2 (l. mole^{-1} sec.$^{-1}$)	0·0056	0·011	0·026	0·058	0·14	0·34	1·2	3·1

(ii)

$HClO_4$ (M)	5·00	4·00	3·00
$NaClO_4$ (M)	1·00	2·00	3·00
$-H_0$	2·77	2·47	2·13
k_2 (l. mole^{-1} sec.$^{-1}$)	1·42	0·78	0·425

(iii)

H_2SO_4 (M)	2·52	3·50	4·48	5·96
$-H_0$	1·13	1·62	2·06	2·74
$-J_0$	2·12	2·98	4·00	5·38
k_2 (l. mole^{-1} sec.$^{-1}$)	0·0044	0·021	0·084	0·78

(E) *Nitrobenzene.*

(i)

$HClO_4$ (M)	2·00	3·00	3·50	4·00	5·00	6·00
$-H_0$	0·76	1·24	1·47	1·71	2·24	3·05
$-J_0$	2·15	3·19	3·70	4·20	5·35	6·55
k_2 (l. mole^{-1} sec.$^{-1}$)	0·0043	0·0099	0·021	0·054	0·35	3·2

(ii)

$HClO_4$ (M)	5·00	4·00	3·00
$NaClO_4$ (M)	1·00	2·00	3·00
$-H_0$	2·77	2·47	2·13
k_2 (l. mole^{-1} sec.$^{-1}$)	1·3	0·66	0·35

(iii)

H_2SO_4 (M)	2·02	3·01	3·99	4·92
$-H_0$	0·87	1·40	1·85	2·26
$-J_0$	1·64	2·54	3·49	4·42
k_2 (l. mole^{-1} sec.$^{-1}$)	0·0029	0·014	0·10	0·40

A few measurements were made in aqueous dioxan, but here the control decomposition was not negligible. Correction was made by determining the initial value of k_1, the first-order velocity-coefficient based on the decomposition of hypobromous acid, both with and without the aromatic compound. The difference was divided by the concentration of aromatic compound to give k_2. The reactions were acid-catalysed, and generally paralleled those in water, but only values determined at the highest acidities were reported, since it was only here that the correction for the control decomposition was small.

Phthalic acid, *ca.* 0·035M; BrOH, *ca.* 0·003M.

(*a*) In 40% dioxan, 4·04M-$HClO_4$ ($-H_0 = 1·68$; $-J_0 = 4·48$): $k_1 = 0·00210$ sec.$^{-1}$, k_1 (control) = 0·00026 sec.$^{-1}$; whence k_2 (corr.) = 0·050 l. mole^{-1} sec.$^{-1}$

(*b*) In 60% dioxan, 4·03M-$HClO_4$ ($-H_0 = 1·83$; $-J_0 = 5·14$): $k_1 = 0·00503$ sec.$^{-1}$, k_1 (control) = 0·00203 sec.$^{-1}$; whence k_2 (corr.) = 0·091 l. mole^{-1} sec.$^{-1}$.

The values of H_0 that we have used and recorded in the above Tables are graphically interpolated from values for aqueous solutions summarised by Paul and Long,[16] and for perchloric acid in aqueous dioxan determined by Bunton *et al.*[17] Values for J_0 for sulphuric acid were obtained similarly from Paul and Long's tabulations; for perchloric acid from data given by Deno *et al.*[18] and tables of the density of aqueous solutions of perchloric acid; and for perchloric acid in aqueous dioxan, from the values of Dahn *et al.*[19] Some of the data are plotted in Figs. 1 and 2.

TABLE 1.

Slopes of acidity-function graphs for bromination by hypobromous acid in water at 25°.

Compound	Catalyst	d[$\log_{10} k_2$]/d[$-H_0$]		d[$\log_{10} k_2$]/d[$-J_0$]	
Benzoic acid	$HClO_4$, 0·5—1·9M	1·16		0·55	
	H_2SO_4, 0·5—2·5M		1·42		0·89
Phthalic acid	$HClO_4$, 2·5—5·8M	1·21		0·57	
o-Nitrobenzoic acid	$HClO_4$, 5·0—9·0M	1·20		0·66	
Nitrobenzene	$HClO_4$, 2·0—6·0M	*ca.* 1·4		*ca.* 0·74	
	H_2SO_4, 2·0—5·0M		*ca.* 1·4		*ca.* 0·78
Trimethylanilinium perchlorate	$HClO_4$, 2·5—6·0M	1·48		0·70	
	H_2SO_4, 2·5—6·0M		1·37		0·67

Product of Bromination of Benzoic Acid.—Benzoic acid (8 g.) was dissolved in distilled water (2·85 l.); 60% perchloric acid (400 ml.) and 0·044M-hypobromous acid (750 ml.) were added. After 30 min., the solution was extracted with ether (4 × 500 ml.). The ether extract was washed with water, dried, and evaporated. A portion (8 g.) of the product which should have contained up to 6·8 g. of bromobenzoic acids was recrystallised from water in order to remove

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[16] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

[17] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

[18] Deno, Berkheimer, Evans, and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344 (correction, p. 6535).

[19] Dahn, Loewe, and Rotzler, *Chem. Ber.*, 1960, **93**, 1572.

benzoic acid. The infrared spectra were measured, and showed the presence of benzoic acid and *m*-bromobenzoic acid. Neither in the crude nor in the recrystallised material was *o*- or *p*-bromobenzoic acid detected by their strong peaks at 794 and 851 cm.$^{-1}$, respectively. It is concluded that *m*-bromobenzoic acid must constitute at least 90%, and probably more, of the brominated product.

In Table 1 are summarised the slopes of the graphs of $\log_{10} k_2$ against H_0 and J_0.

By interpolation or slight extrapolation from the graphs of $\log_{10} k_2$ against H_0, the rate-comparisons in Tables 2 and 3 can be made.

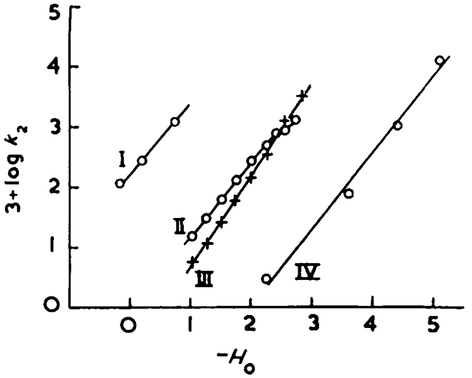

FIG. 1. Dependence of rate on acidity for bromination of aromatic compounds by hypobromous acid in aqueous perchloric acid at 25°.

I, Benzoic acid (slope, 1·16). II, Phthalic acid (slope, 1·21). III, Trimethylanilinium perchlorate (slope, 1·48). IV, *o*-Nitrobenzoic acid (slope, 1·2).

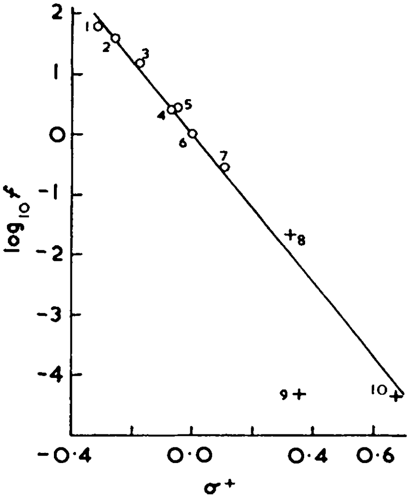

FIG. 2. Plot of partial rate factors ($\log_{10} f$) for acid-catalysed bromination by hypobromous acid against H. C. Brown's electrophilic substituent constants, σ^+.

1, *p*-Me; 2, *p*-Bu^t; 3, *p*-Ph; 4, *m*-Me; 5, *m*-Bu^t; 6, H; 7, *m*-Ph; 8, *m*-CO$_2$H; 9, *m*-NMe$_3^+$; 10, *m*-NO$_2$. ○ In aq. dioxan; + in H$_2$O.

TABLE 2.

Relative reactivities in perchloric-acid-catalysed reactions of hypobromous acid with aromatic compounds.

Compound	$HClO_4$ (M)	$-H_0$	k_2 (l. mole^{-1} sec.$^{-1}$)	k_2/h_0 * (l.^{2} mole^{-2} sec.$^{-1}$)	Rel. rate
Benzene	0·195		3·8	19	1
Benzoic acid	0·50	−0·13	0·11	0·15	$7·5 \times 10^{-3}$
	2·5	1·03	2·3	0·23	($7·5 \times 10^{-3}$)
Phthalic acid	2·5	1·03	$1·6 \times 10^{-2}$	0·0015	$4·9 \times 10^{-5}$
	4·56	2·00	25×10^{-2}	0·0025	($4·9 \times 10^{-5}$)
o-Nitrobenzoic acid	4·56	2·00	$1·04 \times 10^{-3}$	$1·04 \times 10^{-5}$	$1·1 \times 10^{-7}$
Nitrobenzene	2·5	1·03	$5·1 \times 10^{-3}$	$5·0 \times 10^{-4}$	$1·6 \times 10^{-5}$
Trimethylanilinium perchlorate ...	2·5	1·03	$5·0 \times 10^{-3}$	$4·9 \times 10^{-4}$	$1·6 \times 10^{-5}$

* = antilog$_{10}$ ($\log_{10} k_2 + H_0$).

TABLE 3.

Relative reactivities in sulphuric acid-catalysed reactions of hypobromous acid with aromatic compounds.

Compound	H_2SO_4 (M)	H_0	k_2 (l. mole^{-1} (sec.$^{-1}$)	k_2/h_0 (l.^{2} mole^{-2} sec.$^{-1}$)	Rel. rate
Benzoic acid	2·30	1·0	4·7	0·47	($7·5 \times 10^{-3}$)
Nitrobenzene	2·30	1·0	$5·0 \times 10^{-3}$	$5·0 \times 10^{-4}$	$0·79 \times 10^{-5}$
Trimethylanilinium perchlorate...	2·30	1·0	$2·5 \times 10^{-3}$	$2·5 \times 10^{-4}$	$0·40 \times 10^{-5}$

DISCUSSION

(a) *Dependence of Rate on Acidity.*—In Fig. 1 are shown some of the plots * of $\log_{10} k_2$ against $-H_0$. They are all satisfactorily linear, except for phthalic acid at the highest concentrations of perchloric acid. Here the rate does not increase with acidity as much as would be expected, almost certainly because of protonation or dehydration of the phthalic acid.

Plots of $\log_{10} k_2$ against $-J_0$ are not shown, but they are just as satisfactorily linear, so no differentiation between the two possible intermediates, $BrOH_2^+$ and Br^+, can be made on this basis.

The summarised slopes, given in Table 1, show that, whether H_0 or J_0 is taken as the criterion, benzoic acid has a slope significantly different from that for trimethylanilinium perchlorate. The slope does not appear to be determined primarily by the range of acidity used for measurement; *o*-nitrobenzoic acid, the least reactive compound measured, associates itself more closely in slope against H_0 with the most reactive compound, benzoic acid, than with trimethylanilinium perchlorate, of intermediate reactivity.

Neither the slope against H_0 nor that against J_0 is integral; the former is substantially greater than one, and the latter substantially less than one. So a conservative inference is that the nature of the electrophile is not determined by the results and that further discussion of the dependence of rate on acidity is unprofitable.

Since nitration in aqueous sulphuric acid,[9b] when treated similarly, gives slopes of $\log_{10} k_2$ against J_0 substantially greater than one, whereas bromination gives slopes substantially less than one, it seems to us that the balance of probabilities favours the hypothesis that the latter reaction involves the hypobromous acidium ion, $BrOH_2^+$. On this basis,† the following further comments can be made.

First, the fact that the slope is substantially greater than unity indicates that the reaction is subject to a fairly strong salt effect, which superposes itself on the expected rate-dependence. Quite a number of examples of this type of behaviour are now well documented.[20]

Secondly, this effect is different for different aromatic substrates. Benzoic, phthalic, and *o*-nitrobenzoic acid, of widely different reactivity but all clearly brominated through the neutral molecule, have slopes of *ca.* 1·2, whereas trimethylanilinium perchlorate has a significantly higher slope, in the region 1·4—1·5. Nitrobenzene seems also to give a slope of about 1·4, but these results are subject to much more experimental uncertainty.

Thirdly, whereas, for the bromination of nitrobenzene catalysed by sulphuric acid, the rate over quite a range of acidity was the same as at the same H_0 value for perchloric acid, for trimethylanilinium perchlorate the rate was less in sulphuric acid than in perchloric acid of the same H_0 value. So the detailed behaviour is also specific to the catalysing acid.

Fourthly, quite a different behaviour was noted for the bromination of benzoic acid catalysed by sulphuric acid. Here the slope was substantially higher than for perchloric acid; and the rate, which at very low acidities was much the same, at very high acidities was substantially more in sulphuric acid than in perchloric acid of the same acidity. We suggest that this indicates that $BrHSO_4$ is an effective electrophile (cf. ref. 4), promoting an enhanced rate-spread (greater ρ-value) compared with $BrOH_2^+$; so that it begins to

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* Values for nitrobenzene are not included. This compound is rather insoluble in water, so we think that the kinetic measurements are not reliable enough to give a satisfactory value for the slope; the points at low acidity are too scattered.

† Such a deduction by comparison with nitration requires the qualification that the slopes of the plots of $\log_{10} k_2$ against J_0 for nitration vary according to our estimates of them from Deno and Stein's data [9b] over a range which includes the values 1·0 for methoxybenzene, 1·2 for benzene, 1·5 for benzonitrile. It would be very desirable to have comparisons for nitrations in perchloric acid in the region of acidity that we used for bromination.

[20] Cf. Paul, *J. Amer. Chem. Soc.*, 1952, **74**, 141; McIntyre and Long, *ibid.*, 1954, **76**, 3240.

become manifest for slightly deactivated compounds such as benzoic acid, though it is not apparent in the results for the highly deactivated compounds such as nitrobenzene.

Two further points perhaps deserve comment. First, mixtures of sodium perchlorate and perchloric acid give reactivities on the whole greater than expected from their H_0 values. This is consistent with the view that electrolytes have an environmental effect which, when perchloric acid alone is present, gives a slope against H_0 greater than that expected.

Secondly, the reactions in mixtures of dioxan and water are rather slower (by a factor of about 2) than those in pure water, when comparison is made at the same value of $-H_0$ (*i.e.*, in the neighbourhood of $-H_0 = 1{\cdot}7$). This might be taken to imply that the transition state for the process $X^+ + ArH \longrightarrow ArHX^+$ is more solvated than the initia state, a result which seems more reasonable if the charged component of the initial state is the relatively large entity $BrOH_2^+$ than if it is Br^+.

(b) *Structural Effects.*—(i) *Correlation with electrophilic substituent constants.* The present results extend our knowledge of the effects of substituents on partial rate factors for bromination of monosubstituted benzenes by hypobromous acid. We were unable to detect significant amounts of the *ortho*- and *para*-isomers in the product of bromination of benzoic acid, so in calculating partial rate factors we have assumed that this compound, nitrobenzene, and trimethylanilinium perchlorate gave only *meta*-substitution. Derbyshire and Waters's work[4] supports this viewpoint; they obtained *m*-bromobenzoic acid from benzoic acid, and *m*-dinitrobenzene from nitrobenzene, in good yield under quite a variety of experimental conditions in which they considered that Br^+ or $BrOH_2^+$ was the reactive electrophilic species.

Values of the partial rate factors from this and preceding papers,[6,21] together with the electrophilic substituent constants, σ^+, recommended by Brown and Okamoto,[22] are summarised in Table 4 and plotted in Fig. 2.

TABLE 4.

Partial rate factors (f) for bromination of substituted benzenes, RPh, by hypobromous acid with perchloric acid as catalyst at 25°.

(a) *Solvent,* 50% dioxan

Subst. (R)	*p*-Me	*m*-Me	*p*-Bu^t	*m*-Bu^t	*p*-Ph	*m*-Ph
Partial rate factor (f) ...	59	2·5	38·5	2·6	15·6	0·28
$\log_{10} f$	1·77	0·40	1·59	0·42	1·19	−0·55
σ^+	−0·311	−0·066	−0·256	−0·059	−0·179	+0·109

(b) *Solvent,* water

Subst. (R)	*m*-CO_2H	*m*-NO_2	*m*-NMe_3^+
Partial rate factor (f) ...	0·0225	0·000048	0·000048
$\log_{10} f$	−1·65	−4·32	−4·32
σ^+	+0·322	+0·674	+0·359

The value for the NMe_3^+-substituent being left for later consideration, one straight line adequately represents the points both for the more activating substituents (for which the measurements were made in aqueous dioxan) and for the strongly deactivating substituents (for which the measurements were made in water). It seems, therefore, that the results in these two solvents can, from the point of view of substituent effects, be considered together. The slope of the plot, ρ, is $-6{\cdot}2$, a result which confirms[23] the view that this reaction is one with a response to substituent effects which is considerable, and very similar to that found in nitration, but not as large as that found in molecular halogenation.[22,23]

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[21] de la Mare and Harvey, *J.*, 1957, 131; de la Mare and Hassan, *J.*, 1957, 3004.

[22] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[23] de la Mare and Ridd, " Aromatic Substitution—Nitration & Halogenation," Butterworths, London, 1958; (*a*) pp. 239—240; (*b*) pp. 88 ff.

(ii) *The* NMe_3^+-*substituent.* The results for the NMe_3^+-substituent present a specia problem. Our results accord with those for nitration (Lowen *et al.*[9]) and for sulphonation [24] in indicating that the NMe_3^+- and the NO_2-group have about the same effect in deactivating the nucleus for aromatic substitution. For the solvolysis reaction used by Brown and Okamoto to define their electrophilic substituent constants (the solvolysis in 90% acetone of $R{\cdot}C_6H_4{\cdot}CMe_2Cl$), the NMe_3^+-group had a deactivating effect much less powerful than that of the nitro-group; so much so, that for bromination by $BrOH_2^+$, the point for the NMe_3^+-group lies two logarithmic units off the linear plot which to a reasonable approximation takes in, *inter alia*, the carboxyl group and the nitro-group.

In such circumstances it is difficult to know whether the solvolysis or the electrophilic substitution is the one for which the NMe_3^+-group is to be regarded as behaving abnormally. If it is the latter, then aromatic substitutions in solvents of widely differing J_0 (ranging from rather aqueous perchloric acid to concentrated sulphuric acid) behave similarly. If it is the former, no obvious explanation presents itself. Okamoto and Brown [25] suggested that the entropies of activation for the solvolyses of *m*- and *p*-$Me_3N^+{\cdot}C_6H_4{\cdot}CMe_2Cl$ were abnormally high, and that this indicated that for compounds in which the substituent bore a full formal charge the treatment in terms of substituent constants might be expected to be unsatisfactory. It may be noted, however, that if an abnormal entropy of activation for solvolysis of $R{\cdot}C_6H_4{\cdot}CMe_2Cl$ were taken as a criterion for predicting abnormal behaviour of a substituent in affecting this as compared with other reactions, many other groups would also be expected to behave unsatisfactorily. This is illustrated in Fig. 3, where values of σ^+ are plotted against the Arrhenius energy of activation for the solvolysis. The data are from the work of H. C. Brown and his associates.[22, 25, 26] They show that a straight line can be drawn to take in approximately the values for many substituents, but that a number of substituents, including the *m*- and *p*-NMe_3^+ groups, give points which fall

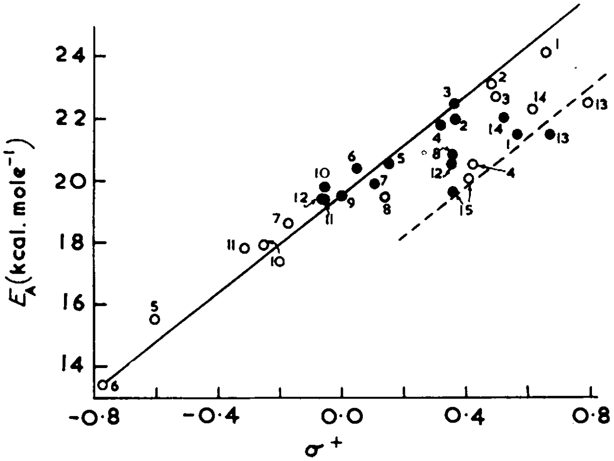

FIG. 3. Plot of electrophilic substituent constants (σ^+) against energy of activation (E_A) for solvolysis of $R{\cdot}C_6H_4{\cdot}CMe_2Cl$ in 90% acetone.*

○ *para*-, ● *meta*-Substituents.

R = 1, CN; 2, CO_2Et; 3, CO_2Me; 4, CO_2H; 5, SMe; 6, OMe; 7, Ph; 8, I; 9, H; 10, Bu^t; 11, Me; 12, F; 13, NO_2; 14, CF_3; 15, NMe_3^+.

* R = NO_2, in 60% acetone; R = *p*-OMe, in 94·8% acetone.

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[24] Brand, *J.*, 1950, 1004.

[25] Okamoto and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4976.

[26] Brown, Brady, Grayson, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897; Brown, Okamoto, and Ham, *ibid.*, p. 1906; Okamoto and Brown, *ibid.*, p. 1909; Brown, Okamoto, and Inukai, *ibid.*, 1958, **80**, 4964; Okamoto, Inukai, and Brown, *ibid.*, p. 4969.

substantially off the line. More particularly it should be noted that, as judged by this criterion, several groups, including the CN-substituent, are just as abnormal as the NMe_3^+-group in energy (and hence in entropy) of activation. So it does not seem reasonable to explain a difference between the NO_2- and the NMe_3^+-group, as revealed by such comparisons as those of Fig. 2, entirely in these terms.

(iii) *The additivity principle.* The rates of bromination of phthalic and benzoic acid show clearly that it is not adequate to treat these reactions as ones in which the carboxyl groups make independent and additive contributions to free energy of activation. For if it is assumed, for example, that the partial rate factors for *ortho-* and *para-*substitution in benzoic acid are equal, the rates for benzoic and phthalic acid allow one to calculate, by using the additivity principle,[23] that there should be only 70% of *meta-*substitution in benzoic acid. This value is not substantially changed by alternative assumptions concerning the *ortho* : *para*-ratio. Actually *meta*-substitution predominates to a much greater extent; we were unable to detect *o*- or *p*-bromobenzoic acid in the product of bromination under our conditions. We thus have a further example illustrating that the additivity principle does not hold quantitatively for compounds containing electron-withdrawing groups, as has been pointed out elsewhere.[23b]

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William Ramsay & Ralph Forster Laboratories,
University College London,
Gower Street, London, W.C.1.

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