Mechanism of Aromatic Bromination by Hypobromous Acid in Aqueous Perchloric Acid. Kinetic Evidence against the Prior Formation of ' Positive Bromine '

By **H. M. Gilow,** Department of Chemistry, Southwestern at Memphis, 2000 North Parkway, Memphis, Tennessee 38112, U.S.A.
John H. Ridd, Department of Chemistry, University College, 20 Gordon Street, London WC1H 0AJ

Results of kinetic studies are used to show that the acid-catalysed mechanism of aromatic bromination by hypobromous acid cannot always involve the prior formation of a positively charged brominating agent. The argument is based on a stepwise comparison of the reactivity of a range of aromatic compounds varying in reactivity from mesitylene to the 2,6-dimethylpyridinium ion. These results, together with the solvent isotope effect, lead to the suggestion of a mechanism for aromatic bromination at low acidities in which the effective electrophile in the rate-limiting step is the hypobromous acidium ion, but where this electrophile is formed by the protonation of a complex of the aromatic compound with hypobromous acid in a pre-equilibrium step. The proposed mechanism has many similarities to that suggested on thermodynamic grounds by Shilov, Vainshtein, and Yasnikov.

AT a given acidity, aromatic bromination by hypobromous acid in aqueous solutions of sulphuric acid or perchloric acid has the expected second-order form [equation (1)],† but the rate coefficient (k_2) is a function

$$\text{Rate} = k_2[\text{ArH}][\text{Hypobromous Acid}] \qquad (1)$$

of the acidity. When the concentration of mineral

acid is low ($[\text{H}^+] < 0\cdot1$ mol l^{-1}), the dependence on acidity is given approximately by equation (2) [1,2] but, in more acidic media, this dependence on $[\text{H}^+]$ is replaced by an approximately linear relationship [3] between log k_2 [equation (1)] and the original Hammett acidity function H_0. The slopes of such plots depend to some extent on the nature of the aromatic substrate: [3] thus the bromination of phthalic acid and of

---

† Hypobromous acid is written out in full in this equation to show that stoicheiometric concentration is implied.

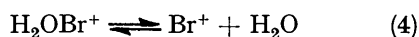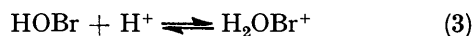[1] E. A. Shilov and N. P. Kanyaev, *Compt. rend. Acad. Sci. U.R.S.S.,* 1939, **24**, 890.

[2] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.,* 1950, 564.

[3] P. B. D. de la Mare and I. C. Hilton, *J. Chem. Soc.,* 1962, 997.

the tri-N-methylanilinium ion in 2·5—6·0M-perchloric acid give slopes of —1·21 and —1·48, respectively.[3]

$$\text{Rate} = k_3[\text{ArH}][\text{Hypobromous Acid}][\text{H}^+] \quad (2)$$

The original [1,2] and still the most common [3,4] interpretation of the acid catalysis assumes that the first equilibrium or both of the equilibria in equations (3) and (4) are maintained in the solution, and that the effective electrophile is either the hypobromous acidium ion (H_2OBr^+) or the bromine cation (Br^+). However,

$$\text{HOBr} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OBr}^+ \quad (3)$$

$$\text{H}_2\text{OBr}^+ \rightleftharpoons \text{Br}^+ + \text{H}_2\text{O} \quad (4)$$

approximate thermodynamic calculations suggest that the concentrations of both electrophiles are too low to explain the observed reaction rate.[5,6] This conclusion is here supported by a purely kinetic argument based on a calculation of the maximum possible concentration of the electrophile consistent with the observed extent of acid catalysis.[7]

The new evidence comes from an extension of the kinetic studies on bromination by ' positive bromine ' to cover a wider range of aromatic reactivity. The reactions have been followed by observing the change in the u.v. spectra of the reactant solutions instead of by titration of samples: this change facilitates the study of fast reactions. For several substrates, the rate coefficients determined spectrophotometrically were shown to accord with those obtained by titration. Product analyses were carried out on examples of very reactive and very unreactive systems.

Second-order rate coefficients [k_2, equation (1)] for the bromination of a series of positive ions are listed in Table 1 and plots of log k_2 against H_0 are shown in Figure 1. The use of H_0 as abscissa is merely to facilitate the calculation of relative reactivities. Values of H_0 for acidities below 0·1M-perchloric acid are equated with —$\log_{10}[\text{H}^+]$ and are otherwise taken from the review by Paul and Long [8] (0·1—1·0M-perchloric acid) and from the work of Yates and Wai [9] (>1·0M-perchloric acid). From the series of stepwise comparisons at the acidities indicated by dotted lines in Figure 1, the reactivity of the 2,6-dimethylpyridinium ion appears to be less than that of the 2-(3,5-dimethylphenyl)ethyltrimethylammonium ion by a factor of $5\cdot6 \times 10^{11}$. From this reactivity ratio and the rate coefficients at the relevant acidities, the second-order coefficient (k_2) for a given substrate should increase by a factor of ca. $1\cdot2 \times 10^{13}$ when the acidity is increased from $H_0 = 3\cdot85$ to —7·45. Since the slopes of the last two rate profiles (both for

protonated pyridinium ions) in Figure 1 are less than those of the adjacent rate profiles for compounds with methylated nitrogen poles, the figure of $1\cdot2 \times 10^{13}$ probably underestimates the acid catalysis of the bromination of these methylated quaternary ions. The lower slopes obtained for the pyridinium ions probably reflect the greater interaction of these protonated ions with the medium: the difference in slope is too small to imply that the pyridinium ions undergo reaction through the corresponding neutral molecules.
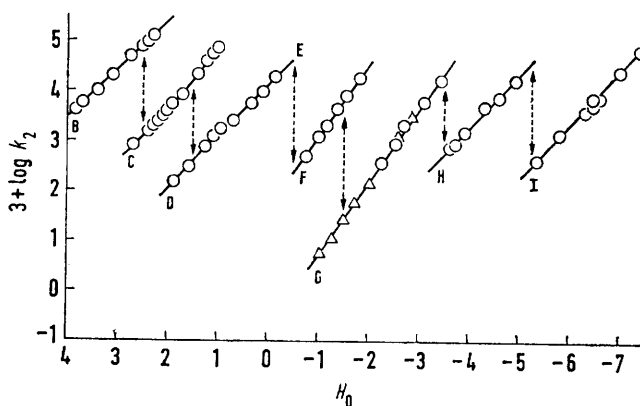

FIGURE 1   Logarithmic plot of the second-order rate coefficient [k_2, equation (1)] against H_0 for the bromination of substituted ammonium ions and pyridinium ions by hypobromous acid in aqueous perchloric acid. The lettering corresponds to that in Table 1. Rate coefficients indicated by triangles came from the work of de la Mare and Hilton (ref. 3). For clarity a few overlapping points have been omitted

In analysing these results, it is convenient to start with the usual assumptions that reaction involves the prior formation of a positive brominating species (' Br^+ ') * and that the increase in k_2 [equation (1)] with acidity derives from an increase in the [' Br^+ ']:[Hypobromous Acid] ratio. Since there is no sign of any curvature in the plot of log k_2 against —H_0 at the highest acidity ($H_0 = -7\cdot45$), the value of this ratio at this acidity must be less than 0·5 : 1. It then follows that the value of [' Br^+ ']/[Hypobromous Acid] at $H_0 = 3\cdot85$ is $<4 \times 10^{-14}$. From this figure and the value of [H^+] at this acidity ($1\cdot42 \times 10^{-4}$ mol l⁻¹), the value of the equilibrium constant for the formation of ' Br^+ ' [K, equation (5)] is calculated to be $<2\cdot8 \times 10^{-10}$. This last calculation involves equating the stoicheiometric concentration of hypobromous acid with the molecular concentration of hypobromous acid, but that is justified at this acidity.

$$K = [\text{' Br}^+ \text{']}/[\text{HOBr}][\text{H}^+] \quad (5)$$

The maximum value of K thus obtained can now be

---

* The symbol ' Br^+ ' is used in this paper as a general representation of the positive brominating species without the structural implications of the symbols Br^+ or H_2OBr^+.

[4] P. B. D. de la Mare and J. H. Ridd, ' Aromatic Substitution, Nitration and Halogenation,' Butterworths, London, 1959, p. 119; R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 122; R. Taylor in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 13, p. 83.

[5] R. P. Bell and E. Gelles, J. Chem. Soc., 1951, 2743.
[6] E. A. Shilov, F. M. Vainshtein, and A. A. Yasnikov, Kinetika i Kataliz, 1961, 2, 214.
[7] This argument has been outlined previously but was then based on a more restricted set of experimental results: A. Gastaminza, H. M. Gilow, and J. H. Ridd, Chem. Comm., 1972, 130.
[8] M. A. Paul and F. A. Long, Chem. Rev., 1957, 57, 1.
[9] K. Yates and H. Wai, J. Amer. Chem. Soc., 1964, 86, 5408.

used to convert the third-order stoicheiometric rate coefficients [k_3, equation (2)] into minimum values of the second-order molecular rate coefficients for reaction

TABLE 1

Second-order rate coefficients [k_2, equation (1)] for the reaction of hypobromous acid with a series of substituted ammonium ions and substituted pyridinium ions in aqueous perchloric acid at $25 \cdot 0 \pm 0 \cdot 1°$

(A) 3-MeO·C$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$

HClO$_4$/mol l^{-1}	$10^{-3}k_2$/ mol^{-1} s^{-1} l
0·000142	1·30

(C) 3-MeC$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$

HClO$_4$/mol l^{-1}	k_2/mol^{-1} s^{-1} l
0·00191	0·81
0·00381	1·47
0·00477	2·02
0·00572	2·34
0·00762	3·11
0·00960	4·01
0·0114	5·53
0·0191	8·30
0·0381	21·5
0·0572	38
0·0762	56
0·0953	72

(E) 4-MeO·C$_6$H$_4$·$\overset{+}{N}$Me$_3$

HClO$_4$/mol l^{-1}	k_2/mol^{-1} s^{-1} l
0·083	1·04
0·167	2·48
0·330	5·50
0·497	9·43
0·820	18·9

(F) 4-MeC$_6$H$_4$·$\overset{+}{N}$Me$_3$

HClO$_4$ (%)	k_2/mol^{-1} s^{-1} l
16·28	0·48
19·96	1·24
22·98	2·06
26·50	4·35
29·42	8·47
32·99	18·7

(H) 2,4,6-Me$_3$C$_5$H$_2$NH$^+$

HClO$_4$ (%)	k_2/mol^{-1} s^{-1} l
51·22	0·77
51·66	0·89
53·04	1·51
55·11	3·70
56·92	7·62
58·21	16·1
58·43	16·9

(B) 3,5-Me$_2$C$_6$H$_3$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$

HClO$_4$/mol l^{-1}	k_2/ mol^{-1} s^{-1} l
0·000142	4·26
0·000191	5·58
0·000381	10·0
0·000955	20·0
0·00191	48
0·00286	76
0·00381	96
0·00477	122

(D) Ph[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$

HClO$_4$/mol l^{-1}	k_2/mol^{-1} s^{-1} l
0·0133	0·144
0·0266	0·294
0·0533	0·737
0·0799	1·21
0·107	1·72
0·133	2·06

(G) Ph$\overset{+}{N}$Me$_3$

HClO$_4$ (%)	k_2/mol^{-1} s^{-1} l
38·50	0·36
41·52	0·91
43·88	2·19
45·65	6·31
49·52	16·9

(I) 2,6-Me$_2$C$_5$H$_3$NH$^+$

HClO$_4$ (%)	k_2/mol^{-1} s^{-1} l
60·39	0·44
62·29	1·37
64·22	3·95
64·82	5·52
64·84	7·36
65·50	7·52
67·16	26
67·21	26
68·67	69
68·78	88

between the aromatic compound and 'Br^+' [k_2', equation (6)]. From equations (2), (5), and (6), these rate coefficients are shown to be related by the equation

$Kk_2' = k_3$. Mean values of k_3 have been calculated for the more reactive substrates from the data in Table 1 and these are given, together with the corresponding values of k_2', in Table 2. The restriction to the more reactive substrates comes from the fact that equation (2) applies only to bromination at low acidities. Even at acidities below [H^+] = $0 \cdot 1$ mol l^{-1}, there is some increase in k_3 with the concentration of perchloric acid: thus, for the bromination of the 3-MeC$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$ ion, the value of k_3 increases from $4 \cdot 2 \times 10^{-2}$ in $1 \cdot 9 \times 10^{-3}$M-perchloric acid to $7 \cdot 6 \times 10^{-2}$ in $9 \cdot 5 \times 10^{-2}$M-perchloric acid. However, for our present purposes, the mean values are sufficient.

$$\text{Rate} = k_2'[\text{ArH}][\text{' }Br^+\text{ '}] \qquad (6)$$

TABLE 2

Third-order stoicheiometric rate coefficients [k_3, equation (2)] and second-order molecular rate coefficients [k_2', equation (6)] for the bromination of the more reactive compounds in Table 1

Substrate	k_3/mol^{-2} s^{-2} l^2	k_2'/mol^{-1} s^{-1} l
3-MeOC$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$	$9 \cdot 1 \times 10^6$	$>3 \cdot 2 \times 10^{16}$
3,5-Me$_2$C$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$	$2 \cdot 6 \times 10^4$	$>9 \cdot 3 \times 10^{13}$
3-MeC$_6$H$_4$·[CH$_2$]$_2$·$\overset{+}{N}$Me$_3$	$5 \cdot 1 \times 10^2$	$>1 \cdot 8 \times 10^{12}$
Ph[CH$_2$]$_2$·NMe$_3$	13·7	$>4 \cdot 9 \times 10^{10}$

The significance of the values of k_2' in Table 2 comes from the fact that they are physically impossible for a bimolecular reaction: even if reaction occurred on encounter, the bimolecular rate coefficient should not exceed 7×10^9 mol^{-1} s^{-1} l.* The values in Table 2 exceed this limit by factors of up to 10^6. Furthermore, from preliminary studies, we have evidence that the rate of bromination continues to increase with acidity up to at least 72·15% perchloric acid ($H_0 = -8 \cdot 37$). The value of K must therefore be considerably less than the upper limit estimated and the values of k_2' correspondingly greater than the lower limits in Table 2. Some work has been carried out on the bromination of neutral substrates and these also yield values of k_2' that greatly exceed the value for reaction on encounter (see Experimental section). Thus, for anisole and mesitylene, the calculated values of k_2' are $>2 \cdot 3 \times 10^{16}$ and $>3 \cdot 6 \times 10^{16}$, respectively.

In seeking an explanation of these high values of k_2' it is helpful to re-examine the assumptions underlying these calculations and to consider first the assumption that the change in k_2 [equation (1)] with acidity comes simply from the change in the ['Br^+ ']/[Hypobromous Acid] ratio. The dependence of the slopes of the rate profiles on the nature of the aromatic substrate shows that this cannot be exactly true. However, the difficulties over the values of k_2' do not arise merely from an unfortunate choice of aromatic substrates: if the slopes of all the rate profiles had been as

* This value is calculated from the equation [10] $k_{en} = 8RT/3000\eta$ where η is the viscosity of the solvent. In principle, a correction should be made because both reactants are positively charged [11] but this has not been done because the charge in the aromatic species is some distance from the point of attack. Such a correction would only strengthen the above argument.

[10] Cf. R. M. Noyes, Progr. Reaction Kinetics, 1961, 1, 129.
[11] P. Debye, Trans. Electrochem. Soc., 1942, 82, 265.

low as unity (a value below that reported for any aromatic compound in ref. 3) the values of k_2' in Table 2 would be reduced by a factor of $<10^2$.

It is more difficult to deal with the possibility that the change in k_2 [equation (1)] with acidity comes partly from the change in the concentration of the brominating agent and partly from a change in the reactivity of the brominating agent. This change in reactivity could be visualised either as a gradual process derived from the change in the solvation of ' Br^+ ' with acidity or as a transition between two distinct positive brominating agents (e.g. H_2OBr^+ and Br^+). Either way, the extent of acid catalysis could not then be used as a guide to the change in the concentration of the brominating agent.

If the change in the reactivity of the brominating agent with acidity were an important factor in determining the extent of acid catalysis, one would expect to observe a change in the selectivity of the brominating agent with acidity. The extent of acid catalysis makes it impractical to determine the relative reactivities of a given group of compounds at widely different acidities but a check on any change in the selectivity of the brominating agent at different acidities is provided by a comparison of the relative reactivites of aromatic

TABLE 3

Reaction rates, relative to benzene, for bromination and nitration in aqueous mineral acids at $25\cdot0 \pm 0\cdot1°$

		Relative rate		
		Bromination		Nitration
Substrate		$HClO_4$	H_2SO_4	H_2SO_4
(A) 3-MeO·C_6H_4·-[CH$_2$]$_2$·$\overset{+}{N}Me_3$		$5\cdot2 \times 10^5$		$6\cdot9$
(B) 3,5-Me$_2$C$_6$H$_3$·-[CH$_2$]$_2$·$\overset{+}{N}Me_3$		$1\cdot5 \times 10^3$		14
(C) 3-MeC$_6$H$_4$·[CH$_2$]$_2$·-$\overset{+}{N}Me_3$		24		$4\cdot5$
(J) Ph[CH$_2$]$_3\overset{+}{N}Me_3$			$3\cdot5$ [a]	$3\cdot2$ [a]
(D) Ph[CH$_2$]$_2\overset{+}{N}Me_3$		$0\cdot70$	$0\cdot51$ [a]	$0\cdot22$ [a]
(E) 4-MeO·C$_6$H$_4$·$\overset{+}{N}Me_3$		$0\cdot53$		$0\cdot33$ [b]
(F) 4-MeC$_6$H$_4$·$\overset{+}{N}Me_3$		$2\cdot9 \times 10^{-3}$		$8\cdot8 \times 10^{-5}$ [e]
(G) Ph$\overset{+}{N}Me_3$		$1\cdot6 \times 10^{-5}$ [d]	$2\cdot6 \times 10^{-6}$ [e]	$3\cdot4 \times 10^{-8}$ [a]
(H) 2,4,6-Me$_3$C$_5$H$_2$NH$^+$		$3\cdot0 \times 10^{-7}$		$3\cdot5 \times 10^{-12}$ [e]
(I) 2,6-Me$_2$C$_5$H$_3$NH$^+$		$2\cdot8 \times 10^{-9}$		
(K) PhCH$_2\overset{+}{N}Me_3$			$1\cdot4 \times 10^{-3}$ [a]	$7\cdot9 \times 10^{-5}$ [a]
(L) Ph$\overset{+}{As}Me_3$			$4\cdot1 \times 10^{-5}$	$1\cdot3 \times 10^{-6}$ [a]
(M) Ph$\overset{+}{P}Me_3$			$8\cdot7 \times 10^{-6}$ [a]	$1\cdot6 \times 10^{-7}$ [a]

[a] A. Gastaminza, J. H. Ridd, and F. Roy, J. Chem. Soc. (B), 1969, 684. [b] R. S. Cook and J. H. Ridd, unpublished observation. [c] J. H. P. Utley and T. A. Vaughan, J. Chem. Soc. (B), 1968, 196. [d] P. B. D. de la Mare and I. C. Hilton, J. Chem. Soc., 1962, 997. [e] C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, and M. Viney, J. Chem. Soc. (B), 1967, 1204.

compounds to bromination and to nitration. Relative reactivities for bromination in perchloric acid and those obtained previously for bromination in sulphuric acid [12]

[12] A. Gastaminza, J. H. Ridd, and F. Roy, J. Chem. Soc. (B), 1969, 684.

are compared with those for nitration in sulphuric acid in Table 3 and Figure 2. The branching of the plot shows that relative reactivities are not quite the same for bromination in the two mineral acids, but both sets of relative reactivities give linear logarithmic plots against the relative reactivities for nitration. This holds up to the point where nitration by nitronium ions occurs on encounter; [13] the rate of nitration then becomes independent of the reactivity of the substrate.

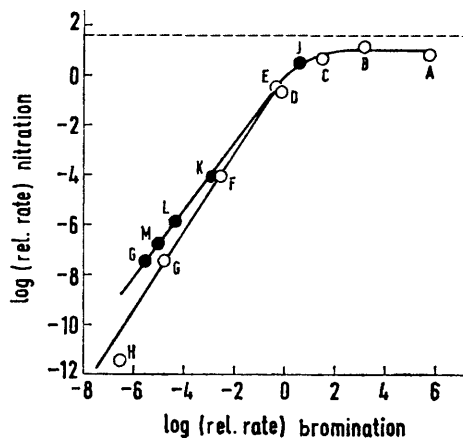The linearity of the plots in Figure 2 is significant

FIGURE 2 The relationship between relative rates (with respect to benzene) for bromination and nitration. Open circles refer to bromination in perchloric acid, dots to bromination in sulphuric acid. The nitration results refer to reaction in sulphuric acid. Lettering as for Table 3. The broken line indicates the reactivity at which nitration becomes a reaction on encounter (ref. 13)

because these substitution reactions cover a wide range of acidity. The results in Figure 2 show therefore that the selectivity of bromination relative to nitration is not a marked function of acidity or aromatic reactivity provided the reactions are not subject to diffusion control. There is good evidence that nitration involves attack by the nitronium ion over the whole of this region of acidity [13,14] and so the linearity in Figure 2 suggests that the nature of the brominating agent is also constant. It therefore appears that we need not consider bromination by two brominating agents (H_2OBr^+ and Br^+) or by a brominating agent whose reactivity is a marked function of the acidity of the medium.

The point for the most deactivated ion in Figure 2 (H = 2,4,6-trimethylpyridinium ion) lies off the linear plot. This deviation could indicate that, at the highest acidities used, the selectivity of bromination decreases relative to nitrogen or the deviation could arise because the interaction of the pyridinium ions with the medium is greater than that of the fully methylated quaternary ions. For a given substrate the acidity used in the kinetic studies of nitration is much greater than that for bromination and so substrates which hydrogen bond

[13] J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge, 1971, p. 27.

[14] J. H. Ridd, Accounts Chem. Res., 1971, 4, 248.

with the solvent would be expected to be more de-activated to nitration than the linear plots in Figure 2 (based on studies with fully methylated quaternary salts) suggest. This apparently occurs with substitution in benzoic acid. From the relative reactivity for bromination in perchloric acid (7.5×10^{-3}),[3] the relative reactivity for nitration should be ca. 8×10^{-4}; the observed relative reactivity [15] is 4×10^{-5}.

The foregoing arguments suggest that the absurdly high values of k_2' in Table 2 do not arise because the brominating agent changes with acidity. We consider therefore that the flaw in the calculations lies in the first assumption: that reaction necessarily occurs with a preformed positive brominating agent. The kinetic form of equation (2) requires only that a positive brominating agent be present in the transition state. The solvent isotope effect on the bromination of benzene $[k(D_2O)/k(H_2O) = 2.2$; see Experimental section] points to a prototropic pre-equilibrium before the rate-limiting step. We have therefore formulated the reaction (see Scheme) in a way which includes this pre-equilibrium and permits but does not require reaction through the preformed positive brominating agent.
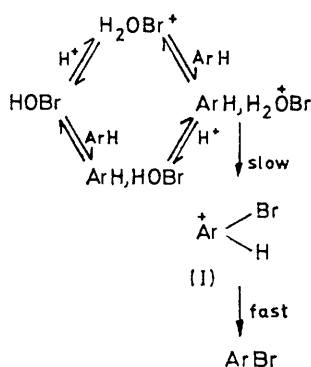
SCHEME

In this Scheme, the π-complex or encounter pair $(ArH,H_2\overset{+}{O}Br)$ is formed from the reactants by two pathways. With highly reactive aromatic substrates and feebly acidic media, the absence of the expected encounter limit requires that the pathway through protonation of the related complex (ArH,HOBr) is by far the more important. As the acidity is increased, the upper pathway should become more significant because the equilibrium concentration of the hypo-bromous acidium ion should increase with acidity more rapidly than the rate of proton transfer to hypobromous acid. A decrease in the reactivity of the aromatic compound should have the same effect, because the basicity of hypobromous acid in the complex

(ArH,HOBr) is probably enhanced by partial electron transfer from the aromatic compound. Hence, although the results require that the lower pathway is the more important at low acidities and with highly reactive substrates, it does not follow that this must remain true for the studies on less reactive compounds at high acidities. Any such change would not modify the selectivity of the bromination reaction because the stages involved occur before the rate-limiting step.

The Scheme is similar to that proposed from approximate thermodynamic calculations by Shilov, Vainshtein, and Yasnikov,[6] the principle difference being that these authors regard the Wheland structure (I) as being in equilibrium with the reactants. The situation can apparently arise when the Wheland structure is very stable (as in the bromination of 7-hydroxynaphthalene-1,3-disulphonic acid) [16] or when steric interactions hinder the forward reaction of the Wheland structure (as in the bromination of 1,3,5-tri-t-butylbenzene) [17] but the absence of an isotope effect in the reaction of hypo-bromous acid with benzene [18] suggests that, in general, the formation of structure (I) is rate-limiting. The value of K' [equation (7)] calculated by these authors [6] from thermodynamic arguments (10^{-11}) is close to the upper limit $(<2.8 \times 10^{-10})$ for the corresponding value of K [equation (5)] obtained in this paper.

$$K' = [H_2OBr^+]/[HOBr][H^+] \qquad (7)$$

The recent reinterpretation of the zeroth-order kinetics for chlorination by hypochlorous acid [19] implies that a similar mechanism to that shown here can now be written for this reaction. However, the clear evidence of a limiting encounter rate in nitration [13] shows that protonation of a (ArH,HNO_3) complex or encounter pair does not provide a pathway for nitration. This is presumably because the nitric acidium ion is not the electrophile in nitration. This distinction between bromination and nitration suggests that strongly acidic electrophiles (in the Brönsted sense) will not give rise to a limiting encounter rate in aromatic substitution and conversely that the observation of such a limiting rate provides useful information on the nature of the electrophile. It may be significant therefore that nitration in acetic anhydride gives rise to a limiting encounter rate [20] with highly reactive substrates: this is a reaction for which there is still some doubt over the nature of the electrophile but recent papers [20,21] have favoured attack by the nitronium ion instead of by protonated acetyl nitrate.

In conclusion, the nature of the electrophile in these acid-catalysed reactions of hypobromous acid is to some extent a matter of definition: the effective electrophile

[15] Ref. 13, p. 178.
[16] M. Christen and H. Zollinger, Helv. Chim. Acta, 1962, 45, 2066.
[17] P. C. Myhre, G. S. Owen, and L. L. James, J. Amer. Chem. Soc., 1968, 90, 2115.
[18] P. B. D. de la Mare, T. M. Dunn, and J. T. Harvey, J. Chem. Soc., 1957, 923.

[19] C. G. Swain and D. R. Crist, J. Amer. Chem. Soc., 1972, 94, 3195.
[20] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, J. Chem. Soc. (B), 1971, 2447.
[21] J. M. A. Baas and B. M. Wepster, Rec. Trav. chim., 1972, 91, 831; S. R. Hartshorn, J. G. Hoggett, R. B. Moodie, K. Schofield, and M. J. Thompson, J. Chem. Soc. (B), 1971, 2461.

in the formation of the Wheland structure is the hypobromous acidium ion but the initial electrophile (at least at the lowest acidities) is hypobromous acid.

EXPERIMENTAL

Materials.— 2-(3-*Methylphenyl*)*ethyltrimethylammonium perchlorate.* Treatment [22] of α-bromo-*m*-xylene with potassium cyanide gave 3-methylbenzyl cyanide. This was reduced with lithium aluminium hydride [23] and the resulting amine was methylated with an excess of methyl iodide in ether to give 3-methylphenethyltrimethylammonium iodide, m.p. 235° (lit.,[24] 236°). The iodide was dissolved in warm water and a saturated aqueous solution of sodium perchlorate was added dropwise until precipitation was complete. The *product* had m.p. 179° (from 95% ethanol) (Found: C, 52·0; H, 7·1; N, 5·0. $C_{12}H_{20}ClNO_4$ requires C, 52·0; H, 7·3; N, 5·0%).

2-(3,5-*Dimethylphenyl*)*ethyltrimethylammonium perchlorate*, prepared in a similar way from α-bromomesitylene, had m.p. 233—234° (from 95% ethanol) (Found: C, 53·6; H, 7·5; N, 4·8. $C_{13}H_{22}ClNO_4$ requires C, 53·5; H, 7·6; N, 4·8%).

2-(3-*Methoxyphenyl*)*ethyltrimethylammonium perchlorate.* *m*-Methoxybenzaldehyde was condensed with nitromethane to give *m*-methoxy-β-nitrostyrene.[25] This was reduced with an excess of lithium aluminium hydride [26] to the amine, which was converted into the quaternary perchlorate as already described. The *product* had m.p. 149—150° (from 95% ethanol) (Found: C, 49·1; H, 7·0; N, 4·7. $C_{12}H_{20}ClNO_5$ requires C, 49·1; H, 6·9; N, 4·8%).

The other quaternary salts were either available from previous work [12] or were prepared from the corresponding aniline derivatives by methylation with methyl iodide followed by treatment with sodium perchlorate. The neutral aromatic substrates were obtained as B.D.H. reagents and were normally purified by distillation. Nitric, sulphuric, and perchloric acids were AnalaR grade reagents. Aqueous solutions of hypobromous acid were prepared [2] from silver nitrate and disodium hydrogen phosphate. The hypobromous acid was distilled in an all-glass blackened apparatus, kept at 5°, and used within 2 days of distillation.

Kinetic Runs.—A solution (3 ml) of the aromatic compound (1×10^{-4}—6×10^{-3} mol l⁻¹) in aqueous perchloric acid of the required concentration was brought to $25·0 \pm 0·1°$ in a spectrophotometer cell and the reaction was started by the injection of a suitable amount of aqueous hypobromous acid (0·100—0·010 ml) so that the concentration of hypobromous acid in the mixture was *ca.* 10^{-4} mol l⁻¹. To minimise heating on dilution of the perchloric acid, the kinetic runs in the higher concentrations of perchloric acid were carried out with the injection of 0·010 ml of hypobromous acid. The formation of the aromatic bromide was followed with a Unicam SP 500 or SP 1800 spectrophotometer by observing the change in the u.v. spectrum at the following wavelengths (the lettering is that in Table 1): A, 240; B, 233; C, 230; D, 225; E, 386; F, 230; G, 220; H, 234; I, 226; benzene, 220; mesitylene, 232; anisole, 232 nm. At least a tenfold excess of the aromatic compound was normally used and the first-order rate coefficient (k_1) obtained from a plot of

log $(D_\infty - D_t)$ against time where D_t and D_∞ are the optical densities at time t and at the end of reaction, respectively. The second-order rate coefficient k_2 [equation (1)] was then calculated from the equation $k_2 = k_1/[\text{ArH}]$. Conditions were chosen so that the half-lives were usually *ca.* 100 s and the infinity readings for a given substrate with a given concentration of hypobromous acid were taken from the fastest reactions.

For the most reactive substrates, this procedure was modified by decreasing the concentration of the aromatic compound so that it was either equal to or about twice that of the hypobromous acid. The corresponding modifications in the calculation of the rate coefficient can be most easily seen by the example in Table 4, which also includes a kinetic run with the most unreactive substrate. Kinetic runs were normally carried out in duplicate, the agreement being usually within $\pm 5\%$ except for the most reactive substrates, mesitylene and anisole, where the reproducibility was less satisfactory.

TABLE 4

Examples of kinetic runs

(A) Bromination of 2,6-dimethylpyridinium perchlorate in 64·28% perchloric acid at $25·0 \pm 0·1°$

$[\text{ArH}] = 2·22 \times 10^{-3}$ mol l⁻¹ $[\text{HOBr}] = 1·0 \times 10^{-4}$ mol l⁻¹

t/s	Optical density (D)	
10	0·107	
20	0·141	
30	0·170	Slope of log $(D_\infty - D_t)$ vs. t
40	0·197	$= -5·23 \times 10^{-3}$
50	0·219	$k_1 = 12·0 \times 10^{-3}$ s⁻¹
60	0·237	
70	0·256	$k_2 = 5·42$ mol⁻¹ s⁻¹ l
80	0·270	
90	0·286	
100	0·295	
∞	0·394	

(B) Bromination of 2-(3,5-dimethylphenyl)ethyltrimethylammonium perchlorate in 0·00191M-perchloric acid at $25·0 \pm 0·1°$

a = $[\text{ArH}] = 3·60 \times 10^{-4}$ mol l⁻¹   b = $[\text{HOBr}] = 1·49 \times 10^{-4}$ mol l⁻¹

t/s	$D_t - D_0$	k_2/mol^{-1} s⁻¹ l
20	0·182	(57)
40	0·274	50
60	0·347	50
80	0·397	50
100	0·431	48
120	0·460	47
150	0·492	47
∞	0·600	

x = $[a(D_t - D_0)]/(D_\infty - D_0)$
$k_2 = [2·303/(a - b)]$ log $[b(a - x)/a(b - x)]$

The calculation of relative rates in Table 3 made it desirable to include the bromination of benzene in this study; the relevant rate coefficients are collected in Table 5 together with the data on bromination in D_2O and rate coefficients for the bromination of anisole and mesitylene. The comparison of these relative rates with those for nitration also required a slight extension of our previous studies of nitration.[12,27] The rate coefficients for the nitration of compounds A, B, and C (Table 3) in 68·3% sulphuric

[22] A. F. Titley, *J. Chem. Soc.*, 1926, 508.
[23] L. H. Amundsen and L. S. Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 242.
[24] A. F. Titley, *J. Chem. Soc.*, 1926, 516.

[25] J. W. Shoesmith and R. J. Connor, *J. Chem. Soc.*, 1927, 2232.
[26] F. A. Ramirez and A. Burger, *J. Amer. Chem. Soc.*, 1950, **72**, 2781.
[27] T. A. Modro and J. H. Ridd, *J. Chem. Soc. (B)*, 1968, 528.

acid at 25° were therefore determined by the method used previously.[27] The results (k_2 in mol^{-1} s^{-1} l) were as follows: A, 0·40; B, 0·79; C, 0·26. These results, in conjunction with that for benzene at this acidity ($k_2 = 0·61$ mol^{-1} s^{-1} l) give relative rates in Table 3.

TABLE 5

Second-order rate coefficients [k_2, equation (1)] for the bromination of neutral substrates by hypobromous acid in aqueous perchloric acid at $25·0 \pm 0·1°$

Benzene		Mesitylene	
HClO₄/mol l^{-1}	k_2/mol^{-1} s^{-1} l	HClO₄/mol l^{-1}	k_2/mol^{-1} s^{-1} l
0·0189	0·354	0·000142	1450
0·0378	0·713		
0·0756	1·61		
0·113	2·46	Anisole	
0·151	3·46	HClO₄/mol l^{-1}	k_2/mol^{-1} s^{-1} l
0·181	4·00	0·000142	910
0·163 [a]	7·77		
0·159 [a]	7·60		

[a] In 94% D$_2$O. The interpolated values of k_2 for reaction in H$_2$O at these acidities are: 0·163M-HClO₄, $k_2 = 3·53$; 0·159M-HClO₄, $k_2 = 3·49$. At both acidities $k(D_2O)/k(H_2O) = 2·2$.

Product Analyses.—The comparison of the rate coefficients obtained by the spectrophotometer method for benzene and the tri-*N*-methylanilinium ion with those reported previously [3,12] provided evidence of the accuracy of this method for compounds of intermediate reactivity. Product analyses were however carried out with examples of the highly reactive and highly unreactive compounds to check that the changes in the u.v. spectrum corresponded to aromatic bromination.

A solution of mesitylene (1·06 × 10^{-3} mol l^{-1}) in aqueous perchloric acid (2 l; 7·32 × 10^{-4} mol l^{-1}) was prepared by shaking the mixture in a darkened winchester for 4 h.

An equivalent amount of hypobromous acid was then added. After 1 h, the solution was extracted with dichloromethane (4 × 150 ml). The extract was dried and evaporated, yielding material (0·196 g, 98%) with the n.m.r. spectrum of bromomesitylene.[28] There was no evidence of starting material, disubstitution, or side-chain bromination.

A solution of 2,4,6-trimethylpyridine (1 × 10^{-3} mol l^{-1}) and hypobromous acid (1 × 10^{-3} mol l^{-1}) in aqueous perchloric acid (100 ml; 56·2%) was kept for 2 h in the dark and then basified with sodium carbonate and extracted (×3) with dichloromethane. The extract was dried (Na$_2$SO$_4$) and evaporated, leaving a product (0·192 g) which, from its ^{1}H n.m.r. spectrum in carbon tetrachloride, contained 12% of the starting material and 88% of a product with three non-equivalent methyl groups and one aromatic proton [τ 3·25 (1H, s) and 7·43, 7·63, and 7·70 (each 3H, s)], as expected for 3-bromo-2,4,6-trimethyl-pyridine.[29] The total material isolated (product plus unchanged reactant) accounted for 90% of the starting material. The presence of the unchanged reactant may arise because of the oxidation of part of the hypobromous acid to bromine during the mixing of the reactants. Since the kinetic studies of these reactions were carried out under pseudo first-order conditions with excess of 2,4,6-trimethylpyridine and with the use of experimental optical densities for complete reaction, the rapid oxidation of part of the hypobromous acid to bromine would change neither the kinetic form nor the observed first-order rate coefficients.

[28] P. Diehl and G. Svegliado, *Helv. Chim. Acta*, 1963, **46**, 461.

[29] J. Abblard, G. Decoret, L. Cronenberger, and H. Pacheco, *Bull. Soc. chim. France*, 1972, 2475.