

107. *The Significance of the Bromine Cation in Aromatic Substitution. Part I. Kinetic Evidence.*

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Hypobromous acid in mineral acid solutions becomes a powerful brominating agent on account of the production of bromine cations: $\text{H}^+ + \text{HOBr} \rightleftharpoons (\text{H}_2\text{OBr})^+$.

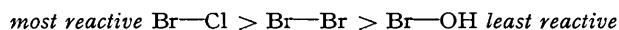
This has been established by brominating sodium toluene- ω -sulphonate with hypobromous acid in the presence of perchloric acid as catalyst and demonstrating that $k_{\text{bi}}/[\text{H}^+]$ is very nearly constant. This reaction exhibits a slight negative "primary salt effect," as would be anticipated on the Brønsted-Bjerrum theory of reaction rates.

Bromination of benzoic acid is a similar reaction, but at high concentrations of the acid catalysts (sulphuric and perchloric acid) the bimolecular reaction velocity rises abnormally. This concentration effect can, in the main, be related to the magnitude of Hammett's "acidity function," H_0 , but in addition a positive linear "salt effect" can be discerned.

At pH 7–8 the relative brominating powers of molecular hypobromous acid and molecular bromine have been compared, by use of sodium *p*-anisate as the reactant. Molecular bromine appears to be about 2000 times as active an agent as hypobromous acid, but buffer salts evidently react with the latter to produce other complex brominating agents, such as $(\text{Br}\cdot\text{HPO}_4)^-$. The ion $(\text{Br}_3)^-$ does not seem to have any detectable brominating power.

Most investigators of bromine substitution seem to concur with the view (Ingold, Smith, and Vass, *J.*, 1927, 1245; Ingold, *Chem. Reviews*, 1934, 15, 271) that the polar reactivity of a reagent

$\text{Br}-\overset{\delta+}{\text{X}}$ depends upon its polarisability to the activated state, $\text{Br}-\overset{\delta-}{\text{X}}$, and can be related to the electron affinity of X, thus:

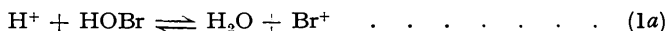


Experimental evidence for this view was put forward by Francis (*J. Amer. Chem. Soc.*, 1925, 47, 2341) who found that at about pH 3 bromine water reacted with *m*-nitrophenol at about a thousand times the speed of free hypobromous acid, and developed the view that the true brominating agent might in each case be the bromine cation, Br^+ . Later, however, his conclusions were criticised severely by Alexander (*J.*, 1938, 729) who studied the bromination of phenols on the surface of *m*/100-sulphuric acid and decided that hypobromous acid was a powerful brominating agent. Much earlier, Stark (*Ber.*, 1910, 43, 671) reported that hypobromous acid, prepared by shaking a 10% suspension of bromine in water with mercuric oxide and filtering the resulting solution, readily brominated both benzene and toluene, and even converted benzoic into *m*-bromobenzoic acid in 89% yield in 24 hours, whereas bromine water had not this reactivity.

Whilst a number of workers (*e.g.*, Baines, *J.*, 1922, **121**, 2810; Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1936, **58**, 467) have studied the effects of acids and of bromide anions on the equilibrium $\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOBr} + \text{H}^+ + \text{Br}^-$ and their implications for addition

and substitution reactions in which polarised molecules, such as $\overset{\delta+}{\text{Br}}-\overset{\delta-}{\text{Br}}$ rather than free bromine cations, Br^+ , may be involved, very few appear to have examined the effects of acids on bromide-free solutions of hypobromous acid. As already reported in brief (*Nature*, 1949, **164**, 446) we were surprised to find that, though free hypobromous acid has no tendency to react with benzene in dilute aqueous solution, yet on the addition of a mineral acid bromination readily occurs. Evidently the discrepancy between the results of Francis and of Alexander is due to the different acidities of their media; the results of Stark, which we have ourselves confirmed, are also explicable by the fact that his reagent is noticeably acidic; it had pH 2—3 when examined with a pH meter using a glass electrode.

As we have stated (*loc. cit.*), this enhanced reactivity of hypobromous acid in acidic media can be explained by the hypothesis that a rapid reversible reaction with hydrogen ions occurs to give either free bromine cations



or the complex hydrated bromine cation $(\text{H}_2\text{OBr})^+$ which is the conjugate acid of the very weak base HOBr :



According to this view, hypobromous acid can behave as a brominating agent in the same way as nitric acid behaves as a nitrating agent (Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277), though since the intensely reactive bromine cation can be formed at much lower acidities than can the NO_2^+ cation it may perhaps react as the solvated entity $(\text{H}_2\text{OBr})^+$, comparable with the nitracidium ion $(\text{H}_2\text{NO}_2)^+$ (*cf.* Halberstadt, Hughes, and Ingold, *Nature*, 1946, **158**, 514).

Though at first we thought that our experimental findings were novel, we have now seen that exactly the same theory had already been advanced by Shilov and Kaniaev in 1939 [*Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1939, **24**, 890] who studied the bromination of the sodium salt of anisole-*m*-sulphonic acid by bromine-free hypobromous acid and showed that it was a second-order reaction which proceeded at a rate which was nearly proportional to the hydrogen-ion concentration of the medium. We now report the results of similar studies of two other aromatic substrates, (a) sodium toluene- ω -sulphonate and (b) benzoic acid, which we selected because they are not attacked by bromine-water.

In *m*/200-aqueous solution at 21.5°, sodium toluene- ω -sulphonate does not react with vacuum-distilled, bromide-free hypobromous acid; a mixture at pH 5.18 (glass electrode) showed no drop in titre during 30 minutes. Similar mixtures brought to pH 2 by the addition of perchloric acid had half-reaction periods of about 15 minutes, and the usual tests of varying $[\text{HOBr}]$ and $[\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}]$ independently showed that the substitution was a process of first order with respect to each of these reactants and strictly second order as a whole, until the substitution was more than 90% complete.

TABLE I.

Bromination of sodium toluene- ω -sulphonate with hypobromous acid at 21.5° in the presence of perchloric acid.

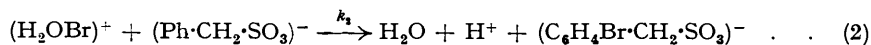
HOBr, M., $\times 10^{-3}$.	Ph·CH ₂ ·SO ₃ Na, M., $\times 10^{-3}$.	HClO ₄ , M., $\times 10^{-2}$.	<i>k</i> (bimolec.), observed (mole/l./sec.).	<i>k</i> _{cat.} (= <i>k</i> _{bi.} /HClO ₄).	Total ionic strength, M.
4.73	7.09	9.41	1.28 ± 0.03	13.5 ₄	0.1013
3.47	14.18	4.71	0.66 ± 0.03	14.0 ₁	0.0613
4.38	7.09	4.71	0.675 ± 0.02	14.3 ₄	0.0542
3.91	7.09	2.36	0.345 ± 0.01	14.7 ₄	0.0306
4.08	7.09	0.942	0.146 ± 0.002	15.4 ₈	0.0165
3.99	7.09	0.471	0.0723 ± 0.0006	15.3 ₅	0.0118
4.61	7.09	2.36 × 10 ⁻² HClO ₄ plus 7.06 × 10 ⁻² NaClO ₄	0.313 ± 0.005	13.2 ₉	0.1013
3.39	7.09	2.36 × 10 ⁻² HClO ₄ plus 2.36 × 10 ⁻² LiCl	falls with time from 0.23 to 0.17		

From Table I, which summarises our results, it will be seen that $k_{\text{cat.}}$ falls by only 12% for a 20-fold change in the perchloric acid concentration, and that it drops steadily as the total ionic strength of the solution is increased. At the dilutions which we have used, both perchloric acid and sodium toluene- ω -sulphonate will be ionised completely. Hence it is the toluene- ω -sulphonate anion which is really substituted and consequently the slight variation of $k_{\text{cat.}}$ with dilution is ascribable to a "primary salt effect" (cf. R. P. Bell, "Acid-Base Catalysis," Chap. 2, Oxford, 1941) as the following analysis will show.

Using the Brønsted-Bjerrum theory of reaction rates in solution we may write the equilibrium (1, b) above as

$$K = \frac{[\text{H}_2\text{OBr}^+]}{[\text{H}^+] \cdot [\text{HOBr}]} \times \left\{ \frac{f_{\text{H}_2\text{OBr}^+}}{f_{\text{H}^+} \cdot f_{\text{HOBr}}} \right\} \dots \dots \dots \quad (\text{A})$$

and the substitution reaction as



$$\text{Velocity of reaction, } v = k_2[\text{H}_2\text{OBr}^+][\text{Ar}^-] \times \left\{ \frac{f_{\text{H}_2\text{OBr}^+} \cdot f_{\text{Ar}^-}}{f_{\text{tr}}} \right\}$$

where Ar^- is the aromatic anion which is brominated and f_{tr} is the activity coefficient of the transition complex of the bromination reaction.

$$\text{Hence } v = Kk_2[\text{H}^+][\text{HOBr}][\text{Ar}^-] \times \left\{ \frac{f_{\text{Ar}^-} \cdot f_{\text{H}^+} \cdot f_{\text{HOBr}}}{f_{\text{tr}}} \right\} \dots \dots \dots \quad (\text{B})$$

Writing $k_{\text{bimolec.}}$ (measured) $\times [\text{HOBr}] \cdot [\text{Ar}^-] = k_{\text{cat.}}[\text{H}^+][\text{HOBr}][\text{Ar}^-]$

$$\text{we have } k_{\text{cat.}} = Kk_2 \left\{ \frac{f_{\text{Ar}^-} \cdot f_{\text{H}^+} \cdot f_{\text{HOBr}}}{f_{\text{tr}}} \right\} \dots \dots \dots \quad (\text{C})$$

At ionic strengths, μ , of under 0.1 mol./litre, the Debye-Hückel expression, $-\log_{10} f_i = Az_i^2 \mu^{\frac{1}{2}}$, may be applied for each ion involved, z_i being the charge on each reactant concerned, and hence equation (C) above gives

$$\log_{10} k_{\text{cat.}} = \log k_0 - A\mu^{\frac{1}{2}}(z_{\text{Ar}^-}^2 + z_{\text{H}^+}^2 - z_{\text{tr}}^2) = \log k_0 - \mu^{\frac{1}{2}} \dots \dots \dots \quad (\text{D})$$

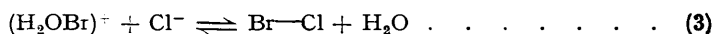
where $\log k_0 = \log_{10} Kk_2$ at infinite dilutions, and μ is the total ionic strength of the solution, since our reaction is one between univalent ions of opposite electrical charge and the theoretical values for A and z_{tr} are 0.5 and zero respectively. Thus in theory we should expect that the reaction would exhibit a *negative* primary-salt effect, and that the graph of $\log_{10} k_{\text{cat.}}$ against $\mu^{\frac{1}{2}}$ should have a limiting gradient of -1 in extremely dilute solution.

Fig. 1 shows that our experimental data accord with an equation of the form (D) though the slope of our plot (found, 0.3) is somewhat lower than the theoretical value. In particular we would draw attention to the fact that point X on the graph, corresponding to the experiment in which 0.0706N-sodium perchlorate was added to a 0.0236N-perchloric acid solution so as to bring μ up to the value for the strongest acid catalyst used, falls satisfactorily on the linear plot.

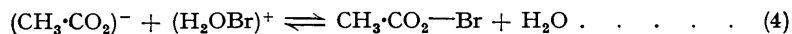
The low gradient of our graph is a natural consequence of the use of solutions somewhat more concentrated than those to which the Debye-Hückel theory is properly applicable, and the deviation may possibly be related to the fact that the transition complex of the attack of the bromine cation on the aromatic nucleus of the toluene- ω -sulphonate anion is not a simple electrically neutral entity but a large dipole, since the bromine cation approaches an uncharged carbon centre remote from the sulphonate group.

It may be noted that a similar negative salt effect seems to influence the substitution studied by Shilov and Kaniaev, in which again the reactants are ions of opposite charge, *viz.*, $(\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)^-$ and $(\text{H}_2\text{OBr})^+$.

Whilst the addition of sodium perchlorate to a reaction mixture had only a small effect on the reaction velocity, the addition of a smaller concentration of lithium chloride has a much greater effect. It noticeably decreased the rate of bromination and complicated the reaction kinetics. This may be ascribed to the setting up of the further equilibrium (3). It would appear that bromine chloride is a less active brominating agent than the bromine cation



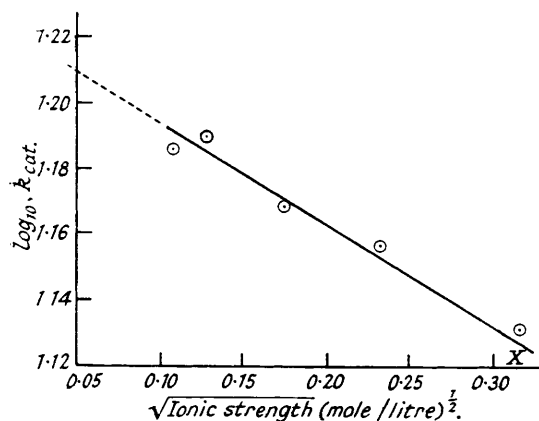
(cf. Shilov and Kaniaev, *loc. cit.*). Since similar equilibria (4), giving other electrically neutral brominating agents of uncertain reactivities, would be set up by adding salts of weak acids to



our reaction mixtures (cf. Mauger and Soper, *J.*, 1946, 71) it is not possible to extend the range of these studies of the reactivity of the bromine cation by carrying out reaction velocity measurements in buffered solutions in the range pH 3—6.

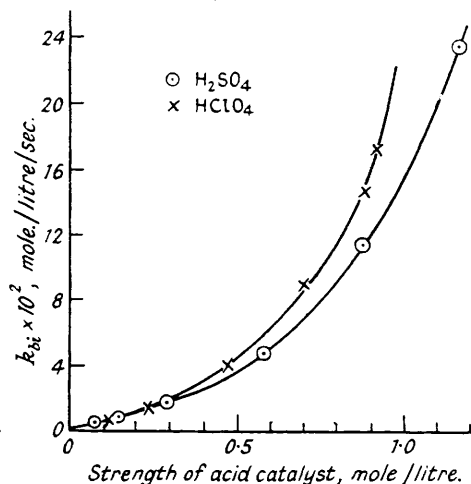
Somewhat different results have been obtained from our study of the bromination of benzoic acid. For this, in order to obtain an adequate concentration of the reactant, we had to use 40% acetic acid as the solvent, and as catalysts we took both perchloric and sulphuric acids over the concentration range 0.1—2.5*N.* Consequently the aromatic substrate was always the undissociated benzoic acid molecule. Tests showed that even in our most concentrated mineral acid catalysts the acetic acid was not attacked by the bromine cation, and a larger-scale preparation confirmed that *m*-bromobenzoic acid was the main reaction product.

FIG. 1.
Bromination of sodium toluene- ω -sulphonate with hypobromous acid.



Relationship between $\log k_{\text{cat.}}$ and $\sqrt{\text{ionic strength}}$.

FIG. 2.
Bromination of benzoic acid with bromine cation.



Relationship between $k_{\text{bi.}}$ and acid concentration.

Fig. 2 shows that both perchloric and sulphuric acid catalyse the reaction between hypobromous and benzoic acids to an extent which is roughly proportional to the mineral acid concentration up to 0.3*N.*, but that at high acid concentrations the value of $k_{\text{cat.}}$ increases as [Acid] increases, and sulphuric acid then becomes somewhat less effective as a catalyst than perchloric acid.

Though the Debye-Hückel theory is unable to predict the nature of the salt effects which influence reactions between ions and neutral molecules, an enhanced catalytic effect at high acid concentrations can be expected from analogy with hydrogen-ion-catalysed reactions, such as sucrose hydrolysis, in strong mineral acid solutions. For such reactions Hammett (*Chem. Reviews*, 1935, 16, 67; "Physical Organic Chemistry," Chap. 9, New York, 1940; Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, 56, 830) from studies of indicators of the type $\text{I} + \text{H}^+ \rightleftharpoons \text{HI}^+$ has defined expressions (E) for experimentally measurable "acidity

$$H_0 = \text{p}K_a - \log_{10} \frac{[\text{HI}^+]}{[\text{I}]} = -\log_{10} \left\{ \alpha_{\text{H}^+} \frac{f_{\text{I}}}{f_{\text{HI}^+}} \right\}; \text{ and } h_0 = \alpha_{\text{H}^+} \frac{f_{\text{I}}}{f_{\text{HI}^+}} \dots (E)$$

functions" H_0 , h_0 , which were found to be independent of the nature of the indicator chosen. He therefore suggested that in strong acid solutions h_0 might be used to replace the activity coefficient factors in the usual Brønsted-Bjerrum salt-effect equations. Indeed he showed experimentally that the kinetic expressions (F)

$$k = \text{Const.} \times h_0 \text{ and } \log_{10} k = -H_0 + \text{Const.} \dots (F)$$

could often replace the ideal equation $k = \text{Const.} \times [\text{H}^+]$ which holds satisfactorily for very dilute solutions only.

Fig. 3, in which Hammett's acidity function H_0 for aqueous sulphuric acid (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827) has been plotted against $\log_{10} k_{\text{observed}}$ for the sulphuric-acid-catalysed bromination, shows that his velocity relationship (F) holds at low acidities, when $k_{\text{cat.}}$ is approximately constant, but that at higher acidities k_{observed} increases rather more rapidly, since $\log_{10} k_{\text{observed}}$ becomes a linear function of H_0 with a gradient of -1.7 instead of the expected value of -1.0 . It is improbable that this discrepancy can be due to the use of 40% acetic acid as the solvent, since Paul and Hammett (*ibid.*, 1936, **58**, 2182) have reported that H_0 for sulphuric acid is almost the same in 50% acetic acid as in water. A similar positive deviation of substitution rates from acidity functions has been noted for aromatic nitrations in 80–90% sulphuric acid (Gillespie and Millen, *loc. cit.*).

Now for the bromination of undissociated benzoic acid we may write (G) :

$$k_{\text{obs.}}[\text{Benz}][\text{HOBr}] = Kk_2[\text{HOBr}][\text{H}^+][\text{Benz}] \left\{ \frac{f_{\text{HOBr}} \cdot f_{\text{H}^+} \cdot f_{\text{Benz}}}{f_{\text{tr}^+}} \right\} \quad \text{(G)}$$

and hence
$$k_{\text{observed}} = Kk_2[\text{H}^+] \left\{ \frac{f_{\text{H}^+} \cdot f_{\text{HOBr}}}{f_{\text{H}_3\text{OBr}^+}} \right\} \times \left\{ \frac{f_{\text{H}_2\text{OBr}^+} \cdot f_{\text{Benz.}}}{f_{\text{tr}^+}} \right\} \quad \text{(H)}$$

If Hammett's acidity function hypothesis is to be followed, then we should compare the activity factor $\left\{ \frac{f_{\text{H}^+} \cdot f_{\text{HOBr}}}{f_{\text{H}_3\text{OBr}^+}} \right\}$ with the expression $\left\{ \frac{f_{\text{H}^+} \cdot f_{\text{I}}}{f_{\text{HI}^+}} \right\}$ for an indicator system, since equilibrium (1b) is exactly that corresponding to a weakly basic indicator. Equation (H) above, however, shows clearly that the bromination which we have studied depends also on the ensuing chemical reaction between the $(\text{H}_2\text{OBr})^+$ cation and the benzoic acid molecule, and for this reaction the further activity factor product $\left\{ \frac{f_{\text{H}_2\text{OBr}^+} \cdot f_{\text{Benz.}}}{f_{\text{tr}^+}} \right\}$ must be taken into account. Since high concentrations of ions and molecules are involved it would be expected that our reaction should exhibit a positive *linear* salt effect (cf. R. P. Bell, *op. cit.*; Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," p. 62, New York, 1941) ascribable to the net value of the activity-coefficient expression given immediately above. The extended Debye-Hückel theory would then lead to the expression (I)

$$\log_{10} k_{\text{observed}} = -H_0 + B\mu + \text{Const.} \quad \text{(I)}$$

and since at high acid concentrations H_0 becomes nearly a linear function of the mineral acid concentration (Hammett and colleagues, *loc. cit.*) the "salt effect" represented by the term $B\mu$ in equation (I) may be written as bH_0 . Equation (I) then reduces to (J)

$$\log_{10} k_{\text{observed}} = -(1 + b)H_0 + \text{Const.} \quad \text{(J)}$$

and in this way the shape of the graphical results of Fig. 3 becomes explicable. This theoretical approach is however far too approximate for any attempt at quantitative treatment.

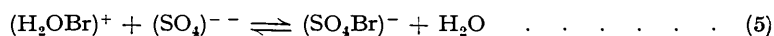
Table II shows that neutral salts still further increase the rate of bromination of benzoic acid in both sulphuric and perchloric acid. This may be due both to the positive salt effect discussed above and to the effect of neutral salts on the acidity function H_0 (Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 828).

TABLE II.

The effect of neutral salts on the bromination of benzoic acid by bromine cations at 21.5°.

Acid.	Salt added.	k_{bi} (found).
H_2SO_4 0.294M.	—	0.01626 mol./l./sec.
H_2SO_4 0.294M.	NaNO_3 1.3M.	0.0689 "
HClO_4 0.448M.	—	0.036 "
HClO_4 0.448M.	NaClO_4 0.448M.	0.0547 "
HClO_4 0.224M.	—	0.012 "
HClO_4 0.224M.	NaClO_4 0.672M.	0.0242 "

In the concentration range which we have used, the acidity functions for sulphuric and perchloric acids are almost identical. The slight deviation in the catalytic reactivities of these two acids may perhaps be due to the intervention of the equilibrium (5)



since the second dissociation constant of sulphuric acid is low enough for the $(\text{SO}_4)^{--}$ anion to function as a base. From the relevant equations for the equilibria concerned, it is easily possible to derive the expression (K)

$$[\text{SO}_4\text{Br}^-] = \text{Const.} [\text{HOBr}][\text{HSO}_4^-] \quad \dots \quad (\text{K})$$

which is similar to those used by Mauger and Soper (*loc. cit.*) in considering the effects of buffers on certain substitution reactions of hypochlorous acid. From equation (K) it can be seen that there should be an increasing conversion of highly active $(\text{H}_2\text{OBr})^+$ cations into inactive $(\text{SO}_4\text{Br})^-$ as the concentration of the sulphuric acid is increased, though this should not be an effect of the same order as the increasing conversion of neutral HOBr into $(\text{H}_2\text{OBr})^+$.

The Relative Reactivities of Hypobromous Acid and Molecular Bromine.—The foregoing work has shown that the relative rates of bromination by means of molecular hypobromous acid and molecular bromine cannot be compared in appreciably acid solution. To confirm the correctness of the polarity theory of Ingold, we have made a direct comparison of the relative

FIG. 3.

Relationship between $\log k_{bl.}$ and Hammett's acidity function H_0 for the bromination of benzoic acid with a sulphuric acid catalyst.

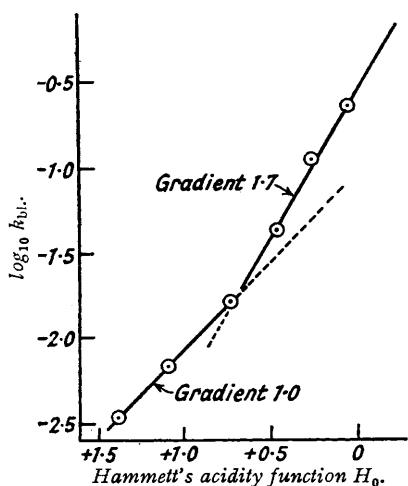
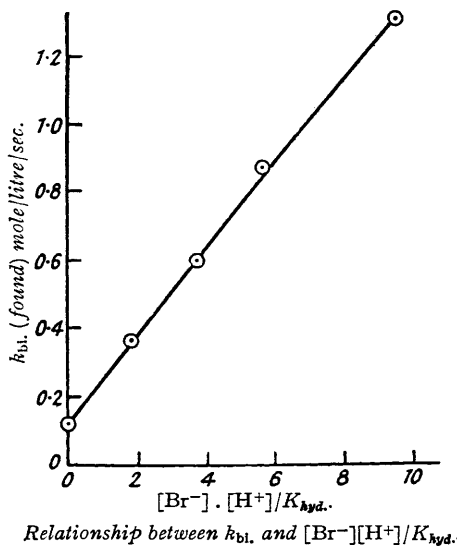


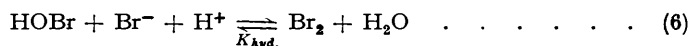
FIG. 4.

Bromination of sodium *p*-anisate with hypobromous acid/bromine mixtures at pH 7.58.



velocities of substitution of sodium *p*-anisate by these two substances in dilute solutions in phosphate buffers in the range pH 7—8, *i.e.*, in circumstances in which hypobromous acid ($K_a = 2.06 \times 10^{-9}$) (cf. Shilov and Gladchikova, *J. Amer. Chem. Soc.*, 1938, **60**, 490) would be undissociated and the aromatic substrate present as the anion. At pH 7.6 hypobromous acid gradually decomposes giving some free bromine, and so when it was used in homogeneous solution the rate of substitution was found to rise after a time. However, by working with a rapidly shaken solution containing suspended silver phosphate it was possible to obtain good second-order velocity constants until more than 75% of the material had been used; these constants corresponded to the initial velocity of the reaction in a similar solution containing no silver phosphate, which therefore acts only to regenerate hypobromous acid from aqueous bromine.

Bromine itself reacts far too rapidly with sodium *p*-anisate for it to be possible to obtain accurate velocity constants, but convincing results were obtained by adding small quantities of potassium bromide to the homogeneous hypobromous acid solutions, when, as our observations show, the equilibrium (6) is set up instantaneously. If we assume

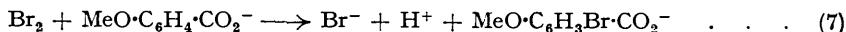


that this is true, and that hypobromous acid and bromine substitute concurrently, and remember that they can be titrated in exactly the same way, we can write (L) :

$$\begin{aligned} \text{Velocity of substitution} &= k_{\text{bi.}} [\text{HOBr}][\text{Ar}^-] \\ &= k_{\text{HOBr}}[\text{HOBr}][\text{Ar}^-] + k_{\text{Br}_2}[\text{Br}_2][\text{Ar}^-] \\ &= [\text{HOBr}][\text{Ar}^-]\{k_{\text{HOBr}} + k_{\text{Br}_2}[\text{Br}^-][\text{H}^+]/K_{\text{hyd.}}\} \quad \dots \quad (\text{L}) \end{aligned}$$

where $K_{\text{hyd.}} = [\text{Br}^-][\text{H}^+][\text{HOBr}]/[\text{Br}_2]$, the equilibrium constant for (6). The latter has been calculated as 4.29×10^{-9} at the temperature used (21.5°) from the equation given by Liebhafsky (*J. Amer. Chem. Soc.*, 1934, **56**, 1500; 1939, **61**, 3513).

Now substitution of an aromatic nucleus by hypobromous acid does not affect the acidity of the solution, and the reaction (7)



(i) regenerates bromide anions as the free bromine is consumed and (ii) reproduces the hydrogen ions used up in the formation of molecular bromine (equation 6), so that in our reaction system both $[\text{Br}^-]$ and $[\text{H}^+]$ remain constant. Consequently, as Fig. 4 shows, the graph of $k_{\text{bi.}}$ against the function $[\text{Br}^-][\text{H}^+]/K_{\text{hyd.}}$ gives a linear plot, from the slope of which k_{Br_2} has been evaluated as 119 mole/l./sec.

The data plotted on Fig. 4 give the ratio $k_{\text{HOBr}} : k_{\text{Br}_2}$ as 1 : 1100, and an approximate ratio of this order was also obtained in attempt to measure k_{Br_2} directly in an identical buffer solution.

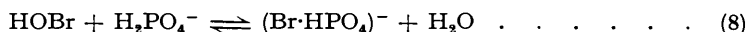
However the figure for k_{HOBr} derived from the data of Fig. 4 is itself that for a composite velocity constant. Lines 1—4 of Table III show that as the normality of the phosphate buffer is increased the velocity of bromination of sodium *p*-anisate (without added bromide) increases also, though the pH of the solution has not changed. On the other hand comparisons between lines 2*a* and 2*b*, and between lines 3*a* and 3*b* of Table III show that if the acid component of the buffer is kept in constant concentration, then, although the pH of the reacting mixture may vary in the range of pH 7—8 which does not sensibly affect the dissociation of molecular hypobromous acid, the velocity of bromination remains nearly constant.

TABLE III.

Bromination of sodium p-anisate with bromine-free hypobromous acid in phosphate buffers at 21.5°.

	Na_2HPO_4 M., $\times 10^{-2}$.	KH_2PO_4 M., $\times 10^{-3}$.	pH (glass electrode).	HOBr , M., $\times 10^{-3}$.	Anisate, M., $\times 10^{-3}$.	$k_{\text{bi.}}$ (found), mol./l./sec.
2 <i>a</i>	1.13	2.00	7.58	4.23	7.03	0.105
1	1.13	2.00	7.58	5.04	14.06	0.112
2 <i>b</i>	2.99	2.00	7.92	4.29	7.03	0.103
3 <i>a</i>	2.26	4.00	7.58	4.29	7.03	0.161
3 <i>b</i>	1.13	4.00	7.40	4.21	7.03	0.166
4	3.39	6.00	7.58	3.99	7.03	0.221
	No buffer salt		7.58	By extrapolation $k_{\text{bi.}} = 0.05$		

These results can be explained, in accordance with the views of Mauger and Soper (*loc. cit.*), by supposing that there can be formed a bromine phosphate which is somewhat more reactive than undissociated hypobromous acid. Thus a change in the potassium dihydrogen phosphate concentration shifts the equilibrium (8), whilst a change of the pH at constant $[\text{H}_2\text{PO}_4^-]$



does not. The second dissociation constant for phosphoric acid ($K_a = 6 \times 10^{-8}$) is much greater than the dissociation constant for water, and this sequence therefore accords with Ingold's views on the relative reactivities of compounds $\text{Br}-\text{X}$.

The extrapolation of the experimental results of Table III shows that the value of k_{HOBr} for the bromination of sodium *p*-anisate in the absence of any buffer is of the order of 1/2000 of the value of k_{Br_2} computed from the data given in Fig. 4. This ratio is about double that of the previous estimates of Francis and of Shilov and Kaniaev, neither of whom however took such careful precautions to eliminate either effects due to acidity or effects due to small traces of free bromine.

The results of the first part of this paper show conclusively that the bromine cation is very much more reactive than molecular bromine, but since the value of the equilibrium constant for the system (1*b*) is unknown we cannot express in figures the relative reactivities of molecular and kationic bromine. Alexander (*loc. cit.*) has ascribed an appreciable brominating power to the complex anion $(\text{Br}_3)^-$. On the other hand, Bradfield, Davies, and Long (*J.*, 1949, 1393)

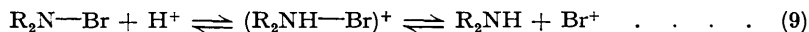
have shown that $(\text{Br}_3)^-$ is a much less active brominating agent than either hypobromous acid or molecular bromine; the same conclusion was reached for bromine addition by Bartlett and Tarbell (*loc. cit.*). Our results show that the ion $(\text{Br}_3)^-$ cannot play an appreciable part in the bromination of sodium *p*-anisate under our conditions of reaction, for if a concurrent substitution by this ion were concerned then the reaction velocity equation (L) (p. 570) would have to include a term

$$k_{\text{Br}_3^-} \cdot \frac{[\text{Br}^-]^2 \cdot [\text{H}^+]}{K_{\text{Br}_3^-} \cdot K_{\text{hyd}}}$$

which is of second order with respect to $[\text{Br}^-]$.

The theoretical curve for Fig. 4 would then become parabolic and not linear. The linearity of the results plotted in Fig. 4 therefore establishes that at pH 7–8 the most active brominating agent present in aqueous solutions is the simple bromine molecule, Br_2 . At this acidity the concentration of the bromine cation (Br^+ or H_2OBr^+) must be quite insignificant because the substitution of sodium *p*-anisate is not pH-dependent in slightly alkaline solution. Again, addition of bromide anion cannot in any way increase the concentration of the bromine cation in the equilibrated system (1) (p. 565), yet it does most markedly increase the rate of aromatic substitution.

Finally we would point out that in polar solvents the substitution reaction of *N*-halogeno-compounds may often be due to the formation of similar systems of cationoid reactivity (*e.g.*, 9).



Schmid (*Helv. Chim. Acta*, 1946, **29**, 1144) for instance has found that *N*-bromosuccinimide can be used to substitute benzene and toluene in the presence of concentrated sulphuric acid. The molecular rearrangements and aromatic substitutions which can be effected by *N*-chloro- and *N*-bromo-compounds are again reactions which proceed *via* their conjugate acids, since they are dependent on general acid catalysis.

EXPERIMENTAL.

Hypobromous Acid.—Aqueous solutions of hypobromous acid were prepared by the method of Shilov and Kaniaev (*J. Gen. Chem. Russia*, 1938, **8**, 445, in Russian) by shaking *ca.* 0.08*N*-bromine-water, made from purified bromine, b. p. 58.1°/747 mm., with an excess of freshly prepared silver phosphate. When the smell of free bromine had disappeared (1 hour), the resulting solution was distilled from a water-bath at 40–50° under a water-pump vacuum, in an all-glass apparatus the outside of which had been covered with a heavy coat of black paint to exclude light. The condenser and receiver were both cooled in ice-water, and the latter was protected by a trap to avoid back-diffusion of impurities arising from interactions of hypobromous acid and rubber connections. The hypobromous acid solutions thus obtained were about 0.02*M.* and had a very pale yellow colour, most of which was due to the presence of traces of free bromine. Nearly all the latter was then removed by extracting the distillate at 0–5° with carbon disulphide-free carbon tetrachloride, and the last traces of the extractant were eliminated by centrifugation. Solutions of hypobromous acid prepared in this way give no precipitate with silver nitrate, though on storage an opalescence gradually develops. Analyses, carried out as described below, show that the product may still contain up to 2% of free bromine, but that it is almost free from bromic acid. It is reasonably stable at 0°, but, when frozen so that ice separates and the remaining liquid becomes much more concentrated, extensive decomposition occurs. Aqueous solutions which have been diluted to about 5×10^{-3} *M.* can be kept for about an hour at summer temperatures (20–25°) without exhibiting any change in titre or noticeable increase in free bromine content.

For the kinetic work these solutions were regularly analysed by the following methods, and allowance was made for the presence of free bromine, after it had been established that this did not react with either benzoic acid or sodium toluene-*o*-sulphonate in the aqueous mixtures used.

Analytical Methods.—(i) $(\text{HOBr} + \text{Br}_2 + \text{HBrO}_3)$ was determined by addition to potassium iodide in dilute sulphuric acid solution followed by thiosulphate titration. (ii) Br_2 was estimated by difference, since it did not react with benzoic acid even in strong sulphuric acid solution. 5 ml. of the hypobromous acid reagent were run into 20 ml. of a solution of 1 g. of benzoic acid in a mixture of 40 ml. each of stabilised glacial acetic and 10*N*-sulphuric acids in a stoppered flask. After 6 minutes, when the HOBr had reacted completely, aliquots of this solution were run into aqueous potassium iodide, and titrated with thiosulphate. (iii) HBrO_3 was determined also by difference, by use of an excess of aqueous crotonic acid to remove both HOBr and Br_2 , as indicated by Shilov and Kaniaev. The remaining HBrO_3 was allowed to liberate iodine from potassium iodide in strong hydrochloric acid in the presence of a few drops of ammonium molybdate solution, added as a catalyst. A typical analysis gave the values: HOBr, 0.018*M.*; Br_2 , 5×10^{-4} *M.*; HBrO_3 under 4×10^{-5} *M.*

*Quantitative Bromination of Sodium Toluene-*o*-sulphonate.*—Sodium toluene-*o*-sulphonate (Fromm and Seixas Palma, *Ber.*, 1906, **39**, 3309) was crystallised first from hot water and then from absolute alcohol, and finally dried in a vacuum at 100°. It was neutral, stable to cold permanganate solution, and gave no precipitate with silver nitrate or barium chloride solutions. A stock solution in distilled water was mixed as required with standardised perchloric acid prepared from AnalaR chloride-free

material. For kinetic measurements, freshly prepared dilute hypobromous acid was added to the prepared samples of the acidified aromatic compound contained in blackened glass-stoppered flasks immersed in a thermostat at $21.5^\circ \pm 0.05^\circ$, the initial volume regularly being 50 ml. At intervals, 5-ml. portions were withdrawn for titration with $N/100$ -thiosulphate, by a semi-micro-burette. Since the temperature of the thermostat was very close to that of the laboratory the time of reaction could be measured to as high a degree of accuracy as that of half-addition of the mixtures to acidified potassium iodide solution. Immediately after each experiment the purity of the hypobromous acid solution was checked.

The examples in Table IV show the accuracy of the determinations of the second-order reaction velocity coefficient.

TABLE IV.

Bromination of sodium toluene- ω -sulphonate with hypobromous acid.

(A) $\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na} = 7.09 \times 10^{-3}\text{M.}$, $\text{HOBr} = 4.73 \times 10^{-3}\text{M.}$, $\text{HClO}_4 = 0.0942\text{N.}$

Time:		Titre	HOBr	k (bimol.),
min.	sec.	(corr. for Br_2), ml.	remaining, %.	calc.
0	0	4.59	100	—
0	37	3.37	73.5	1.306
1	11	2.68	58.4	1.263
2	10	1.89	41.2	1.268
3	58	1.10	24.0	1.286
6	2	0.66	14.4	1.279
8	20	0.41	8.9	1.154

Mean $k_{\text{bl.}} = 1.275 \pm 0.03$ mole/litre/sec.

(B) $\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na} = 7.09 \times 10^{-3}\text{M.}$, $\text{HOBr} = 4.079 \times 10^{-3}\text{M.}$, $\text{HClO}_4 = 0.00942\text{N.}$

Time:		Titre	HOBr	k (bimol.),
min.	sec.	(corr. for Br_2), ml.	remaining, %.	calc.
0	0	3.96	100	—
0	58	3.73	94.2	0.1477
3	15	3.26	82.3	0.1479
5	41	2.88	72.7	0.1440
8	43	2.46	62.1	0.1460
15	21	1.83	46.3	0.1448
25	25	1.23	31.1	0.1446

Mean $k_{\text{bl.}} = 0.146 \pm 0.002$ mol./litre/sec.

Quantitative Bromination of Benzoic Acid.—AnalaR benzoic acid was dissolved in purified acetic acid (Orton and Bradfield, *J.*, 1924, 125, 960), and the solutions were diluted with the chosen specimens of dilute sulphuric or perchloric acids so that the final mixture contained 40% of acetic acid by volume. Velocity measurements were conducted at 21.5° by the procedure described above. The examples in Table V show that the bromination is strictly a second-order reaction.

TABLE V.

Bromination of benzoic acid with hypobromous acid.

(A) $\text{Ph}\cdot\text{CO}_2\text{H} = 7.876 \times 10^{-3}\text{M.}$, $\text{HOBr} = 3.747 \times 10^{-3}\text{M.}$, $\text{H}_2\text{SO}_4 = 2.352\text{N.}$

Time:		Titre	HOBr	k (bimol.),
min.	sec.	(corr. for Br_2), ml.	remaining, %.	calc.
0	0	3.92	100	—
1	18	3.38	86.2	0.2503
4	35	2.44	62.2	0.2432
8	56	1.59	40.6	0.2577
12	18	1.20	30.6	0.2568
17	21	0.80	20.2	0.2580
24	14	0.48	12.2	0.2590
33	11	0.26	6.6	0.2586

Mean $k_{\text{bl.}} = 0.255 \pm 0.004$ mole/litre/sec.

(B) $\text{Ph}\cdot\text{CO}_2\text{H} = 7.876 \times 10^{-3}\text{M.}$, $\text{HOBr} = 4.035 \times 10^{-3}\text{M.}$, $\text{HClO}_4 = 0.1176\text{N.}$

Time:		Titre	HOBr	k (bimol.),
min.	sec.	(corr. for Br_2), ml.	remaining, %.	calc.
0	0	4.14	100	—
8	12	3.43	82.8	0.00487
15	1	2.89	69.8	0.00511
20	58	2.51	60.6	0.00511
29	7	2.07	50.0	0.00511
37	43	1.69	40.8	0.00512
47	29	1.36	32.8	0.00507

*Bromination of Sodium *p*-Anisate with Hypobromous Acid.*—Hypobromous acid, prepared as described above, was shaken with freshly prepared silver phosphate at 0° for 4 hours, filtered through sintered glass, and added to a buffered solution of sodium *p*-anisate maintained at 21.5° in a thermostat. Table VI indicates the ensuing rate of reaction. The pH given was determined by means of a glass electrode standardised against pure potassium hydrogen phthalate.

TABLE VI.

*Reaction of hypobromous acid with sodium *p*-anisate at pH 7.58.*

$\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na} = 7.03 \times 10^{-3}\text{M.}$, $\text{HOBr} = 4.20 \times 10^{-3}\text{M.}$, $\text{Na}_2\text{HPO}_4 = 0.0113\text{M.}$, $\text{KH}_2\text{PO}_4 = 0.0020\text{M.}$ } Buffer pH = 7.58.

Time:		Titre (corr. for Br_2), ml.	k (bimol.),	Time:		Titre (corr. for Br_2), ml.	k (bimol.),
min.	sec.		calc.	min.	sec.		calc.
0	0	4.15	—	12	19	1.96	0.1776
4	10	3.45	0.1105	17	5	1.36	0.2075
8	27	2.58	0.1529	22	0	0.94	0.2339

Since solutions of hypobromous acid when stored at pH 7—8 in the absence of the aromatic reactant gradually developed a yellow colour, this increase in $k_{\text{bl.}}$ was ascribed to the slow formation of free bromine. To obviate this, a similar mixture containing silver phosphate still in suspension was

agitated mechanically whilst the bromination with sodium *p*-anisate was carried out. Under these conditions the result recorded in Table VII was obtained.

TABLE VII.

Reaction of hypobromous acid with sodium p-anisate in presence of solid silver phosphate at pH 7.58; temp. 21.5°.

MeO·C₆H₄·CO₂Na = 1.406 × 10⁻²M., HOBr = $\left. \begin{array}{l} \text{Na}_2\text{HPO}_4 = 0.0113\text{M.} \\ \text{KH}_2\text{PO}_4 = 0.0020\text{M.} \end{array} \right\}$ Buffer pH = 7.58.
5.043 × 10⁻³M.

Time:		Titre	HOBr	<i>k</i> (bimol.),	Time:		Titre	HOBr	<i>k</i> (bimol.)
min.	sec.	(corr. for Br ₂), ml.	remaining, %.	calc.	min.	sec.	(corr. for Br ₂), ml.	remaining, %.	calc.
0	0	4.98	100	—	8	59	2.33	46.8	0.1127
2	1	4.08	81.9	0.1212	12	52	1.78	35.7	0.1101
4	10	3.41	68.5	0.1148	17	30	1.20	24.1	0.1100
6	7	2.89	58.0	0.1150					

Mean $k_{bi.} = 0.113 \pm 0.003$ mole/litre/sec.

In subsequent experiments, in which potassium bromide was added to the reaction mixtures to provide a low, but constant, concentration of bromide anions, filtered hypobromous acid solutions were used. The extrapolation of the results so obtained (cf. Fig. 4) confirms the validity of the result given in Table VII and indicates that heterogeneous catalysis does not intervene.

Table VIII indicates typical results obtained in the presence of low concentrations of bromide anions.

TABLE VIII.

Bromination of sodium p-anisate with a hypobromous acid-bromine mixture at pH 7.58; temp. 21.5°.

MeO·C₆H₄·CO₂Na = 7.03 × 10⁻³M., HOBr = $\left. \begin{array}{l} \text{Na}_2\text{HPO}_4 = 0.0113\text{M.} \\ \text{KH}_2\text{PO}_4 = 0.002\text{M.} \end{array} \right\}$ Buffer pH = 7.58 (glass electrode).
4.355 × 10⁻³M., KBr = 1.68 × 10⁻³M.

Time:		Titre	HOBr	<i>k</i> (bimol.),	Time:		Titre	HOBr	<i>k</i> (bimol.),
min.	sec.	(corr. for Br ₂), ml.	remaining, %.	calc.	min.	sec.	(corr. for Br ₂), ml.	remaining, %.	calc.
0	0	4.30	100	—	3	3	1.28	31.0	1.308
0	38	3.12	75.6	1.323	4	7	0.92	22.3	1.323
1	13	2.44	59.1	1.304	5	42	0.59	14.3	1.336
2	3	1.80	43.6	1.289	7	50	0.34	8.2	1.346

Mean $k_{bi.} = 1.32 \pm 0.02$ mole/litre/sec.

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