706. *The Mechanism of Bromine Substitution in Aqueous Solution.*

By W. J. Wilson and F. G. Soper.

Benzene and o-nitroanisole are brominated by bromine water at conveniently measurable rates. It is found that molecular bromine is the brominating agent in bromine water and that the tribromide ion is inactive. In hypobromous acid solutions bromination is slight, but the reactivity of hypobromous acid is increased by hydrogen-ion concentration to values much exceeding that of bromine. This is interpreted as due to bromination by positive bromine ion, H_2OBr^+. In buffer solutions at constant pH, bromination occurs at a rate dependent on the product of the concentration of the hypobromous acid and of the free acid of the buffer, indicating bromination by acyl hypobromite. The latter rate may also exceed that of bromination by molecular bromine.

THE fact that molecular bromine is a more powerful brominating agent than hypobromous acid in water was demonstrated by Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340). This would be expected from the calculated relative ease of ionisation of these substances into positive bromine, the ratio of the hypothetical ionisation constants of bromine and hypobromous acid into positive halogen being given by K_h/K_w, where K_h is the hydrolysis constant of bromine and equals 5.8×10^{-9} (Liebhafsky, *ibid.*, 1934, **56**, 1500), and K_w is the ionic product of water. This relative ease of ionisation would be expected to be approximately related to the ease with which

the electrophilic brominating molecule can supply positive bromine to the nucleophilic centre. Schilov and Kaniaev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 890), in studying the reaction of hypobromous acid with anisole-*m*-sulphonic acid, observed a marked increase in reaction rate as the hydrogen-ion concentration was increased, which was attributed to the formation of a bromine cation by displacement of the reaction $H^+ + HOBr \rightleftharpoons Br^+ + H_2O$. As pointed out, however, by Bradfield and Jones (*Trans. Faraday Soc.*, 1941, **37**, 726), Schilov and Kaniaev did not consider the effect of increase in hydrogen-ion concentration on the ionization and reactivity of anisole-*m*-sulphonic acid. The hypothesis of the bromine cation, nevertheless, explains satisfactorily many of the reactions of hypobromous acid (Hinshelwood, *J.*, 1947, 694). The production of bromine cations from molecular bromine, $Br_2 \rightleftharpoons Br^+ + Br^-$, should be assisted by low concentrations of Br^-, and it is possible that the retarding effect of increase in concentration of the latter may be due partly to repression of the ionisation of bromine into bromine cations. Alexander (*J.*, 1938, 729), using monolayer technique, measured the bromination of *p*-hexadecylphenol and found that the rate of interaction with bromine water was *increased* to a marked extent on addition of bromide ions. From comparison with bromination by hypobromous acid it was concluded that the tribromide ion was four times as effective as hypobromous acid. It is possible that formation of Ph·OBr derivatives is a complicating factor in the above work where the phenolic groups are preferentially available in the monolayer.

Precise work on the reactivity of aqueous hypobromous acid in substitution reactions is handicapped by its decomposition to bromic and hydrobromic acids, the latter then reacting with hypobromous acid to produce bromine. The decomposition of hypobromous acid (Prutton and Maron, *J. Amer. Chem. Soc.*, 1935, **57**, 1652) follows the equation $v = k_4[HOBr]^3[OH^-]$, where k_4 at 25° has the value $4 \cdot 4 \times 10^8$ l.³ mol.⁻³ min.⁻¹. This corresponds, in a solution of M/100-hypobromous acid, to 0·44% decomposition in 1 min. at pH 7, with proportionally less decomposition in more acid solutions and greatly increased stability in more dilute solutions. This instability of hypobromous acid necessitates a careful selection of reaction so that the speed of the latter, whilst not too rapid for examination, is sufficiently fast to avoid complication by appreciable decomposition of the hypobromous acid. Reactions of hypobromous acid with *o*-nitroanisole and with benzene have been found to be satisfactory in this respect.

Utilising *o*-nitroanisole and bromine water, the effect of bromide has been examined in view of the unusual result observed in the interfacial reaction. The effect of bromide, which converts bromine into the tribromide ion, normally results in a retardation of the bromination rate (cf. Bradfield, Jones, and Orton, *J.*, 1929, 2810). This has been again confirmed in the present work on the bromination of *o*-nitroanisole by bromine water. The specific rates k_2, given by $v = k_2[Br_2 + Br_3^-][\text{nitroanisole}]$, which are observed on decreasing the percentage of free bromine from 86·8 to 6·2% by additions of potassium bromide, are shown in the table, the equilibrium constant of $Br_2 + Br^- \rightleftharpoons Br_3^-$ (Lewis and Randall, "Thermodynamics," 1923, 520) being taken as 15·2 at 25°. Values of $k_2^{Br_3}$, defined by $v = k_2^{Br_2}[Br_2][\text{nitroanisole}]$ and equal to $k_2[Br_2 + Br_3^-]/[Br_2]$, are satisfactorily constant.

| [Br₂.]	[o-Nitroanisole].	[Br⁻].	k_2.	$\dfrac{[Br_2]}{[Br_2 + Br_3^-]}$.	$k_2^{Br_3}$.
0·001	0·005	0·010	3·21	0·868	3·74
0·001	0·005	0·021	2·81	0·755	3·68
0·001	0·005	0·087	1·49	0·404	3·70
0·001	0·005	0·010	0·232	0·062	3·74

Hydrolysis of the bromine to hypobromous acid, by the reaction $Br_2 + H_2O \rightleftharpoons HOBr + H^+ + Br^-$, was reduced to a negligible extent in the above experiments by the presence of hydrogen ion at a concentration of 5×10^{-3} M., as well as by the presence of bromide ion. Hydrogen-ion concentration was found to have no appreciable effect on the specific rate of bromination by bromine water as shown in the figure, and hence bromination by the latter cannot be due to the presence of equilibrium hypobromous acid. The fact that the specific rate, $k_2^{Br_2}$, after correction for the presence of inactive tribromide, is unaffected by a 100-fold change in bromide-ion concentration, further indicates that the activity of molecular bromine is not due to the presence of small amounts of positive bromine cations, formed in the equilibrium, $Br_2 \rightleftharpoons Br^- + Br^+$, for this ionisation would be greatly affected by the increase of bromide-ion concentrations.

Comparison of the effect of hydrogen ion on the rate of bromination by bromine and by hypobromous acid is shown in the figure, the [H⁺] being varied from 5×10^{-3} to 3×10^{-2} by additions of perchloric acid. At the latter hydrogen-ion concentration, the specific rate of bromination by hypobromous acid is some six times greater than that by bromine, and the effect

cannot, therefore, be due to conversion of the hypobromous acid into bromine. A similar effect is observed in the bromination of an aqueous solution of benzene. In neither case can the effect be attributable to change in reactivity of the substance undergoing substitution, and must, therefore, be associated with the displacement of the equilibrium $HOBr \rightleftharpoons Br^+ + OH^-$, giving increased concentration of active bromine cations.

The effect of acids on the bromination of nitroanisole by HOBr and Br$_2$.
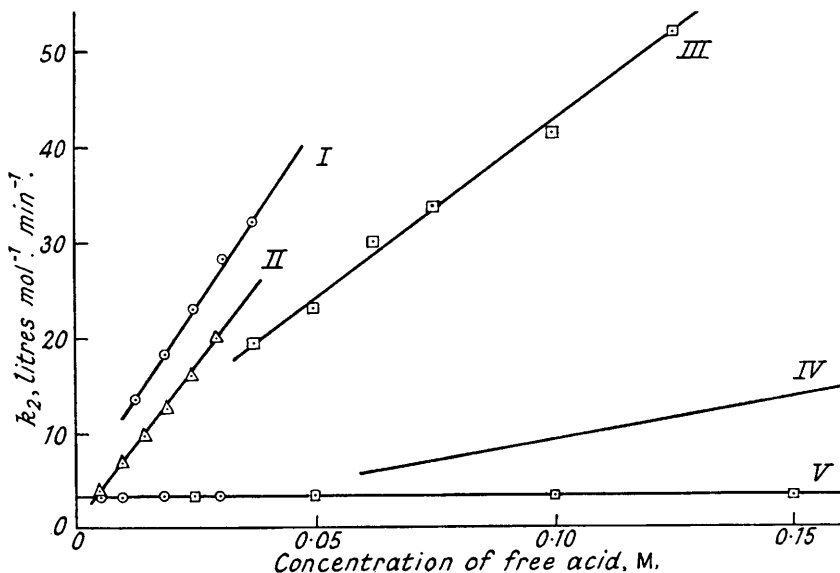
I. HOBr, CH$_2$Cl·CO$_2$H *buffer, pH* = 2·74.
II. HOBr, H$_3$O$^+$ (HClO$_4$).
III. HOBr, H$_3$PO$_4$ + NaH$_2$PO$_4$ *buffer, pH* = 1·72.
IV. HOBr, CH$_3$·CO$_2$H *buffer, pH* = 4·87.
V. Br$_2$ + *acids.* —○— HClO$_4$. —□— CH$_2$Cl·CO$_2$H.

The electron deficiency of the bromine cations and the donor properties of the oxygen of water would suggest H_2O,Br^+ for its form in aqueous solution. That no effect is observed on the reactivity of molecular bromine with increase in hydrogen-ion concentration would be expected from the non-participation of hydrogen-ion in the equilibrium $Br_2 \rightleftharpoons Br^+ + Br^-$.

Catalysis by acyl hypohalogenites has now been observed in *N*-chlorination (Mauger and Soper, *J.*, 1946, 71) and in iodination (Painter and Soper, *J.*, 1947, 342). Similar catalysis is shown in the bromination of *o*-nitroanisole and of benzene using hypobromous acid and increasing concentration of buffer at constant pH. A half-neutralised chloroacetic acid buffer being used at pH 2·74, where the specific rate of bromination by hypobromous acid in the absence of chloroacetic acid is approximately 1 l. mol.$^{-1}$ min.$^{-1}$, the specific rate is progressively increased with increase of buffer concentration to values, *e.g.*, 30 l. mol.$^{-1}$ min.$^{-1}$, much exceeding the specific rate by bromine water. The effect of such additions of buffer at constant pH is shown in the figure for chloroacetic, phosphoric, and acetic acid buffers. Variation of the sodium acetate concentration in the acetic acid buffer was found to be without appreciable effect. With 0·5M-acetic acid and 0·05, 0·15, and 0·2M-sodium acetate, the specific rates observed were respectively 30·7, 29·4, and 29·6. No catalytic effect is observed on addition of chloroacetic acid buffer at pH 2·74 to mixtures containing bromine water. Evidently, inappreciable amounts of acyl hypobromite are formed in acid solutions under the experimental conditions by the reaction, $Br_2 + AcOH \rightleftharpoons AcOBr + H^+ + Br^-$, although in the iodination of phenol by iodine in near-neutral solutions a marked effect of the buffer acid is observed. This is probably due to the difference in the acidity of the solutions examined in the two cases. Both hydrogen ion and un-ionised acids have a marked catalytic effect on the reactions of hypobromous and hypoiodous acids. Since the halogen cation may be written as H_2OX^+, and other acid derivatives as AcOX, the enhanced electrophilic reactivity may be regarded as due in the former to the addition of a proton to the HOX molecule, and in the latter to the replacement of the hydrogen by groups such as acyl with decreased electron-donor properties.

Comparison of the halogenating properties of aqueous solutions of bromine and iodine, indicates that, in both, acyl hypohalogenites and halogen cations are highly effective in causing substitutive halogenation, but that, unlike molecular iodine, molecular bromine is also reactive.

EXPERIMENTAL.

The reaction rate was followed iodometrically, all reactions being carried out in stoppered flasks at a temperature of $25 \cdot 0° \pm 0 \cdot 02°$. The reaction between bromine water and o-nitroanisole was shown to be dependent on the concentrations of both reactants. With initial concentrations $[Br^-] = 0 \cdot 01M.$, $[Br_2] = 0 \cdot 001M.$, $[H^+] = 10^{-3}N.$, doubling the initial concentration of o-nitroanisole from $0 \cdot 0025$ to $0 \cdot 0050M.$ gave specific bimolecular rates of $3 \cdot 47$ and $3 \cdot 37$ uncorrected for tribromide formation. A typical experiment in which the initial concentrations were $[Br_2] = 0 \cdot 00192M.$; [nitroanisole) $= 0 \cdot 005M.$; $[Br^-] = 0 \cdot 01M.$; $[H^+] = 0 \cdot 005N.$ is given below:

Time, mins.	0	6	12	18	24	30	36	42
Titre of 10 c.c. in c.c. of $0 \cdot 00296N$-$Na_2S_2O_3$	13·00	11·94	10·82	9·94	9·02	8·00	7·58	7·12
k_2, l. mol.$^{-1}$ min.$^{-1}$	—	2·89	3·18	3·14	2·94	3·53	3·30	3·18

With benzene, the specific rate, k_2, with bromine water in the presence of $0 \cdot 01M$-bromide, was $0 \cdot 166$ l. mol.$^{-1}$ min.$^{-1}$, whilst with hypobromous acid and perchloric acid to increase the hydrogen-ion concentration, results obtained were :

$[H^+] \times 10^2$, M.	1	1·58	2·0	2·31	3·98	6·00
k_2, l. mol.$^{-1}$ min.$^{-1}$	5·7	9·0	12·0	13·8	20·0	32·5

With chloroacetic acid buffer pH 2·8, the effect of increase of the concentration of the free chloroacetic acid, by increasing the total amount of the buffer, was to increase the specific rate as in the case of o-nitroanisole :

$[CH_2Cl \cdot CO_2H]$, M.	0·04	0·08	0·12	0·16	0·20	0·24
k_2, l. mol.$^{-1}$ min.$^{-1}$	2·16	2·80	3·60	4·00	5·30	6·22

The figures for the catalytic effect of acids on the rate of bromination by hypobromous acid are probably subject to errors due to partial conversion of the hypobromous acid into bromine owing to the displacement of the equilibrium, $HOBr + H^+ + Br^- = Br_2 + H_2O$, in the more acid solutions. Any bromine formed in this way would not show an enhanced reactivity due to the presence of acid and hence the true reactivity of hypobromous acid in the presence of acid may be greater than that recorded. The recorded figures are, however, greatly in excess of reactivities due to bromine and show a progressive increment with increase of acid concentration.

Hypobromous acid was prepared by three methods : (a) by centrifuging bromine water with yellow mercuric oxide, (b) distillation of solutions prepared as in (a), (c) by centrifuging bromine water with silver phosphate. Samples of hypobromous acid give rise spontaneously to bromic and hydrobromic acids, only the latter being removed by silver phosphate and mercuric oxide. Iodometric titration of solutions of hypobromous acid treated with 5 c.c. of M/100-phenol for 30 secs. to remove all the hypobromous acid, and then with potassium iodide and M-phosphoric acid gave the bromic acid content, and comparison with titrations omitting the preliminary treatment with phenol gave the hypobromous acid content by difference. Bromic acid was present in the hypobromous acid to an extent of 10% or less. Reaction rates using hypobromous acid (plus added acid to give a measurable speed) revealed no differences due to the method of preparation. Presence of small amounts of bromic acid appeared to have no effect on the reaction rate, and estimation of bromic acid before and after a reaction showed no appreciable formation of this acid in 15 minutes, within which period the reactions involving hypobromous acid were examined.

UNIVERSITY OF OTAGO, DUNEDIN, NEW ZEALAND.