Kinetics and Mechanism of Aromatic Halogenation by Hypohalous Acids. Part I. Bromination of Aromatic Ethers by Hypobromous Acid.

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The reactivity of hypobromous acid with aromatic ethers in 75% acetic acid at 19·8° is extremely high, and the rates become measurable only when the ethers contain one or more powerful deactivating substituents. The kinetics of the bromination of *p*-nitroanisole and *p*-nitrophenetole show that the reaction is bimolecular, and of first order with respect to each of the reactants.

The rate of substitution is much higher than with either bromine or bromine chloride in the same medium, although Derbyshire and Waters (*J.*, 1950, 564) found that at pH 7 the velocities of bromination of sodium *p*-anisate by bromine and by hypobromous acid are in the ratio 2000 to 1.

The formation of the hydrated bromine cation by the equilibrium $H^+ + HOBr \rightleftharpoons BrOH_2^+$ has been postulated to explain the acid-catalysed bromination of sodium toluene-ω-sulphonate, and a similar explanation is now advanced for the enhanced reactivity of hypobromous acid in 75% acetic acid solution. Experiment shows that the reaction with *p*-nitroanisole is catalysed by mineral acid, the value of $k_{bl}/[H^+]$ remaining virtually constant for $[H^+]$ in the range 0·005—0·090M.
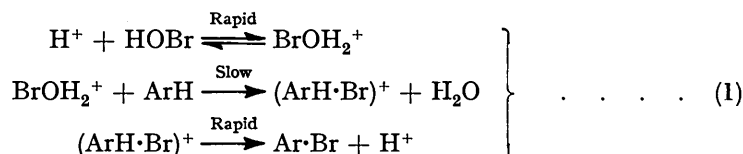
A decrease in the rate of bromination on the addition of acetate ion to the solution, and an increase in rate in the presence of neutral salts, confirm that bromination by the brominium ion Br^+ or by the solvated cation $BrOH_2^+$ is of predominant importance in the medium used.

ALTHOUGH much attention has been given to the study of substitution by bromine, little was known until recently of the nature of the various brominating agents, or of the influence of solvents, particularly of acid media, in modifying their reactivity. As a result, the relative brominating powers of such agents have, through a conflict of evidence, remained obscure. This is especially true of molecular bromine, bromine water, and hypobromous acid (Bradfield and Brynmor Jones, *Trans. Faraday Soc.*, 1941, **37**, 734, and references cited therein).

It is generally accepted that the brominating power of a reagent Br–X is not only related to the electron affinity of X, but is also determined by its polarisability to the activated state, $\overset{\delta+}{Br}$–$\overset{\delta-}{X}$ (Ingold, Smith, and Vass, *J.*, 1927, 1245; Ingold, *Chem. Reviews*, 1934, **15**, 271). The brominium ion Br^+ should therefore be the most powerful, and

hypobromous acid one of the weakest of brominating agents. In acid media, however, hypobromous acid has been found to be a most effective reagent. This was first observed by Shilov and Kanjaev (*Doklady Akad. Nauk S.S.S.R.*, 1939, **24**, 890), who showed that in weakly alkaline solution the bromination of sodium anisole-*m*-sulphonate (ArH) by bromine-free hypobromous acid proceeds in accordance with the equation $d[HOBr]/dt = k_2[ArH][HOBr]$. On the addition of sulphuric or nitric acid k_2 increased in value, but $k_2/[H^+]$ remained approximately constant. The rate of reaction could be represented by $d[HOBr]/dt = k_1[ArH][HOBr][H^+]$, where $k_1 = k_2/[H^+]$, and $[HOBr][H^+]$ is a measure of the formation of the bromine cation, in accordance with the equilibrium, $H^+ + HOBr \rightleftharpoons H_2O + Br^+$. This view has been confirmed recently by Derbyshire and Waters (*loc. cit.*) for the bromination of sodium toluene-ω-sulphonate and of benzoic acid. In aqueous solution at pH 5·18, sodium toluene-ω-sulphonate is not attacked by bromine-free hypobromous acid at 21·5°, but on the addition of perchloric acid, and at pH 2, bromination becomes rapid, and is a reaction of the first order with respect to each reactant, and second order as a whole for 90% of the reaction. In the light of these results it becomes clear, as Derbyshire and Waters have pointed out, that the conflicting evidence relating to the relative effectiveness of bromine and hypobromous acid arises from the different acidities of the media used.

Direct confirmation of the presence of bromine cations in acidified solutions of hypobromous acid has been obtained from electrodialytic experiments by Gonda-Hunwald, Graf, and Körösy (*Nature*, 1950, **166**, 68), but thermodynamic calculations by Bell and Gelles (*J.*, 1951, 2734) have shown that the bare halogen cation cannot exist in appreciable concentration in aqueous solution, although the solvated cation is much more stable. If this, then, is the reagent in acid media, the bromination of aromatic compounds by hypobromous acid in the presence of added acid may be represented as follows :

$$
\left.
\begin{aligned}
H^+ + HOBr &\xrightleftharpoons{\text{Rapid}} BrOH_2^+ \\
BrOH_2^+ + ArH &\xrightarrow{\text{Slow}} (ArH\cdot Br)^+ + H_2O \\
(ArH\cdot Br)^+ &\xrightarrow{\text{Rapid}} Ar\cdot Br + H^+
\end{aligned}
\right\} \quad \cdots \cdots \quad (1)
$$

Although the mechanism of the acid-catalysed bromination of organic compounds in water would seem to be established, little is known concerning the mechanism in solvents such as aqueous acetic acid. Recently, however, Derbyshire and Waters (*loc. cit.*) have found that the kinetics of the bromination of benzoic acid in 50% acetic acid points to bromination by the solvated bromine cation, $BrOH_2^+$, and, in some preliminary experiments in 75% acetic acid, Bradfield, Davies, and Long (*J.*, 1949, 1389) obtained approximate bimolecular rate constants for the reaction of hypobromous acid with two phenolic ethers.

In the present study the rates of bromination at 19·8° of a wide range of *p*-substituted and 2 : 4-disubstituted alkyl phenyl ethers have been determined in 75% acetic acid solution. In all cases the reaction has been found to be of the second order, and satisfactory rate constants have been obtained over 80—90% of the reaction range. (For

TABLE 1. *Initial rates :* p-*nitrophenetole in* 75% *acetic acid at* 19·8°.

Initial concns. (mole l.$^{-1}$)		Initial rate, $10^6 dx/dt$	$(dx/dt)/[\text{Ether}][\text{HOBr}]$
[Ether]	[HOBr]		
0·0050	0·00334	5	0·30
0·0100	0·00325	10	0·31
0·0050	0·00643	10	0·31

a preliminary report of the main results see Branch and Brynmor Jones, *Research*, 1952, **5**, 334.) The reaction between *p*-nitrophenetole and hypobromous acid was shown by initial rate measurements to be of the first order with respect to each reactant. Results typical of many are given in Table 1. Attempts to confirm the order of reaction by the " half-life " method proved tedious because of the difficulty of obtaining accurately reproducible concentrations of hypobromous acid. It was found, however, that the ratios

of the fractional life times in two sets of experiments were very close to the calculated values, as shown in Table 2.

TABLE 2.   p-*Nitrophenetole : order of reaction from fractional life periods.*

[Ether]$_1$ = 0·00500M				[Ether]$_2$ = 0·00500M		
[HOBr]$_1$ = 0·00334M				[HOBr]$_2$ = 0·00643M		
Reaction, %	10	20	30	40	50	60
(t_1/t_2), calc.	1·29	1·26	1·25	1·24	1·23	1·22
(t_1/t_2), obs.	1·30	1·26	1·24	1·24	1·22	1·22

[Ether]$_1$ = 0·00500M				[Ether]$_2$ = 0·00250M			
[HOBr]$_1$ = 0·00583M				[HOBr]$_2$ = 0·00556M			
Reaction, %	10	20	30	40	50	60	70
(t_1/t_2), calc.	0·98	1·00	1·03	1·07	1·12	1·19	1·27
(t_1/t_2), obs.	0·96	1·00	1·03	1·07	1·11	1·18	1·26

Another complication, which may be overcome by careful choice of experimental conditions, is the instability of hypobromous acid. In 75% acetic acid the most carefully purified specimens decompose slowly to give free bromine, and it was necessary, therefore, to determine the relative reactivities of bromine and hypobromous acid towards aromatic ethers, especially since Derbyshire and Waters had found that at pH 7—8 bromine attacks sodium *p*-anisate about 2000 times as rapidly as does hypobromous acid.

The rate of bromination of *p*-nitroanisole by molecular bromine in 75% acetic acid was expected from earlier halogenation studies to be slow, and it was in fact found to be inappreciable compared with its rate of bromination by hypobromous acid. Because of the formation of HBr$_3$, and the consequent complexity of the kinetics (Bradfield, Brynmor Jones, and Orton, *J.*, 1929, 2810), the bimolecular coefficient for bromination by bromine falls as the reaction proceeds : nevertheless, the initial value obtained by extrapolation from the present measurements in 75% acetic acid was no greater than 2×10^{-5} l. mole^{-1} sec.$^{-1}$. This value is almost low enough to be accounted for by bromination by HOBr resulting from the hydrolysis of bromine (2), and is in marked contrast to the value 0·162 l. mole^{-1} sec.$^{-1}$ for the bromination of *p*-nitroanisole by hypobromous acid itself.

$$Br_2 + H_2O \rightleftharpoons HOBr + HBr \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Addition of small amounts of bromide ion to the reaction solution containing pure hypobromous acid leads to the immediate formation of free bromine in accordance with

$$HOBr + Br^- \rightleftharpoons Br_2 + OH^- \qquad . \quad . \quad . \quad . \quad . \quad (3)$$
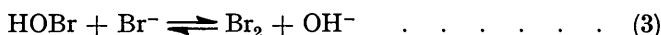
equation (3) and rate coefficients, calculated from the initial concentrations of hypobromous acid and aromatic ether, fall rapidly as the reaction proceeds. When, however, the values are re-calculated, with allowance for HOBr removed in this way, satisfactory constants are obtained. These constants agree with those found later when using bromine-free hypobromous acid. This is illustrated by the results given in Table 3.

TABLE 3.   p-*Nitrophenetole at* 19·8°.

Initial concn. of aromatic ether, a; initial concn. of HOBr, b_1; concn. of added bromide ion, b_2.

$a = 0·00500$M; $b_1 = 0·00295$M; $b_2 = 0$.   Mean $k_{bi} = 0·328$ l. mole^{-1} sec.$^{-1}$.
$a = 0·00250$M; $b_1 = 0·00359$M; $b_2 = 0·00050$M.

Time (sec.)	150	460	920	1310
$\log_{10} [a(b_1 - b_2 - x)/(b_1 - b_2)(a - x)]$	0·0127	0·0393	0·0728	0·1061
k_{bi}	0·330	0·334	0·322	0·316

Addition of chloride ion in an amount greater than that of the hypobromous acid brought the reaction virtually to a standstill, and this, no doubt, may be attributed to the formation of bromine chloride as in equation (4). Although this reagent would be

$$H_2OBr^+ + Cl^- = BrCl + H_2O \qquad . \quad . \quad . \quad . \quad . \quad (4)$$
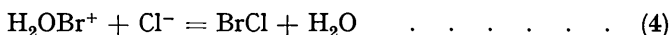
expected to be more reactive than free bromine, the fact that no fall in titre was observed during the experiments in 30 min. shows that its brominating power is
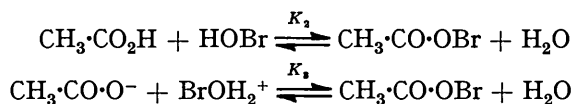
extremely low compared with that of hypobromous acid at pH 2. These experiments indicate that hypobromous acid in 75% acetic acid is a much more active brominating agent than bromine, bromine chloride, and the hypobromous acid molecule.

TABLE 4. *Bromination of* p-*nitroanisole : catalysis by mineral acid at* 19·8°.

Concn. of added mineral acid (M)	k_{bi}	$k_{cat.} = (k_{bi} - k_0)/[H_2SO_4]$
—	0·162 (k_0)	—
0·005	0·248	17·2
0·010	0·324	16·2
0·017	0·434	16·0
0·030	0·660	16·6
0·043	0·820	15·8
0·088	1·61	16·5

That the high reactivity of such a solution may be ascribed to the solvated bromine cation is supported by the observation that the reaction of *p*-nitroanisole with hypobromous acid in acetic acid solution is catalysed linearly by mineral acid, the catalytic coefficient remaining almost constant for amounts of added sulphuric acid in the range 0·005—0·090M (see Table 4). It can be calculated from the catalytic coefficient that the rate of reaction in 75% acetic acid corresponds to a hydrogen-ion concentration in this solvent of 0·010 mole l.$^{-1}$. The value calculated from the dissociation constant of acetic acid is 0·015 mole l.$^{-1}$.

It has been suggested by Mauger and Soper (*J.*, 1946, 71) that the brominating agent in acetic acid solution may be the acyl hypobromite. This could be formed by the establishment of either of the following equilibria in acetic acid solutions of HOBr :

$$CH_3 \cdot CO_2H + HOBr \underset{}{\overset{K_2}{\rightleftharpoons}} CH_3 \cdot CO \cdot OBr + H_2O$$

$$CH_3 \cdot CO \cdot O^- + BrOH_2^+ \underset{}{\overset{K_3}{\rightleftharpoons}} CH_3 \cdot CO \cdot OBr + H_2O$$

If the hypobromite is formed according to the first equation, and the following reaction ensues, $CH_3 \cdot CO \cdot OBr + ArH \overset{k_2}{\longrightarrow} CH_3 \cdot CO_2H + ArBr$, the overall rate of reaction is given by the expression

$$-d[HOBr]/dt = k_2 K_2 [CH_3 \cdot CO_2H][HOBr][ArH] \quad . \quad . \quad . \quad . \quad (5)$$

and the observed bimolecular constant by

$$k_{obs.} = k_2 K_2 [CH_3 \cdot CO_2H] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If, on the other hand, the acyl hypobromite results from the second equilibrium, the corresponding relationship becomes

$$-d[HOBr]/dt = k_2 K_1 K_3 K_{HOAc}[CH_3 \cdot CO_2H][HOBr][ArH] \quad . \quad . \quad . \quad (7)$$

where K_{HOAc} is the dissociation constant of acetic acid, and K_1 is the constant for the equilibrium, $H^+ + HOBr \overset{K_1}{\rightleftharpoons} BrOH_2^+$. In this case

$$k_{obs.} = k_2 K_1 K_3 K_{HOAc}[CH_3 \cdot CO_2H] \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For bromination by the solvated cation mechanism the reaction is $BrOH_2^+ + ArH \overset{k_1}{\longrightarrow} ArBr + H_3O^+$, which leads to the expression

$$k_{obs.} = k_1 K_1 [H^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

To distinguish between the alternative mechanisms of bromination by the solvated bromine cation and by acyl hypobromite, a study was made of the bromination of *p*-nitroanisole in various acetic acid–water mixtures, and the manner in which the rate constant varies with the composition of the medium is shown in Table 5. The shape of the curve obtained by plotting the rate constants against the composition of the medium may be accounted for qualitatively on the basis of bromination by the solvated cation. As acetic acid is added to the aqueous solution the rate increases rapidly from 0·021 to

0·183—a result which arises from the formation of hydrogen ions by the dissociation of the acetic acid. This increase in rate is counteracted, however, by a decrease in the dielectric constant of the medium, as the percentage of acetic acid is increased, so that over quite a range of concentration the observed velocity coefficient remains virtually constant. The rapid decrease in rate which then follows in solutions of high acetic acid content may be

TABLE 5. *Variation in velocity coefficient for the bromination of* p-*nitroanisole with composition of the solvent at* 19·8°.

Weight, %, of acetic acid ...	0	10	25	50	65	75	85
k_{bi}	0·021	0·183	0·194	0·189	0·183	0·162	0·134
			0·190	—	0·175	0·163	0·136

due to two factors. In this region (75—90%), the concentration of acetic acid and of acetic acid monohydrate decreases rapidly, while the concentration curve for the dimer rises steeply (Kipling, *J.*, 1952, 2858). This, combined with the decreasing dielectric constant of the medium, could account for the rapid fall in the rate of bromination observed in 80—90% acetic acid solutions. It is less easy to see how a curve of this form could arise when the acyl hypobromite is the effective brominating agent. Equation (9) may be written in the form

$$k_{obs.} = k_1 K_1 K_{HOAc}[CH_3 \cdot CO_2 H]/[CH_3 \cdot CO \cdot O^-] \quad . \quad . \quad . \quad . \quad (10)$$

and on comparing this with equations (6) and (8) it is seen that the addition of acetate ion to the reaction solution should lead to a decrease in the bimolecular constant only when bromination occurs by the mechanism of the solvated cation. The figures in Table 6 show that this decrease is observed experimentally. That the fall in the constant is here not

TABLE 6. *Effect of added acetate ion : bromination of* p-*nitroanisole at* 19·8°.

Concn. of added acetate ion (M)	—	0·010	0·050	Satd. soln.
$k_{obs.}$	0·162	0·135	0·122	0·085

as marked as might be expected from equation (10) may be due to an increase in rate in solutions of higher ionic strength, as a result of the operation of a positive secondary salt effect.

An increase in rate in the presence of neutral salts has also been observed (Table 7) and this, presumably, is to be attributed to the same secondary salt effect.

TABLE 7. *Effect of neutral salts on the rate of bromination of* p-*nitroanisole at* 19·8°.

Salt added	Concn. (M)	Observed velocity constant	$\log_{10} (k/k_0)$
—	—	0·162 (k_0)	—
Na_2HPO_4	0·005	0·164	0·005
Na_2SO_4	0·020	0·170	0·021
Li_2SO_4	0·030	0·176	0·036

Direct confirmation that bromination by this mechanism is of predominant importance may be obtained from a study of the catalytic effect of hydrogen ion on the rate of bromination of *p*-nitroanisole in water. If 75% acetic acid is taken to have a pH of 2, the value of the rate constant in 0·015M-aqueous sulphuric acid should be at least as great as in 75% acetic acid containing 0·005M of added mineral acid. Any differences in dielectric constant between the two media would operate to increase further the catalysed rate in water. The values found experimentally were 0·276 l. mole^{-1} sec.$^{-1}$ in acidified aqueous solution, and 0·248 l. mole^{-1} sec.$^{-1}$ in 75% acetic acid containing sulphuric acid.

It would appear, therefore, that the kinetics of the bromination of *p*-nitroanisole and *p*-nitrophenetole by hypobromous acid in 75% acetic acid solution are consistent with bromination by the solvated bromine cation. Catalysis by mineral acid, and the effects of added acetate ion and of neutral salts, indicate that bromination by the acyl hypobromite cannot be of significance under the experimental conditions in this investigation. It is not impossible, however, for the brominating agent in concentrated acetic acid to be the ion, $Br \cdot \overset{+}{O} \overset{H}{\underset{CO \cdot CH_3}{\diagdown}}$, that is, a bromine ion solvated by an acetic acid molecule. The kinetics of bromination by such an ion would be similar to those by the solvated cation

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$BrOH_2^+$, but it is not possible to make a distinction between them on the basis of the present kinetic studies. In 75% acetic acid solution, it is concluded, therefore, that the active brominating agent is either the solvated cation, $BrOH_2^+$, or the brominium ion Br^+.

EXPERIMENTAL

Acetic acid was purified by distillation from 2% chromium trioxide (" AnalaR "), followed by redistillation from 0·2% naphthalene-2-sulphonic acid and the theoretical amount of " AnalaR " acetic anhydride (Orton and Bradfield, *J.*, 1927, 983). Considerable head and tail fractions were rejected, and the final distillate had m. p. 16·4°. This was analysed for excess of acetic anhydride (Orton and Bradfield, *loc. cit.*) and the average content was 0·003 ml. per 100 ml. of purified acid. The reaction medium, containing 75% of acetic acid by weight (n_D^{20} 1·3756), was prepared by adding the calculated volume of acetic acid (after allowance for the slight water content of the purified acid) to a known volume of distilled water.

Hypobromous Acid.—Considerable difficulty was encountered at first in obtaining hypobromous acid sufficiently pure for the kinetic measurements. A few preliminary experiments by Bradfield, Davies, and Long (*loc. cit.*) showed a constant bimolecular coefficient for the bromination of benzyl *p*-nitrophenyl ether by HOBr in 75% acetic acid, whereas their values for *p*-nitrophenetole showed a downward drift. Repetition of these experiments, with carefully purified *p*-nitrophenetole and *p*-nitroanisole, and hypobromous acid prepared by the method of Bradfield, Davies, and Long, confirmed that the rate coefficients decrease as the reaction proceeds. It was suspected, and later confirmed, that this decrease arose from the presence of free bromine in the hypobromous acid. In these experiments the initial titres were, therefore, a measure of total bromine—that due to hypobromous acid and that due to free bromine in solution. The fall in titre during the course of the reaction with the aromatic ether, on the other hand, was a measure of its rate of bromination by hypobromous acid alone. Later an equation was derived which enabled these rate values to be corrected for the presence of free bromine in the HOBr.

If a and b_1 are the initial concentrations of ether and HOBr respectively, and b_2 the concentration of free bromine in solution (the total bromine being $b_1 + b_2 = B$), R_t the observed rate constant after time t, and k the rate constant for bromination by HOBr, then

$$R_t = \frac{1}{t(B-a)} \ln \frac{a(B-x)}{B(a-x)} \quad . \quad . \quad . \quad . \quad (11)$$

and
$$R_t(a-x)(B-x) = dx/dt = k(a-x)(b_1-x) \quad . \quad . \quad . \quad (12)$$

whence
$$R_t = k - kb_2(B-x)^{-1} \quad . \quad . \quad . \quad . \quad (13)$$

Since the values of R_t for substitution in this expression are obtained from equation (11), which is derived by integration of (12) on the assumption that R_t does not vary with t, equation (13) is not strictly valid. It was found, however, that by using the value of x corresponding to $t/2$ so that equation (13) becomes

$$R_t = k - [Kb_2(B-x)_{t/2}^{-1}] \quad . \quad . \quad . \quad . \quad (14)$$

the graph of R_t against $(B-x)_{t/2}^{-1}$ was a straight line of slope $-Kb_2$, and intercept K, for concentrations of bromine not greater than 25% of the concentration of hypobromous acid. Some examples of the results after correction in this way are given in Table 8. These rate constants agree well with the values 0·162 and 0·328 found later, when using purified hypobromous acid.

TABLE 8.

Ether	Observed rate coefficient, R_t Initial value (l. mole^{-1} sec.$^{-1}$)	Final value	Graphically extrapolated values b_2 (M)	K
p-Nitroanisole	0·120	0·109	0·00021	0·163
p-Nitrophenetole	0·175	0·126	0·00067	0·325
	0·149	0·110	0·00033	0·328

The constancy of the bimolecular coefficients found by Bradfield, Davies, and Long for benzyl *p*-nitrophenyl ether probably arose from a compensation of two opposing factors. It has now been established that with pure, bromine-free hypobromous acid the rate of bromin-

ation of this particular ether increases as the reaction proceeds. For the reasons already given, this increase could be masked if the hypobromous acid contained free bromine, and carefully conducted experiments with hypobromous acid purified by the method given below showed that the constant values found by these earlier workers were in fact fortuitous. The values now obtained are given in Table 9, and it will be seen that the increase in rate persists after the ether had been repeatedly crystallised, and the ratio of ether to hypobromous acid varied five-fold.

TABLE 9. *Bromination of benzyl* p-*nitrophenyl ether by hypobromous acid in* 75% *acetic acid at* 19·8°.

(1) [Ether] = 0·00250 mole/l.; [HOBr] = 0·00644 mole/l.

Time (sec.)	212	465	850	1320	1540
k (l. mole^{-1} sec.$^{-1}$)	0·114	0·118	0·135	0·184	0·241

Ether recrystallised from ethyl alcohol :

(2) [Ether] = 0·00250 mole/l.; [HOBr] = 0·00578 mole/l.

Time (sec.)	215	513	790	1165
k (l. mole^{-1} sec.$^{-1}$)	0·113	0·121	0·134	0·159

Ether recrystallised twice from ethyl alcohol and twice from methyl alcohol :

(3) [Ether] = 0·01250 mole/l.; [HOBr] = 0·00498 mole/l.

Time (sec.)	200	410	555	825
k (l. mole^{-1} sec.$^{-1}$)	0·116	0·118	0·123	0·131

It was suspected that this anomalous behaviour in the case of the benzyl ether arose from the slow formation of free nitrophenol as a result of the debenzylation, and this was in some measure confirmed by qualitative tests, although no derivative of nitrophenol could be isolated.

Pure hypobromous acid was prepared by shaking bromine (3 ml.; " AnalaR "), water (1 l.), and silver sulphate (15 g.) until the heavy precipitate settled, leaving a clear, pale straw-coloured supernatant solution. After filtration, the aqueous solution of hypobromous acid was distilled under reduced pressure (*ca.* 15 mm.) from a water-bath at 40—50°. The all-glass distillation apparatus was coated with a thick layer of black paint to exclude light, and the distillate was collected and stored over carbon tetrachloride in a dark bottle. Only samples of hypobromous acid which had been distilled during the previous 48 hr. were used for kinetic measurements. Traces of bromine were removed from the stored solution as completely as possible by shaking and allowing the carbon tetrachloride to settle. Immediately before each experiment a 25-ml. sample of the aqueous layer was removed and shaken with a further 10 ml. of pure carbon tetrachloride. Solutions of HOBr purified in this way, and diluted to give 75% w/w acetic acid solution, gave no appreciable titre due to bromine during 30 min. at 20°, as shown herewith :

Time (sec.)	0	175	290	580	680	950	1385
HOBr titre, ml.	12·80	—	—	12·80	—	12·80	—
Br$_2$ titre, ml.	—	0·00	0·00	—	0·00	—	0·02

(Titres in ml. of 0·00500N-sodium thiosulphate for 5-ml. portions of 0·00640 mole/l. HOBr in 75% acetic acid.)

The free bromine was estimated by running the 5-ml. portions of hypobromous acid solution into an excess of benzoic acid in 75% acetic acid to remove the HOBr, adding potassium iodide, and titrating the liberated iodine against the thiosulphate. The total hypobromous acid and bromine was estimated by direct titration against standard thiosulphate in the usual way.

Kinetic Measurements.—All measurements were made at 19·8° ± 0·02°. Because of the high reactivity of hypobromous acid towards the aromatic ethers it was essential to reduce the time taken to mix the solutions, and thereby minimise errors in timing. For this, a special reaction vessel was made consisting of two small long-necked flasks with ground glass stoppers, and connected in such a way as to form an H-shaped vessel with bulbs at both feet. The reactants were introduced into separate limbs, and the reaction initiated by inverting and rapidly shaking the vessel. The progress of the reaction was followed by running 5-ml. samples into aqueous potassium iodide, containing a little solid carbon dioxide to reduce the oxidation of the liberated hydrogen iodide during the determination. The liberated iodine was titrated against 0·005N-sodium thiosulphate. Individual values of the bimolecular coefficient in any experiment usually varied over approximately 3%, but the mean values obtained in different

experiments were usually within 2% of one another. The following values for p-nitroanisole are typical.

(1) p-*Nitroanisole in* 75% *acetic acid at* 19·8°.

[Ether] = 0·00500 mole/l.; [HOBr] = 0·00633 mole/l.

Time (sec.)	0	240	494	750	1024
Titre, ml.	25·55	21·46	18·46	16·45	14·73
10^3x (mole/l.)		1·01	1·75	2·26	2·68
k_{bi} (l. mole^{-1} sec.$^{-1}$)		0·163	0·164	0·160	0·160

(2) p-*Nitroanisole in* 75% *acetic acid with* 0·088M-H_2SO_4.

[Ether] = 0·00500 mole/l.; [HOBr] = 0·00182 mole/l.

Time (sec.)	46	75	115	205
10^3x (mole/l.)	0·54	0·76	1·02	1·36
k_{bi} (l. mole^{-1} sec.$^{-1}$)	1·64	1·58	1·63	1·63

p-Nitroanisole, m. p. 53°, p-nitrophenetole, m. p. 59°, and benzyl p-nitrophenyl ether, m. p. 106°, were prepared by standard methods and purified by repeated crystallisation from absolute alcohol.

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