296. *The Halogenation of Phenolic Ethers and Anilides. Part XV. The Kinetics of Bromination in 75% Acetic Acid.*

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The rate of bromination of *p*-chlorophenyl ethers in 75% acetic acid by bromine solutions is represented by the expression: $dx/dt = k_b[E][Br_2] + k_t[E][Br_2]^2$, the ratio k_t/k_b being constant. The same expression is applicable to *o*-chlorophenyl ethers, but the ratio k_t/k_b is approximately one fifth of that found for the *p*-chloro-series. Hypobromous acid is a powerful brominating agent for ethers in this medium, but analysis of the kinetics of the reaction shows that it plays little, if any, part in bromination by bromine solutions. The significance of the term involving $[Br_2]^2$ is discussed.

(*Symbols.*—The following symbols are used throughout with the meaning shown, concentrations being in g.-mols./l.$^{-1}$:

a = total initial concentration of bromine.
b = total initial concentration of hydrobromic acid.
c = initial concentration of phenol ether.
$[Br_2]$ = concentration of bromine not combined as HBr_3
$= \frac{1}{2}\{\sqrt{(K + b - a + 2x)^2 + 4K(a - x)} - (K + b - a + 2x)\} = y.$
$[HBr]$ = concentration of hydrobromic acid not combined as $HBr_3 = b + x - (a - x - y)$.
$[E]$ = concentration of phenolic ether.
$K = [Br_2][HBr]/[HBr_3] = 0{\cdot}0110$ in 75% acetic acid at 20°).

Kinetically, the reaction between bromine and phenol ethers in 50% acetic acid is, in the first place, complicated by retention of part of the bromine as HBr_3 by the hydrobromic acid added initially or formed during the reaction, the HBr_3 being inactive as a brominating agent in this medium. It was found by Bradfield, Jones, and Orton (*J.*, 1929, 2810) that, provided that 5—10 molecular proportions of hydrobromic acid were present throughout the reaction, the rate of reaction could be represented reasonably well as a bimolecular reaction between " free " bromine and ether :

$$dx/dt = k_b[E][Br_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The bimolecular constant k_b tends to fall somewhat as the reaction progresses, this fall being less marked when ten than when five molecular proportions of bromine are present initially. An important observation of these authors was that, when two different ethers of the *p*-chloro- or *p*-bromo-series are brominated under identical conditions, and the times t_1 and t_2, respectively, taken for a given percentage change compared, the ratio $t_1 : t_2$ is constant at all stages of the reaction, *i.e.*, the relative rates of bromination are equal to the inverse ratio of the times taken for a given percentage change. From this it was inferred that, for the ethers examined, the law governing the rate of reaction may be expressed by an equation containing only one constant characteristic of the ether employed, *i.e.*, of the form :

$$dx/dt = k\phi([E], [Br_2], [HBr]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

notwithstanding the possible existence of complex equilibria between the various molecular species which may be present.

There is good reason to believe that, with bromine solutions, the bromine molecule is not the only brominating agent, particularly in aqueous media. Thus, to account for the large accelerating influence of water on the bromination of phenol in carbon tetrachloride, Baines (*J.*, 1922, 2810) assumed that the bromine molecule is but a weak brominating agent, while hypobromous acid, formed by hydrolysis, is very powerful. On the other hand, Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340) found that *m*-nitrophenol is brominated about 1000 as fast by bromine-water as by aqueous hypobromous acid and ascribed the activity of bromine-water to bromine atoms, probably carrying positive charges. A somewhat similar view is held by Schilov and Naniaev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 890), who found that the rate of bromination of anisole-*m*-sulphonic acid in water by hypobromous acid can be represented by the equation : $-d[HOBr]/dt = k[A][HOBr][H^{\bullet}]$, and suggested that $[HOBr][H^{\bullet}]$ is a measure of the formation of the bromine cation : $HOBr + H^{\bullet} \longrightarrow Br^{\bullet} + H_2O$, as a very powerful brominating agent. On the other hand, Alexander (*J.*, 1938, 729), overcoming the difficulty presented by the extreme rapidity of bromination of phenols in aqueous solution by spreading *p*-hexadecylphenol as a monolayer on an aqueous substrate, found that in bromine-water the effective brominating agents are the tribromide ion and the hypobromous acid molecule, the former being four times as active as the latter. Israel, Tuck, and Soper (*J.*, 1945, 547) showed that in chloroform solution a brominating agent is produced, from a bromo-amine and acetic acid, which they consider to be the acyl hypobromite and which is capable of brominating anisole and phenetole.

In acetic acid, Robertson and his collaborators (*J.*, 1943, 276; 1948, 100) found that the order of reaction between bromine and a variety of substances varies between two and four as the concentration of the bromine is increased, and put forward the expression :

$$dx/dt = k[A][Br_2] + k'[A][Br_2]^2 + k''[A][Br_2]^3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As their measurements were generally confined to the early stages of the reaction, the formation of HBr_3 was neglected, and the bromine concentrations terms represent the total bromine concentration. No attempt was made to apply this equation in detail. The interpretation placed on the term involving the square of the bromine concentration is considered later.

The present investigation is concerned primarily with an attempt to elucidate further the kinetics of bromination by bromine in 75% acetic acid; velocity measurements have been made with *o*- and *p*-chlorophenyl ethers, the initial conditions being varied. Some experiments on bromination by hypobromous acid in the same medium have also been made.

EXPERIMENTAL.

Perbromide Equilbrium Constant.—The perbromide equilibrium constant in 75% acetic acid was determined by the aspiration method of W. J. Jones (*J.*, 1911, **99**, 392), using an apparatus in which all connections in contact with bromine vapour were of ground glass, lubricated with phosphoric acid. For the solubility coefficient of bromine at 20°, a value of 260 was found. The following table gives illustrative figures of the equilibrium-constant determinations at 20°, for which a mean value of $K = 0{\cdot}0110$ was found.

$a - b$ = c.c. of 0·01734N-thiosulphate equivalent to bromine carried over by V c.c. of air.

	Initial concentrations. g.-mols./l.				
V.	Total Br.	Total HBr.	$a - b$.	Concn. of free Br.	K.
1038	0·0375	0·0188	11·49	0·0246	0·0111
996	0·0371	0·0188	10·81	0·0241	0·0107
873	0·0283	0·00953	8·68	0·0220	0·0114
1127	0·0189	0·01875	5·05	0·00991	0·0107

Determination of Velocity of Bromination by Bromine.—Materials were prepared or purified and velocity determinations carried out by the method of Bradfield, Jones, and Orton (*J.*, 1929, 2810). The solvent used consisted of a mixture of purified acetic acid and water in the proportion of 3 : 1 by weight. Two series of measurements were made of the rate of bromination at 20° of the ethers of *o*- and *p*-chlorophenol, respectively, with the initial concentration of hydrobromic acid varied from ten times the bromine concentration to zero. The data obtained were plotted as x–t curves, and with each series of ethers, relative rates were obtained directly from the curves representing experiments in which the initial conditions were identical. The same constancy of the ratio $t_1 : t_2$ is observed when $b = 0$ as when $b = 5a$ or $10a$.

The necessity of allowing for HBr_3 formation leads to a somewhat unwieldy expression when the differential equation corresponding to a bimolecular reaction between bromine and ether is integrated. To simplify the task of testing the alternative hypotheses concerning the reaction mechanism, it was therefore decided to make direct use of values of dx/dt obtained from the x–t curves. To overcome the well-known difficulty of drawing accurate tangents to a curve of large radius of curvature, the device of Groocock, Ingold, and Jackson (*J.*, 1930, 1039) was at first employed by us, but later more accurate values for the tangents were calculated in the following manner It was found that the curves representing the disappearance of bromine could be accurately reproduced by empirical equations of the following form : $t = \alpha n + \beta n^2 + \gamma n^3 + \delta n^4$, where n is the fraction of the bromine which has disappeared in t minutes. In each case, from a smooth curve drawn through the experimental points, values of t corresponding to $n = 0{\cdot}1, 0{\cdot}2$, etc., were read off, and from these figures the constants α, β, γ, and δ were evaluated. Since $na = x$, $\frac{dn}{dx} = \frac{1}{a}$ and $\frac{dt}{dx} = \frac{dn}{dx} \cdot \frac{dt}{dn} = \frac{1}{a} \cdot \frac{dt}{dn}$, while $\frac{dt}{dn} = \alpha + 2\beta n + 3\gamma n^2 + 4\delta n^3$, numerical values of dt/dx and hence of dx/dt are easily calculated. Substitution of numerical values of dx/dt and of the concentration terms in equation (1) and the other differential equations considered below has been used throughout this paper as a substitute for integration for the evaluation of the constants k_b, etc.

As examples of the experimental figures, data are given in Table I for the bromination of *p*-chlorophenyl *iso*propyl ether at 20°.

TABLE I.

(Concentrations in g.-mols./l., t = time in minutes, $S = dx/dt \times 10^6$.)

Exps. I—IV $\left\{\begin{array}{l} a = 0{\cdot}0075 \\ c = 0{\cdot}0375 \end{array}\right.$ Exp. V $\left\{\begin{array}{l} a = 0{\cdot}01875 \\ c = 0{\cdot}01875 \end{array}\right.$ Exp. VI $\left\{\begin{array}{l} a = 0{\cdot}0375 \\ c = 0{\cdot}01875 \end{array}\right.$

Exp.	% change :	30	35	40	45	50	55	60
	t =	378	463	556	666	792	938	1102
= 10a)	S =	4·81	4·20	3·65	3·17	2·76	2·41	2·12
II	t =	214	265	325	392	467	549	651
($b = 5a$)	S =	7·68	6·76	5·93	5·22	4·60	4·06	3·61
III	t =	136	170	209	253	307	367	437
($b = 3a$)	S =	11·9	10·4	9·01	7·76	6·66	5·69	4·85
IV	t =	63	80·5	99	122	151	185	226
($b = a$)	S =	24·4	20·9	17·7	14·8	12·3	10·3	8·53
V	t =	41	58	79	108	148	210	298
($b = 0$)	S =	72·5	52·4	36·6	25·4	17·9	12·9	9·46
VI	t =	8·2	10·6	13·6	17·2	21·7	27·7	35
($b = 0$)	S =	438	350	290	229	180	142	112

The rate is practically the same when five molecular proportions of sodium bromide are added initially as when the equivalent amount of hydrobromic acid is used. Again, in the absence of added hydrobromic acid, the presence of three molecular proportions of β-naphthalenesulphonic acid is without appreciable effect. It would be expected, of course, that the buffering effect of the 75% acetic acid would largely mask any possible consequence of small variations of strong-acid content on the rate of bromination.

Bromination by Hypobromous Acid.—A solution of hypobromous acid was prepared by shaking bromine, water, and yellow mercuric oxide. Acetic acid was added to this solution to bring the composition to 75% acetic acid. To estimate the small amount of bromine sometimes present, use was made of the fact that *p*-chlorophenyl 4-nitrobenzyl ether reacts almost instantaneously with hypobromous acid in 75% acetic acid and is scarcely attacked by bromine. A measured quantity of the hypobromous acid solution was added to an excess of this ether, and the remaining bromine could then be titrated. Allowance for the bromine present was made when necessary.

The hypobromous acid solution reacted almost instantaneously with equimolecular accounts of *o*- or *p*-chloroanisole or similar ethers. In some cases the product was isolated. For example, *p*-chlororophenyl 4-nitrobenzyl ether (1·253 g.) in 75% acetic acid was mixed with 0·05M-hypobromous acid (100 c.c.) and made up to 500 c.c. When the mixture was shaken, the product crystallised. It had m. p. 142—143°, and, after crystallisation from alcohol, m. p. 146—147° (0·1279 G. of the crude product gave 0·1211 g. of mixed silver halides. Calc. for $C_{13}H_9NO_3ClBr$: 0·1237 g. 0·1107 G. of the recrystallised substance gave 0·1068 g. of silver halides. Calc.: 0·1070 g.). Similarly from *p*-nitrophenetole, 2-bromo-4-nitrophenetole, m. p. 97—98°, was obtained.

The rate of bromination by hypobromous acid was, in most cases, much too rapid to be measured. Approximate values, calculated for a bimolecular reaction, were, however, obtained for *p*-nitrophenetole and *p*-nitrophenyl benzyl ether, as shown below:

$[HOBr] = [Ether] = 0{\cdot}008$ g. mols./l.

p-Nitrophenetole.

t.	% change.	*k.*
7·4	62·4	18·8
11·4	74·8	17·8

p-Nitrophenyl benzyl ether.

t.	% change.	*k.*
13·3	54·0	8·19
24·5	73·9	8·17

DISCUSSION.

In Table II is shown the effect of varying the molecular proportion of hydrobromic acid initially present on the bimolecular coefficient k_b for the bromination of *p*-chlorophenyl *iso*propyl ether, calculated from equation (1) by the method described above. It will be seen that, when $b = 0$, k_b is not only far from constant, but numerically from about two to six times greater than when $b = 10a$. On the other hand, a moderately good termolecular constant, k_t,

$$\frac{dx}{dt} = k_t[E][Br_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

derived from equation (4) may be calculated for Experiment VI.

In view of these results, the possibility of the simultaneous occurrence of a bimolecular and a termolecular reaction, as represented by equation (5) was examined. Suitable pairs of equations

$$\frac{dx}{dt} = k_b[E][Br_2] + k_t[E][Br_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

were solved for k_t/k_b. For *p*-chlorophenyl *iso*propyl ether, a mean value of $k_t/k_b = 319$ was adopted and k_b calculated, with the results shown in Table III. In Table IV are given the values of k_b for the methyl, ethyl, and *n*-propyl ethers of *p*-chlorophenol, using the same fixed value of $k_t/k_b = 319$.

Because of the retention of part of the bromine in an inactive form as HBr_3, the experiments quoted in Table III represent a more considerable range than is at first apparent. The initial "free" bromine concentration increases from 0·00103 g.-mol./l. (13·8% of the total bromine) in Exp. I to 0·0375 g.-mol./l. in Exp. VI. Correspondingly the initial values of the ratio

TABLE II.

Values of k_b *and* k_t, *calculated by equations* (1) *and* (4) *for the bromination of* p-*chlorophenyl* iso*propyl ether in* 75% *acetic acid.*

Exp.	% change:	30	35	40	45	50	55	60
I ($b = 10a$)	k_b =	0·199	0·191	0·183	0·176	0·172	0·170	0·172
IV ($b = 5a$)	k_b =	0·222	0·210	0·200	0·190	0·180	0·173	0·167
V $\begin{Bmatrix} b = 0 \\ a = c \end{Bmatrix}$	k_b =	0·531	0·468	0·403	0·352	0·316	0·296	0·291
VI $\begin{Bmatrix} b = 0 \\ a = 2c \end{Bmatrix}$	k_b =	1·22	1·14	1·06	0·97	0·90	0·84	0·80
	k_t =	43·1	42·7	41·8	40·8	40·1	40·0	40·8

TABLE III.

Bromination of p-*chlorophenyl* iso*propyl ether.*
Values of k_b *calculated by equation* (5), *with* $k_t/k_b = 319$.

Exp.	% change: 30	35	40	45	50	55	60	Mean.
I ($b = 10a$)	0·163	0·159	0·154	0·151	0·150	0·150	0·154	0·154
II ($b = 5a$)	0·128	0·127	0·127	0·127	0·130	0·134	0·140	0·130
III ($b = 3a$)	0·119	0·119	0·119	0·119	0·120	0·121	0·123	0·120
IV ($b = a$)	0·111	0·110	0·110	0·110	0·109	0·110	0·112	0·110
V $\begin{Bmatrix} b = 0 \\ a = c \end{Bmatrix}$	0·123	0·119	0·113	0·109	0·108	0·112	0·122	0·115
VI $\begin{Bmatrix} b = 0 \\ a = 2c \end{Bmatrix}$	0·122	0·120	0·116	0·113	0·110	0·109	0·110	0·114

TABLE IV.

Values of k_b *calculated by equation* (5) *with* $k_t/k_b = 319$.

Exp. VII. *p*-Chloroanisole
Exp. VIII. *p*-Chlorophenetole
Exp. IX. *p*-Chlorophenyl *n*-propyl ether
Concns. as in Exp. V.

Exp.	% change : 30	35	40	45	50	55	60	Mean.
VII.	0·0141	0·0138	0·0136	0·0135	0·0133	0·0135	0·0140	0·0137
VIII.	0·0375	0·0365	0·0351	0·0337	0·0325	0·0319	0·0320	0·0341
IX.	0·0485	0·0467	0·0451	0·0438	0·0431	0·0433	0·0426	0·0447

$[E]/[Br_2]$ vary from 36·4 : 1 to 0·5 : 1. In the slowest reaction (experiment I), 792 minutes are required for disappearance of 50% of the bromine, with $dx/dt = 2{\cdot}77 \times 10^{-6}$ at this point; the corresponding figures for the most rapid (experiment VI) are 21·75 minutes and $dx/dt = 180 \times 10^{-6}$. Bearing in mind that, because of the smoothing off of experimental errors effected by the method of calculating dx/dt, these errors do not appear as random errors in the individual values of k_b, but as a trend up or down in a given experiment, the applicability of equation (5) over this wide range of speeds is very satisfactory. Quite distinct from this trend in some experiments, there is a steady change in the mean value of k_b from 0·154 in experiment I ($b = 10a$) to about 0·113 in experiments IV, V, and VI ($b = a$ or 0). This change is similar to that shown by the bimolecular velocity coefficients for the chlorination of *p*-chloroanisole in 99% acetic acid, Bradfield and Jones (*J.*, 1928, 1006) finding k = 1·41, 1·32, and 1·22 when 7·0, 4·0, and 0·2 molecular proportions, respectively, of hydrochloric acid over and above that required to liberate chlorine from the chloro-amine were present in the reaction mixture.

A more limited number of measurements have been made with *o*-chlorophenyl ethers, for which the rate of bromination is intrinsically greater than for the corresponding *p*-chlorophenyl ethers. It is found that, in the *o*-chloro-series, k_t/k_b is 63·5, *i.e.*, about 1/5th of its value in the *p*-chloro-series. Calculated values of k_b for *o*-chloroanisole are given in Table V, showing that in this case also equation (5) is applicable, though with this ether the direction of change in the mean value of k_b with changing concentration of hydrobromic acid is the reverse of that observed with *p*-chlorophenyl *iso*propyl ether.

TABLE V.

Bromination of o-*chloroanisole.*
Values of k_b *calculated by equation* (5) *with* $k_t/k_b = 63{\cdot}5$.

Concns. : $a = 0{\cdot}0075$, $c = 0{\cdot}0150$ g.-mol./l.

Exp.	% change : 30	35	40	45	50	55	60	Mean.
X ($b = 5a$)	2·81	2·75	2·71	2·67	2·65	2·65	2·69	2·70
XI ($b = a$)	3·53	3·41	3·29	3·14	3·09	3·04	3·05	3·22
XII ($b = 0$)	3·26	3·31	3·36	3·35	3·33	3·29	3·29	3·31

We consider equation (5), viewed as an empirical equation, to represent our results satisfactorily. The constancy of k_t/k_b for each series of ethers also satisfies the requirements of equation (2). Before attempting to interpret equation (5), however, alternatives must be considered and suggestions which have been put forward regarding the nature of the brominating agents responsible for the bromination of phenols must be examined.

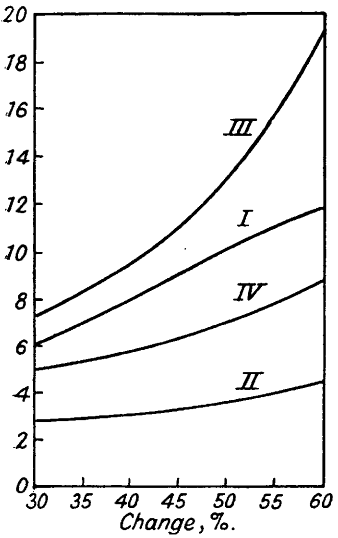
In 75%, as in 50%, acetic acid, the very marked retarding influence of hydrobromic acid implies that HBr_3 can be, at most, only a weak brominating agent. On the other hand, we find hypobromous acid to be extremely reactive, reaction in 75% acetic acid being almost instantaneous when any of the *o*- or *p*-chloro-ethers is treated with an approximately equimolecular proportion of this reagent. Isolation of the product in several typical cases showed it to be the normal chloro-bromo-ether, identical with that obtained by the action of bromine. In an attempt to obtain measurable rates, we examined the action of hypobromous acid on *p*-nitrophenetole and *p*-nitrophenyl benzyl ether, substances which do not react appreciably with bromine in this medium. Even with these substances, bromination is extremely rapid—in the case of the former, the development of a yellow colour suggests some accompanying oxidation. Such measurements as could be made lead to approximate values of k = 18 and 8, respectively, for the bimolecular velocity coefficients for bromination by hypobromous acid. It is estimated that the corresponding value of k for *p*-chlorophenyl *iso*propyl ether would be 15,000—20,000. Obviously, although there is no independent evidence of bromine undergoing hydrolysis in aqueous acetic acid, the conception of bromination as due to a very low concentration of hypobromous acid provides an attractive hypothesis, and it is imperative to examine it closely.

Bromination by hypobromous acid may be represented by equations (6) and (7). Nothing

$$\mathrm{Br_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOBr + HBr} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$\mathrm{HOBr + EH \xrightarrow{k_2} EBr + H_2O} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

is known of the relative magnitudes of k_1 and k_2, and thus three cases fall to be considered, (1) $k_1 \ll k_2$, (2) $k_1 \gg k_2$, (3) k_1 and k_2 of comparable magnitude. In each case, also, bromination must be considered as due (*a*) solely to hypobromous acid, and (*b*) partly to bromine and partly to hypobromous acid. It will be shown by reference to data from experiments V and VI above that none of these hypotheses suffices to explain the experimental results.



It is convenient first to describe the setting out of the requisite data in the figure. The initial concentration of ether, *c*, is the same in both experiments V and VI, but, whilst in experiment V, $a = c$, in experiment VI, $a = 2c$. Consider the experimental values of $(dx/dt)_P$ from experiment VI and $(dx/dt)_P{}'$ from experiment V for the same percentage change *P*. The ratio, $R = (dx/dt)_P/(dx/dt)_P{}'$ is plotted against *P* in curve I. In curve II are plotted the ratios of the calculated amounts of " free " bromine, *i.e.*, $[\mathrm{Br_2}]/[\mathrm{Br_2}]'$, $[\mathrm{Br_2}]$ and $[\mathrm{Br_2}]'$ referring to experiments VI and V, respectively. Similarly, in curve III the ratios, $[\mathrm{Br_2}]^2/[\mathrm{Br_2}]'^2$, are shown, while in curve IV are set out the ratios $([\mathrm{Br_2}][\mathrm{HBr}]')/([\mathrm{Br_2}]'[\mathrm{HBr}])$ in which [HBr] and [HBr]′ refer to values calculated for experiments VI and V, respectively.

In passing, to illustrate the use of these data, it may easily be shown that whilst the reaction is neither simply bimolecular nor termolecular, the data are compatible with equation (5) above. For, if bromination may be represented by $dx/dt = k_b[E][\mathrm{Br_2}]$, then $R = (k_b[E][\mathrm{Br_2}])/(k_b[E]'[\mathrm{Br_2}]') = [\mathrm{Br_2}]/[\mathrm{Br_2}]'$, since $[E] = [E]'$. Curve I should then coincide with curve II. Similarly, if $dx/dt = k_t[E][\mathrm{Br_2}]^2$, $R = [\mathrm{Br_2}]^2/[\mathrm{Br_2}]',^2$ and curve I should coincide with curve III. If $dx/dt = k_b[E][\mathrm{Br_2}] + k_t[E][\mathrm{Br_2}]^2$, then $\mathrm{R} = (k_b[\mathrm{Br_2}] + k_t[\mathrm{Br_2}]^2)/(k_b[\mathrm{Br_2}]' + k_t[\mathrm{Br_2}]'^2)$. The numerical side of the right-hand side must lie between $[\mathrm{Br_2}]/[\mathrm{Br_2}]'$ and $[\mathrm{Br_2}]^2/[\mathrm{Br_2}]'^2$, and therefore curve I should lie between curves II and III. As it does, equation (5) is compatible with the data.

Returning now to bromination by hypobromous acid, the three cases set out above will be examined.

Case (1). Hydrolysis of bromine slow, substitution of ether very rapid, *i.e.*, $k_1 \ll k_2$.

(*a*) Bromination by HOBr only. $dx/dt = k_1[\mathrm{Br_2}]$, $R = [\mathrm{Br_2}]/[\mathrm{Br_2}]'$.

(*b*) Bromination by $\mathrm{Br_2}$ and HOBr.

$$dx/dt = k_b[E][\mathrm{Br_2}] + k_1[\mathrm{Br_2}].$$

$$R = \frac{[\mathrm{Br_2}](k_b[E] + k_1)}{[\mathrm{Br_2}]'(k_b[E]' + k_1)} = [\mathrm{Br_2}]/[\mathrm{Br_2}]' \text{ since } [E] = [E]'.$$

In both cases the values of *R* should coincide with curve II, a conclusion not in accord with experiment.

Case (2). Hydrolysis of bromine very fast, substitution of ether slow, *i.e.*, $k_1 \gg k_2$. In this case, [HOBr] may be taken as having its equilibrium value. It is further assumed that [HOBr] is negligible compared with $[\mathrm{Br_2}]$, and that therefore $[\mathrm{Br_2}]$ may be calculated in the usual way without significant error.

(*a*) Bromination by HOBr only.

$$[\mathrm{HOBr}] = k_1[\mathrm{Br_2}]/k_{-1}[\mathrm{HBr}].$$

$$dx/dt = k_2[E][\mathrm{HOBr}] = (k_1k_2[E][\mathrm{Br_2}])/k_{-1}[\mathrm{HBr}]\,; \quad R = ([\mathrm{Br_2}][\mathrm{HBr}]')/([\mathrm{Br_2}]'[\mathrm{HBr}]).$$

As the values of *R* do not coincide with curve IV, this is not in accord with experiment.

(*b*) Bromination by HOBr and Br_2.

$$dx/dt = k_b[E][Br_2] + k_1k_2[E][Br_2]/k_{-1}[HBr]\,; \quad R = \frac{[E](k_b[Br_2] + k_1k_2[Br_2]/k_{-1}[HBr])}{[E]'(k_b[Br_2]' + k_1k_2[Br_2]'/k_{-1}[HBr]')}$$

The numerical value of R should lie between $[Br_2]/[Br_2]'$ and $([Br_2][HBr]')/([Br_2]'[HBr])$, *i.e.*, curve I should lie between curves II and IV. This is not in accord with experiment.

Case 3. Hydrolysis of bromine and substitution of ether proceed at comparable rates. Then, for a stationary concentration of HOBr

$$[HOBr] = k_1[Br_2]/(k_{-1}[HBr] + k_2[E]).$$

(*a*) Bromination by HOBr only.

$$dx/dt = k_2[E][HOBr] = (k_1k_2[E][Br_2])/(k_{-1}[HBr] + k_2[E]).$$

$$R = \left(\frac{[Br_2]}{k_{-1}[HBr] + k_2[E]}\right)\Big/\left(\frac{[Br_2]'}{k_{-1}[HBr]' + k_2[E]'}\right).$$

The numerical value of this expression lies between $[Br_2]/[Br_2]'$ and $([Br_2][HBr]')/([Br_2]'[HBr])$, *i.e.*, R should lie between curves II and IV. This is not in accord with experiment.

(*b*) Bromination by HOBr and Br_2.

$$dx/dt = k_b[E][Br_2] + k_1k_2[E][Br_2]/(k_{-1}[HBr] + k_2[E])$$

$$R = \frac{[E]\{k_b[Br_2] + k_1k_2[Br_2]/k_{-1}[HBr] + k_2[E])\}}{[E]'\{k_b[Br_2]' + k_1k_2[Br_2]'/(k_{-1}[HBr]' + k_2[E]')\}}$$

The numerical value of this expression lies between $[Br_2]/[Br_2]'$ and the numerical value of the expression deduced in (*a*) above, *i.e.*, R should lie between curve II and some curve which it has been deduced should lie between curves II and IV. This also is not in accord with experiment.

Notwithstanding the activity of HOBr as a brominating agent in 75% acetic acid, it thus appears that it does not participate appreciably in the bromination by bromine in this medium. The alternative formation of acetyl hypobromite in place of hypobromous acid (cf. Israel, Tuck, and Soper, *J.*, 1945, 547), $AcOH + Br_2 \rightleftharpoons AcOBr + HBr$, would not be distinguishable by our experiments. The conception of "positive bromine" as the brominating agent, in the sense used by Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340) and Schilov and Naniaev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 890), *i.e.*, a positively charged bromine atom as a separate entity, as distinct from a mesomeric polarization, may be dismissed, since the concentration of $Br^{\bullet}$ would be proportional to $[Br_2]/[HBr]$ if bromine dissociates, or to $[HOBr][H^{\bullet}]$ (Schilov and Naniaev). From what has already been said it will be clear that neither conception is compatible with the experimental results.

Returning then to the interpretation of equation (5), it seems unlikely that we are dealing with a single, unknown brominating agent X, whose concentration is a function of the "free" bromine concentration, which can be expressed, at least to a near approximation, as $[X] = \alpha[Br_2] + \beta[Br_2]^2$, for then, by hypothesis, β/α should be independent of the nature of the ether, whereas for *o*- and *p*-chloro-ethers different values of k_t/k_b are observed.

We concluded that the first term of equation (5) represents a true bimolecular reaction between the bromine molecule and the ether. As an interpretation of the second term, involving $[Br_2]^2$, either of the two mechanisms proposed by Robertson and his collaborators (*J.*, 1943, 276; 1948, 100) would suffice :

$$(a)\quad AH + Br_2 \rightleftharpoons AHBr_2\,;\ AHBr_2 + Br_2 \longrightarrow ABr + HBr + Br_2.$$

$$(b)\quad Br_2 + Br_2 \rightleftharpoons Br_4\,;\ AH + Br_4 \longrightarrow ABr + HBr + Br_2.$$

Of these we prefer (*b*), although no independent evidence of the existence of Br_4 molecules is available. It is implied by our calculations that the concentration of Br_4 molecules compared with Br_2 molecules is very low. The constant k_t in equation (5), on this interpretation, is really $k_b'K_B$, where k_b' is the bimolecular constant for the reaction between Br_4 and the ether, and $K_B = [Br_4]/[Br_2]^2$. It is perhaps slightly surprising to find that, for the *p*-chloro-series of ethers, k_b'/k_b is constant, as a relationship of the form, $\log k_b = m \log k_b' + \textit{constant}$, might have been expected, if Br_2 and Br_4 may be regarded as two distinct reagents. It should, however, be noted that the range of velocities represented by the present series of ethers is rather small. In the case of the *o*-chloro-series, a different value of k_b'/k_b is not incompatible with this interpretation.

Finally, Table VI shows the relative effects of alkyl groups on the rate of bromination.

These values are independent of the kinetic interpretation of the measurements given above. In each series the value for the chloroanisole is taken as 100. Comparing the *o*- with the *p*-chloro-series, k_b for *o*-chloroanisole is 242 × k_b for *p*-chloroanisole. The relation of some of these relative rates of bromination to the relative rates of chlorination of the same ethers has been briefly discussed by Bradfield and Jones (*Trans. Faraday Soc.*, 1941, **37**, 726).

TABLE VI.

Relative effects of R *in ethers,* $RO\cdot C_6H_4\cdot Cl$ *on the rate of bromination in* 75% *acetic acid.*

R =	$C_6H_5\cdot CH_2$.	Me.	Et.	Pr^n.	Pr^i.
p-Series	55	100	255	336	837
o-Series	—	100	254	289	546

The work described above was carried out at the University College of N. Wales, and much of the present discussion was incorporated in a thesis by one of us (G. I. D., University of Wales, 1931). The authors wish to express their thanks to Professor Gwyn Williams for friendly and critical discussion of the present manuscript.

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