13. *Kinetics of the Bromination of Some Anisoles and Phenols.*

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Kinetic measurements have been made on the bromination of four anisoles and six phenols in aqueous solution. The potential of a redox electrode was used to follow the disappearance of bromine in very dilute solution, and velocity constants up to 3×10^4 l. mole^{-1} sec.$^{-1}$ were measured. Measurements at varying acidities were used to derive separately the bromination velocities of phenol molecules and phenoxide ions, the latter having velocity constants up to 8×10^9 l. mole^{-1} sec.$^{-1}$. In most of the reactions studied no reaction of tribromide ions could be detected, but in the bromination of phenoxide ions their reactivity amounted to 1—3% of that of molecular bromine.

Previous work with aromatic amines[1] and with *m*-nitrophenol[2] has shown that it is possible by means of electrical methods to measure the very high rate constants (10^2 to 10^{10} l. mole^{-1} sec.$^{-1}$) for reaction of these substances with bromine. With the more reactive species, such as the dimethylanilines and the *m*-nitrophenoxide ion, it is possible to detect reaction with the tribromide ion as well as with molecular bromine, but with the less reactive *m*-nitrophenol molecule no reaction with tribromide ion can be detected. The present paper describes further work on *m*-nitrophenol by a different method, and measurements are also reported for other phenols and for anisoles, special attention being paid to the relative reactivity of Br_2 and Br_3^-.

Experimental

Materials.—Anisole and *o*-bromoanisole were fractionally distilled several times at atmospheric pressure, this process being repeated until the products from two successive fractionations gave identical kinetic results. No phenolic impurities were detectable by alcoholic ferric chloride. *p*-Bromo-, *m*-fluoro-, *o*-chloro-, and *p*-chloro-anisole were tested for phenolic impurities and distilled twice.

m-Nitrophenol, recrystallized three times from chloroform, had m. p. 98°. 2-Bromo-5-nitrophenol was prepared from *m*-nitrophenol as described by Henley and Turner[3] and recrystallized three times from carbon tetrachloride (m. p. 119°). 2,4-Dinitrophenol was recrystallized three times from water (m. p. 113°), and 2,6-dinitrophenol three times from aqueous alcohol (m. p. 61°). 2,4-Dibromophenol was prepared by brominating phenol as described by Pope and Wood:[4] the crude product was fractionally distilled at atmospheric pressure and then recrystallized from carbon tetrachloride (m. p. 35°). *p*-Bromophenol was recrystallized from carbon tetrachloride. Phenol was used without further purification.

[1] Bell and Ramsden, *J.*, 1958, 161.

[2] Bell and Spencer, *J.*, 1959, 1156.

[3] Henley and Turner, *J.*, 1930, 937.

[4] Pope and Wood, *J.*, 1912, **101**, 1824.

All inorganic substances were of "AnalaR" quality, and the water used was redistilled from potassium permanganate in a glass still.

Measurement of Reaction Velocity.—The course of the reaction was followed by measuring the change of redox potential, as previously described.[1] A platinum-gauze electrode was used, in conjunction with a calomel electrode ending in a fine capillary tip. The potential was measured with a Tinsley potentiometer with mirror-galvanometer. The bromine concentration was usually followed over the range 10^{-5} to 10^{-8}M. Below about 10^{-9}M-bromine the potential does not decrease as quickly as it should do, and behaves erratically, often changing if the potentiometer is temporarily unbalanced. Erratic behaviour was sometimes encountered at higher bromine concentrations and could only be cured by remaking the electrode. It occurred less often if the electrode was kept immersed in a concentrated bromine solution between experiments. If the initial concentration of bromine is 10^{-6}M or less, an appreciable proportion of it reacts slowly with some impurity in the water used. This complication could be avoided by first adding enough bromine to react with the impurity and then leaving the solution until all the excess of bromine had evaporated: an experiment was then carried out in the usual way.

Provided that the concentration of bromide ion remains constant, the observed e.m.f. is given by

$$E = E_0 + 0{\cdot}0295 \log [\mathrm{Br_2}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

at 25°, the numerical factor at 0° being 0·0319. E_0 involves the bromide-ion concentration and any junction potentials present. If the organic substance is present in large excess the reaction will follow a first-order course, and the second-order velocity constant k at 25° is given by

$$k = -\frac{1}{c}\frac{\mathrm{d}\ln[\mathrm{Br_2}]}{\mathrm{d}t} = -\frac{1}{c}\frac{\mathrm{d}\ln[\mathrm{Br_3^-}]}{\mathrm{d}t} = \frac{-78{\cdot}2\,.\,\mathrm{d}E}{c\,.\,\mathrm{d}t} \quad . \quad . \quad . \quad . \quad (2)$$

where c is the concentration of organic substance. At 0° the numerical factor has the value 71·7. Experiments carried out under these conditions did in fact give an accurately linear relation between E and t. If the organic substance is initially present in only moderate excess (say three-fold), c will become effectively constant after the bromine concentration has fallen by a power of ten (corresponding to 0·03 v), and a linear relation will hold after a curved initial section. Equation (2) can again be used, though the value of c will now differ from the initial concentration. If the concentrations of bromine and organic substance are more closely equivalent, then $[\mathrm{Br_2}]$ can be calculated from equation (1), using the initial e.m.f. to obtain E_0, and the value of k calculated from the usual second-order equation, which can also be applied to the curved initial section in the previous case. All these methods have been used to calculate k, with concordant results. The values thus obtained do not discriminate between different forms of bromine (*e.g.*, Br_2 and Br_3^-) or of the organic substance (*e.g.*, phenol and phenoxide ion), so that they may vary with the concentration of bromide or hydrogen ions.

The volume of the reaction mixture was usually 100 ml., and it was stirred at a constant speed of 1500 r.p.m.; preliminary experiments showed that the same results were obtained with any speed between 800 and 2500 r.p.m. The reaction was started by adding one of the reactants from a calibrated pipette of about 1 ml. capacity. If possible, the organic substance was added last, so that the initial potential in the bromine solution could be measured. For the faster reactions it was convenient to set the potentiometer at successive 10 mv intervals, and to record the times at which the galvanometer spot passed through zero. By using initial concentrations down to 10^{-5}M it was possible to measure second-order velocity constants up to about 3×10^4 l. mole^{-1} sec.$^{-1}$.

Results for the Bromination of Anisoles.—Provided that Br_2 and Br_3^- are the only brominating species, the observed velocity constant for the bromination of an anisole should be represented by

$$k = (k_1 + Kk'_1[\mathrm{Br^-}])/(1 + K[\mathrm{Br^-}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k_1 and k_1' are the second-order velocity constants for the reaction of anisole with the species Br_2 and Br_3^- respectively, and K is the equilibrium constant $[\mathrm{Br_3^-}]/[\mathrm{Br_2}][\mathrm{Br^-}]$. K was assumed to be 16 at 25°, and 20 at 0°; these values are not accurately known,[5] but the conclusions reached are not affected by any reasonable choice of constants. The initial bromination

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[5] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 101.

products are much less reactive towards bromine than the original substances, so that no correction is necessary for further bromination. Product analysis was not attempted, but there is good evidence [6,7] that bromination takes place mainly in the *para*-position.

The results are given in Tables 1 and 2. The velocity constants are expressed in l. mole^{-1} sec.$^{-1}$ and most of the values represent the mean of 2—6 experiments. Unless otherwise stated, the hydrogen-ion concentration was $9{\cdot}94 \times 10^{-4}$ (perchloric acid).

TABLE 1. *Bromination of anisole at* 0°.

(*a*) Variable $[\mathrm{Br}^-]$ and ionic strength (I); no added salt.

$[\mathrm{Br}^-]$	0·199	0·494	0·586	1·48
k	1160	606	416	342
$k(1 + K[\mathrm{Br}^-])$	5810	6610	8620	10,700

(*b*) Variation of $[\mathrm{Br}^-]$ at constant $I = 0{\cdot}5$ ($\mathrm{NaClO_4}$ added).

$[\mathrm{Br}^-]$	0·124	0·247	0·370	0·493
k	2140	1150	780	607
$k(1 + K[\mathrm{Br}^-])$	7340	6860	6560	6620

(*c*) Variation of $[\mathrm{Br}^-]$ at constant $I = 0{\cdot}2$ ($\mathrm{NaNO_3}$ added).

$[\mathrm{Br}^-]$	0·00115	0·0107	0·0254	0·0500	0·149	0·178
k	5150	4500	3750	2790	1520	1200
$k(1 + K[\mathrm{Br}^-])$	5270	5460	5620	5590	6040	5990

TABLE 2. *Bromination of* o-*bromoanisole at* 25°.

(*a*) Variation of $[\mathrm{H}^+]$ at constant $I = 1{\cdot}51$ and constant $[\mathrm{Br}^-] = 0{\cdot}509$ ($\mathrm{NaClO_4}$ added).

$10^4[\mathrm{H}^+]$	9·92	99·2	99·2	4980	9920
k	42·7	44·7	41·3	37·7	32·8

(*b*) Variation of $[\mathrm{H}^+]$ at constant $I = 0{\cdot}202$ and constant $[\mathrm{Br}^-] = 0{\cdot}0521$ ($\mathrm{NaClO_4}$ added).

$10^4[\mathrm{H}^+]$	9·92	150	506
k	131	122	124

(*c*) Variable $[\mathrm{Br}^-]$ and I; no added salt.

$[\mathrm{Br}^-]$	0·0134	0·0530	0·103	0·153	0·202
k	153	106	72	57	46
$k(1 + K[\mathrm{Br}^-])$	185	194	189	196	194

(*d*) Variation of $[\mathrm{Br}^-]$ at constant $I = 0{\cdot}1$ ($\mathrm{NaNO_3}$ added).

$[\mathrm{Br}^-]$	0·00253	0·0225	0·0521	0·0719	0·100
k	216	158	110	92	72
$k(1 + K[\mathrm{Br}^-])$	225	215	201	198	189

(*e*) Variation of $[\mathrm{Br}^-]$ at constant $I = 0{\cdot}2$ ($\mathrm{NaClO_4}$ added).

$[\mathrm{Br}^-]$	0·0521	0·102	0·151	0·200
k	131	84	61	46
$k(1 + K[\mathrm{Br}^-])$	240	222	207	194

(*f*) Variation of $[\mathrm{Br}^-]$ at constant $I = 1{\cdot}51$ ($\mathrm{NaClO_4}$ added).

$[\mathrm{Br}^-]$	0·063	0·113	0·162	0·212	0·262	0·509	0·757	1·01	1·26	1·50
k	309	217	156	122	94·7	44·7	28·9	18·2	14·3	9·5
$k(1 + K[\mathrm{Br}^-])$	621	610	560	536	492	409	379	313	288	238

(*g*) Variation of I at constant $[\mathrm{Br}^-] = 0{\cdot}0521$ ($\mathrm{NaClO_4}$ or $\mathrm{NaNO_3}$ added).

I	0·053	0·103	0·152	0·202	0·301	0·549	0·797	1·29	1·54
$k(\mathrm{NaClO_4})$	106	110	119	131	135	178	229	318	370
$k(\mathrm{NaNO_3})$	106	110	115	122	130	153	173	214	227

The results for *o*-bromoanisole are the more extensive, and will be considered first. Tables 2 (*a*) and (*b*) show that, as expected, the rate is little affected by hydrogen-ion concentration. The small decrease at high acidities is no greater than the salt effects discussed below. Equation 3 predicts that the quantity $k(1 + K[\mathrm{Br}^-])$ should be independent of $[\mathrm{Br}^-]$ if molecular bromine is the only brominating agent, but should increase with $[\mathrm{Br}^-]$ if tribromide ion is also effective. Table 2 (*c*), in which only bromide is added, suggests no detectable effect of $\mathrm{Br_3}^-$, while the experiments at constant ionic strength [2 (*d*), (*e*), and (*f*)] all show a decrease of $k(1 + K[\mathrm{Br}^-])$ with $[\mathrm{Br}^-]$, which cannot be accounted for by equation 3. This behaviour is undoubtedly due to kinetic salt effects. Table 2 (*g*) shows that sodium perchlorate and sodium nitrate exert large positive effects of different magnitudes, and the results with varying bromide ion at constant ionic strength can be explained if potassium bromide exerts a smaller positive salt effect than either sodium perchlorate or sodium nitrate. A positive kinetic salt effect is to

[6] de la Mare and Vernon, *J.*, 1951, 1761.

[7] Stock and Brown, *J. Amer. Chem. Soc.*, 1960, **82**, 1942.

be expected on theoretical grounds [8] for a reaction between uncharged molecules in which charge separation occurs in the transition state, and there may also be a salt effect on the constant K. There is thus no experimental evidence for reaction between *o*-bromoanisole and tribromide ion, but by extrapolating the values in Table 2 (*c*) to infinite dilution we obtain a reliable value $k_1 = 185$ l. mole^{-1} sec.$^{-1}$ for the velocity constant of the reaction with bromine at 25° and zero ionic strength.

The results for anisole follow a similar pattern. The addition of high concentrations of bromide alone [Table 1 (*a*)] causes an increase in $k(1 + K[\mathrm{Br}^-])$, which, taken by itself, would suggest $k_1'/k_1 \approx 0{\cdot}04$; *i.e.*, the reactivity of tribromide is about 4% of that of bromine. However, measurements with the ionic strength maintained at 0·2 by the addition of sodium nitrate show a considerably smaller increase [Table 1 (*c*)], and with addition of sodium perchlorate to an ionic strength of 0·5 [Table 1 (*b*)] a decrease is observed. There is thus no firm evidence for tribromide reactivity. The velocity constant for reaction with molecular bromine is about 6100 l. mole^{-1} sec.$^{-1}$ at 0°.

Some approximate measurements were made with a number of other anisoles at 25°, and the results are collected in Table 3, it being assumed that molecular bromine is the only active reagent. The value for *o*-nitroanisole is taken from the work of Wilson and Soper.[9]

TABLE 3. *Bromination of various anisoles at 25°.*

Subst.	—	*m*-F	*o*-Br	*o*-Cl	*p*-Br	*o*-NO$_2$
k_1	4×10^4	1×10^4	2×10^2	2×10^2	5	6×10^{-3}

Results for the Bromination of Phenols.—Solutions of phenols contain two reactive species, the molecule and the anion, and in principle both of these could react with either molecular bromine or the tribromide ion. Actually no evidence was found for reaction between phenol molecules and tribromide ion, and the results can be represented in terms of three velocity constants, k_1 (bromine + phenol), k_2 (bromine + phenoxide), and k_3 (tribromide + phenoxide). Provided that most of the phenol is present in the un-ionized form the expression for the observed velocity constant is:

$$k(1 + K[\mathrm{Br}^-]) = k_1 + K_a(k_2 + k_3K\phi[\mathrm{Br}^-])/f_{\pm}^2[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad (4)$$

In this equation, K_a is the thermodynamic dissociation constant of the phenol, and $f_{\pm}^2$ the correction needed to obtain the phenoxide concentration in a solution of finite ionic strength: similarly, k_3 refers to zero ionic strength, and the factor $\phi = f_1^2/f_2$ represents the primary salt effect for the reaction between the two negatively charged ions. Most of the experiments were carried out at $I = 0{\cdot}2$, for which $f_{\pm}$ has been taken as 0·778 (the value for 0·2M-perchloric acid) while ϕ is estimated as 2·0. Some experiments (not recorded) in which the ionic strength was varied by adding sodium nitrate or sodium perchlorate showed little variation in the observed velocity constant. This finding is difficult to interpret quantitatively, since the observed salt effect is compounded of the effect on three velocity constants and two equilibria.

The most detailed study was carried out with *m*-nitrophenol, which had been previously investigated by Bell and Spencer,[2] the limiting current at a rotating platinum cathode being used to follow the disappearance of bromine. Although introduction of the first bromine lowers the reactivity towards further substitution, the resulting monobromo-derivative is a stronger acid than the original phenol and is therefore present to a larger extent as the highly reactive anion: thus Bell and Spencer had to make a correction of up to 15% for dibromination, although only a few per cent of the phenol was brominated. The greater sensitivity of the method employed here made it possible to use much lower bromine concentrations, the initial concentrations being normally 10^{-3}M-*m*-nitrophenol and 5×10^{-6}M-bromine. Under these conditions the correction for further bromination does not exceed 5% even at the lowest acidities, and the velocity constants given in Table 4 have been corrected in this way. The interpretation of the present results is further simplified by the use of a constant ionic strength $I = 0{\cdot}2$ in place of the high and varying values of I studied by Bell and Spencer.

It also appears that the correction for dibromination was not correctly applied by Bell and

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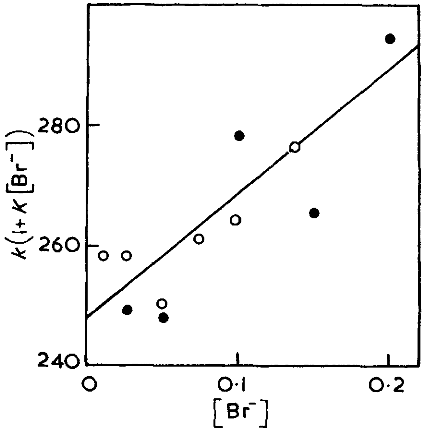
[8] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Son, London 1953, Chapter VII.

[9] Wilson and Soper, *J.*, 1949, 3376.

Spencer. Relying on an early paper[10] they assumed that the first product of bromination was a bromonitrophenol of m. p. 147°, assumed to be 2-bromo-3-nitrophenol. More recent work[3] shows that this compound (actually 4-bromo-3-nitrophenol) is formed from bromine vapour and *m*-nitrophenol at high temperatures, but that reaction in acetic acid solution (which more closely resembles our conditions) produces 2-bromo-5-nitrophenol, m. p. 120°. The correction for dibromination ought therefore to be based on measurements with the last compound: the point is unimportant in the present work, but makes an appreciable difference to some of the results of Bell and Spencer. Corrections on this basis have been applied to their results in 0·06M-perchloric acid and are compared with our own data in the Figure, which also serves to show the degree of reproducibility. It is clear that the two different electrical methods lead to substantially the same velocity constants.



Bromination of m-*nitrophenol.*
○, *Results from this paper.*
●, *Bell and Spencer's results* (*corrected*).

Our results for *m*-nitrophenol are given in Table 4, each being the mean of 2—4 experiments. The calculated velocity constants are from equation (4), with $K = 16$, $K_a = 3{\cdot}98 \times 10^{-9}$ (ref. 11), $\phi = 2{\cdot}0$, $f_\pm = 0{\cdot}778$, $k_1 = 101$, $k_2 = 1{\cdot}32 \times 10^9$, $k_3 = 2{\cdot}8 \times 10^7$.

The other phenols were studied less extensively, and only the velocity constants are given in Table 5. The three disubstituted phenols will give, with one molecule of bromine, products

TABLE 4. *Bromination of* m-*nitrophenol at* 25°.

$[HClO_4]$	0·0195	0·0195	0·0195	0·0195	0·0293	0·0293	0·0586	0·0586
$[Br^-]$	0·0494	0·0981	0·147	0·176	0·0494	0·166	0·0104	0·0250
k obs.	301	230	173	165	228	116	220	184
k calc.	309	222	175	160	225	117	214	185
$[HClO_4]$	0·0586	0·0586	0·0586	0·0586	0·146	0·146	0·146	0·146
$[Br^-]$	0·0494	0·0738	0·0981	0·137	0·0104	0·0250	0·0299	0·0494
k obs.	140	120	103	87	138	105	114	85
k calc.	141	117	100	82	137	114	115	88

TABLE 5. *Bromination of various phenols at* 25°.

Compound	K_a	Ref.	k_1	k_2	k_3	k_3/k_2
Phenol	$1{\cdot}1 \times 10^{-10}$	13	$1{\cdot}8 \times 10^5$	—	—	—
p-Bromophenol	$4{\cdot}6 \times 10^{-10}$	14	$3{\cdot}2 \times 10^9$	$7{\cdot}8 \times 10^9$	—	—
2,4-Dibromophenol	$1{\cdot}6 \times 10^{-8}$	*	$5{\cdot}5 \times 10^2$	$1{\cdot}5 \times 10^9$	$5{\cdot}0 \times 10^7$	0·033
m-Nitrophenol	$4{\cdot}0 \times 10^{-9}$	11	$1{\cdot}0 \times 10^2$	$1{\cdot}3 \times 10^9$	$2{\cdot}8 \times 10^7$	0·022
2,6-Dinitrophenol	$1{\cdot}8 \times 10^{-4}$	15	—	$5{\cdot}4 \times 10^6$	$1{\cdot}0 \times 10^5$	0·018
2,4-Dinitrophenol	$8{\cdot}4 \times 10^{-5}$	16	—	$1{\cdot}0 \times 10^6$	$1{\cdot}3 \times 10^4$	0·013

* This value is estimated from $K_a = 1{\cdot}4 \times 10^{-8}$ for 2,4-dichlorophenol.[17]

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[10] Linden, *Ber.*, 1885, **18**, 612.
[11] Biggs, *Trans. Faraday Soc.*, 1956, **52**, 35.
[12] Pope and Wood, *J.*, 1912, **101**, 1824.
[13] Hahn and Klockmann, *Z. physikal. Chem.*, 1931, *A*, **157**, 206.
[14] Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 1058.
[15] Kertes, *J.*, 1955, 1386.
[16] Bale and Monk, *Trans. Faraday Soc.*, 1957, **53**, 450.
[17] Judson and Kilpatrick, *J. Amer. Chem. Soc.*, 1949, **71**, 3115.

substituted in the 2-, 4-, and 6-positions and therefore will not be brominated further. *p*-Bromophenol gives 2,4-dibromophenol as its first bromination product,[12] but the results for this compound were not sufficiently accurate to justify a correction for further bromination. *p*-Bromophenol is such a weak acid that most of the bromination velocity involves the undissociated molecule, and no estimate of k_3 could be made. With phenol itself the reaction is so fast even in strongly acid solution that neither k_2 nor k_3 could be measured, and the value of k_1 is of low accuracy. The two dinitrophenols are acids of considerable strength, and even in acid solutions only bromination of the anion can be detected.

DISCUSSION

The results for the substituted anisoles (Table 3) show the expected deactivating effect of the electronegative *ortho*- and *meta*-substituents. Substitution in the *para*-position has a much greater effect, since it blocks the favoured position of bromination. The very large deactivating effect of an *o*-nitro-group is of course due to its mesomeric effect, which can stabilize the initial state, but not the transition state in bromination. No bromination by tribromide ion could be detected in any of these reactions, though because of the large salt effects a low reactivity would not have been established with certainty. The results for the bromination of phenols suggest that the most reactive anisoles might be about 1% as reactive towards tribromide ion as towards molecular bromine, which would escape detection.

The same deactivating substituent effects are observed in the bromination of both phenol molecules and phenoxide ions (Table 5). The latter also react detectably with tribromide ion, and although the velocity constants for this reaction are not accurately known, there is good evidence that the reactivity of tribromide relative to molecular bromine increases with increasing reactivity of the organic substance.

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