228. *Kinetics of the Bromination of* m-*Nitrophenol in Aqueous Solution.*

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Kinetic measurements have been made of the bromination of *m*-nitrophenol in aqueous solution. The initial concentrations of phenol and bromine were respectively about 3×10^{-4}M and 10^{-5}M, and the disappearance of bromine was followed by measuring the limiting current at a rotating platinum cathode. Velocity constants are derived for the reactions of bromine with the *m*-nitrophenol molecule and anion, and for the reaction of the tribromide ion with the *m*-nitrophenol anion.

Little kinetic information is available about the rapid reaction between phenols and bromine in aqueous solution. Francis[1] studied the relative rates of bromination of different phenols by competition methods, but his results cannot be interpreted in any simple manner since he used solutions of varying acidity and did not take into account the widely different reactivities of the phenol molecule and the phenoxide ion. Robertson, de la Mare, and Swedlund[2] report direct measurements of the rate of bromination of phenol in acetic acid solution, and estimate that the hydroxyl group activates the benzene ring by a factor of 10^{11}. In these measurements the main reactive species is certainly the undissociated phenol molecule, since the solvent is strongly acidic and the addition of sulphuric acid does not decrease the rate. Recent work on the iodination of phenol[3] involves iodination by an iodine cation, the iodine molecule being inactive.

This paper deals with bromination in aqueous solution under conditions where Br_2 and Br_3^- are the only effective agents, and measurements over a range of acidity make it possible to separate the contribution of the phenol molecules and the phenoxide ions.

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[1] Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2211, 2340.
[2] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.
[3] Berliner, *J. Amer. Chem. Soc.*, 1951, **73**, 4307.

The use of an electrical method for following the bromine concentration makes it possible to work with concentrations 10^{-4}—10^{-6}M and to follow reactions with half-times of a few seconds. Even so, the reaction of phenol itself with bromine was too fast to measure, and it was necessary to use the less reactive *m*-nitrophenol.

EXPERIMENTAL

m-Nitrophenol, recrystallised from carbon disulphide, had m. p. 96·5—97°. 2-Bromo-3-nitrophenol, prepared by direct bromination as described by Linden[4] and recrystallised twice from water, had m. p. 147°. Inorganic reagents were " AnalaR " or of pure quality. The acidity was fixed by adding perchloric acid, and bromide was added as sodium bromide on account of the low solubility of potassium perchlorate.

The decrease in bromine concentration was followed polarographically by measuring the limiting current between a rotating platinum cathode and a stationary platinum anode, as described by Kolthoff and his co-workers.[5,6] The cathode was of platinum wire 0·5 mm. in diameter and 7 mm. long and projected horizontally near the bottom of a vertical glass shaft which rotated at a constant speed of 560 revolutions per min. The shaft terminated in a single-bladed glass stirrer which mixed the reactants. The anode was of platinum gauze, 2 × 2 cm., and was fixed horizontally a short distance below the stirrer. The reaction vessel was a 150 c.c. beaker and 100 c.c. of reaction mixture were used. A potential of 0·2 v (corresponding to the flat part of the polarographic curve) was applied across the electrodes, and the current measured directly by a mirror galvanometer, resistance 40 ohms, period 2 sec., full sensitivity 200 mm./μA. For some of the fastest reactions a Cambridge " Flik " galvanometer was used, having a period of 0·2 sec. and a full sensitivity of 100 mm./μA. In each experiment the sensitivity was adjusted by a shunt so that the initial bromine concentration gave a full-scale deflection. All measurements were made at 25° ± 0·01°. Tests showed that under these conditions the galvanometer deflection is a linear function of the bromine concentration in the range 10^{-4}—10^{-6}M: the absolute bromine concentrations are not required here since the reactions are of first order. This method of following the bromine concentrations is more accurate than the method previously described[7] based on redox potentials, though it will not cover such a wide concentration range. After being used for some time the electrodes often become unresponsive to changes in bromine concentration (cf. Lingane and Anson[8]). This could usually be cured by cleaning with hot concentrated nitric acid, but in extreme cases it was necessary to heat the electrodes to bright redness and to re-make them.

The reaction mixtures contained initially about 3×10^{-4}M-phenol and 10^{-5}M-bromine The reaction was started by adding a small quantity of phenol solution from a syringe to a solution containing bromine, sodium bromide, and perchloric acid. Galvanometer readings were taken at intervals of 2—10 sec., a calibrated metronome being used for the faster reactions. The course of the reactions was of strictly first order up to at least 90% of reaction, and the apparent first-order velocity constants were obtained by plotting log $(r_\infty - r_t)$ against t, where r is the galvanometer reading at time t. Second-order constants were then obtained by dividing the first-order constants by the phenol concentration. These second-order constants had to be corrected for the subsequent bromination of the 2-bromo-3-nitrophenol first formed, since although this compound reacts more slowly than *m*-nitrophenol it is a stronger acid and is therefore present to a greater extent as the reactive anion. The rate of bromination of 2-bromo-3-nitrophenol was measured under the same conditions of acidity and bromide concentration, and the observed velocity with *m*-nitrophenol was corrected by subtracting the velocity corresponding to the amount of 2-bromo-3-nitrophenol present at 50% of reaction. Kinetic analysis shows that this procedure is legitimate when the correction is small, and in our experiments it ranged between 5% and 15%. It was not possible to obtain reliable velocity constants for low values of $[H^+]$ or $[Br^-]$, since under these conditions the correction becomes too large. The corrected constants are given in the Table.

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[4] Linden, *Ber.*, 1885, **18**, 612.

[5] Laitenen and Kolthoff, *J. Phys. Chem.*, 1941, **45**, 1079.

[6] Kolthoff and Reynolds, *Discuss. Faraday Soc.*, 1954, **17**, 167.

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

[8] Lingane and Anson, *Analyt. Chem.*, 1956, **28**, 1871.

Bromination of m-*nitrophenol at* 25°.

Velocity constants in l. mole^{-1} sec.$^{-1}$, corrected for second-stage bromination. Calculated values in parentheses.

	[HClO$_4$]	0·06	0·2	0·5	1·0
[NaBr]	0·025	178 (179)	101 (104)	80 (80)	64 (70)
	0·05	138 (140)	76 (81)	61 (61)	53 (54)
	0·1	107 (101)	56 (57)	44 (42)	41 (37)
	0·15	78 (80)	44 (44)	34 (33)	29 (28)
	0·2	67 (68)	36 (37)	25 (27)	25 (23)

DISCUSSION

Under our conditions the most likely brominating agents are Br_2 and Br_3^-. Hypobromous acid will be present only in very small amounts, because of the high concentration of hydrogen ions and bromide ions: it is in any case a much less effective reagent than molecular bromine.[1,9] Similarly, the conditions are unfavourable for the presence of kinetically significant quantities of a cationic bromine species. The fact that the rate is decreased by an increase in the concentration of either bromide ions or hydrogen ions shows that Br_2 is more reactive than Br_3^-, and that the nitrophenoxide anion is more reactive than the undissociated molecule. Actually the experimental results provide no evidence for any reaction between the two least reactive species, Br_3^- and phenol molecule, and can be accounted for quantitatively in terms of the three reactions phenol + Br_2, phenoxide ion + Br_2, and phenoxide ion + Br_3^-. If the second-order velocity constants for these reactions are k_1, k_2, and k_3 respectively, the observed velocity constant k is given by

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

where K_a is the dissociation constant of *m*-nitrophenol ($5{\cdot}3 \times 10^{-9}$),[10] and K the equilibrium constant $[\mathrm{Br_3}^-]/[\mathrm{Br_2}][\mathrm{Br}^-] = 18$.[11] The activity coefficient $f_{\pm}$ refers to the ions of *m*-nitrophenol, but in the absence of information about these we have used the values for perchloric acid. The values in parentheses in the Table are calculated from

$$k(1 + 18[\mathrm{Br}^-]) = 91 + (6{\cdot}9 + 12[\mathrm{Br}^-])/f_{\pm}^2[\mathrm{H}^+] \quad . \quad . \quad . \quad . \quad (2)$$

and comparison with eqn. (1) gives the following velocity constants, all in l. mole^{-1} sec.$^{-1}$: *m*-$NO_2{\cdot}C_6H_4{\cdot}OH + Br_2$, $k_1 = 91$; *m*-$NO_2{\cdot}C_6H_4{\cdot}O^- + Br_2$, $k_2 = 1{\cdot}3 \times 10^9$; *m*-$NO_2{\cdot}C_6H_4{\cdot}O^- + Br_3^-$, $k_3 = 1{\cdot}3 \times 10^8$. The value of k_1 is higher than that found by Robertson, de la Mare, and Swedlund[2] for phenol itself in acetic acid, but the change of solvent would account for a discrepancy in this direction. k_2 represents an extremely fast reaction, and is of the same order of magnitude as previously found for the reaction of bromine and iodine with enolate ions[12,13,14] and of bromine with *NN*-dialkylanilines.[7] It seems likely that a second-order velocity constant of 10^9—10^{10} l. mole^{-1} sec.$^{-1}$ represents an upper limit for reactions in aqueous solution, and that none of these reactions involves any appreciable energy of activation. This would explain why in the present instance the nitro-group exerts no detectable de-activating effect on k_2, though it undoubtedly does so in aromatic species of lower intrinsic reactivity, such as the phenol molecule.

Several investigators have found[15,16] that the tribromide ion has negligible reactivity as a brominating agent compared with the bromine molecule, and we have not been able to detect any reaction between tribromide ion and the molecule of *m*-nitrophenol. On the

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[9] Derbyshire and Waters, *J.*, 1950, 564.
[10] Lunden, *Z. physikal. Chem.*, 1910, **70**, 249.
[11] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 101.
[12] Bell and Spiro, *J.*, 1953, 429.
[13] Bell and Engel, *J.*, 1957, 247.
[14] Bell and Vogelsong, *J.*, 1958, 243.
[15] Bradfield, Davies, and Long, *J.*, 1949, 1389.
[16] Wilson and Soper, *J.*, 1949, 3376.

other hand, there is clear evidence of reaction between tribromide ion and the *m*-nitrophenoxide ion, though the exact value of k_3 is sensitive to the value assumed for the tribromide equilibrium constant. Evidence for the reactivity of tribromide ion has been found in the bromination of the enol and enolate of malonic ester [12] and of *NN*-dialkylanilines,[7] and the tri-iodide ion similarly shows a measurable activity in the iodination of various enols and enolate ions.[13,14] All these reactions have velocity constants in the range 10^4—10^{10}, and it is reasonable that species of such high reactivity should show little discrimination between different halogenating agents: thus iodine and bromine react at closely similar rates with the enol and with the enolate ion of malonic ester, though their reactivities differ greatly towards less reactive organic species. Another example of the same principle occurs in relations between catalytic power and basic strength, where the exponent β in $k_B = GK_B{}^{\beta}$ decreases steadily with the increasing reactivity of the substrate in a series of ketones and similar substances covering a range of 10^{10} in reaction velocity.[17]

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[17] Bell and Lidwell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 88; Bell, Gelles, and Möller, *ibid.*, 1949, *A*, **198**, 308.