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The Bromination of *p*-Nitrophenol in Acetic Acid

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Bromination of aromatic substrates like *p*-bromophenol, anisole, *etc.* by molecular bromine in acetic acid follows the rate expression, Rate$=k[\mathrm{ArH}][\mathrm{Br_2}]+k'[\mathrm{ArH}][\mathrm{Br_2}]^2$. For the bromination of *p*-nitrophenol in acetic acid, variable orders in bromine and *p*-nitrophenol have been observed on varying the concentrations of reactants. A rate expression of the type, Rate$=k[\mathrm{ArH}][\mathrm{Br_2}]+k'[\mathrm{ArH}][\mathrm{Br_2}]^2+k''[\mathrm{ArH}]^2[\mathrm{Br_2}]$ has been proposed. The observations conform to a general mechanism for bromination provided a bromine molecule, a substrate molecule or solvent molecules can be the electrophile in the rate determining step, depending upon the conditions employed for the reaction.

Bromination of aromatic compounds by molecular bromine in acetic acid medium usually exhibits complex kinetics, the overall orders being dependent on the relative concentration of substrate and bromine.[1,2] The rate is usually expressed in the form

$$\text{Rate} = k[\mathrm{ArH}][\mathrm{Br_2}] + k'[\mathrm{ArH}][\mathrm{Br_2}]^2.$$

The accepted mechanism for the third order process involves the electrophilic attack of the complex formed between the substrate and bromine by a molecule of bromine in the rate-determining step.[3] In the second order process, it has been suggested that the complex undergoes electrophilic attack by the solvent molecules.[2] That certain substrates can also act as electrophiles has been shown in the bromination of *p*-bromophenol in $\mathrm{CCl_4}$.[4] In acetic acid however, it has not been possible to establish conditions where *p*-bromophenol acts as an electrophile. A more powerful electron-withdrawing group like $-\mathrm{NO_2}$ in the *para* position of phenol might make it function as an electrophile capable of competing with both $\mathrm{Br_2}$ and $\mathrm{CH_3COOH}$, leading to a second order in substrate and first order in $\mathrm{Br_2}$. The bromination of *p*-nitrophenol (ArH) in acetic acid has been taken up to investigate this possibility.

Experimental

Glacial acetic acid (GR, SM) was purified according to Orton's procedure,[5] potassium permanganate being used instead of chromic acid. Bromine (AR, BDH) was used without further purification. *p*-Nitrophenol was recrystallized from two percent hydrochloric acid. The kinetics of the bromination of *p*-nitrophenol was followed by determining the concentration of bromine iodometrically as a function of time. The reactions were carried out by the batch method.[6] The orders have been determined by the isolation method using the initial rates. This procedure eliminates the influence of the products formed in the reaction. The slopes at various concentrations were taken from the concentration-time curve by the mirror method.[7] For each experiment a plot of log rate *vs.* log concentration was made from which the initial rate was obtained for the corresponding initial concentration. The initial rate was also evaluated by the method of least-squares. The values obtained for initial rates by both methods were within 5% deviation. With the use of these initial rates, orders were obtained by plotting the logarithms of initial rates against the corresponding initial concentrations. The orders and rate constants were again evaluated by the least-squares analysis of the data. The deviations in rate constants in most cases were within 10%.

Results and Discussion

The interaction of *p*-nitrophenol with bromine in acetic acid follows 1 : 1 stoichiometry. At higher concentrations of reactants (0.29—0.14M) under equimolar conditions, the overall order is three and at lower concentrations of reactants (0.099—0.018M) it is less than three (Fig. 1). It is apparent that the reaction is complicated by the occurence of variable orders. The individual ordres are given in Table 1.

The variation in order in ArH from 0.80 to 1.58 is more than to be expected from experimental error.

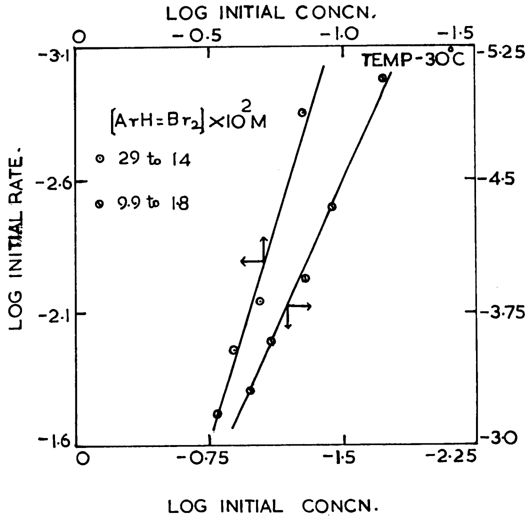

Fig. 1. Logarithmic plots of initial rates *vs.* initial concentrations for the determination of overall order.

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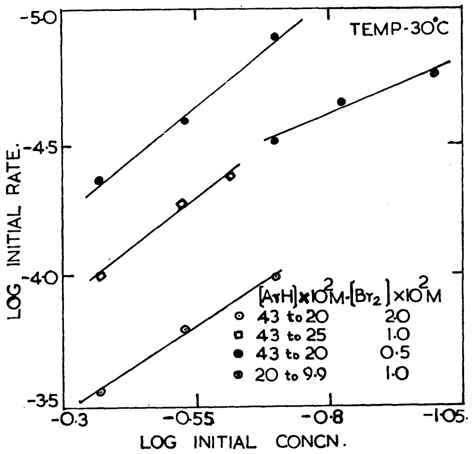

Fig. 2. Logarithmic plots of initial rates *vs.* initial concentrations for the determination of order in *p*-nitrophenol.

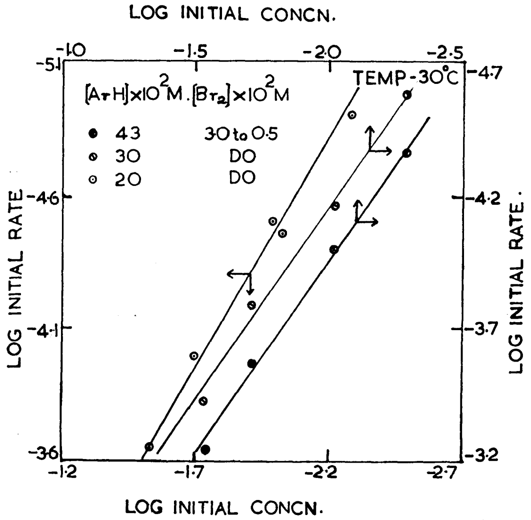

Fig. 3. Logarithmic plots of initial rates *vs.* initial concentrations for the determination of the order in bromine.

Table 1. Individual orders at different concentration ranges

Order in *p*-nitrophenol (Fig. 2) Concentrations (mol/l) ArH	Br$_2$	order	Order in bromine (Fig. 3) Concentrations (mol/l) ArH	Br$_2$	order
0.43—0.20	0.020	1.40	0.43	0.03—0.005	1.56
0.43—0.25	0.010	1.58	0.30	0.03—0.005	1.50
0.43—0.20	0.005	1.40	0.20	0.03—0.005	1.64
0.20—0.10	0.010	0.80			

The fractional orders observed in ArH and bromine at different concentrations of reactants suggest the possibility of either substrate molecules or bromine molecules or solvent molecules playing a vital role in the rate-determining step of the general mechanism:

$$ArH + Br_2 \rightleftharpoons ArHBr_2$$

$$ArHBr_2 + E \xrightarrow{\text{slow}} ArHBr^+ + EBr^-$$

$$ArHBr^+ \xrightarrow{\text{fast}} ArBr + H^+$$

$$H^+ + EBr^- \xrightarrow{\text{fast}} HBr + E$$

E can be ArH, bromine or solvent. When the bromine concentration is comparatively high, the electrophile will be bromine itself. As the concentration of ArH is increased, the substrate, being in excess, may satisfy the role of electrophile. This is possible in the case of *p*-nitrophenol, due to the highly electron-withdrawing nature of the nitro group which will make the molecule more electrophilic towards the removal of Br$^-$ from the ArHBr$_2$ complex. Hence the fractional orders in reactants observed in the bromination of *p*-nitrophenol suggest a rate expression of the type

$$\text{Rate} = k[\text{ArH}][\text{Br}_2] + k'[\text{ArH}][\text{Br}_2]^2 + k''[\text{ArH}]^2[\text{Br}_2]$$

This equation can be rearranged as

$$\frac{\text{Rate}}{[\text{ArH}][\text{Br}_2]} = k + k'[\text{Br}_2] + k''[\text{ArH}]$$

At constant concentrations of bromine, the values on the left hand side of this equation can be plotted against [ArH]. The value of k'' can be obtained from the slope (Fig. 4). Different values of intercepts will be

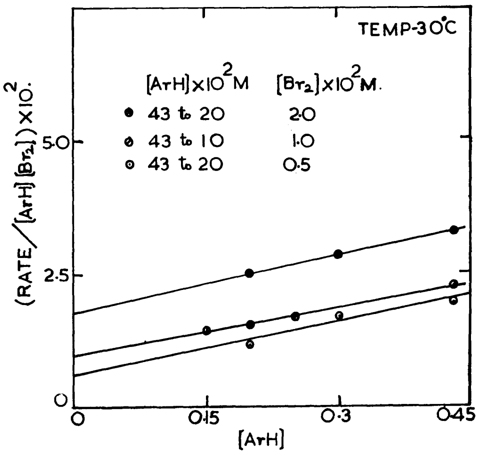

Fig. 4. Composite order plots.

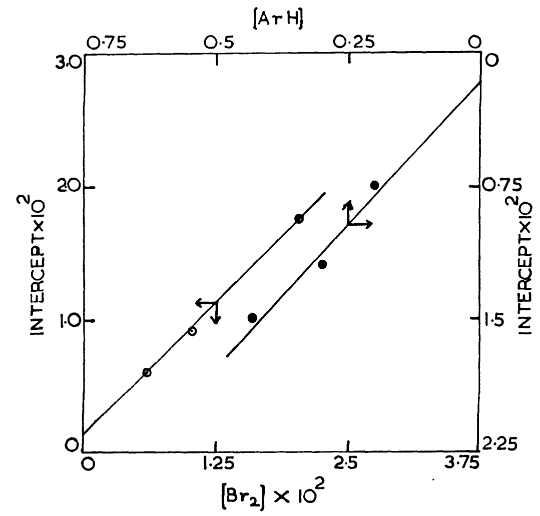

Fig. 5. ⊙ Intercept *vs.* [bromine] for different constant concentrations of bromine. ● Intercept *vs.* [*p*-nitrophenol] for different constant concentrations of *p*-nitrophenol.

TABLE 2. RATE CONSTANTS

Data from Figs. 4 and 5			Data from Figs. 5 and 6			Data from Fig. 6
k (1 mol^{-1} min^{-1})	k' (1^2 mol^{-2} min^{-1})	k'' (1^2 mol^{-2} min^{-1})	k (1 mol^{-1} min^{-1})	k' (1^2 mol^{-2} min^{-1})	k'' (1^2 mol^{-2} min^{-1})	$(k'+k'')$ (1^2 mol^{-2} min^{-1})
		0.02991		1.088		
0.00102	0.884	0.03296	0.0011	1.066	0.03055	0.7299
		0.03254		0.996		

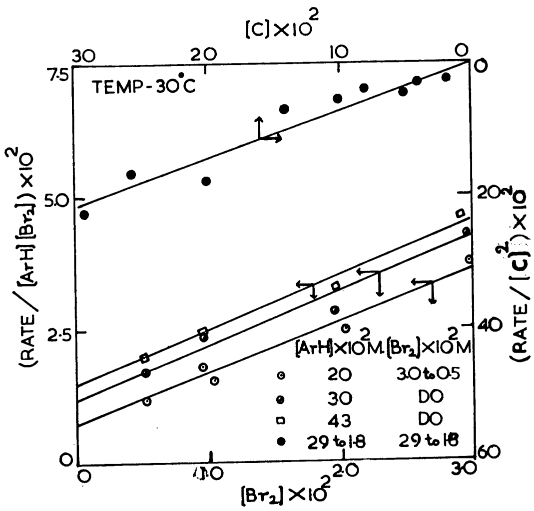

Fig. 6. Composite order plots.

obtained for different constant concentrations of bromine. A plot of the values of the intercepts obtained against the corresponding [Br$_2$] should give a straight line with a slope k' and an intercept k (Fig. 5). Similar analysis of the data can be made for experiments where the concentration of ArH is kept constant and that of bromine is varied. The linear relationship is actually verified (Fig. 6) and another set of values of k, k', and k'' are obtained (Table 2). There is satisfactory agreement between these two sets of values. For the experiments carried out to determine the overall order, since equimolar concentrations are used, the rate expression can be written as

$$\text{Rate} = k[\text{C}]^2 + (k'+k'')[\text{C}]^3$$

where [C]=[ArH]=[Br$_2$]. The plot of Rate/[C]^2 *versus* [C] should be a straight line. This is verified as can be seen in Fig. 6. The intercept in agreement with value of k already determined is almost zero. The value of $(k'+k'')$ obtained is presented along with the rate constants obtained from the other analysis, in Table 2. The overall second order process may not be significant under these conditions.

The values of the rate constants indicate that the process in which bromine acts as the electrophile is much faster than the one in which ArH acts as the electrophile, which in turn is faster than the one in which the solvent molecules take an active part. The appearance of higher orders in substrate indicates that structural features induce a molecule to play an active role in the rate-determining step. In the case of *p*-nitrophenol, this may be due to the inductive effect of the nitro group which makes the substrate more electrophilic for the removal of Br$^-$ from the ArHBr$_2$ complex than *p*-bromophenol.

Since ArH is in excess of bromine, even if there is a significant complex formation between the reactants, the total concentration of ArH and the free concentration of ArH are not different. But the total bromine concentration and the free bromine concentration will be different. Hence

$$\text{Rate} = \frac{k_1[\text{ArH}][\text{Br}_2]_\text{T}}{1+K[\text{ArH}]} + \frac{k_1'[\text{ArH}][\text{Br}_2]_\text{T}^2}{(1+K[\text{ArH}])^2} + \frac{k_1''[\text{ArH}]^2[\text{Br}_2]_\text{T}}{1+K[\text{ArH}]}$$

where K is the equilibrium constant for the complex formation. On transformation this expression can be written as

$$\frac{\text{Rate}}{[\text{ArH}][\text{Br}_2]_\text{T}} = \frac{k_1}{1+K[\text{ArH}]} + \frac{k_1'[\text{Br}_2]_\text{T}}{(1+K[\text{ArH}])^2} + \frac{k_1''[\text{ArH}]}{1+K[\text{ArH}]}$$

At constant concentration of ArH, the left hand side of the above expression can be plotted against [Br$_2$]$_\text{T}$ to give a straight line. The experimental results plotted in this manner yields a straight line with an intercept equal to $(k_1+k_1''[\text{ArH}])/(1+K[\text{ArH}])$. From the different values of the intercepts for different concentrations of ArH, the values of K, k_1, and k_1'' can be calculated. The value of K thus obtained is about 23. Eventhough the value of k_1'' obtained is positive, the value of k_1 is negative which is absurd. A similar plot made for the results obtained for varying concentrations of ArH but constant concentration of bromine is also a straight line. This should not be so if there is significant complex formation. Spectroscopic studies also suggest that the concentration of the complex is very small. It is therefore justified to consider that actually K is very small and the free bromine concentration can be taken to be equal to the total bromine concentration.

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