Autocatalysis in the Bromination of Anisole in Carbon Tetrachloride

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Summary The kinetics of the autocatalysed bromination of anisole (ArH) in CCl_4 has been found to be first order in ArH, Br_2, and HBr, but with IBr as catalyst, the orders are 1, 1, and 2, respectively; a common mechanism is believed to operate.

BROMINATION of aromatic substrates by molecular bromine in CCl_4 is catalysed by IBr,[1] HBr,[2,3] *etc.* In the IBr-catalysed bromination the rate passes through a maximum if the concentration of iodine is increased while that of the substrate and bromine is kept constant. This has been investigated and it has been shown that the ratio of total iodine to total bromine (Y/X) is related to the order in IBr (m).[4,5] The catalysis by HBr has not been investigated in detail. The bromination of anisole in CCl_4 has been shown to be first order in ArH and second order in Br_2 and the reaction has also been reported to be autocatalytic.[3] The main product of bromination was *p*-bromoanisole. A detailed kinetic investigation of this reaction and also the catalysis by IBr is reported. The concentration of Br_2 was determined spectrophotometrically in the bromination of ArH and iodometrically in the IBr-catalysed reaction.

Previous investigations[5] used IBr as a source of bromine. Here, the molar concentration of total Br_2 was maintained higher than that of iodine to ensure that IBr acts only as a catalyst.[4] The orders in ArH, free Br_2, and IBr are found to be 1, 1, and 2, respectively. The catalytic maximum occurs at the predicted ratio (Y/X) of 0·5, and the rate constant k_C is $4{\cdot}39 \times 10^3\ l^3\ mol^{-3}\ s^{-1}$.

At sufficiently low concentrations of IBr, the concentration *vs.* time curves show evidence of autocatalysis. The bromination of ArH in CCl_4 shows a considerable period of induction which decreases as the concentration of Br_2 increases for a constant concentration of ArH. Isolation experiments carried out with a large constant excess of ArH appear to conform to equation (1) up to *ca.* 20% reaction

$$k't = [2{\cdot}303/(a + b)]\log[a(b + x)/b(a - x)] \qquad (1)$$

where a is the initial concentration of Br_2, x is the amount of Br_2 that has reacted at any time t, b is the concentration of HBr that accumulates by the end of the induction period, and k' is an apparent rate constant. The rate constant k_a was calculated from equation (2). After this stage, when

$$k_a = k'/[ArH] \qquad (2)$$

the concentration of HBr in solution appears to remain constant, the reaction follows pseudo-second-order kinetics up to *ca.* 80% reaction and the corresponding rate constant k_2' when divided by [HBr] (*ca.* 8 mM, corresponding to the upper flat portion of the autocatalysis curve) gives values of k_a which are in good agreement with those previously obtained (see Table). These results suggest that the order in HBr is 1. When HBr is added initially, the induction period is not observed and the order, as calculated from the initial rates, is found to be 1 in HBr. With [HBr] > 8 mM the reaction follows second-order kinetics even from the beginning.

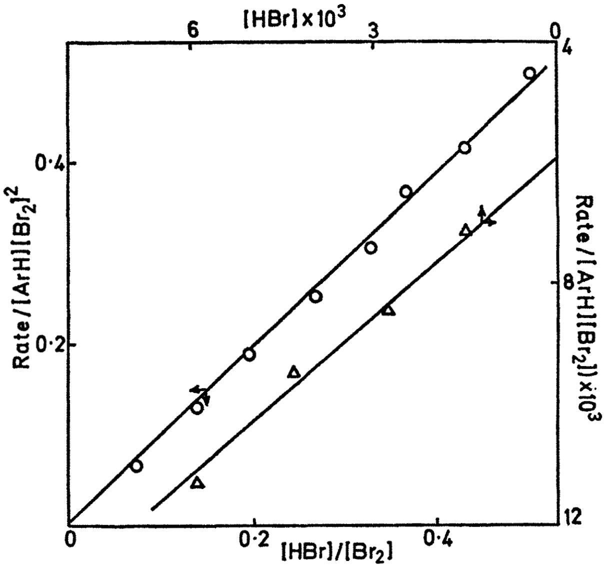

FIGURE. *Linear plots of equations* (3) ○ *and* (4) △.

TABLE[a]

			$k_a/l^2\ mol^{-2}\ s^{-1}$ Autocatalysis		
$[Br_2] \times 10^2$/M	$[HBr] \times 10^3$/M	Induction period (min)	To constant [HBr]	After constant [HBr]	Initially added HBr
5·36		7·5	0·911	0·909	
4·02		8·0	0·904	0·920	
3·02		15·0	0·910	0·921	
3·80	9·0				0·910
3·80	4·5				0·961
3·80	3·0				0·952

[a] In CCl_4, at 30°, with [ArH] = 0·1042M.

The rate of bromination of anisole can therefore be represented by equation (3) where k_0 is the rate constant for

$$\text{Rate} = k_0[ArH][Br_2]^2 + k_a[ArH][Br_2][HBr] \qquad (3)$$

the uncatalysed reaction. The linear plot (see Figure) with a negligible intercept indicates that k_0 is small. In view of the autocatalysis by HBr, the rate in the IBr-catalysed reaction can be represented by equation (4), neglecting the

$$\text{Rate} = k_c[\text{ArH}][\text{Br}_2][\text{IBr}]^2 + k_a[\text{ArH}][\text{Br}_2][\text{HBr}] \qquad (4)$$

contribution from the uncatalysed reaction. A plot of equation (4) is again linear (see Figure). The values of k_c ($3{\cdot}99 \times 10^3$ l^3 mol^{-3} s^{-1}) and k_a ($0{\cdot}95$ and $0{\cdot}89$ l^2 mol^{-2} s^{-1}) calculated from these linear plots agree well with those obtained previously (see Table).

Mechanistically these results support the general scheme involving the interaction between one molecule of the complex ArH,Br_2 initially formed and one molecule of an electrophile in the rate-determining step advanced for third-order kinetics observed in brominations by molecular Br_2.[6] The higher order in IBr has not been satisfactorily explained. Probably, substances like anisole, benzene, and mesitylene, for which higher orders in IBr have been reported, form strong 1:1 complexes because of their greater π-basicities. In order to polarise and remove Br^- from these complexes more than one molecule of IBr may be needed. Thus in the IBr catalysis two molecules of IBr act as the electrophile and in the reaction involving HBr one molecule of HBr acts as the electrophile.

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