

## Autocatalysis in the Bromination of Anisole in Carbon Tetrachloride

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**Summary** The kinetics of the autocatalysed bromination of anisole (ArH) in  $\text{CCl}_4$  has been found to be first order in ArH,  $\text{Br}_2$ , 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  $\text{CCl}_4$  is catalysed by IBr,<sup>1</sup> HBr,<sup>2,3</sup> 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 ( $m$ ).<sup>4,5</sup> The catalysis by HBr has not been investigated in detail. The bromination of anisole in  $\text{CCl}_4$  has been shown to be first order in ArH and second order in  $\text{Br}_2$  and the reaction has also been reported to be autocatalytic.<sup>3</sup> 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  $\text{Br}_2$  was determined spectrophotometrically in the bromination of ArH and iodometrically in the IBr-catalysed reaction.

Previous investigations<sup>5</sup> used IBr as a source of bromine. Here, the molar concentration of total  $\text{Br}_2$  was maintained higher than that of iodine to ensure that IBr acts only as a catalyst.<sup>4</sup> The orders in ArH, free  $\text{Br}_2$ , 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  $4.39 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ .

At sufficiently low concentrations of IBr, the concentration *vs.* time curves show evidence of autocatalysis. The bromination of ArH in  $\text{CCl}_4$  shows a considerable period of induction which decreases as the concentration of  $\text{Br}_2$

was calculated from equation (2). After this stage, when

$$k_a = k'/[\text{ArH}] \quad (2)$$

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  $[\text{HBr}]$  (*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

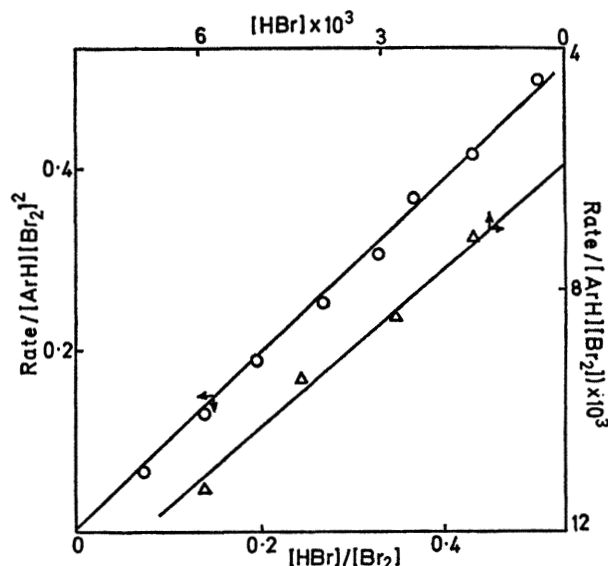


FIGURE. Linear plots of equations (3) ○ and (4) △.

TABLE<sup>a</sup>

$[\text{Br}_2] \times 10^2/\text{M}$	$[\text{HBr}] \times 10^3/\text{M}$	Induction period (min)	$k_a/\text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$		
			Autocatalysis		Initially added HBr
			To constant $[\text{HBr}]$	After constant $[\text{HBr}]$	
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

<sup>a</sup> In  $\text{CCl}_4$ , at 30°, with  $[\text{ArH}] = 0.1042\text{M}$ .

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

$$k't = [2.303/(a + b)] \log[a(b + x)/b(a - x)] \quad (1)$$

where  $a$  is the initial concentration of  $\text{Br}_2$ ,  $x$  is the amount of  $\text{Br}_2$  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  $k_a$

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  $[\text{HBr}] > 8 \text{ mM}$  the reaction follows second-order kinetics even from the beginning.

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

$$\text{Rate} = k_0[\text{ArH}][\text{Br}_2]^2 + k_a[\text{ArH}][\text{Br}_2][\text{HBr}] \quad (3)$$

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

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

contribution from the uncatalysed reaction. A plot of equation (4) is again linear (see Figure). The values of  $k_c$  ( $3.99 \times 10^3 \text{ l}^3 \text{ mol}^{-3} \text{ s}^{-1}$ ) and  $k_a$  (0.95 and  $0.89 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ) 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  $\text{ArH}\cdot\text{Br}_2$  initially formed and one molecule of an

electrophile in the rate-determining step advanced for third-order kinetics observed in brominations by molecular  $\text{Br}_2$ .<sup>6</sup> 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  $\pi$ -basicities. In order to polarise and remove  $\text{Br}^-$  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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