

## Kinetics of the Autoxidation of Toluenes Catalysed by Cobalt(III) Acetate. Part III.<sup>1</sup> Effects of Organic Bromides

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The effect of organic bromides on the rate of the autoxidation of toluene to benzoic acid, catalysed by cobalt(III) acetate in acetic acid at 90°, has been studied. The addition of organic bromides such as bromobenzene, 1,2-dibromoethane, *n*-butyl bromide, and benzyl bromide increases the rate and the conversion curves show several inflections. The number of inflections varies with the toluene concentration but not with the concentrations of catalyst and bromides.

We previously reported<sup>1</sup> that the autoxidation of *m*- and *p*-bromotoluene catalysed by cobalt(III) acetate in acetic acid proceeded much faster than predicted by Hammett's  $\sigma$  value and that the autoxidation of toluene was accelerated by the addition of bromobenzene. It is well known that autoxidations of methylbenzenes catalysed by cobalt(II) acetate in acetic acid are accelerated by the addition of substances giving rise to bromide ions such as hydrogen bromide, sodium bromide, *etc.*<sup>2</sup> The present study was initially intended to disclose the extent of acceleration by organic bromides; to our surprise, however, the addition of bromobenzene gave an inflected conversion curve. This report deals with this phenomenon.

The autoxidation of toluene (*ca.* 1M) catalysed by cobalt(III) acetate (0.1241M) in acetic acid at 90° was accelerated by the addition of a relatively high concentration (>0.4M) of bromobenzene and the absorption of oxygen followed an inflected curve (Figure 1), which was accurately reproducible. The number of inflections increased with increasing concentration of toluene, *i.e.* two with 0.5M-toluene and four with 2M-toluene. Different toluene concentrations gave nearly the same absorption curve below 50% conversion; thus the rate is independent of the toluene concentration. Two reports<sup>3</sup> describe the acceleration of autoxidation by organic bromides, but this phenomenon has not been previously reported and it seems to be specific for this particular system.

Increase in the concentration of bromobenzene resulted in increase in the rate of oxygen absorption, but no change in the number of inflections and the shape of the curve. Increases in rate occur at similar extents of conversion, if the concentration of toluene is constant, whatever the concentration of bromobenzene. At a higher catalyst concentration, a higher concentration of organic bromide is necessary for the appearance of the inflected curve. For example, 0.379M-bromobenzene is sufficient at 0.1241M-cobalt(III) acetate but more than 0.950M-bromobenzene must be used at 0.2482M-catalyst.

<sup>1</sup> Part II, T. Morimoto and Y. Ogata, *J. Chem. Soc. (B)*, 1967, 1353.

<sup>2</sup> D. A. S. Ravens, *Trans. Faraday Soc.*, 1959, **55**, 1768; Y. Kamiya, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1966, **69**, 897; T. Takaya, T. Koga, and T. Hara, *Bull. Chem. Soc. Japan*, 1966, **39**, 654; Y. Kamiya, T. Nakajima, and K. Sakoda, *ibid.*, 1966, **39**, 2211; K. Sakoda, Y. Kamiya, and N. Ohta, *ibid.*, 1968, **41**, 641.

This tendency is shown in Figure 2, which indicates the change in the curve with change in catalyst concentration at constant concentrations of toluene and bromobenzene. The inflected curve is observed when the ratio of [PhBr] to [Co<sup>III</sup>] is more than 2 : 1.

The concentrations of bromobenzene, benzaldehyde, and toluene at various times were measured by g.l.c. with chlorobenzene as internal standard. Before analysis

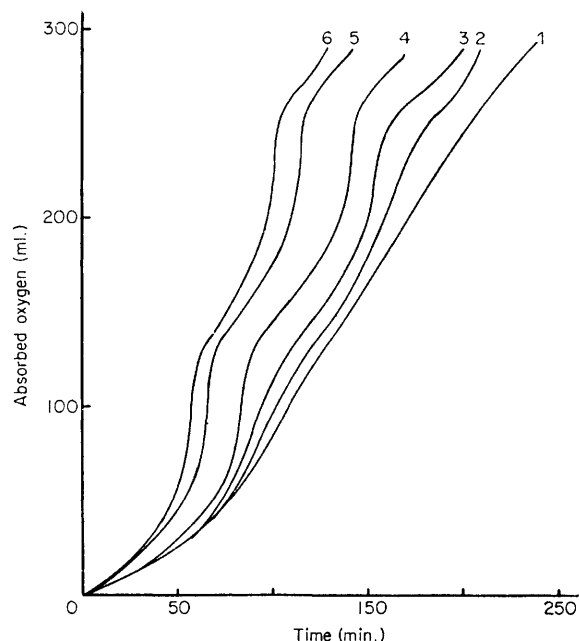


FIGURE 1 Absorption curves for oxygen with various concentrations of bromobenzene with constant concentrations of toluene (1.01—1.04M) and catalyst (0.1862M) at 90°; bromobenzene concentrations: 1, 0.379M; 2, 0.514M; 3, 0.763M; 4, 0.951M; 5, 1.43M; 6, 1.95M

the reaction mixture was poured into water and extracted with ether and the extract was dried (Na<sub>2</sub>SO<sub>4</sub>). As shown in Figure 3, the concentration of organic bromide was nearly constant. This was confirmed by the fact that no precipitation of silver bromide occurred on addition of silver nitrate to the aqueous layer of the extract of the reaction mixture. Therefore liberation of bromide ion from the parent bromide is negligibly small.

<sup>3</sup> A. S. Hay and H. S. Blanchard, *Canad. J. Chem.*, 1965, **43**, 1306; A. Suzuki, K. Iwase, and J. Nakamura, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1964, **67**, 1550.

The concentration of benzaldehyde increased gradually at first, passed through a maximum, and sharply decreased; this increase and decrease were repeated several

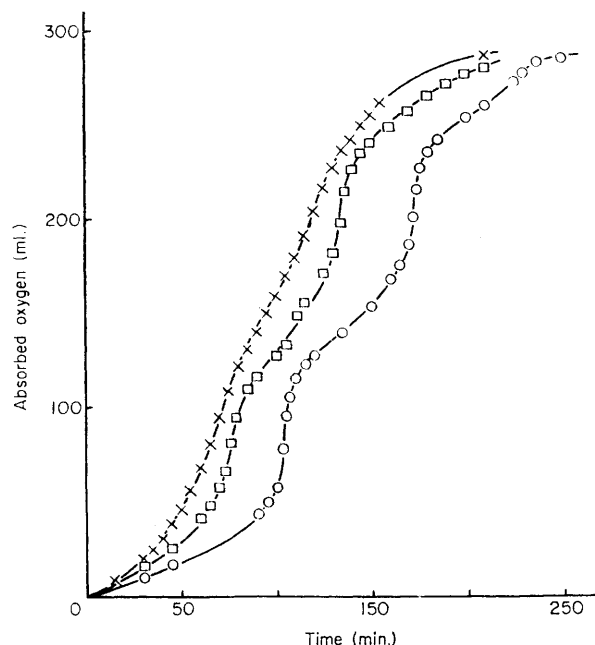


FIGURE 2 Variation in the absorption curves for oxygen with change in catalyst concentration at constant concentrations of toluene (0.8059M) and bromobenzene (1.0422M) at 90°; catalyst concentrations: (—○—) 0.1241M, (—□—) 0.1862M, (—×—) 0.2482M

times. A rapid decrease in the concentration of benzaldehyde accompanies a rapid decrease in concentration of toluene and increase in rate of oxygen absorption. The maximum concentration of benzaldehyde formed was not affected by the concentrations of catalyst, substrate, and bromide; this is consistent with the fact that nearly the same amount of oxygen is absorbed in the

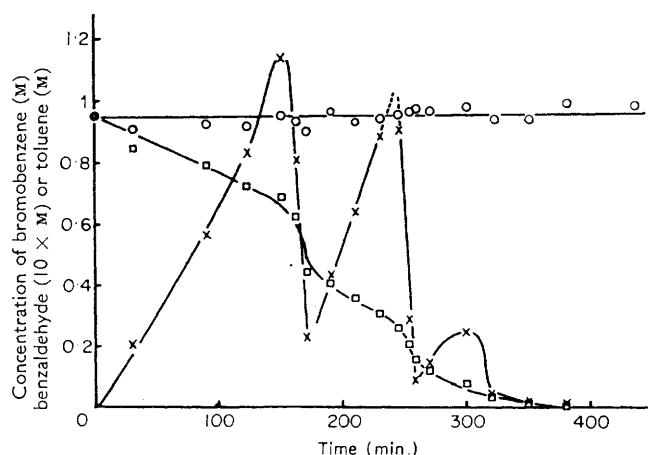


FIGURE 3 Change in concentrations of bromobenzene, benzaldehyde, and toluene with time at 90°; [PhMe] = 0.951M, [Co] = 0.1201M, [PhBr] = 0.95M; (—○—) bromobenzene, (—×—) benzaldehyde, (—□—) toluene

fast reaction even when the concentrations of catalyst, substrate, and bromide are varied.

Molecular bromine can also accelerate the reaction even at a very low concentration, and gives an inflected conversion curve. Benzyl bromide also considerably accelerates the reaction. The similarity between the curves for molecular bromine and benzyl bromide (Figure 4) implies that bromine from bromide ion liberated by the solvolysis of benzyl bromide acts as a promoter. In fact, bromide ion was detected by a silver nitrate test on the aqueous layer after the autoxidation with added benzyl bromide.

1,2-Dibromoethane, n-butyl bromide, and cyclohexyl bromide caused the same phenomenon and were unchanged after completion of the reaction; this was confirmed by the silver nitrate test and g.l.c. Hence, organic bromides in general seem to be effective.

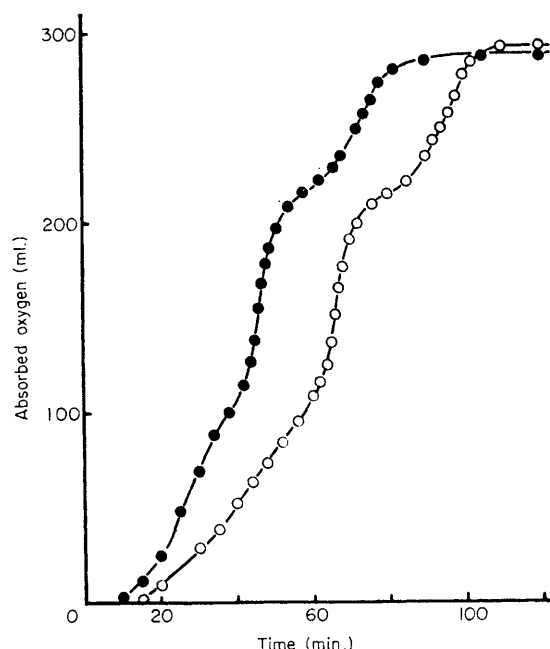


FIGURE 4 Comparison of absorption curve for reaction accelerated by bromine with that for reaction accelerated by benzyl bromide at constant concentrations of toluene (0.796M) and catalyst (0.1241M) at 90°; (—○—) [PhCH<sub>2</sub>Br] = 0.042M, (—●—) [Br<sub>2</sub>] = 0.019M

As seen from the Figures, this reaction is separable into two stages, *i.e.* a slow autoxidation where benzaldehyde accumulates, and a rapid autoxidation where benzaldehyde is consumed. If the concentration of abstracting radicals becomes constant after an induction period, the conversion curve should not be inflected, but smooth as observed in the case without bromide.<sup>1</sup> We therefore suppose that bromides can cause another type of oxidation which has a long induction period but which, after starting, proceeds rapidly with consumption of benzaldehyde and toluene. This rapid reaction is chain-branching, *i.e.* the concentration of radicals increases, and it needs the presence of bromide. Organic and inorganic bromide and atomic bromine form complexes

with cobalt ions and these complexes may abstract a hydrogen atom and may catalyse the second rapid reaction, where inorganic bromide is more effective than organic bromide. In the second reaction, the consumption of benzaldehyde is so fast that it soon almost disappears to give a very low ratio of  $[\text{PhCHO}]$  to  $[\text{PhMe}]$  at the steady state; thus the reaction is slowed down, since benzaldehyde is a chain carrier. The similar decrease in benzaldehyde concentration has been observed in  $\text{Co}^{3+}$ -catalysed autoxidation of toluene when a high concentration of benzaldehyde is added without bromides.<sup>4</sup> After the retardation caused by the disappearance of benzaldehyde, the slower process, which is catalysed by benzaldehyde and cobalt ions alone and has a shorter induction period, takes over. Further study is still necessary for elucidation of this phenomenon.

<sup>4</sup> T. Morimoto and Y. Ogata, *J. Chem. Soc. (B)*, 1967, 62.

<sup>5</sup> G. R. Robertson, *Org. Synth.*, Coll. Vol. I, 1956, 138.

#### EXPERIMENTAL

Toluene and acetic acid were purified as described previously.<sup>4</sup> Cobalt(III) acetate was prepared by dropwise addition of peracetic acid to a suspension of cobalt(II) acetate in acetic acid. Bromobenzene (b.p. 156—156.5°) was washed with sulphuric acid and water, and distilled. n-Butyl bromide (b.p. 100.8—101.6°)<sup>5</sup> and benzyl bromide (b.p. 86—87°/18 mm.)<sup>6</sup> were synthesised by known methods. Commercial 1,2-dibromoethane, cyclohexyl bromide, and elemental bromine were used without further purification.

*Rate Measurements.*—The apparatus and method were as described in Part I.<sup>4</sup>

*Measurement of Concentrations of Toluene, Benzaldehyde, and Bromobenzene.*—The apparatus and method were as described in Part II<sup>1</sup> except that a column (2 m.) packed with 2.5% polyethylene glycol 20M instead of 15% Apiezon L was used.

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<sup>6</sup> E. F. J. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, 1907, 1695.