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THE AUTOXIDATION OF TETRALIN CATALYSED BY COBALT SALT AND SODIUM BROMIDE IN ACETIC ACID

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Abstract—The rate of cobalt-catalysed autoxidation of tetralin in acetic acid is considerably increased in the presence of sodium bromide, and it is concluded that this is due to the participation of a new type of propagation step between peroxy radical and cobalt monobromide. Derived kinetic equations, first order with respect to hydrocarbon concentration as well as to cobalt monobromide, have shown good agreement with the experiments. Cobalt dibromide is inactive as a catalyst but is easily converted to monobromide in the presence of sodium acetate. The induction period, due to an inhibitor, is markedly reduced in the oxidation of tetralin catalysed with cobalt salt and sodium bromide.

INTRODUCTION

IN PREVIOUS papers, it was shown that the limiting rate of cobalt-catalysed autoxidation of tetralin in acetic acid[1] and in pure tetralin[2] is in good agreement with the theoretical prediction of Tobolsky and also the limiting rate can be excellently correlated as a function of dielectric constant[3] of the solvent, when fatty acids were used as the solvent.

In recent years, a mixture of metal salts and various bromides have been used as catalyst in the autoxidation of *p*-xylene[4] to terephthalic acid in acetic acid. Although the oxidation of *p*-xylene is successful by this process, its reaction mechanism is still far from certain. Ravens[5] suggested that the effect of bromide which increases remarkably the rate of cobalt-catalysed oxidation is due to an initiation step as follows:

$$HBr + O_2 \rightarrow HO_2^{\cdot} + Br^{\cdot} \qquad (1)$$

This, however, appears energetically improbable because of the highly endothermic reaction and the competitive cobalt-catalysed decomposition of hydroperoxide. Although Ravens experimentally derived his kinetic equation as a function of the partial pressure of oxygen, the oxygen pressure used might not be so high that the dissolving rate of oxygen into the solution could be excluded.

Instead, the effect of bromide may be attributed to the following propagation step:

$$HBr + RO_2^{\cdot} \rightarrow ROOH + Br^{\cdot} \qquad (2)$$

Not only is Eq. 2 energetically more probable than Eq. 1, but it has been suggested in the gas phase oxidation of paraffins.[6]

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[1] Y. Kamiya, S. Beaton, A. Lafortune and K. U. Ingold, *Canad. J. Chem.* **41**, 2020 (1963).

[2] Y. Kamiya, S. Beaton, A. Lafortune and K. U. Ingold, *Canad. J. Chem.* **41**, 2034 (1963).

[3] Y. Kamiya, *Bull. Chem. Soc. Japan* **38**, 2156 (1965).

[4] A. Saffer and R. S. Barker, U.S. Pat., 2,833,816; Belg. Pat. 546,191; De. E. Burney and G. H. Weisemann, *Petrol. Refiner* **38**, (8) 186 (1959).

[5] D. A. S. Ravens, *Trans. Faraday Soc.* **55**, 1768 (1959).

[6] F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.* **41**, 2595 (1949).

In order to investigate the catalytic effect of a cobalt salt and bromide in acetic acid solution, tetralin was chosen as its autoxidation has been studied kinetically in detail.

RESULTS AND DISCUSSION

Oxygen absorption curve and the effect of bromides

The rate of cobalt-catalysed autoxidation of tetralin in acetic acid reaches a maximum value and before decreasing slowly remains at the stationary state until about 10% of tetralin is consumed. The induction period, the intercept of the extrapolated maximum rate on the time axis, is less than 10 min at cobalt concentrations above 5×10^{-3} mole/l. At lower concentrations the induction period is considerably increased. At a given tetralin concentration the maximum rate of oxidation is independent of the Co concentration in the range 5×10^{-2} to 1×10^{-1} mole/l., as shown previously. In this range, the rate is proportional to the square of tetralin concentration from 0·4 to 4·0 mole/l.

By adding sodium bromide to the solution of cobalt in acetic acid, the color changes from pink to blue showing that cobalt is converted to the bromide. Sodium bromide does not affect the general shape of the oxygen absorption curve although the rate is considerably increased, e.g., by a factor of four at 5×10^{-2} mole/l. of Co concentration (Fig. 3). In general, cobalt dibromide gives about 15% higher rate of oxidation than a mixture of cobalt decanoate and sodium bromide. On the other hand, the addition of ammonium bromide instead of sodium bromide results in the lower rate of oxidation especially if the Co concentration are above 1×10^{-2} mole/l. In the case of sodium and ammonium bromides the induction period is always several minutes less regardless of the amount of cobalt and bromide present. However, in the case of cobalt dibromide a pronounced induction period was observed as a function of the concentration of cobalt dibromide and temperature as shown in Fig. 1. It is clear that cobalt dibromide has little activity as a catalyst as it takes a long time to convert the dibromide to monobromide at low temperatures in acetic acid. The addition of sodium acetate entirely eliminates this induction period suggesting that Eq. 4 proceeds very rapidly. When 4×10^{-1} mole/l. hydrogen bromide is added to a solution of 5×10^{-2} mole/l. cobalt, no appreciable oxygen absorption takes place within 4 hr. High concentrations of hydrogen bromide appear to convert the cobalt salt to dibromide and to inhibit the oxidation.

$$CoBr_2 + CH_3COOH \xrightarrow{slow} CoBr(CH_3COO) + HBr \tag{3}$$

$$CoBr_2 + CH_3COONa \xrightarrow{fast} CoBr(CH_3COO) + NaBr \tag{4}$$

Spectrometric analysis has shown that the absorption at 700 mμ due to cobalt dibromide is rapidly and markedly reduced by adding equimolar amounts of sodium acetate.

Benzyl bromide, reported to be an effective organic bromide[7] in the oxidation of *p*-toluic acid, was added to the solution of 10^{-2} and 5×10^{-2} mole/l. cobalt at the molar ratio of bromide to cobalt 3:1. As no change in the rate of oxidation of tetralin was observed, organic bromide may only be effective at higher temperatures.

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[7] Y. Takegami, T. Okano, T. Fujii and S. Uemura, *J. Japan Petrol. Institute* **7**, 560 (1964).

The concentration of sodium bromide

Although hydrogen bromide can be formed by the reaction

$$\mathrm{NaBr} + \mathrm{CH_3COOH} \overset{K}{\rightleftarrows} \mathrm{HBr} + \mathrm{CH_3COONa} \qquad (5)$$

its concentration must be very low, since the equilibrium constant is very small. If the marked increase in the rate of oxidation due to sodium bromide is caused by Eq. 1, a comparable rate to $R_{Br} - R_0$, i.e., the rate increased by adding bromide, should be obtained even in the absence of cobalt. Since the addition of 2×10^{-1} mole/l. sodium bromide to the acetic acid solution of tetralin results in no appreciable absorption of oxygen within 1 hr at 50°, hydrogen bromide is not responsible for the initiating reaction in the presence of small amounts of hydroperoxide. The decomposition rate of tetralin hydroperoxide in a 1:1 by volume benzene–acetic acid solution with 2×10^{-3} mole/l. cobalt decanoate at 50° is increased about 20% by adding 4×10^{-3} mole/l. sodium bromide, showing that the rate of initiation by cobalt is affected only slightly in the presence of sodium bromide.

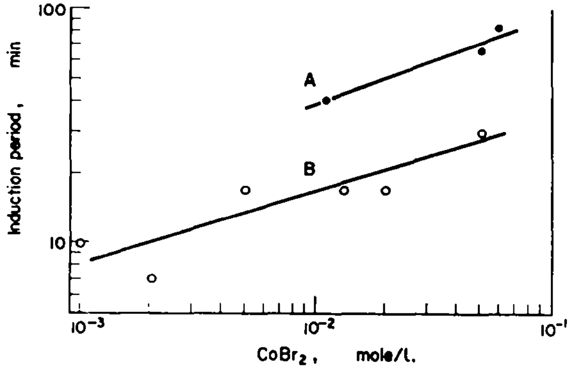

FIG. 1. Induction period in the oxidation of tetralin in acetic acid with cobalt dibromide as a function of the concentration of cobalt dibromide at 35° (A) and 50° (B).

The effect of hydrogen bromide on the propagation step has been studied by the oxidation of tetralin in acetic acid with 1×10^{-2} mole/l. azobisisobutyronitrile (AIBN) at 50°. By adding $2{\cdot}76 \times 10^{-2}$ mole/l. sodium bromide the rate of oxidation tends to increase with time and reaches the rate of $4{\cdot}6 \times 10^{-6}$ mole/l. sec after 250 min as compared with the rate of $3{\cdot}4 \times 10^{-6}$ mole/l. sec in the absence of sodium bromide. This effect may be attributed to the induced decomposition of tetralin hydroperoxide by hydrogen bromide, because the concentration of hydroperoxide which is the main oxidation product is increased with time. It has been confirmed that in the AIBN-initiated autoxidation of α-methylstyrene in acetic acid, which yields polyperoxide and no reactive hydroperoxide, the increase in the rate due to hydrogen bromide, resulting from sodium bromide, is less than 10% and is unchanged as the oxidation proceeds.

Hydrogen bromide, resulting from sodium bromide and acetic acid, may be an effective catalyst for the propagation step even though its concentration is very low.

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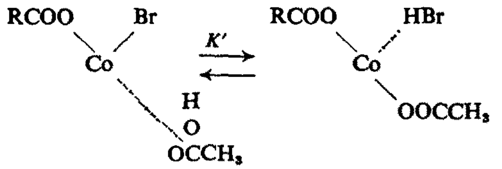
[8] F. R. Mayo, A. A. Miller and G. A. Russell, *J. Amer. Chem. Soc.* **80**, 2500 (1958).

In the autoxidation catalysed with cobalt and sodium bromide, hydrogen bromide as compared with cobalt monobromide may only play a minor role, since cobalt dibromide, which can liberate equimolar amounts of hydrogen bromide gives a little higher rate of oxidation than is the case with sodium bromide and cobalt decanoate. Very recently, Hay and Blanchard[9] have shown that the initial rate of AIBN-initiated autoxidation of cumene is considerably increased in the presence of $2{\cdot}2 \times 10^{-2}$ mole/l. hydrogen bromide. The rate of oxidation of tetralin initiated with 10^{-2} mole/l. AIBN at 50° is increased by a factor of forty in the presence of 2×10^{-2} mole/l. HBr, but the effect almost disappears after 1·2 ml oxygen per 1 ml solution had been absorbed. Therefore, hydrogen bromide can not be an effective catalyst for as long a time as a mixture of cobalt and sodium bromide.

Experiments in which the molar ratio of sodium bromide to cobalt was varied (Fig. 2) proved that the effective catalyst for the propagation step in the oxidation catalysed with cobalt and sodium bromide is not free hydrogen bromide but cobalt monobromide or a derivative. The rate of oxidation with 5×10^{-2} mole/l. of cobalt increases as NaBr:Cobalt is increased but very slowly at NaBr:Cobalt above 1:1. On the other hand, at 1·22 mole/l. of tetralin the rate reaches a limiting value at NaBr:Cobalt of 1:1 and starts to decrease at NaBr:Cobalt above 5:1. The induced decomposition of tetralin hydroperoxide by hydrogen bromide can be completely excluded at a cobalt concentration as high as 5×10^{-2} mole/l., since the steady concentration of hydroperoxide is very low.

When NaBr:Cobalt is nearly 1:1, the concentration of free hydrogen bromide must be extremely low, because most of bromide will be complexed with cobalt and the equilibrium constant of Eq. 5 will be small. Therefore, if hydrogen bromide and not cobalt monobromide is the true catalyst for the propagation, a sharp increase in the rate of oxidation should occur at NaBr:Cobalt above 1:1 and also the rate should continue to increase over a large NaBr:Cobalt range, and, moreover the addition of sodium acetate to the solution of cobalt dibromide should result in the marked decrease in the rate of oxidation in contrast to the experimental results.

It has been concluded[1,3] that the cobalt salt in acid solution is coordinated with the acid, and the cobalt monobromide and cobalt–hydrogen bromide complex $Co(RCOO)_2HBr$ may be reversible according to hydrogen transfer, as follows:



Experimental results support that cobalt monobromide can take the structure of $Co(RCOO)_2HBr$. First, hydrogen bromide can be evolved from the acetic acid solution of cobalt monobromide at higher temperatures. Second, the lower the concentration of sodium bromide the sooner the rate of oxidation decreases at a temperature as low as 35°, and this result can be attributed to the loss of hydrogen bromide from the solution.

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[9] A. S. Hay and H. S. Blanchard, *Canad. J. Chem.* **43**, 1306 (1965).

$\mathrm{Co(RCOO)_2HBr}$ (written as $\mathrm{Co^{2.+}HBr}$ below) may be able to react with peroxy radical and to transfer chain as follows:

$$\mathrm{Co^{2.+}HBr + RO_2^{\cdot} \rightarrow products + (Co^{2+} + Br^{\cdot})} \quad \text{or} \quad \mathrm{(Co^{3+}Br^{-})} \tag{6}$$

$$\mathrm{Co^{2+} + Br^{\cdot} + RH \rightarrow Co^{2.+}HBr + R^{\cdot}} \tag{7}$$

Kinetics

When the autoxidation of tetralin catalysed with cobalt salt and sodium bromide in acetic acid solution proceeds as follows:

$$\mathrm{ROOH + (Co)_2} \xrightarrow{k_1'} \mathrm{radical} \xrightarrow{\mathrm{RH}} \mathrm{R^{\cdot}} \tag{8}$$

$$\mathrm{R^{\cdot} + O_2} \xrightarrow{k_2} \mathrm{RO_2^{\cdot}} \tag{9}$$

$$\mathrm{RO_2^{\cdot} + RH} \xrightarrow{k_3} \mathrm{ROOH + R^{\cdot}} \tag{10}$$

$$\mathrm{RO_2^{\cdot} + Co^{2.+}HBr} \xrightarrow{k_3'} \mathrm{products + (Co^{2+} + Br^{\cdot})} \quad \text{or} \quad \mathrm{(Co^{3+}Br^{-})} \tag{6}$$

$$\mathrm{Co^{2+} + Br^{\cdot} + RH} \xrightarrow{k_4} \mathrm{Co^{2.+}HBr + R^{\cdot}} \tag{7}$$

$$\mathrm{RO_2^{\cdot} + RO_2^{\cdot}} \xrightarrow{k_6} \mathrm{products + O_2} \tag{11}$$

where $\mathrm{(Co)_2}$ represent the effective form of cobalt for the decomposition of hydroperoxide, $k_1'\ \mathrm{(Co)^2(ROOH)}$ is affected a little by adding sodium bromide as described above. When k_2 and k_4 are large enough compared with k_3 and k_3', the rate of oxidation at stationary conditions is given by:

$$-\mathrm{dO_2/dt} = [k_3\mathrm{(RH)} + k_3'\mathrm{(Co^{2.+}HBr)}](k_1')^{1/2}\mathrm{(ROOH)^{1/2}(Co)}/2k_6 \tag{12}$$

$$\mathrm{R_{Br} - R_0} = k_3'(k_1')^{1/2}\mathrm{(Co^{2.+}HBr)(ROOH)^{1/2}(Co)}/2k_6 \tag{13}$$

When the rate of hydroperoxide decomposition equals its rate of formation:

$$\mathrm{(ROOH)}\infty = k_3^2\mathrm{(RH)^2}/2k_1'k_6\mathrm{(Co)^2} \tag{14}$$

$$-\mathrm{dO_2/dt} = k_3\mathrm{(RH)}[k_3\mathrm{(RH)} + k_3'\mathrm{(Co^{2.+}HBr)}]/2k_6 \tag{15}$$

Therefore,

$$\mathrm{R_{Br} - R_0} = k_3k_3'\mathrm{(RH)(Co^{2.+}HBr)}/2k_6 \tag{16}$$

In order to confirm the derived kinetic equations, the concentration of hydroperoxide in the course of oxidation[1] was measured with 6 × 10^{-3} mole/l. cobalt in the presence and in the absence of 6 × 10^{-3} mole/l. sodium bromide. In both experiments, the concentration of hydroperoxide was steady over a long time range and almost equal in value to 2·1 × 10^{-2} mole/l. and 2·25 × 10^{-2} mole/l. (with sodium bromide), even though the rate of oxidation increases by a factor of three in the presence of sodium bromide. Provided the propagation step due to $\mathrm{Co^{2.+}HBr}$ proceeds by Eq. 17, $\mathrm{(ROOH)}\infty$ will be expressed by $[k_3\mathrm{(RH)} + k_3'\mathrm{(Co^{2.+}HBr)}]/2k_1'k_6\mathrm{(Co)^2}$, hence $\mathrm{(ROOH)}\infty$ will be increased by a factor of three in the presence of bromide.

$$\mathrm{Co^{2.+}HBr + RO_2^{\cdot} \rightarrow Co^{2+} + Br^{\cdot} + ROOH} \tag{17}$$

The results of the steady concentration of hydroperoxide support the reaction scheme suggested above, since this concentration of hydroperoxide is independent of sodium bromide according to Eq. 14.

In acid solution cobalt monobromide can be easily formed as follows:

$$\mathrm{Co(RCOO)_2 + NaBr \overset{K_1}{\rightleftarrows} CoBr(RCOO) + RCOONa} \tag{18}$$

As suggested above, $\mathrm{Co^{2+}HBr = K'[CoBrRCOO]}$, therefore

$$\mathrm{Co^{2+}HBr = (\mathit{K}_1K')^{1/2}(Co)^{1/2}(NaBr)^{1/2} = (\mathit{K}_1K')^{1/2}[(Co) - (Co^{2+}HBr)]^{1/2} \times (NaBr)^{1/2}} \tag{19}$$

When the ratio of sodium bromide to cobalt is relatively small, $\mathrm{Co^{2+}HBr}$ as well as the rate of oxidation according to Eq. 16 is expected to be half order with respect to sodium bromide. The log–log plots of $(R_{Br} - R_0)$ against (NaBr: Cobalt) at 5×10^{-2} mole/l. cobalt are shown in Fig. 2, and $(R_{Br} - R_0)$ is found to be almost half order with respect to (NaBr: Cobalt) at (NaBr: Cobalt) below 1:2.

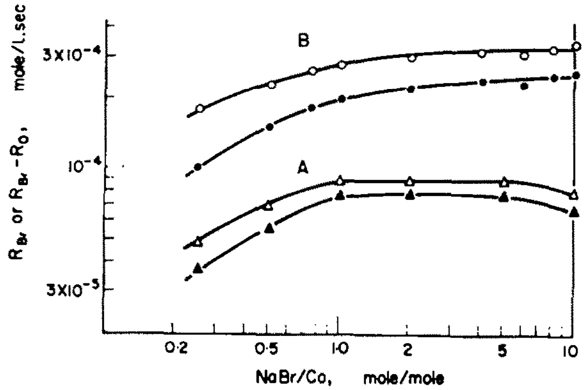

FIG. 2. The steady rate of oxidation of tetralin in acetic acid with 5×10^{-2} M cobalt and sodium bromide as a function of (NaBr/Cobalt) at 35° at 1·22 M (A) and 3·67 M (B) tetralin. Solid points represent $(R_{Br} - R_0)$, i.e., the rate increased with sodium bromide.

The effect of cobalt concentration

In Fig. 3, the log of the steady rate of oxidation of tetralin is plotted against log of cobalt concentration in the presence and absence of sodium bromide. The rate of oxidation of tetralin in acetic acid,[1] is increased slowly at cobalt above 5×10^{-3} mole/l. and reaches the limiting value of $k_3^2(\mathrm{RH})^2/2k_6$ at 5×10^{-2} mole/l. cobalt. On the other hand, the rate of oxidation in the presence of sodium bromide is roughly first order with respect to cobalt at concentrations below 1×10^{-2} mole/l., and tends to increase slowly as the cobalt is increased. Two moles of sodium bromide per one mole of cobalt are used in the experiments in Fig. 3, since at this ratio the rate has shown the maximum or nearly maximum value as the amount of sodium bromide is varied.

The difference of two rate curves due to the addition of sodium bromide to the solution, i.e., $(R_{Br} - R_0)$ is very small at low concentrations of cobalt and is increased as a function of cobalt.

If $\mathrm{Co^{2+}HBr}$ is proportional to cobalt, then by Eq. 15, $(R_{Br} - R_0)$ is required to be proportional to cobalt and by Eq. 13 to be proportional to the square of cobalt. Observed orders in cobalt are 2.0 at 10^{-3} mole/l., 1.0 at 10^{-2} mole/l. and 0.5 at 5×10^{-2} mole/l. These results suggest that an almost linear relation exists between cobalt and $\mathrm{Co^{2+}HBr}$ when the cobalt is not as high as 5×10^{-2} mole/l.

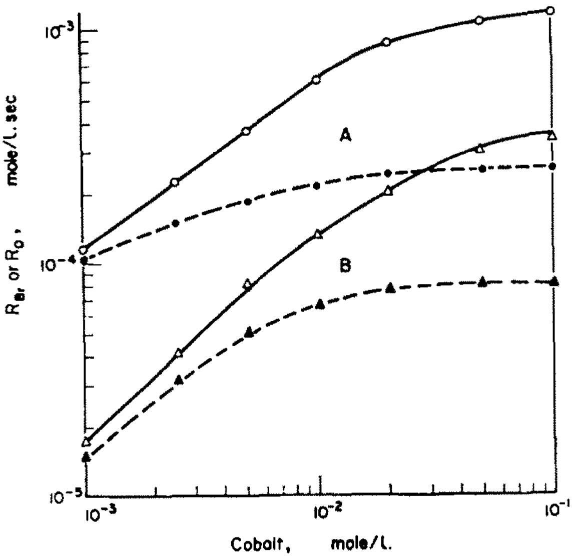

FIG. 3 The steady rate of oxidation of tetralin in acetic acid in the presence of two moles of sodium bromide per one mole of cobalt (R_{Br}) as a function of cobalt concentration at 35° (A) and 50° (B). Broken lines represent the rate without bromide (R_0).

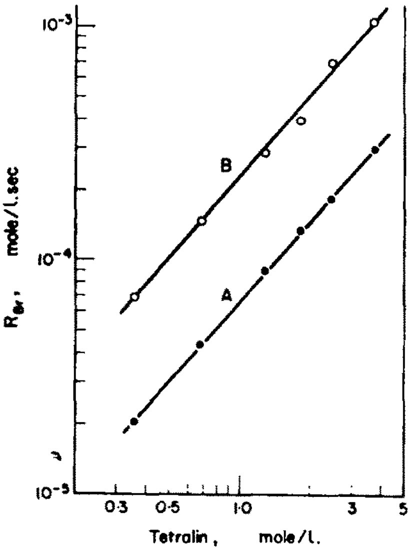

FIG. 4. The rate of oxidation of tetralin with 5×10^{-2} M cobalt and 1×10^{-1} M sodium bromide in acetic acid as a function of tetralin concentration at 35° (A) and 50° (B).

The effect of tetralin concentration

Although the tetralin concentration affects the rate of oxidation markedly as shown in Fig. 4, the hydrogen abstraction step from tetralin by Eq. 10 is not as important as the limiting rate region of simple cobalt-catalysed autoxidation in which the rate is proportional to $(RH)^2$.

The log–log plots of $(R_{Br} - R_0)$ against (RH) are shown in Fig. 5. The rate of hydroperoxide decomposition will equal its rate of formation at 5×10^{-2} mole/l. cobalt, since the limiting rate can be observed in the simple cobalt-catalysed autoxidation of tetralin in Fig. 3. As can be seen, $(R_{Br} - R_0)$ is exactly first order with respect to the concentration of tetralin over a range from 0·35 to 3·67 mole/l. as required by Eq. 16, showing excellent agreement with the theory.

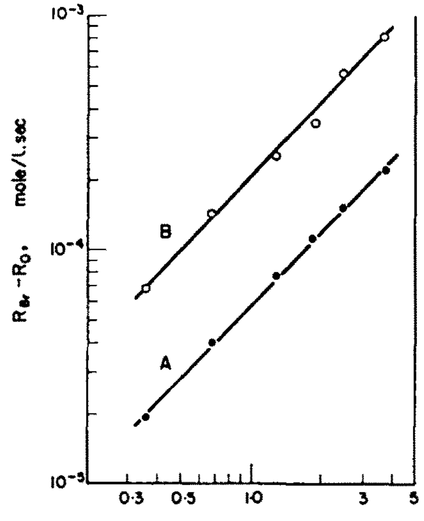

FIG. 5 $(R_{Br} - R_0)$ with 5×10^{-2} M cobalt and 1×10^{-1} M sodium bromide as a function of tetralin concentration at 35° (A) and 50° (B).

The effect of acid strength

Previously,[3] it was shown that $k_3/k_6^{1/2}$ derived from the limiting rate of oxidation of tetralin can be excellently correlated with the dielectric function of $(D - 1)/(2D + 1)$ when fatty acids are used as the solvent. The effect on the rate of oxidation due to bromide, as given in Table 1, decreases as the carbon number of fatty acid is increased and in the order of acid strength. $Co^{2+}HBr$ can be produced by the reaction between organic acid and sodium bromide as shown in Eq. 18, therefore a weak acid solvent results in a smaller equilibrium constant, i.e., smaller $Co^{2+}HBr$ concentration. It should be mentioned that when butyric or nonanoic acids are used as the solvent, the color of the solution remains yellow and does not change to blue color due to cobalt monobromide.

The partial pressure of oxygen

Ravens reported that the rate of oxidation of *p*-toluic acid catalysed with cobalt bromide is half order with respect to the partial pressure of oxygen and the initiating reaction of the oxidation must be Eq. 1. The effect of the partial pressure of oxygen under various conditions are listed in Table 2. It is clear that the oxidation of tetralin in acetic acid with cobalt and bromide is independent of the partial pressure of oxygen at atomospheric pressure, and so the possibility of Eq. 1 can be discarded.

The effect of inhibitor

The effect of sodium bromide on the oxidation is demonstrated in the presence of an antioxidant. With 5×10^{-3} mole/l. cobalt and $1{\cdot}2 \times 10^{-2}$ mole/l. 2,6-di-butyl-phenol the induction period of tetralin is more than 120 min, but by adding sodium bromide from 5×10^{-3} to 3×10^{-2} mole/l. reduces the induction period by several minutes without materially affecting the rate of oxidation catalysed with NaBr and cobalt. Since the bromide is effective even when the concentration of sodium bromide is lower than inhibitor and the rate does not vary, the effect can be not attributed to the reaction between hydrogen bromide and inhibitor.

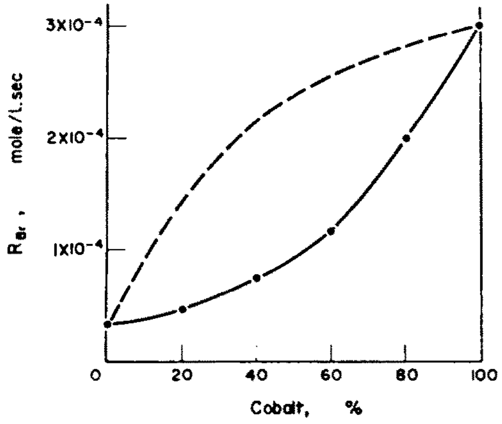

Fig. 6. The mixing effect of cobalt with manganese at 5×10^{-3} M of total concentration and 1×10^{-2} M sodium bromide at 35°. Broken line represents the rate in the absence of manganese.

$$RO_2^{\cdot} + IH \rightarrow ROOH + I^{\cdot} \tag{20}$$

$$I^{\cdot} + HBr \rightarrow HI + Br^{\cdot} \tag{21}$$

Equation 20 may be competitive with Eq. 6, but Eq. 21 may not proceed because the induction period observed is very short. Oxalic acid,[3] which inhibits the oxidation of tetralin in acetic acid by precipitating cobalt at the molar ratio of 1:1, completely stops the oxidation even in the presence of sodium bromide.

The mixing effect of metal catalysts

A synergistic effect of catalyst was reported by Ravens[5], i.e., by replacing 20% of the cobalt by manganese an approximately five fold increase in the rate of oxidation of *p*-toluic acid was observed showing that the metals are strongly synergistic in the presence of sodium bromide.

In the case of tetralin, as shown in Fig. 6, an antagonistic effect is observed, i.e., the activity of cobalt is very much lowered by mixing with manganese. A similar result is seen in the absence of bromide. As previously suggested,[10,11] manganous manganese reacts with the peroxy radical and terminates the chain. Therefore, produces an antagonistic effect but this becomes synergistic when the manganese increases the rate of Eq. 6 because of a strong affinity for the peroxy radical.

TABLE 1. THE EFFECT OF ACID SOLVENT ON THE OXIDATION OF TETRALIN IN A 1:1 BY VOLUME FATTY ACID-TETRALIN SOLUTION WITH 5×10^{-3} mole/l. COBALT AND 1×10^{-1} mole/l. SODIUM BROMIDE AT 35°

Acid	R_0(mole/l. sec)	R_{Br}(mole/l. sec)	R_{Br}/R_0
Acetic	$8{\cdot}1 \times 10^{-5}$	$3{\cdot}0 \times 10^{-4}$	3·75
Propionic	$7{\cdot}1 \times 10^{-4}$	$1{\cdot}2 \times 10^{-4}$	1·69
Butyric	$6{\cdot}8 \times 10^{-5}$	$8{\cdot}2 \times 10^{-5}$	1·21
Nonanoic	$6{\cdot}0 \times 10^{-5}$	$6{\cdot}2 \times 10^{-5}$	1·03

TABLE 2. THE EFFECT OF PARTIAL PRESSURE OF OXYGEN ON THE RATE OF TETRALIN OXIDATION IN ACETIC ACID WITH 5×10^{-3} mole/l. COBALT AND 1×10^{-1} mole/l. SODIUM BROMIDE AT 35°.

Tetralin concentration (mole/l.)	$-dO_2/dt$(mole/l. sec) P_{O_2}:720 mm Hg	 P_{O_2}:400 mm Hg
1·22	$9{\cdot}1 \times 10^{-5}$	$9{\cdot}2 \times 10^{-5}$
1·83	$1{\cdot}34 \times 10^{-4}$	$1{\cdot}34 \times 10^{-4}$
3·67	$3{\cdot}0 \times 10^{-4}$	$3{\cdot}0 \times 10^{-4}$

EXPERIMENTAL

The technique used has been described previously.[1,2] Tetralin was oxidised at 35° and 50° in a 1:1 by volume fatty acid–tetralin solution (3·67 M tetralin) unless otherwise stated. NaBr or NH_4Br were used with cobalt dibromide. In addition cobalt and manganese were used as the decanoates.

[10] Y. Kamiya and K. U. Ingold, *Canad. J. Chem.* **42**, 1207 (1964).
[11] Y. Kamiya and K. U. Ingold, *Canad. J. Chem.* **42**, 2424 (1964).