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The Autoxidation of *p*-Xylene Catalyzed with Cobalt Monobromide in Acetic Acid

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The rate of the cobalt-catalyzed autoxidation of *p*-xylene by adding sodium bromide reaches the steady state within several minutes and increases remarkably at high cobalt concentrations. Although *p*-tolualdehyde as well as water, the main oxidation products of *p*-xylene at the initial stage, strongly affect the rate of oxidation, the apparent rate is kept constant over a long period. When cobalt dibromide is used, a pronounced induction period can be observed at high cobalt concentrations, and the rate of oxidation starts to decrease after a short while. The effect of the ratio of sodium bromide to cobalt has shown that cobalt monobromide is an effective catalyst for the propagation step. The rate of the oxidation of *p*-xylene is found to be of the order of from 1.5 to 2.0 with respect to cobalt at concentrations from 10^{-3} to 5×10^{-2} mol./l. and at temperatures from 65 to 95°C, and to be first-order with respect to the *p*-xylene concentration; these findings show excellent agreement with the theory. When cobalt is partly replaced by manganese, a strong synergistic effect can be observed.

Although several papers[1-5] have been published on the autoxidation of methyl-substituted benzene catalyzed with cobalt bromide, the reaction mechanism is still far from certain. We have shown very recently that the rate of the cobalt-catalyzed autoxidation of tetralin[6] in acetic acid is increased remarkably in the presence of sodium bromide and have kinetically proved that this effect can be attributed to the participation of a new type of propagation reaction between cobalt monobromide and the tetralyl peroxy radical; the kinetic scheme can be represented as follows:

$$\mathrm{ROOH} + (\mathrm{Co})_2 \xrightarrow{k_1'} \text{radical} \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{RH} \xrightarrow{k_2} \mathrm{RO_2}\cdot \tag{2}$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot \tag{3}$$

$$\mathrm{RO_2}\cdot + \mathrm{Co^{2+}BrH} \xrightarrow{k_3'} \text{products} + (\mathrm{Co^{2+}} + \mathrm{Br}\cdot) \tag{4}$$

$$(\mathrm{Co^{2+}} + \mathrm{Br}\cdot) + \mathrm{RH} \xrightarrow{k_4} \mathrm{Co^{2+}BrH} + \mathrm{R}\cdot \tag{5}$$

$$\mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} \text{products} + \mathrm{O_2} \tag{6}$$

$\mathrm{Co^{2+}BrH}$ represents the cobalt-hydrogen bromide complex, which we suggest is the effective catalyst

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

[2] N. Ohta, E. Takahashi and H. Horikiri, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 1353 (1962).

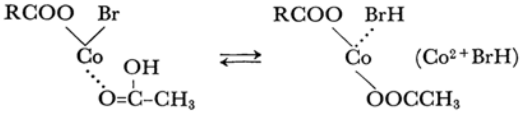
[3] M. Shigeyasu, ibid., **67**, 1396 (1694).

[4] A. Suzuki, K. Iwasa and J. Nakamura, ibid., **67**, 1550 (1964).

[5] Y. Takegami, T. Okano, T. Fujii, S. Uemura and S. Okaya, *J. Japan Petrol. Inst.*, **7**, 560, 723, 727 (1964).

[6] Y. Kamiya, *Tetrahedron*, **22**, 2029 (1966).

for the propagation and the alternative structure of cobalt monobromide in acetic acid.



However, the reaction scheme in the autoxidation of *p*-xylene catalyzed with cobalt bromide should be considerably different from the one shown above; the rate of the cobalt-catalyzed autoxidation of *p*-xylene in acetic acid is extremely slow at temperatures as low as 80°C, even at the cobalt concentration of 5×10^{-2} mol./l., and so the rate of propagation step must be very slow. Previously,⁶⁾ it has been suggested that another propagation reaction 7 between $Co^{2+}BrH$ and the peroxy radical, proceeds to a minor extent as compared with Eq. 4, because the steady state concentration of tetralin hydroperoxide observed increases a little when sodium bromide is added to the solution.

$$\begin{aligned}&RO_2\cdot + Co^{2+}BrH + RH\\&\xrightarrow{k_3''} ROOH + (Co^{2+} + Br\cdot) + R\cdot \qquad (7)\end{aligned}$$

When the hydroperoxide is formed by Eq. 7 instead of Eq. 4, and when k_2 and k_4 are large enough compared with k_3' and k_3'', the overall rate of oxidation under stationary-state conditions is given by:

$$\begin{aligned}-dO_2/dt &= [k_3' + k_3''(RH)](k_1'/2k_6)^{1/2}\cdot\\&\quad(Co)(Co^{2+}BrH)(ROOH)^{1/2} \qquad (8)\end{aligned}$$

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

$$\begin{aligned}-dO_2/dt &= k_3''(RH)[k_3' + k_3''(RH)]\cdot\\&\quad(Co^{2+}BrH)/2k_6 \qquad (9)\end{aligned}$$

Provided k_3' is much larger than $k_3''(RH)$, as in the case of tetralin autoxidation,

$$-dO_2/dt = k_3'k_3''(RH)(Co^{2+}BrH)^2/2k_6 \qquad (10)$$

Experimental

The experimental techniques⁷⁾ have been described previously. *p*-Xylene was oxidized at 65, 80 or 95°C using a 50-ml. long-necked flask in a 1 : 1 (by volume) acetic acid-*p*-xylene solution except when noticed. The bromides used were sodium or ammonium bromides and cobalt dibromide. Cobalt, manganese and copper were used as decanoates. The amount of *p*-tolualdehyde was determined by gas chromatography using 2.5 m. of a PEG succinate ester column at 180°C. The *p*-toluic acid was titrated with an aqueous solution of sodium hydroxide in the presence of EDTA as a chelating reagent after drying off the solvent with an infrared lamp.

Results and Discussion

Oxygen Absorption Curve.—The rate of cobalt-catalyzed autoxidation of *p*-xylene in acetic acid increases slowly as the oxidation proceeds and as *p*-tolualdehyde is accumulated in the solution. On the other hand, when sodium bromide is added the rate reaches the steady state in several minutes and is increased by a factor of three hundred at cobalt concentration of 5×10^{-2} mol./l. and at the sodium bromide concentration of 1×10^{-1} mol./l. Typical oxygen absorption curves are shown in Fig. 1 at the cobalt concentration of 2×10^{-2} mol./l. With cobalt decanoate and sodium bromide, the rate of oxidation is kept constant over a long period. Generally, the addition of ammonium bromide instead of sodium bromide results in about a 10% lower rate. On the other hand, with cobalt dibromide the initial rate is about 20% higher than that obtained with cobalt and sodium bromide, but the rate suddenly decreases after 30 min. (that is, the catalyst is deactivated). Hay and Blanchard⁸⁾ obtained similar results in the autoxidation of cumene. They concluded that these results can be attributed to the formation of phenol due to the decomposition of cumene hydroperoxide by hydrogen bromide. However, in the case of *p*-xylene almost no phenolic inhibitor is formed by the decomposition of *p*-xylene hydroperoxide. In the present state these peculiar results remain unclarified.

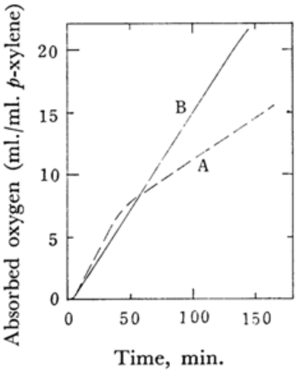


Fig. 1. Oxygen absorption curves in the autoxidation of *p*-xylene in acetic acid catalyzed with 10^{-2} mol./l. $CoBr_2$ (A) and with 10^{-2} mol./l. $CoDe_2$ and 2×10^{-2} mol./l. NaBr (B) at 80°C.

Benzyl bromide, reported by Takegami⁵⁾ and his coworkers to be one of the most effective organic bromides for the oxidation of *p*-toluic acid, has been shown to have a moderate effect on the rate of oxidation, showing the value of 1.9×10^{-4} mol./l.sec. compared with 8.0×10^{-4} mol./l.sec. in the case of NaBr at cobalt 5×10^{-2} mol./l. and at the bromide-to-cobalt ratio of 3.0.

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7) Y. Kamiya, S. Beaton, A. Lafortune and K. U. Ingold, *Can. J. Chem.*, **41**, 2034 (1963).

8) A. S. Hay and H. S. Blanchard, ibid., **43**, 1306 (1965).

A high concentration of cobalt dibromide shows a very pronounced induction period, during which the rate of oxygen absorption is extremely small. This induction period can be increased by increasing the concentration of cobalt dibromide as well as by decreasing the temperature; it can become, for example, 37 min. at cobalt 2×10^{-2} mol./l., and more than 120 min. at cobalt 1×10^{-1} mol./l. at 65°C. The induction period due to cobalt dibromide can be entirely eliminated in the presence of an equimolar amount of sodium acetate; this shows that cobalt monobromide is the effective catalyst, as has been observed in the autoxidation of tetralin. As is shown in Fig. 2, the oxidation products at the initial stage are mainly composed of *p*-tolualdehyde, accompanied by an equimolar amount of water and relatively small amounts of *p*-toluic acid and *p*-toluyl alcohol. The rate of oxidation should be increased as the aldehyde is accumulated, since the effect of aldehyde on the rate is remarkable, as Fig. 3 shows. On the other hand, water is found to deactivate the catalyst strongly; i. e., the rate is decreased by a factor of three by adding 0.69 mol. of water to 1.0 mol. of *p*-xylene at 2×10^{-2} mol./l. of cobalt and 4×10^{-2} mol./l. of sodium bromide, but it is not affected when 0.069 mol. of water is added. Moreover, as *p*-xylene is consumed the rate of oxidation should tend to decrease, because the rate is proportional to *p*-xylene, as Figs. 3 and 7 show. In spite of various effects, however, the apparent rate of oxidation is kept constant over a long period. Therefore, the rate of autoxidation of *p*-xylene catalyzed with cobalt monobromide is apparently independent of the hydrocarbon concentration in the course of oxidation, and it is first-order with respect to the initial hydrocarbon concentration (see Fig. 7).

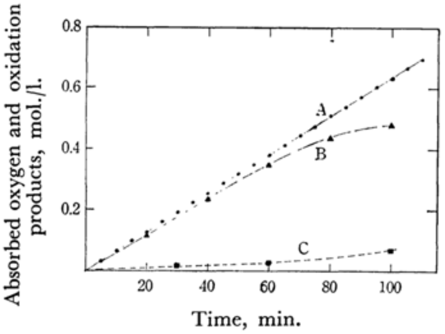

Fig. 2. Absorbed oxygen (A) and oxidation products, *p*-tolualdehyde (B) and *p*-toluic acid (C), as a function of time in the oxidation of *p*-xylene in acetic acid with 2×10^{-2} mol./l. cobalt and 4×10^{-2} mol./l. NaBr at 65°C.
—— O_2 ---- *p*-Tolualdehyde
······ *p*-Toluic acid

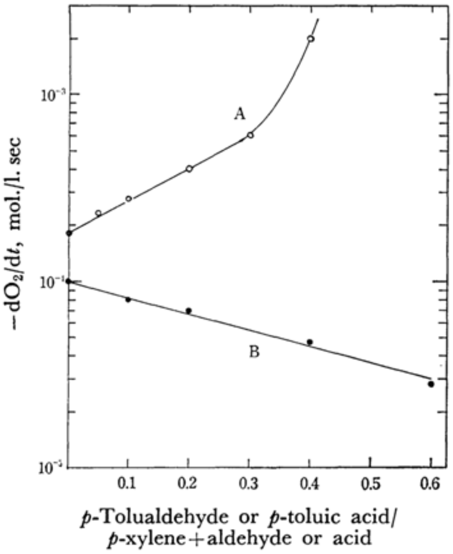

Fig. 3. The effect acid of *p*-tolualdehyde (A) at 80°C and of *p*-toluic acid (B) at 65°C.
○ *p*-Tolualdehyde, 80°C, Co: 2×10^{-2} mol./l., NaBr: 4×10^{-2} mol./l.
● *p*-Toluic acid, 65°C, Co: 2×10^{-2} mol./l., NaBr: 4×10^{-2} mol./l.

The Ratio of Sodium Bromide to Cobalt.—The effect of the ratio of sodium bromide to cobalt is shown in Figs. 4 and 5. Just as in the case of tetralin oxidation, the rate shows a limiting value at a 1 : 2 ratio of sodium bromide to cobalt at temperatures below 80°C. It is confirmed that the increase in the rate of oxidation upon the addition of bromide is due not to free hydrogen bromide but to cobalt monobromide, since the rate reaches a limit or nearly so at sodium bromide/cobalt 1.0. At this ratio, the concentration of free hydrogen bromide should be extremely low, because most of the bromide can be complexed with cobalt and the equilibrium constant of Eq. 11 is very small:

$$CH_3COOH + NaBr \rightleftarrows HBr + CH_3COONa \tag{11}$$

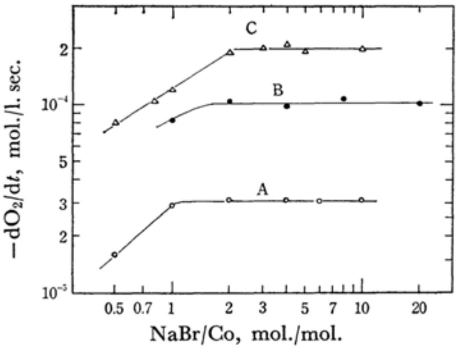

Fig. 4. The steady rate of oxidation of *p*-xylene in acetic acid as a function of the ratio of NaBr/Co, with 5×10^{-2} mol./l. cobalt at 65°C (A), with 2×10^{-2} mol./l. cobalt at 65°C (B) and with 2×10^{-2} mol./l. cobalt at 80°C (C).

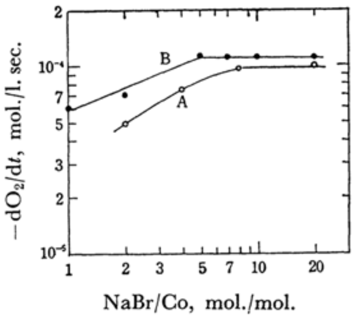

Fig. 5. The steady rate of oxidation of *p*-xylene as a function of the ratio of NaBr/Co in acetic acid with 1×10^{-2} mol./l. cobalt at 95°C (A) and in butyric acid with 5×10^{-2} mol./l. cobalt at 80°C (B).

Although, at 95°C, the rate of oxidation tends to increase until sodium bromide/cobalt is reached at 8.0, as is shown in Fig. 5, the rate has shown a limiting value at sodium bromide/cobalt 2.0 at such higher cobalt concentrations as 5×10^{-2} mol./l. These results might be due to the decrease of the concentration of hydrogen bromide by the formation of inactive organic bromides. The organic bromides can be expected to increase at high temperatures, but the influence on the rate of oxidation will be small at high concentrations of sodium bromide.

It has already been proved that hydrogen bromide is not effective in the initiating reaction, since with just the addition of hydrogen bromide to the solution, in the absence of metal salt or an initiator, the oxidation of tetralin[6] does not proceed, and the induction period[8] due to a phenol can not be decreased.

The Effect of Cobalt Concentration.—The limiting rates of the oxidation of *p*-xylene, as the ratio of sodium bromide to cobalt is varied, are plotted against the cobalt concentration at temperatures from 65°C to 95°C in Fig. 6. At all temperatures the curves show the same characteristics. The rate of oxidation is nearly second-order with respect to cobalt at concentrations below 2×10^{-2} mol./l.; the order in cobalt tends to decrease to the extent of 0.75 as the cobalt is increased. (Incidentally, quite a similar relation was obtained at the *p*-xylene concentration of 1.22 mol./l.). The rate of oxidation is required to be second-order with respect to cobalt according to Eqs. 8 and 10, provided $Co^{2+}BrH$ is proportional to cobalt. Therefore, $Co^{2+}BrH$ seems to be almost proportional to cobalt at low concentrations, but the order of $Co^{2+}BrH$ with respect to cobalt seems to decrease a little as the amount of cobalt is increased.

The Effect of the *p*-Xylene Concentration.—The rate of the autoxidation of *p*-xylene is plotted against the concentration of *p*-xylene in Fig. 7 at 65°C and 80°C; it is found to be exactly first-order with respect to *p*-xylene, as is required by Eq. 10, showing excellent agreement with the theory. On the other hand, the rate tends to be independent of *p*-xylene at low concentrations; this result suggests that the following reaction

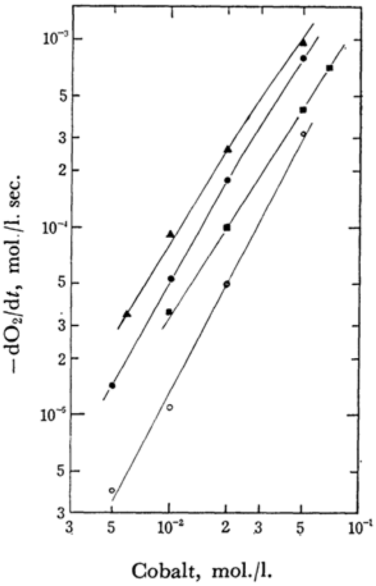

Fig. 6. The maximum rate of oxidation of *p*-xylene in acetic acid in the presence of NaBr as the ratio of NaBr/Co is varied as a function of cobalt concentration.

■ 65°C, *p*-xylene/acetic acid 1/1 (ml./ml.) NaBr/Co 2
● 80°C, *p*-xylene/acetic acid 1/1 (ml./ml.) NaBr/Co 2
▲ 95°C, *p*-xylene/acetic acid 1/1 (ml./ml.) NaBr/Co 8
○ 80°C, *p*-xylene/acetic acid 1/5 (ml./ml.) NaBr/Co 2

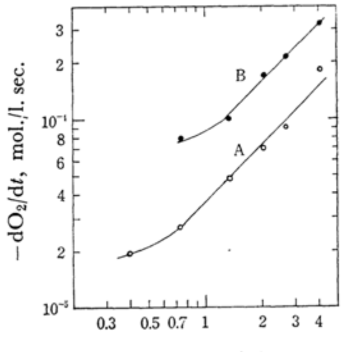

Fig. 7. The steady rate of oxidation of *p*-xylene in acetic acid as a function of *p*-xylene concentration with 2×10^{-2} mol./l. cobalt and 4×10^{-2} mol./l. NaBr at 80°C (A) and with 5×10^{-2} mol./l. cobalt and 1×10^{-1} mol./l. NaBr at 65°C (B).

becomes more important than Eq. 7 at low concentrations of *p*-xylene:

$$Co^{2+}BrH + RO_2\cdot \xrightarrow{k_3'''} (Co^{2+} + Br\cdot) + ROOH \qquad (12)$$

When Eq. 7 is replaced by Eq. 12, the rate of oxidation, instead of with Eq. 10, can be represented by:

$$-dO_2/dt = k_3'k_3'''(Co^{2+}BrH)^2/2k_6 \qquad (13)$$

The Effect of Acid Strength.—When a higher fatty acid is used instead of acetic acid, the rate of oxidation shows a lower value as the carbon number of the fatty acid is increased. However, further experiments show that the rate reaches a limit at a higher ratio of sodium bromide to cobalt in a higher fatty acid solvent. For example, at a cobalt concentration of 2×10^{-2} mol./l., the rate of oxidation in butyric acid shows a maximum value of 1.1×10^{-4} mol./l.sec. at the sodium bromide/cobalt ratio of 4.0 as compared with the maximum rate of 1.8×10^{-4} mol./l.sec. at a sodium bromide/cobalt ratio of 2.0 in acetic acid. When bromoacetic or chloroacetic acids are used instead of acetic acid, the initial rate of oxidation results in a small decrease (about 10%), and the catalyst is gradually deactivated as the reaction proceeds.

The Synergistic Effect of the Metal Catalyst.—When 20% of the cobalt is replaced by manganese, an approximately five-fold increase in the rate of the oxidation of *p*-xylene was observed, showing that the metals are strongly synergistic, as is shown in Fig. 8. As has previously been suggested,⁹⁾ manganeous salt easily reacts with peroxy radicals and terminates the chain. Therefore, the synergistic effect may occur when manganese increases the rate of Eq. 7 because of a strong affinity to the peroxy radical. However, the synergistic effect due to manganese and the rate of oxidation catalyzed with manganese bromide are rapidly decreased as oxidation proceeds; i. e., the manganese is found to be deactivated easily. In contrast to the synergistic effect of manganese, cupric salt has shown a very strong antagonistic effect, showing that the rate of the oxidation of *p*-xylene is reduced by a factor of ten when 20% of the cobalt is replaced by copper.

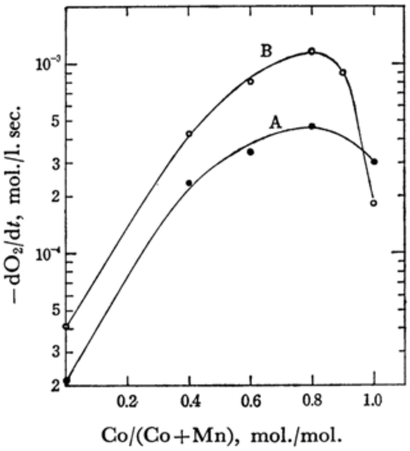

Fig. 8. The mixing effect of cobalt with manganese at 5×10^{-2} mol./l. of total metal concentration and 1×10^{-1} mol./l. NaBr at 65°C (A) and at 2×10^{-2} mol./l. of total metal concentration and 4×10^{-2} mol./l. NaBr at 80°C (B).

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9) Y. Kamiya and K. U. Ingold, ibid., *Can. J. Chem.*, **42**, 1027 (1964).