February, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 481—484 (1974) 481

Autoxidation of Aromatic Hydrocarbons Catalyzed with Cobaltic Acetate in Acetic Acid Solution. III. Oxidation of *p*-Toluic Acid[1]

Mikito KASHIMA and Yoshio KAMIYA[2]

Polymer Research Laboratory, Ube Ind. Ltd., 8-2, Goi, Ichihara-city, Chiba, 290

(Received March 20, 1973)

The oxidation of *p*-toluic acid catalyzed with cobaltic acetate was studied kinetically in acetic acid. The maximum absorption rate of oxygen was obtained in the initial stage of reaction, being represented by the same equation as in the case of toluene, ethylbenzene and cumene. That is, the kinetic equation is of first order with respect to the initial concentration of *p*-toluic acid, of second order with respect to the initial concentration of Co(III), and of inverse first order with respect to the initial concentration of Co(II). The relative reactivity of *p*-toluic acid per active hydrogen was lower than that of toluene, but higher than that of ethylbenzene and cumene. The apparent chain-length in the oxidation of *p*-toluic acid was much shorter than that of *p*-xylene oxidation.

Many procedures have been developed for obtaining terephthalic acid by the autoxidation of *p*-xylene under applied oxygen pressure with cobaltous salts of aliphatic acids as catalyst, together with various promoters such as aldehydes[3,4] and ketones.[5,6] The roles of transition metal ion used as the catalyst are not yet fully clarified since the main purpose of these methods was to increase the yield of terephthalic acid.

Recently, aromatic oxidation catalyzed with cobaltic acetate has received considerable attention.[7–9] The reactions were mainly studied under nitrogen atmosphere for academic purposes, but they should be carried out under oxygen atmosphere for practical purposes. Thus we have reported the reaction mechanism and the role of catalyst in the liquid-phase oxidation of aromatic hydrocarbons catalyzed with cobaltic acetate under oxygen atmosphere.

It has been clarified that *p*-toluic acid was easily oxidized to terephthalic acid with cobaltic acetate under oxygen pressure in acetic acid. The oxidation of *p*-toluic acid to terephthalic acid was apparently initiated by the electron transfer equilibrium between *p*-toluic acid and cobaltic acetate. The oxidation proceeds with a short chain-length comparable to the one obtained in the oxidation of toluene catalyzed with Co(III).

Experimental

Materials. Glacial acetic acid of reagent grade was used. *p*-Toluic acid was vigorously stirred in boiling water and filtered after cooling. The procedure was repeated until no chloride ion was detected. It was then recrystallized from methanol-water solution. Cobaltous acetate was of special grade. The preparation and titration of cobaltic acetate, and the determination of water content in the solution were carried out by the same method as reported in part I.[10]

Procedure. The reaction mixture was charged into a 300 ml. stainless-steel autoclave, and temperature was increased gradually under applied oxygen pressure. The amount of absorbed oxygen was calculated on the basis of pressure drop. To keep oxygen pressure as constant as possible, fresh oxygen was charged into the autoclave as fresh oxygen was charged into the autoclave as soon as a pressure drop of 1 kg/cm^2 had been observed.

Analysis. The solid materials formed by the addition of 150 ml. of water into the reaction mixture were filtered from the aqueous solution, and washed twice with 50 ml of methanol. The crude terephthalic acid was dried at 100 °C.

The filtrate and methanol washings were mixed and concentrated to a syrup containing catalyst, *p*-toluic acid and other substances. It was dissolved in 10% sodium carbonate aqueous solution. The resulting solution was filtered and then acidified with hydrochloric acid. The resulting precipitate was filtered, washed twice with water, and dried at 60 °C to give unreacted *p*-toluic acid and terephthalaldehydic acid. A known weight of this precipitate was dissolved in a portion of M/10 sodium hydroxide. Hydrochloric acid of M/10 was added to this alkaline solution until pH of solution decreased to 3.8. An ethanol solution of hydroxylamine hydrochloride was then added to the solution and pH was again adjusted to 3.8 by adding M/10 sodium hydroxide. The amount of terephthalaldehydic acid contained in the precipitate was calculated by the following equation.

$$\text{Yield of terephthalaldehydic acid (\%)} = 1.50(x-y)/w$$

where x and y are the values of volume (ml) of NaOH and HCl aqueous solution, respectively, and w is weight (g) of precipitate.

Results and Discussion

Rate Law. When *p*-toluic acid (TA) was oxidized with cobaltic acetate under applied oxygen pressure in acetic acid at 80 °C, the reaction proceeded without an induction period. The maximum rate of oxygen absorption (v_m) was obtained in the initial stage of reaction.

The effect of oxygen partial pressure on v_m was studied in the case of the constant concentration of TA (0.333 M) and cobaltic acetate (0.084 M) in acetic acid at 100 °C with an agitation velocity of 1000 rpm. The maximum rate of oxygen absorption was independent of oxygen pressure above 4 kg/cm^2. All experiments were therefore carried out under oxygen pressure of 5 kg/cm^2 unless otherwise stated.

The relation between TA concentration and the maximum rate of oxygen absorption is shown in Fig. 1. The rate of oxidation is proportional to TA concentration below about 2 in the molar ratio of TA to cobaltic acetate, and is inversely proportional to that above the molar ratio 2. Two factors might be considered for explaining the above result: (a) acetate anions on cobaltic ion are replaced by *p*-toluate anions to form a less active cobaltic ion,[11] and (b) the solubility tof TA in acetic acid may be constant from the fac

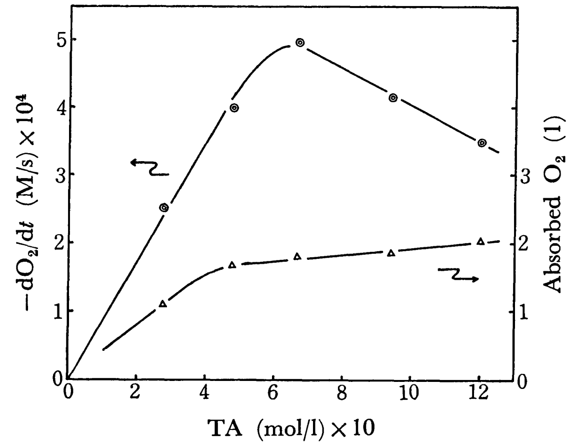


Fig. 1. The effect of TA concentration on the oxidation rate and the amount of O_2 absorbed at 80 °C under 5 kg/cm².
Co(III), 0.253 M; Co(II), 0.005 M.

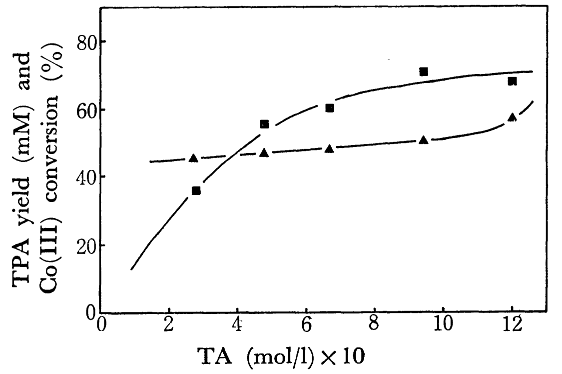


Fig. 2. The effect of TA concentration on TPA yield and Co(III) conversion under the same condition as Fig. 1.
■ TPA yield, ▲ Co(III) conversion

that the yield of terephthalic acid and the amount of oxygen absorbed are constant even when the ratio of TA to cobaltic acetate exceeds 2 (see Fig. 2). The cohesion of undissolved TA may cause a decrease in the apparent concentration of cobaltic acetate.

The effect of the initial concentration of cobaltous acetate on the maximum rate of oxygen absorption and the induction period are shown in Fig. 3. It is clear that cobaltous ion inhibits oxidation remarkably and the induction period increases with the concerntration of Co(II). The reaction proceeds very slowly when the ratio Co(III)/Co(II) is nearly equal to 1. Figure 4 shows a plot of v_m against the square of the initial concentration of cobaltic ion when the concentrations of *p*-toluic acid and cobaltous ion are maintained constant. It is evident that the reaction is of second order with respect to the concentration of Co(III).

Thus v_m obtained in oxidizing TA with cobaltic acetate under oxygen pressure can evidently be represented by the equation

$$v_m = k[TA][Co(III)]^2[Co(II)]^{-1} \qquad (I)$$

which is similar to the equation obtained in the oxidation of toluene,[10] ethylbenzene and cumene.[1]

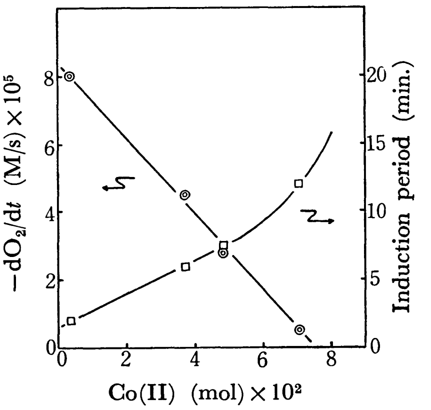


Fig. 3. The effect of Co(II) concentration on the oxidation rate and induction period at 80 °C under 5 kg/cm².
TA, 0.333 M; Co(III), 0.128 M.

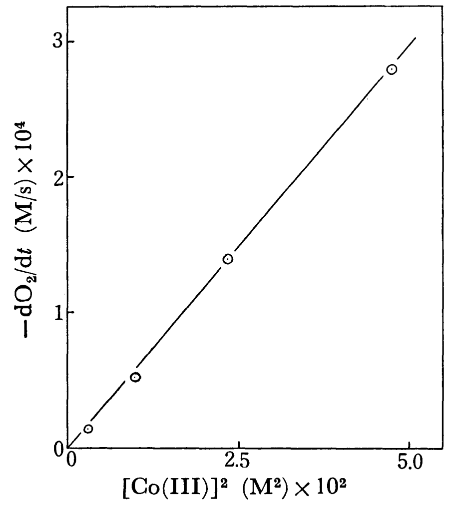
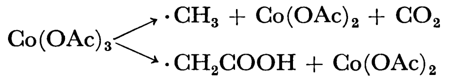


Fig. 4. The effect of Co(III) concentration on the oxidation rate at 80 °C under 5 kg/cm².
TA, 0.467 M; Co(II), 0.0116 M.

Thus the oxidation of TA catalyzed with cobaltic acetate is also initiated by the electron transfer equilibrium between TA and cobaltic acetate.

Effect of Temperature. The rate of oxygen absorption becomes maximum at 100 °C. Both the yield of terephthalic acid (TPA) and the amount of absorbed oxygen showed a similar change in the temperature range 60—120 °C, giving maximum value at 100 °C (see Fig. 5). However, the molar ratio of TPA formed to cobaltic ion consumed decreased gradually with temperature rise. The tendency was most remarkable above 100 °C. This indicates that the self-decomposition of cobaltic acetate occurs considerably above 100 °C as follows:



$$Co(OAc)_3 \begin{cases} \rightarrow \cdot CH_3 + Co(OAc)_2 + CO_2 \\ \rightarrow \cdot CH_2COOH + Co(OAc)_2 \end{cases}$$

In view of the fact the yield of TPA shows only a slow decrease above 100 °C, methyl and carboxymethyl radicals do not seem to contribute to the formation of TPA. The apparent activation energy was cal-

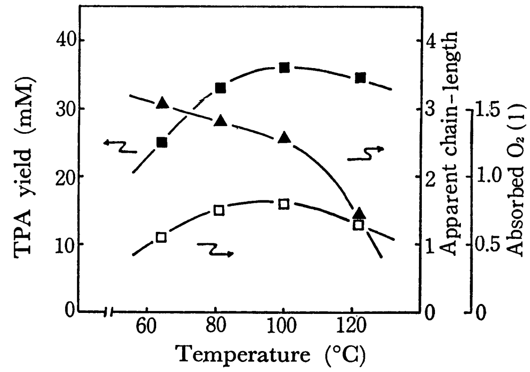


Fig. 5. The effect of temperature on TPA yield, the amount of absorbed O_2, and the apparent chain-length in the oxidation of TA (50 mM).
■ TPA yield, □ absorbed O_2,
▲ apparent chain-length

culated to be 10 kcal/mol, comparable to the one obtained by Kamiya *et al.*[12)]

We have reported that the decreasing order of relative reactivities toward cobaltic acetate was as follows; primary>secondary>tertiary hydrogen, which was entirely inverse to the order for free radicals. The reactivity of TA per active hydrogen toward Co(III) was slightly smaller than that found in the oxidation of toluene with Co(III), but larger than that obtained for ethylbenzene and cumene (see Table 1). This result is not explicable in terms of the C–H bond rupture process, but supports the view that the electron transfer process is rate-determining step.

Table 1. Relative reactivities per active hydrogen of aromatic compounds toward Co(III) at 60 °C

Hydrocarbon	$k\times10^5$, (M^{-1} s.$^{-1}$)	Ratio
Toluene	3.08	1
p-Toluic acid	2.29	0.74
Ethylbenzene	1.67	0.54
Cumene	1.57	0.51

Reaction Products. Terephthalic acid was mainly obtained by the oxidation of TA with cobaltic acetate in acetic acid. A small amount of terephthalaldehydic acid (TAA) was also obtained as a by-product. The yield of TPA increased gradually with time, taking the constant value of 42% after 90 min, while the yield of TAA reached the steady value of 2% soon after the reaction started (see Fig. 6). It is thus apparent that the reaction proceeds successively TA→TAA→TPA, and that the oxidation of TAA is very fast.

The conversion of Co(III) and the ratio of Co(III)/(total Co) were found to take the constant value, 55% and 0.35, respectively after 90 min. Accordingly, the molar ratio of the yield of TPA to the consumed Co(III) was calculated to be 3.1 after 90 min, indicating that the apparent chain-length is much shorter than that obtained in the autoxidation of *p*-xylene. This suggests that the reaction is continued not by the abstraction of hydrogen from TA with peroxy radical, but by the regeneration of Co(III) from the oxidation of Co(II) with peracid or peroxy radical.

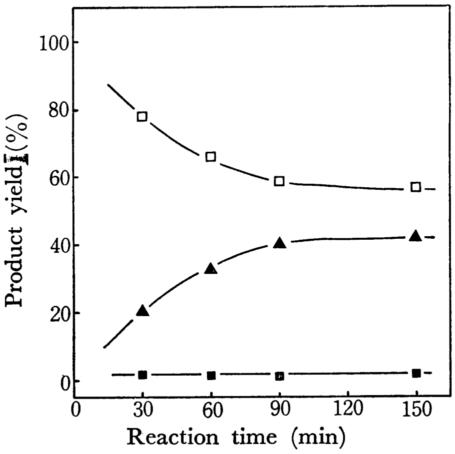


Fig. 6. Product yield and TA conversion in the oxidation of TA at 100 °C under 10 kg/cm².
TA, 0.333 M; Co(III), 0.081 M; Co(II), 0.02 M.
□ TA conversion, ▲ TPA, ■ TAA

Reaction Mechanism. It is clear that the oxidation of TA catalyzed with cobaltic acetate also proceeds through the electron transfer equilibrium as in the case of toluene, ethylbenzene and cumene, since the rate of oxygen absorption can be represented by the same equation independent of substrates, the apparent activation energies are almost equal to each other, and the relative reactivity of TA toward Co(III) is only a little smaller than that of toluene.

For the kinetics of second-order dependence on Co(III) and inverse first-order dependence on Co(II) of v_m, the following elementary reactions might play an important role in the early stage of reaction assuming that the active species of catalyst is the dimer of cobaltic acetate.

$$2\mathrm{Co(III)} \overset{K_1}{\rightleftharpoons} \mathrm{Co(III)_2} \qquad (1)$$

$$\begin{aligned}&\mathrm{R\text{-}CH_3 + Co(III)_2} \overset{K_2}{\rightleftharpoons} \mathrm{[R\text{-}CH_3{}^{+}AcO^{-}Co(III)]}\\ &\quad + \mathrm{Co(II)}\end{aligned} \qquad (2)$$

$$\begin{aligned}&\mathrm{[R\text{-}CH_3{}^{+}AcO^{-}Co(III)]} \xrightarrow{k_3} \mathrm{R\text{-}CH_2\cdot + Co(III)}\\ &\quad + \mathrm{AcOH}\end{aligned} \qquad (3)$$

$$\mathrm{R\text{-}CH_2\cdot + O_2} \xrightarrow{k_4} \mathrm{R\text{-}CH_2OO\cdot} \qquad (4)$$

$$\begin{aligned}&\mathrm{R\text{-}CH_2OO\cdot + Co(III)} \xrightarrow{k_5} \mathrm{R\text{-}CHO + Co(II)}\\ &\quad + \mathrm{(1/2)O_2 + AcOH}\end{aligned} \qquad (5)$$

When the concentration of *p*-tolyl and *p*-tolylperoxy radicals reaches a stationary concentration in the early stage of reaction, the following equation can be introduced.

$$[\mathrm{R\text{-}CH_2\cdot}] = k_3[\mathrm{X}],\ [\mathrm{R\text{-}CH_2OO\cdot}] = k_3k_5^{-1}[\mathrm{X}][\mathrm{Co(III)}]^{-1}$$

where (X) is $K_1K_2k_3[\mathrm{R\text{-}CH_3}][\mathrm{Co(III)}][\mathrm{Co(II)}]^{-1}$ and R is C_6H_4COOH. The absorption rate of oxygen can then be represented by $(-\mathrm{d}O_2/\mathrm{d}t)=(1/2)k_3[\mathrm{X}]$. Then, v_m is abbreviated as

$$v_m = (1/2)K_1K_2k_3[\mathrm{R\text{-}CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1} \qquad (\mathrm{II})$$

This equation is qualitatively in agreement with the experimental results. However, it will become more complicated or changed as the oxidation proceeds, since the oxidation of aldehyde plays an important part.

We postulated that the active species of catalyst was the dimer of cobaltic acetate since no spectroscopic evidence could be found for the formation of Co(IV). However, it is possible that the active species of catalyst is Co(IV) produced by the disproportionation,

$$2\mathrm{Co(III)} \overset{K_1'}{\rightleftarrows} \mathrm{Co(IV)} + \mathrm{Co(II)}$$

We can thus consider the following elementary reactions in the early stage of reaction.

$$\mathrm{R\text{-}CH_3} + \mathrm{Co(IV)} \xrightarrow{k_2'} \mathrm{R\text{-}CH_2\cdot} + \mathrm{Co(III)} + \mathrm{AcOH}$$

$$\mathrm{R\text{-}CH_2\cdot} + \mathrm{O_2} \xrightarrow{k_3'} \mathrm{R\text{-}CH_2OO\cdot}$$

$$\mathrm{R\text{-}CH_2OO\cdot} + \mathrm{Co(III)} \xrightarrow{k_4'} \mathrm{R\text{-}CHO} + \mathrm{Co(II)} + (1/2)\mathrm{O_2} + \mathrm{AcOH}$$

Resolving these elementary reactions by the same method as mentioned above, we obtain

$$v_\mathrm{m} = K_1'k_2'[\mathrm{R\text{-}CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1}$$

This equation is also in agreement with Eqs. (1) and (II).

References

1) Part II, Y. Kamiya and M. Kashima, This Bulletin, **46**, 905 (1973).

2) Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo.

3) J. Yamashita, K. Kurashima, M. Hida, and H. Hashimoto, *Kogyo Kagaku Zasshi*, **67**, 1153 (1965).

4) D. C. Hull, U. S. P. 2,673,217/1954.

5) W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).

6) T. Koga and T. Hara, This Bulletin, **39**, 664 (1966).

7) T. Morimoto and Y. Ogata, *J. Chem. Soc. B*, **1967**, 62.

8) T. A. Cooper and W. A. Waters, *ibid.*, **1967**, 687.

9) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr. *J. Amer. Chem. Soc.*, **91**, 6830 (1969).

10) Y. Kamiya and M. Kashima, *J. Catal.*, **25**, 326 (1972).

11) R. Kawai and Y. Kamiya, *Nippon Kagaku Kaishi*, **1973**, 1538.

12) Y. Kamiya, M. Ohzu, and N. Ohta, *Kogyo Kagaku Zasshi*, **71**, 999 (1968).