The Autoxidation of Toluene Catalyzed with Cobalt Monobromide in Acetic Acid

Koichiro SAKOTA, Yoshio KAMIYA and Nobuto OHTA

Department of Fuel Technology, The University of Tokyo, Hongo, Tokyo

(Received August 17, 1967)

The kinetics of cobalt-catalyzed autoxidation of toluene have been studied in acetic acid in the presence of sodium bromide. The reaction is found to proceed of apparent zero-order in the concentration of toluene for a long duration and of first-order in its initial concentration and of second-order in cobalt ion concentration. In case of ethylbenzene or cumene the rate of oxidation is of first-order in its concentration. This zero-order dependence is explained as a result of the co-oxidation of toluene and its intermediate reaction product, benzaldehyde. A reaction scheme is proposed, which has been shown to be consistent with experimental data by solving out the rate equations simultaneously with a computer, co-oxidation of toluene and benzaldehyde being taken into consideration.

The profound accelerating effect of the bromide on the rate of the autoxidation of aromatic hydrocarbons catalyzed by cobalt salt in organic acid media has been recognized and commercially in practice. Several papers have been published on this reaction mechanism after Revens' paper in 1959. Recently Hay and Blanchard[1] made some experimentals to examine the elementary reactions. We also have made kinetical experimentals treating with tetralin and ethylbenzene to obtain the detail of the reaction mechanism and extended our study to the oxidation of *p*-xylene under its low conversions. The characteristics of the cobalt-catalyzed autoxidation of methylbenzenes in the presence of bromide were as follows.

The rate of oxidation of methylbenzenes keeps constant for a long duration in spite of the decrease of their concentrations, even though the rates are of first-order dependence with respect to their initial concentrations. There are many complexities in the oxidation of methylbenzenes, since the aromatic aldehydes produced as intermediate products of reaction are easily oxidized and the reaction turns into co-oxidation of toluene and benzaldehyde. In this paper we studied the oxidation of toluene kinetically in detail in stead of *p*-xylene to avoid the difficulties caused by the number of the intermediate products which prevent us from satisfactory kinetical analysis when high conversions are attained. The co-oxidation reaction of toluene and benzaldehyde was taken into consideration.

Results and Discussion

The Effects of Hydrocarbons. The oxygen uptake took place after a few minutes of induction period, when toluene was oxidized with oxygen in
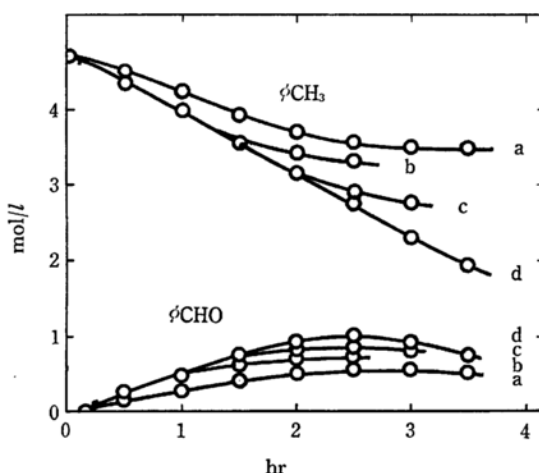

Fig. 1. Oxidation of toluene at 80°C.
Co: 2.0×10^{-2} mol/*l*
NaBr: a, 2.0×10^{-2}; b, 4.0×10^{-2}; c, 8.0×10^{-2}; d, 1.6×10^{-1} mol/*l*

acetic acid solution with cobalt acetate and sodium bromide as catalysts. It was observed that the rate of oxidation was increased by a factor of about 300 in the presence of bromide. As is observed in Fig. 1, there is a long duration where the rates of the consumption of toluene and of the accumulation of benzaldehyde kept constant. We regard these phenomena characteristic in the oxidation of methylbenzenes in a cobalt bromide-acetic acid-system. Kinetical experiments were made to obtain the accounts. The fact that so much of benzaldehyde was accumulated may be partly attributed to the low temperatures of reaction but

1) A. S. Hay and H. S. Blanchard, *Can. J. Chem.*, **43**, 1306 (1965).

strongly suggests that the reaction of the hydrogen abstraction from toluene is more profoundly accelerated than that from benzaldehyde by the catalysis of bromide. It was observed in this case that the stronger the C–H bond, the more profoundly catalyzed the hydrogen abstraction reaction from the hydrocarbons, say, in the case of ethylbenzene (*ca.* 30 fold) and of tetralin (*ca.* 4 fold). This may be explained from the difference of the degree of the C–H bond rupture in the transition state of the hydrogen abstraction stage by peroxy radicals and by cobalt-bromide complexes. The profound effect of bromide implies that cobalt-bromide complex is more active than peroxy radicals. So the stretching of C–H bond in transition state is thought to be larger for peroxyradicals than for cobalt-bromide complex. The larger the stretching of a C–H bond, the more the contribution of the C–H bond energy to the activation energy of the process. And the order of acceleration by bromide was observed as *p*-toluic acid > toluene > ethylbenzene > tetralin. The bond formation between peroxyradical and toluene, $ROO\cdots H-CH_2-\phi$, may be less favoured than between bromide and toluene, $Co-Br\cdots H-CH_2-\phi$, because bromine atom is more capable of covalent bond formation and less oriented to form a bond due to the presence of d-orbitals and its larger size than oxygen. These properties may explain that the activation energy of the reaction catalyzed by bromine is less affected by the bond energy of the C–H bond to be broken. Benzaldehyde is oxidized into perbenzoic acid *via* benzoyl radical. Perbenzoic acid suffers homolytic decomposition by cobalt salt to give radicals. These radicals can abstract the hydrogen atom from toluene or increase the concentration of the active cobalt complex, which can also abstract hydrogen atom from toluene. In other words, benzaldehyde can accelerate the consumption of toluene—co-oxidation of toluene
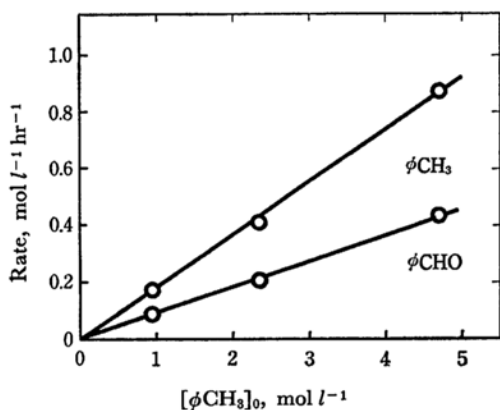
and benzaldehyde—. The behaviors of benzaldehyde explain qualitatively the apparent zero-order dependence of the rate of toluene consumption on the concentration of toluene. It was observed also in case of *p*-xylene and *p*-toluic acid that the profile of the reaction was the same as in case of toluene. To determine the effect of the concentration of the hydrocarbon, the initial concentration of toluene was varied. As presented in Fig. 2, the variation of the initial concentration of toluene with constant concentrations of cobalt acetate and sodium bromide showed first-order dependence of the rate of toluene consumption and of accumulation of benzaldehyde. It follows from this fact the hydrogen abstraction stage is the rate-determining step. Benzaldehyde and benzoic acid were produced mainly, with a little amount of benzyl alcohol. The concentration of peroxidic compounds was less than 10^{-3} mol/*l*. Ethlbenzene and cumene were oxidized to give acetophenone mainly. In either case, the rates of oxygen uptake and of consumption of hydrocarbon were proportional to the concentration of their own during the oxidation, namely the rate of oxidation is of first-order with respect to the concentration of hydrocarbon in contrast to the case of toluene (Fig. 3).
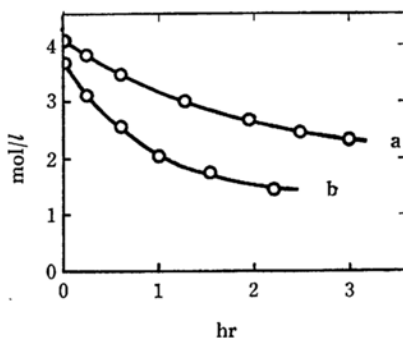

Fig. 3. Oxidation of ethylbenzene and cumene at 80°C with 2×10^{-2} mol/*l* cobalt and 4×10^{-2} mol/*l* sodium bromide.
a, ethylbenzene; b, cumene

This difference of the reaction profile is ascribed to the difference between the stability of benzaldehyde and acetophenone against oxidation. The facts above make it necessary that the oxidation of toluene is treated kinetically as co-oxidation when high conversions of toluene are reached. In general, it might be said in the oxidation of aromatic hydrocarbons in cobalt bromide-acetic acid-system that: (1) the oxidation of the hydrocarbons with only primary hydrogens in the side chains, proceeds of apparent zero-order dependence on the concentration during the oxidation and shows first-order dependence on the initial concentration of the hydrocarbons to be oxidized, (2) the oxidation of hydrocarbons with secondary and/or
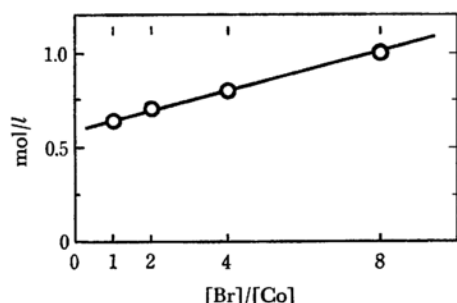

Fig. 2. The rates of toluene consumption and of accumulation of benzaldehyde at 80°C with 2×10^{-2} mol/*l* cobalt, 4×10^{-2} mol/*l* sodium bromide.

Fig. 4. The maximum amount of benzaldehyde accumulated *vs.* ratio of sodium bromide to cobalt.

Fig. 6. Electronic spectra of reaction solution at 80°C with 5×10^{-3} mol/l cobalt and 1×10^{-2} mol/l sodium bromide.
1: 0 min; 2: 25 min; 3: 65 min; 4: 85 min; 5: 105 min; 6: 120 min

tertiary hydrogens in the side chains, is of first-order dependence on the concentration and gives corresponding ketones as oxidation products.

The Effect of The Concentration of Sodium Bromide. As mentioned above the bromide seems to catalyze the process where toluene is oxidized into benzaldehyde, and the amount of bromide added has a profound effect on the oxidation rate (Figs. 1 and 4). The rate of toluene consumption increased continuously as the concentration of bromide increased until the ratio of [bromide]/[cobalt acetate] attained near two and kept constant when the ratio became higher than two. We conclude from the facts mentioned above and other papers[2,3] that the catalytic species is cobalt monobromide. It seems, however, that our proposed reaction mechanism may be insufficient to explain the length of the duration where the rate of toluene consumption kept constant and the maximum amount of accumulated benzaldehyde became larger according to the increase of the amount of the added bromide. But these behaviors can be fully understood from the data in Fig. 5. The line (a) stands for the change of the concentration of the bromide anion and has good corre-
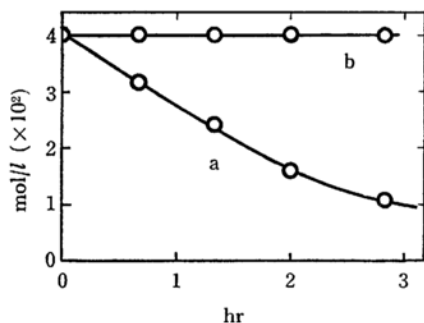
spondence to the toluene consumption curve. It implies that bromine atoms were consumed proportionally to the extent of the reaction. When bromide was analyzed quantitatively after the reaction solution was diluted with alkaline solution and refluxed sufficiently, the values obtained were equal to the initial concentration of bromide (the line (b)). Bromine atom seems to be consumed as benzyl bromide. The number of toluene molecule oxidized per one bromine atom was about 25. This number is temperature dependent and becomes larger at higher temperatures because organic bromides may be decomposed to regenerate bromine atoms. The electronic spectra of the reaction solution are shown in Fig. 6. Optical density readings were taken at the reaction temperature. Oxygen feed and time count were started when the temperature of the solution reached the designated value. The decrease in the optical densities at 14.5 kK corresponded satisfactorily to the change of the concentration of the bromide anion shown in Fig. 5. The increases in optical densities in the ultraviolet region are due to the increase in the concentration of benzaldehyde formed. The shape of the electronic spectra changed and had a stronger ·resemblance to that of cobaltous acetate after the consumption of bromine atom. The reaction rate also began to tail off according to the decrease of the concentration of the bromide. Now it was understood easily that the more the added amount of bromide, the longer the length of the duration where the sufficient amount of bromide anion is present to maintain the catalytic activities of the cobalt-bromide complex.

The Effect of Cobalt Concentration. The dependence of the rate of oxygen uptake was shown in Fig. 7. At the concentrations from 5×10^{-3} to 4×10^{-2} mol/l of cobalt acetate, the rate of oxygen uptake was of second-order with respect to the

Fig. 5. Concentration of bromide anidn *vs.* reaction time at 80°C with 2×10^{-2} mol/l cobalt.

2) Y. Kamiya, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 897 (1966); Y. Kamiya, *Tetrahedron*, **22**, 2029 (1966).
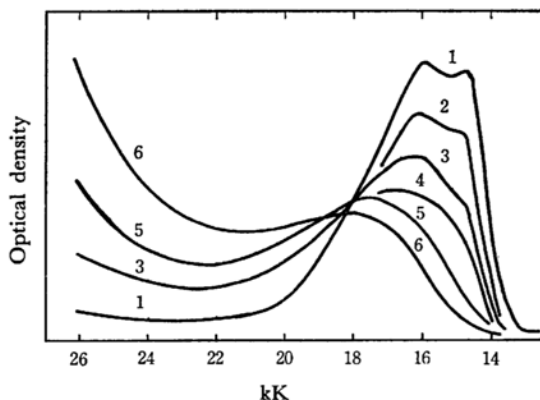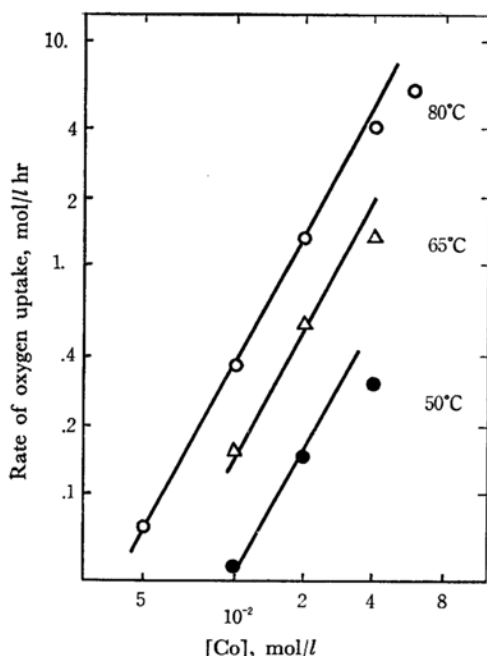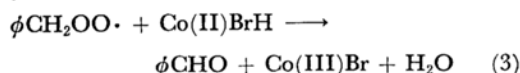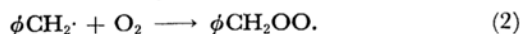3) Y. Kamiya, J. Nakajima and K. Sakoda, This Bulletin, **39**, 2211 (1966).
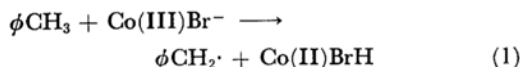
Fig. 7. The rates of oxygen uptake *vs.* concentration of cobalt acetate at $[NaBr]/[Co(OcA)_2 \cdot 4H_2O] = 2$.

concentration of cobalt salt, showing some departure from linearity at high concentrations of cobalt salt. This may be partly due to the limitation of solubility of sodium bromide to maintain the ratio of [bromide]/[cobalt acetate] higher than about two, which assures the maximum concentration of cobalt monobromide. If the cobalt ion only affects the catalysis of decomposing hydroperoxides, the rate of toluene consumption will be of less first-order to the concentration of cobalt acetate assuming a bi-molecular termination process. Since the decomposition of hydroperoxide by cobalt ions in glacial acetic acid (referred to as (Co)) is expressed as follows[4] under the conditions employed here.

$$hpo + 2(Co) \longrightarrow radicals$$
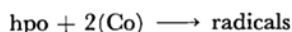
The second-order dependence to cobalt ion implies the following reactions with participation of cobalt ion into propagation steps.

$$\phi CH_3 + Co(III)Br^- \longrightarrow$$
$$\phi CH_2 \cdot + Co(II)BrH \qquad (1)$$

$$\phi CH_2 \cdot + O_2 \longrightarrow \phi CH_2OO. \qquad (2)$$

$$\phi CH_2OO \cdot + Co(II)BrH \longrightarrow$$
$$\phi CHO + Co(III)Br + H_2O \qquad (3)$$

Benzaldehyde can behave like initiator. So the concentration of active species which are capable

4) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **41**, 2020 (1964).

to abstract hydrogen atom from methyl groups may increase, as the concentration of benzaldehyde increases. It seems inadequate to apply stationary state treatment in this system when the amount of benzaldehyde accumulated is considerable. Co-existence of active species, such as $\phi CH_2OO\cdot$, $\phi COOO\cdot$ and $Co(III)Br^-$, and the occurrance of cross-termination prevent from solving out equations directly to show the second-order dependence on cobalt concentration, the apparent zero-order dependence on toluene concentration, *etc.*

The Cobalt-Bromide Complexes. It has been reported that $Co(H_2O)_6{}^{2+}$, $Co(H_2O)_4Cl_2$ are octahedral and $CoBr_4{}^{2-}$ is tetrahedral. Cobalt acetate will be changed into $CoBr^+(Oh)$, $CoBr_2$ $(Oh), \cdots CoBr_4{}^{2-}(Td)$ step by step according to the addition of bromide. The absorption band at 14.5 kK in Fig. 8 is considered to be caused by the transition $^4T_1 \leftarrow {}^4A_2$ of $CoBr_4{}^{2-}$, because it has the strongest intensity and is located at the longest wavelength and the intensity at 14.5 kK decreased continuously according to the extent of the reaction (Fig. 6). The bands around 16 kK may be the bands splitted and shifted of that of cobalt acetate at 18.7 kK by the lowering of the symmetry caused by the coordination of bromide anion to cobalt ion. The Co–Br bond is expected to be more covalent than the Co–OAc bond from the values of nephelauxetic ratios and nuclear quadrupole resonance data and so on. This covalency will make the electron transfer easier from bromide anion to cobaltic cation which is formed *via* oxidation of Co(II) by hydroperoxides or peroxyradicals. This tranfer will stabilize the Co(III) state and as a result, give the radical character to the bromine ligated to the Co(III). And the bromine may gain the ability of hydrogen abstraction. Because of the presence of *d*-orbitals and its larger size, bromine is less oriented and easier for hydrogen to form a bond with than oxygen in acetate or cobalt ion is. This favours the bond formation with hydrogen atom of alkyl groups.
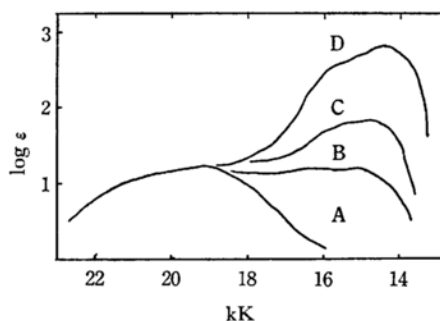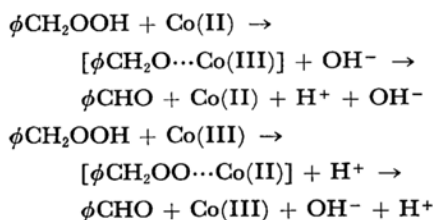

Fig. 8. Electronic spectra of cobalt acetate in the presence of sodium bromide in acetic acid solution.

[sodium bromide]/[cobalt acetate]:
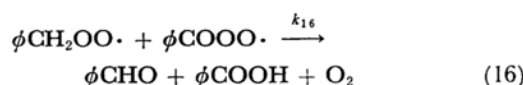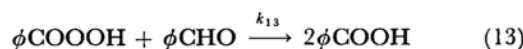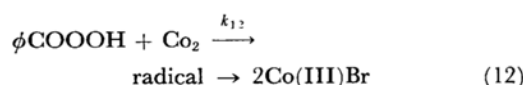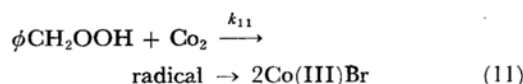A, 0; B, 0.5; C, 2.0; D, 100

The Reaction Mechanism. The detailed mechanism of initiation steps is not still fully explained but we gave some discussions in other papers.[2,3] When the reaction proceeds to some extent and the concentration of benzaldehyde becomes considerable, the initiation reaction (12) is predominant over other initiation processes. When benzylhydroperoxide is decomposed catalytically by cobalt ion, benzyloxy and benzylperoxy radicals are formed in equal amount. Benzyloxy radical abstracts hydrogen and become benzylalcohol. If benzylperoxy radical became benzylhydroperoxide, benzylalcohol would be accumulated to considerable amount. Because benzylalcohol was rather stable and oxidized at the rate of 5% of that of toluene. But little amount of benzylalcohol was detected in experiments. This suggests thatthe contribution of the reac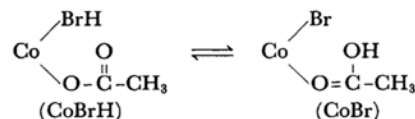tion (4) is small. An alternative mechanism below, where benzaldehyde is formed from benzylhydroperoxide without formation of benzylalcohol,

$$\phi CH_2OOH + Co(II) \rightarrow$$
$$[\phi CH_2O \cdots Co(III)] + OH^- \rightarrow$$
$$\phi CHO + Co(II) + H^+ + OH^-$$
$$\phi CH_2OOH + Co(III) \rightarrow$$
$$[\phi CH_2OO \cdots Co(II)] + H^+ \rightarrow$$
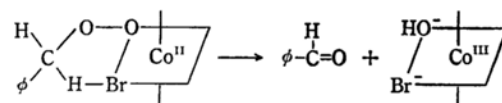$$\phi CHO + Co(III) + OH^- + H^+$$

may not be operative. Because it may be unreasonable that above reactions proceed without migration of radicals formed from hydroperoxide out of the solvent cage around the cobalt ion. The reaction (3) is probable. The following elementary reactions will explain the experimental observations after the initial stage of the reaction.
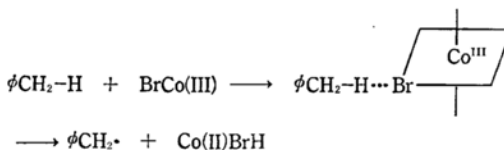
$$\phi CH_3 + Co(III)Br \xrightarrow{k_1}$$
$$\phi CH_2\cdot + Co(II)BrH \quad (1)$$

$$\phi CH_2\cdot + O_2 \xrightarrow{k_2} \phi CH_2OO\cdot \quad (2)$$

$$\phi CH_2OO\cdot + Co(II)BrH \xrightarrow{k_3}$$
$$\phi CHO + Co(III)Br + H_2O \quad (3)$$

$$\phi CH_2OO\cdot + \phi CH_3 \xrightarrow{k_4}$$
$$\phi CH_2OOH + \phi CH_2\cdot \quad (4)$$

$$\phi CH_2OO\cdot + \phi CHO \xrightarrow{k_5}$$
$$\phi CH_2OOH + \phi CO\cdot \quad (5)$$

$$\phi CHO + Co(III)Br \xrightarrow{k_6}$$
$$\phi CO\cdot + Co(II)BrH \quad (6)$$

$$\phi CO\cdot + O_2 \xrightarrow{k_7} \phi COOO\cdot \quad (7)$$

$$\phi COOO\cdot + Co(II)BrH \xrightarrow{k_8}$$
$$\phi COOOH + Co(III)Br \quad (8)$$

$$\phi COOO\cdot + \phi CH_3 \xrightarrow{k_9}$$
$$\phi COOOH + \phi CH_2\cdot \quad (9)$$

$$\phi COOO\cdot + \phi CHO \xrightarrow{k_{10}}$$
$$\phi COOOH + \phi CO\cdot \quad (10)$$

$$\phi CH_2OOH + Co_2 \xrightarrow{k_{11}}$$
$$radical \rightarrow 2Co(III)Br \quad (11)$$

$$\phi COOOH + Co_2 \xrightarrow{k_{12}}$$
$$radical \rightarrow 2Co(III)Br \quad (12)$$

$$\phi COOOH + \phi CHO \xrightarrow{k_{13}} 2\phi COOH \quad (13)$$

$$2\phi CH_2OO\cdot \xrightarrow{k_{14}} \phi CHO + \phi CH_2OH \quad (14)$$

$$2\phi COOO\cdot \xrightarrow{k_{15}} (\phi COO)_2 + O_2 \quad (15)$$

$$\phi CH_2OO\cdot + \phi COOO\cdot \xrightarrow{k_{16}}$$
$$\phi CHO + \phi COOH + O_2 \quad (16)$$

The equilibrium below exists and reactions (3) and (1) are expressed as follows.

(CoBrH)   (CoBr)

reaction (3):

$$\phi CH_2OO\cdot + Co(II)BrH \longrightarrow$$
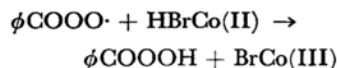

reaction (1):

$$\longrightarrow \phi CH_2\cdot + Co(II)BrH$$
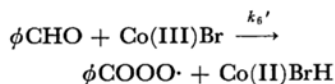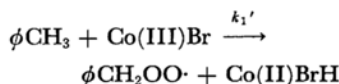
Benzoyloxy radical has not hydrogen atom and cannot proceed *via* reaction (3), so might be converted to perbenzoic acid.

$$\phi COOO\cdot + HBrCo(II) \rightarrow$$
$$\phi COOOH + BrCo(III)$$

The reactions (2) and (7) are very fast, therefore can be simplified as follows.

$$\phi CH_3 + Co(III)Br \xrightarrow{k_1'}$$
$$\phi CH_2OO\cdot + Co(II)BrH$$

$$\phi CHO + Co(III)Br \xrightarrow{k_6'}$$
$$\phi COOO\cdot + Co(II)BrH$$

Above reactions are rewritten as ordinary differential equations.

$$-d[\phi CH_3]/dt = k_1'[\phi CH_3][Co(III)Br]$$
$$+ k_4[\phi CH_3][\phi CH_2OO\cdot]$$
$$+ k_9[\phi CH_3][\phi COOO\cdot]$$

$$d[\phi CH_2OO\cdot]/dt = k_1'[\phi CH_3][Co(III)Br]$$
$$- k_3[\phi CH_2OO\cdot][Co(II)BrH]$$
$$- k_5[\phi CHO][\phi CH_2OO\cdot]$$
$$+ k_9[\phi CH_3][\phi COOO\cdot] - 2k_{14}[\phi CH_2OO\cdot]^2$$
$$- k_{16}[\phi CH_2OO\cdot][\phi COOO\cdot]$$

$$d[\phi CHO]/dt = k_3[\phi CH_2OO\cdot][Co(II)BrH]$$
$$- k_5[\phi CHO][\phi CH_2OO\cdot]$$
$$- k_6'[\phi CHO][Co(III)Br]$$
$$- k_{10}[\phi CHO][\phi COOO\cdot]$$
$$- k_{13}[\phi CHO][\phi COOOH] + k_{14}[\phi CH_2OO\cdot]^2$$
$$+ k_{16}[\phi CH_2OO\cdot][\phi COOO\cdot]$$

$$d[\phi COOO\cdot]/dt = k_5[\phi CHO][\phi CH_2OO\cdot]$$
$$+ k_6'[\phi CHO][Co(III)Br]$$
$$- k_8[\phi COOO\cdot][Co(II)BrH]$$
$$- k_9[\phi CH_3][\phi COOO\cdot] - 2k_{15}[\phi COOO\cdot]^2$$
$$- k_{16}[\phi CH_2OO\cdot][\phi COOO\cdot]$$

$$d[\phi COOOH]/dt = k_8[\phi COOO\cdot][Co(II)BrH]$$
$$+ k_9[\phi CH_3][\phi COOO\cdot]$$
$$+ k_{10}[\phi CHO][\phi COOO\cdot]$$
$$- k_{12}[\phi COOOH][Co(II) + Co(III)]^2$$

$$d[Co(III)Br]/dt = - k_1'[\phi CH_3][Co(III)Br]$$
$$+ k_3[\phi CH_2OO\cdot][Co(II)BrH]$$
$$- k_6'[\phi CHO][Co(III)Br]$$
$$+ k_8[\phi COOO\cdot][Co(II)BrH]$$
$$+ 2k_{12}[\phi COOOH][Co(II) + Co(III)]^2$$

As the concentration of benzaldehyde become higher according to the consumption of toluene, the concentration of perbenzoic acid may increase. Perbenzoic acid is decomposed to give radicals. This increase may raise the rate of initiation step and compensate the decrease of toluene concentration to keep the rate of toluene consumption constant for a long time. But this explanation is only qualitative. Above simultaneous six first-order ordinary differential equations have been solved after Runge-Kutta Gill's method with a OKITAC 5090 electronic computer to see the dependence on the initial concentration of the toluene and cobalt salt. The meaningful results may be obtained in spite of some arbitraliness of the values of rate constants used.

The values of rate constants were changed little by little in order that the curves of the concentrations of toluene and benzaldehyde against reaction time have stronger resemblance to those obtained in experiments. One set of the rate constants which gave satisfiable calculation results are as follows.

k_1': 1×10^{-2}, k_3: 1, k_4: 1×10^{-5}, k_5: 5×10^{-5},
k_6': 1.5×10^{-2}, k_8: 2, k_9: 1×10^{-4}, k_{10}: 2×10^{-4},
k_{12}: 2×10^1, k_{13}: 5×10^{-3}, k_{14}: 3×10^{-1},
k_{15}: 3×10^{-1}, k_{16}: 3×10^{-1}, $mol^{-1} l^{-1} sec^{-1}$

except k_{12} ($mol^{-2} l^2 sec^{-1}$)

According to the assumed predominance of the reaction (12) in initiation steps mentioned above, the initial conditions for intermediates, $\phi CH_2OO\cdot$, ϕCHO, $\phi COOO\cdot$, $\phi COOOH$, $Co(III)Br$, were given as 5×10^{-3}, 5×10^{-2}, 2×10^{-4}, 2×10^{-3}; 1—4×10^{-3}, $mol\, l^{-1}$, respectively.

The calculation results suggest that above elementary reactions are consistent with the observations: the apparent zero-order dependence of the rate of toluene consumption on the concentration of toluene in the solution, and the constancy of the ratio of $d[\phi CH_3]/d[\phi CHO]$ in the earlier stage of the reaction and the first-order dependence on the initial concentration of toluene and the second-order with respect to the concentration of cobalt acetate. The ratio of k_1' to k_6' suggests that the oxidation of toluene was more efficiently catalyzed than that of benzaldehyde.

Experimental

Reagents. Hydrocarbons such as toluene, were washed with sulfuric acid till the solutions were not colored and with alkaline solution, then distilled as usually. Acetic acid, cobalt acetate and sodium bromide of guaranteed grade were used without further purification.

Reaction Vessels. All runs were carried out in a 50 ml glass flask connected to the oxygen reservoir and the pressure was kept constant automatically in a thermostatted water bath. All measurements of absorption spectra were made by means of a Hitachi EPS-2 spectrophotometer, using 10 mm quartz cell mounted in a thermostated cell holder under temperature controll to ±0.5°C. The cells are equipped with a condenser, a oxygen inlet tube and a glass thermister to controll the reaction temperature automatically. The solution was stirred by oxygen gas.

Analysis. Quantitative analysis was made by gas chromatography and polarography, under the conditions—polyethylene glycol 6000, 20 wt%, on Flusin-T; and 50% alcoholic McIlvaine buffer solution, respectively. The concentration of bromide was determined by potentiometric titration with a siver electrode coated with argentous bromide by a standard argentous nitrate solution.