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The Autoxidation of Aromatic Hydrocarbons Catalyzed with Cobaltic Acetate in Acetic Acid Solution

I. The Oxidation of Toluene

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The kinetics of the oxidation of toluene catalyzed by cobaltic acetate in acetic acid have been studied at 60°C. The oxidation proceeds without induction period, and the maximum absorption rate of oxygen as well as the maximum reduction rate of cobaltic ion were observed at the beginning of the reaction. Both maximum rates can be expressed as follows,

$$-dO_2/dt = k[\phi\text{-CH}_3][\text{Co(III)}]^2[\text{Co(II)}]^{-1}$$

$$-d\text{Co(III)}/dt = k'[\phi\text{-CH}_3][\text{Co(III)}]^2[\text{Co(II)}]^{-1}$$

with $k'/k \sim 1.7$. The oxidation product was exclusively benzaldehyde at the early stage of oxidation. The following mechanisms are proposed: (1) The oxidation of toluene to benzyl radical proceeds by the reaction of toluene with a dimer of cobaltic ion; (2) Benzylperoxy radical is oxidized to benzaldehyde by a cobaltic ion.

INTRODUCTION

Although the oxidation of alkylbenzenes with cobaltic salts in acetic acid has been extensively studied (*1–5*), the nature of the interaction between cobaltic ion and hydrocarbon at the early stage of the reaction is not yet fully clarified. The oxidation of toluene with cobaltic acetate proceeds through an electron transfer equilibrium (*6*), as does the oxidation of *p*-methoxytoluene with manganic acetate (*7*), since the rate of oxidation is inversely proportional to the concentration of cobaltous ion, and toluene is oxidized more easily than isopropylbenzene.

To study the electron transfer equilibrium further, the results obtained in the presence of oxygen should be compared with those obtained in the absence of oxygen. In this article, we present a rate law, to propose a reaction mechanism, and examine the effect of benzylalcohol and sodium acetate as well as the solvent effect in the oxidation of toluene with cobaltic acetate in acetic acid.

EXPERIMENTAL

Material. Toluene was repeatedly shaken with concentrated sulfuric acid until no color was observed. After washing and drying, it was fractionally distilled. Acetic acid, benzylalcohol, and cobaltous acetate were of reagent grade. Cobaltic acetate was prepared by the oxidation of cobaltous acetate by passing ozone in acetic acid. The concentration of cobaltic ion was determined by potentiometric titration. The amount of water in the solution was determined by Karl Fischer titration.

Procedure. The oxidation apparatus is shown in Fig. 1. The oxygen pressure was maintained constant at atmospheric, regulated by a gas stocker (C) from a gas which was evolved by electrolysis of water. The electrolysis was controlled by an electric relay. The mixed solution of toluene, co-

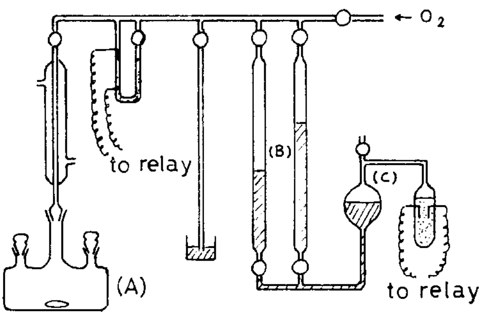

FIG. 1. The apparatus employed to study the kinetics.

baltic acetate, and acetic acid was poured into the reaction vessel (A), and then (A) and the gas burette (B) were filled with oxygen. When the reaction vessel was immersed in the water bath at 60°C, the oxidation started.

The initial absorption rate of oxygen was calculated from the tangent on the plot of oxygen absorbed against time. Similarly, the initial reduction rate of cobaltic ion was obtained from the plot of the consumption of cobaltic ion against time.

Reaction product. After the reaction the solution was poured into an equal volume of water and thoroughly extracted with ether. The extracted solution was washed with aqueous sodium hydroxide and dried over calcium chloride.

Analysis was carried out by gas chromatography employing a 2.2 m column packed with D.O.P. on Celite 545 at flow rate of helium, 50 ml min^{-1}, at 140°C. The formation of benzaldehyde and a small amount of benzylalcohol and benzylacetate were confirmed by analysis. After the alkaline solution was acidified, benzoic acid was extracted with benzene.

RESULTS AND DISCUSSION

Rate law. When cobaltic acetate is employed as a catalyst, toluene is oxidized with oxygen even at 60°C. The oxidation proceeded without induction period and the maximum absorption rate of oxygen was observed to be equal to the initial rate of oxidation. As described previously (*8*), water in the solution has a marked effect on the initial absorption rate of oxygen and the initial reduction rate of cobaltic ion. Therefore, the amount of water should be maintained constant.

The initial absorption rate of oxygen was plotted against the initial concentration of toluene, as shown in Fig. 2. In this case, the initial concentration of cobaltic ion was maintained constant. Thus the overall reaction is of first order with respect to toluene.

Figure 3 shows a plot of the initial rate against the reciprocal of the initial concentration of cobaltous ion. It is evident that the reaction is of inverse first order with respect to cobaltous ion. This suggests that the reaction involves an electron transfer equilibrium between cobaltic ion and toluene. Figure 4 shows a plot of the initial rate against the initial concentration of cobaltic ion, when the concentration of toluene and the molar ratio of cobaltic to total cobalt ions was maintained constant; here again a linear plot was obtained.

Taking account of the inverse first order dependence of the oxidation rate on the concentration of cobaltous ion, the overall reaction must be of second order with respect to cobaltic ion concentration.

These results obtained in the presence of oxygen indicate that the kinetics of the reaction are consistent with the following rate law:

$$-dO_2/dt = k[\phi\text{-}CH_3][Co(III)]^2[Co(II)]^{-1} \quad (I)$$

To check this, we also examined the reduction rate of cobaltic ion in the presence of oxygen at 60°C. In this case, similarly, the maximum reduction rate of cobaltic ion was observed just after the reaction was started.

Figure 2 also shows a plot of the maximum rate of cobaltic ion against the initial concentration of toluene, when the initial concentration of cobaltic and cobaltous ion was maintained constant. The linearity of this plot indicates that the reduction rate of cobaltic ion is of first order with respect to toluene. However, the line does not pass through the origin: this fact may be explained by the self-decomposition of co-

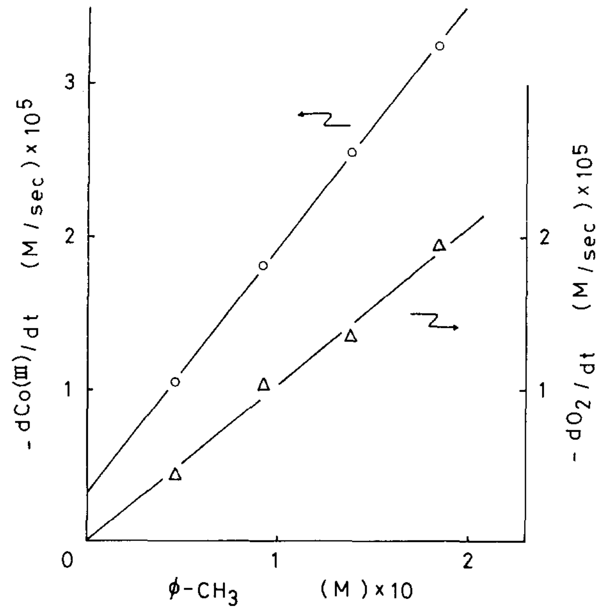

FIG. 2. Effect of toluene on the reduction rate of Co(III) and on the initial rate of oxidation. Co(III): 0.157 *M*, Co(II): 0.020 *M*, H_2O: 1.25 *M*, at 60°C under 1 atm of O_2.

baltic ion. Although it is considered that methyl radicals ($\cdot CH_3$) (*9*) or carboxymethyl radicals ($\cdot CH_2COOH$) (*10*) are produced by the self-decomposition of cobaltic ion, the contribution of them could be negligible at a high concentration of toluene in our experiments.

Figure 4 shows a plot of the initial reduction rate of cobaltic ion against the total concentration of cobalt when molar ratio of cobaltic to total cobalt ions is maintained constant. Evidently, the reduction rate of cobaltic ion is of first order with respect to total cobalt concentration. However, taking account of the inverse first order dependence of the reduction rate of cobaltic ion on the concentration of cobaltous ion, the reduction rate of cobaltic ion also is of second order with respect to cobaltic ion.

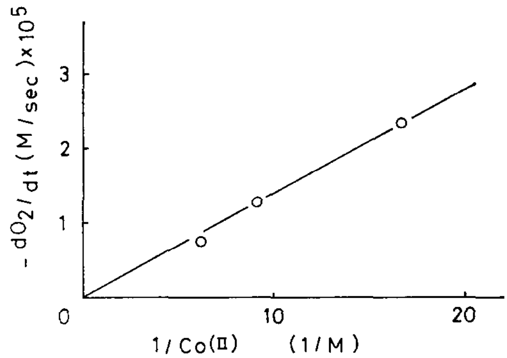

FIG. 3. Effect of Co(II) on the initial rate of oxidation. ϕ-CH_3: 1.57 *M*, Co(III): 0.155 *M*, H_2O: 1.98 *M*, at 60°C under 1 atm of O_2.

Hence, the reduction rate of cobaltic ion is expressed as the following equation.

$$-d\mathrm{Co(III)}/dt = k'[\phi\text{-}\mathrm{CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1} \quad \mathrm{(II)}$$

This equation is similar to Eq. (I) and consistent with the following equation obtained in the absence of oxygen.

$$-d\mathrm{Co(III)}/dt = k''[\phi\text{-}\mathrm{CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1} \quad \mathrm{(III)}$$

If cobaltic acetate only reacts with toluene, the reduction rate of Co(III) in the presence of oxygen should be proportional to that in the absence of oxygen. However, as shown in Fig. 5, there is considerable difference between both rates even at the early stage of the reaction, and this difference increases as the reaction proceeds, that is, the ratio of the rate constant

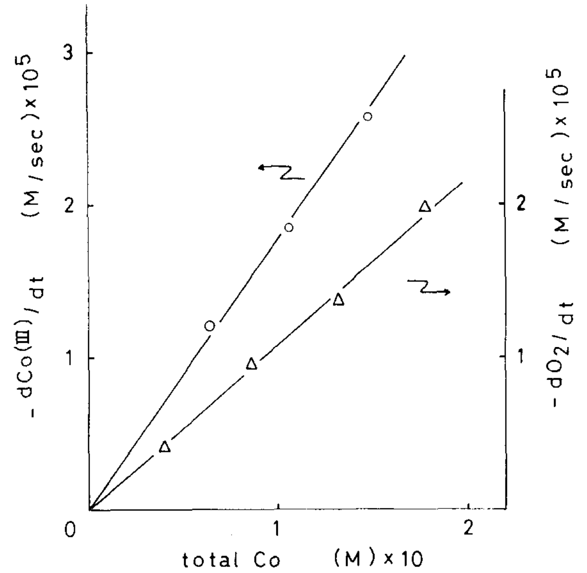

FIG. 4. Effect of total cobalt ion on the reduction rate of Co(III) and on the initial rate of oxidation. ϕ-CH_3: 0.184 *M*, θ: 0.837, H_2O: 1.25 *M*, at 60°C under 1 atm of O_2.

(k') in the presence of oxygen to that (k'') in the absence of oxygen increases from 1.5 to 2.2. Hence, it seems that cobaltic ion is regenerated by some oxidation process under oxygen atmosphere, probably by the reaction of cobaltous ion with perbenzoic acid.

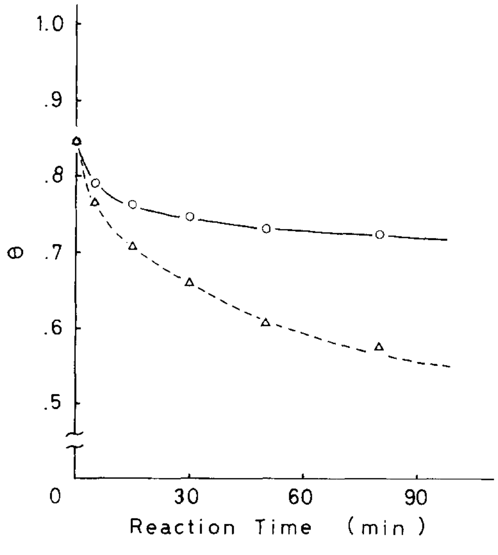

FIG. 5. Consumption curve of cobaltic ion under O_2 (○) (*M*) and Ar (△). ϕ-CH_3: 0.184 *M*, Co (III): 0.150 *M*, Co(II): 0.027 *M*, H_2O: 1.25 *M*, at 60°C.

From Eqs. (I) and (II) it follows that the initial absorption rate of oxygen will be proportional to the initial reduction rate of cobaltic ion. The ratio k'/k obtained from Fig. 2 (or Fig. 4) is calculated to be around 1.7. When the apparent chain length is long, the ratio k'/k will be smaller than one. Hence, this result indicates that the apparent chain length is very short and the following redox type reactions are not so important in the oxidation of toluene with cobaltic acetate.

$$\phi\text{-}CH_2OOH + Co(III) \rightarrow \phi\text{-}CH_2OO\cdot + Co(II) + H^+$$

$$\phi\text{-}CH_2OOH + Co(II) \rightarrow \phi\text{-}CH_2O\cdot + Co(III) + OH^-$$

Thus, the initiation step consists of the same mechanism either under oxygen or argon atmosphere.

Reaction products. The main oxidation products of toluene with cobaltic acetate were benzaldehyde, benzoic acid and small amounts of benzyl alcohol and benzyl acetate (see Fig. 6). The salient points on the constitution of products are as follows:

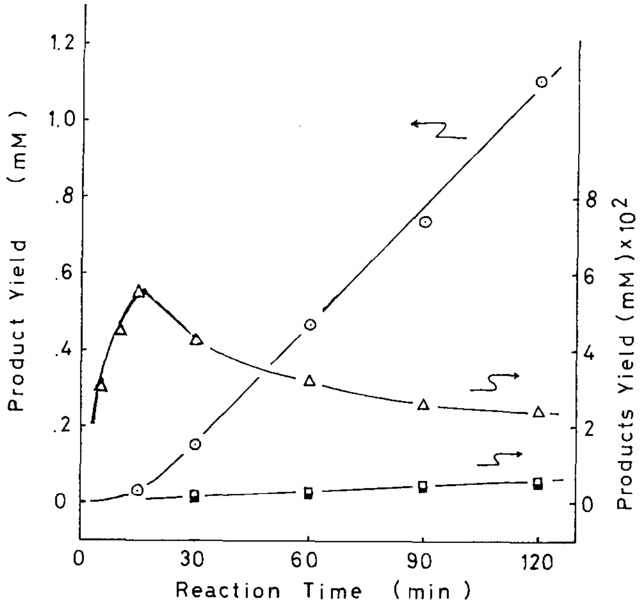

FIG. 6. Yields of ϕ-COOH (○), ϕ-CHO (△), ϕ-CH_2OH (□) and ϕ-CH_2OAc (■) in the oxidation of ϕ-CH_3 at 60°C under 1 atm of O_2.

(a) At the early stage of oxidation (within 15 min) benzaldehyde is the sole oxidation product of toluene and the molar ratio of benzaldehyde to benzyl alcohol is higher than ten within 60 min.

(b) The yield of benzyl acetate is very small as compared with those of benzaldehyde and benzoic acid.

After 15 min, the regeneration of Co(III) from the oxidation of Co(II) by perbenzoic acid will take place appreciably, since benzoic acid is produced from benzaldehyde via perbenzoic acid.

To provide further insight into the oxidation reaction, we studied the effect of addition of alcohol on the initial rate. The initial absorption rate of oxygen decreases linearly as the amount of benzyl alcohol increases and becomes constant, as shown in Fig. 7, although the reduction rate of Co(III) is faster in the oxidation of ϕ-CH_2OH than in the oxidation of ϕ-CH_3. It is well known that a *sec*-alcohol easily forms complexes with higher valency metal ion to produce a ketone by two-electron oxidation (*11–13*). Hence, if ϕ-CH_2OH is produced considerably, it will be oxidized to ϕ-CHO with Co(III) through the same mechanism as *sec*-alcohol, showing a higher reduction rate of Co(III). But benzylalcohol should not be produced by the bimolecular termination of benzylperoxy radical, because the rate of oxidation of benzyl alcohol was not higher than that of benzaldehyde and the oxidation product was entirely benzaldehyde.

The formation of benzaldehyde can be attributed to the reaction of cobaltous ion with peroxy radicals (*14–16*), but this explanation contradicts the result that the molar ratio of Co(III) to absorbed oxygen is about 1.7.

$$\phi\text{-}CH_2OO\cdot + Co(II) \rightarrow \phi\text{-}CHO + Co(III) + OH^-$$

Since more than two molecules of Co(III) were reduced per molecule of hydroperoxide and benzaldehyde was produced predominantly, Scott (*17*) recently suggested the following scheme in the reaction of benzyl hydroperoxide with cobaltic acetate:

$$2Co(III) + \phi\text{-}CH_2OOH \rightarrow 2Co(II) + \phi\text{-}CHO + 2H^+ + \tfrac{1}{2}O_2$$

We propose a similar reaction scheme in order to explain our experimental results,

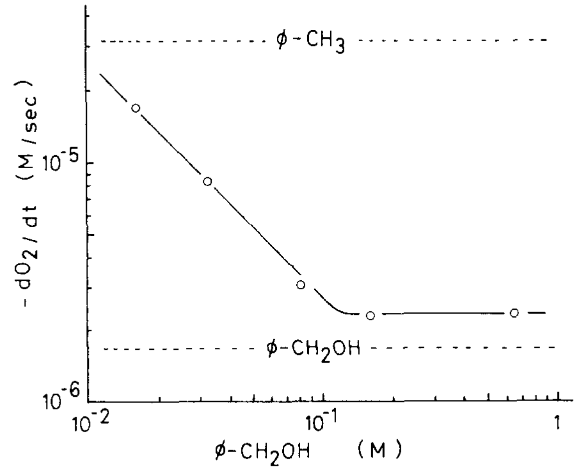

FIG. 7. Effect of benzylalcohol on the initial rate of oxidation of toluene. ϕ-CH_3: 0.622 *M*, Co(III): 0.121 *M*, Co(II): 0.026 *M*, at 60°C under 1 atm of O_2. A broken line (ϕ-CH_3) represents the rate of oxidation of toluene in the absence of benzylalcohol and a broken line (ϕ-CH_2OH) the rate of oxidation of pure benzylalcohol at the same reaction conditions described above.

although the details of the mechanism seem more complicated:

$$\mathrm{Co(III)} + \phi\text{-}\mathrm{CH_2OO\cdot} \rightarrow \mathrm{Co(II)} + \phi\text{-}\mathrm{CHO} + \mathrm{H^+} + \tfrac{1}{2}\mathrm{O_2}$$

Effect of sodium acetate. In oxidizing toluene with cobaltic acetate in acetic acid, the initial absorption rate of oxygen as well as the initial reduction rate of Co(III) are remarkably accelerated by the addition of sodium acetate (see Table 1). This result can be explained as follows. Since the dissociation constant of sodium acetate in acetic acid is relatively large (1.3×10^{-6} (*18*), a cobaltic ion is easily coordinated with an extra acetate anion and forms an active cobalt with coordination number higher than three, and the initial rate of oxidation can be greatly enhanced with these active cobalt species.

Solvent effect. In oxidizing toluene with Co(III) in acetic acid under oxygen atmosphere, a remarkable positive solvent effect was observed on addition of benzene or monochlorobenzene. As shown in Table 2, the initial rate of oxidation increases linearly as the amount of benzene or monochlorobenzene is increased. The state of solvation of acetic acid around the cobaltic ion is probably disturbed by the addition of neutral solvents in acetic acid solution. Accordingly, cobaltic ion can be reacted more easily with toluene.

Reaction mechanism. Previously we proposed that an electron transfer equilibrium

TABLE 1

THE EFFECT OF SODIUM ACETATE ON THE INITIAL RATE OF OXIDATION OF TOLUENE[a]

NaOAc	$-dO_2/dt$ ($M \times 10^5$)
0	0.51
0.018	0.75
0.055	1.07
0.135	1.94
0.457	2.82
1.35	2.00

[a] Co(III): 0.135 *M*; Co(II): 0.014 *M*; 60°C; O_2 pressure 1 atm. Initial concentration ϕ-CH_3 1.18 *M*.

TABLE 2

SOLVENT EFFECT ON ϕ-CH_3 OXIDATION[a]

ϕ-CH_3 (ml)	AcOH (ml)	ϕ-Cl (ml)	ϕ-H (ml)	$-(dO_2/dt)$ (M/sec)
5	60	—	—	2.05×10^{-5}
5	45	15	—	3.22
5	30	30	—	5.17
5	30	—	30	5.39

[a] Co(III): 0.108 *M*; Co(II): 0.080 *M*; 60°C; O_2 pressure 1 atm.

exists between toluene and cobaltic acetate, and also that the rate-determining step consisted of the reaction of the ionic pair with cobaltic acetate according to the kinetic result shown by Eq. (III).

However, the rate law in the presence of oxygen can also be expressed similarly to that in the absence of oxygen: the absorption rate of oxygen and the reduction rate of Co(III) are of second order with respect to cobaltic ion concentration and inversely first order to cobaltous ion concentration. In order to explain these kinetic results, the active species of cobalt may be considered as a dimer of cobaltic ion (*19*, *20*) or a quadrivalent cobalt ion rather than cobaltic ion monomer. Since we are not able to show any spectroscopic evidence about the formation of Co(IV) represented by the following disproportionation reaction,

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

we are disinclined to consider the contribution of a quadrivalent cobalt ion. If a dimer of Co(III) is one of the active species (*2*, *3*), the initiation step can be explained by the following reactions.

$$\mathrm{Co(III)_2} + \phi\text{-}\mathrm{CH_3} \rightleftarrows \phi\text{-}\mathrm{CH_3^+AcO^-Co(III)} + \mathrm{Co(II)}$$

$$\phi\text{-}\mathrm{CH_3^+AcO^-Co(III)} \rightarrow \phi\text{-}\mathrm{CH_2\cdot} + \mathrm{Co(III)} + \mathrm{AcOH}$$

Then, in the absence of oxygen, the following reaction takes place:

$$\phi\text{-}\mathrm{CH_2\cdot} + \mathrm{Co(III)_2} \rightarrow \phi\text{-}\mathrm{CH_2OAc} + \mathrm{Co(III)} + \mathrm{Co(II)}$$

In the presence of oxygen, however, benzyl radical produced by the decomposition of ionic pair reacts with oxygen to yield benzylperoxy radical.

The following reactions will mainly contribute to the oxidation of toluene with cobaltic acetate at the early stage of reaction:

$$2\mathrm{Co(III)} \overset{K_1}{\rightleftarrows} \mathrm{Co(III)_2} \quad (1)$$

$$\phi\text{-}\mathrm{CH_3} + \mathrm{Co(III)_2} \overset{K_2}{\rightleftarrows} \phi\text{-}\mathrm{CH_3^+AcO^-Co(III)} + \mathrm{Co(II)} \quad (2)$$

$$\phi\text{-}\mathrm{CH_3^+AcO^-Co(III)} \xrightarrow{k_3} \phi\text{-}\mathrm{CH_2\cdot} + \mathrm{Co(III)} + \mathrm{AcOH} \quad (3)$$

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

$$\phi\text{-}\mathrm{CH_2OO\cdot} + \mathrm{Co(III)} \xrightarrow{k_5} \phi\text{-}\mathrm{CHO} + \mathrm{Co(II)} + \mathrm{H^+} + \tfrac{1}{2}\mathrm{O_2} \quad (5)$$

$$\phi\text{-}\mathrm{CH_2OO\cdot} + \mathrm{Co(II)} \xrightarrow{k_6} \phi\text{-}\mathrm{CHO} + \mathrm{Co(III)} + \mathrm{OH^-} \quad (6)$$

When the rate determining step is reaction (3), the rate of oxygen absorption can be expressed as follows:

$$-d\mathrm{O_2}/dt = k[\phi\text{-}\mathrm{CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1}$$

where $k = (k_5 + 2k_6)/(2k_5 + 2k_6)$.

The rate of reduction of Co(III) can be calculated as follows

$$-d\mathrm{Co(III)}/dt = k'[\phi\text{-}\mathrm{CH_3}][\mathrm{Co(III)}]^2[\mathrm{Co(II)}]^{-1}$$

where $k' = 2k_5/(k_5 + k_6)$.

It should be mentioned that the rate equations will be more complicated or quite changed as the oxidation proceeds, since the consumption of Co(III) by benzaldehyde as well as the regeneration of Co(III) by peroxidic products as perbenzoic acid and the bimolecular termination of peroxy radicals will also play an important part.

REFERENCES

1. Cooper, T. A., and Waters, W. A., *J. Chem. Soc.* 1358 (1964).
2. Richardson, W. H., *J. Amer. Chem. Soc.* **87,** 1096 (1965).
3. Lande, S. S., and Kochi, J. K., *J. Amer. Chem. Soc.* **90,** 5196 (1968).
4. Heiba, E. I., and Koehl, W. J., *J. Amer. Chem. Soc.* **91,** 6830 (1969).
5. Morimoto, T., and Ogata, Y., *J. Chem. Soc.* B 62 (1967).
6. Sakota, K., Kamiya, Y., and Ohta, N., *Can. J. Chem.* **47,** 387 (1969).
7. Andrulis, P. J., Dewar, M. J. S., and Hunt, R. L., *J. Amer. Chem. Soc.* **88,** 5473 (1966).
8. Kamiya, Y., Ohsu, M., and Ohta, N., *J. Chem. Soc. Jap.* (Ind. Chem. sect.) **71,** 999 (1968).
9. Eberson, L., *J. Amer. Chem. Soc.* **89,** 4669 (1967).
10. Heiba, E. I., Dessau, R. M., and Koehl, W. J., *J. Amer. Chem. Soc.* **91,** 138 (1969).
11. Mosher, W. A., and Whitmore, F. C., *J. Amer. Chem. Soc.* **70,** 2544 (1948).
12. Hampton, J., Leo, A., and Westheimer, F. H., *J. Amer. Chem. Soc.* **78,** 306 (1956).

13. Nave, P. M., and Trahanovsky, W. S., *J. Amer. Chem. Soc.* **92**, 1120 (1970).
14. Kamiya, Y., and Ingold, K. U., *Can. J. Chem.* **42**, 1027, 2424 (1964).
15. Betts, A. T., and Uri, N., Advances in Chemistry Series **76**, 160 (1968).
16. Sheredin, V. P., and Denisov, E. T., *Izvest. Akad. Nauk. SSSR. Ser. Khim* 1428 (1967).
17. Scott, E. J. Y., *J. Phys. Chem.* **74**, 1174 (1970).
18. Martin, R. J. L., *Aust. J. Chem.* **15**, 409 (1962).
19. Sharp, J. A., and White, A. G., *J. Chem. Soc.* 110 (1952).
20. Koubek, K., and Edward, J. O., *J. Inorg. Nucl. Chem.* **25**, 1401 (1963).