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The Metal-Catalyzed Autoxidation of Cumene

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The catalysis of metal carboxylates and metal phthalocyanines in the autoxidation of cumene was kinetically studied. The limiting rate of oxidation of cumene was just over half the theoretical rate of $k_p{}^2(\mathrm{RH})^2/2k_t$ suggesting that the induced decomposition of cumyl hydroperoxide due to cumyloxy radical proceeds rapidly. The effect of metal catalyst in the autoxidation of cumene was concluded to be caused by the decomposition of hydroperoxide and not by the activation of oxygen, since the rate of oxidation increased with the increase in the rate of metal-catalyzed decomposition of hydroperoxide. The synergistic effect on the metal-catalyzed autoxidation of cumene was proved to result from the synergistic effect of metal salts on the decomposition of hydroperoxide. The oxidation products of cumene varied remarkably according to reaction conditions.

The rate of oxidation of hydrocarbons catalyzed by metal salts reaches a constant value as the metal concentration is increased, and the value is in good agreement with the theoretical value of $k_p{}^2(\mathrm{RH})^2/2k_t$ in the cases of tetralin[1,2] and ethylbenzene.[3] These results strongly suggest that the metal catalysis is caused by the production of radicals from the hydroperoxide decomposition.

$$\mathrm{ROOH} + \mathrm{Metal} \longrightarrow \text{radicals } (\mathrm{RO\cdot} \text{ and } \mathrm{RO_2\cdot}) \qquad (1)$$

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \qquad (2)$$

$$\mathrm{RO_2\cdot} + \mathrm{RH} \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R\cdot} \qquad (3)$$

$$\mathrm{RO_2\cdot} + \mathrm{RO_2\cdot} \xrightarrow{k_t} \text{inactive products} + \mathrm{O_2} \qquad (4)$$

The autoxidation of cumene has been studied by a number of workers,[4-9] but its metal catalysis has not yet been completely clarified. Blanchard[4] concluded that the role of metal salt in the autoxidation is not to initiate chain by the activiation of oxygen but to produce radicals by the decomposition of hydroperoxide. Kropf[5] suggested that the chain initiation due to copper phthalocyanine-oxygen complex occurs by the hydrogen abstraction from cumene because there is an almost quantitative production of hydroperoxide at temperatures below 105°C when copper phthalocyanine was used as the catalyst. However, Minkov[7] has shown that cumyl hydroperoxide can be decomposed by copper phthalocyanine.

Recently, we found that copper phthalocyanine remarkably initiates the chain of autoxidation of α-methylstyrene[10] by the addition mechanism. The following mechanism can be postulated.

$$\mathrm{CuPc} + \mathrm{O_2} \longrightarrow (\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-} \qquad (5)$$

$$(\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-} + \rangle\mathrm{C{=}C}\langle \longrightarrow$$

$$(\mathrm{CuPc})^{\delta+}\mathrm{O_2}^{\delta-}\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\cdot \xrightarrow{\text{olefin, } \mathrm{O_2}} (\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-}\mathrm{O_2}\text{-})_n \qquad (6)$$

It was intended to make clear by precise experiments the two kinds of catalytic effect in the autoxidation of cumene owing to metal catalyst, that is, the production of radicals by the decomposition of hydroperoxide and the activation of oxygen molecule.

Experimental

The oxidation technique has been described previously.[1] All experiments were carried out at 60°C except otherwise stated. The catalysts used are cobaltous and manganous acetates and the cobaltous, manganous and cupric decanoates along with cobalt phthalocyanine-(CoPc) and α- and β-copper phthalocyanine(CuPc). Oxygenated copper phthalocyanine was prepared by the oxidation of copper phthalocyanine with 45% nitric acid at −5 to 0°C as reported by Bansho and coworkers.[11] The analysis of oxygenated copper phthalocyanine gave the formula CuPc-$\mathrm{O_2}$-CuPc, which was converted to copper phthalocyanine after reduction.

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[1] Y. Kamiya, S. Beaton, A. Lafortune and K. U. Ingold, *Can. J. Chem.*, **41**, 2020, 2034 (1963).

[2] Y. Kamiya and K. U. Ingold, *ibid.*, **42**, 1027 (1964).

[3] Y. Kamiya, *Kogyo Kagaku Zasshi*, **69**, 897 (1966).

[4] H. S. Blanchard, *J. Amer. Chem. Soc.*, **82**, 2014 (1960).

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[7] A. I. Minkov and N. P. Keier, *Kinetika i Kataliz*, **8**, 160 (1967).

[8] T. G. Traylor and C. A. Russell, *J. Amer. Chem. Soc.*, **87**, 3698 (1965).

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The oxidation products of cumene were determined by gas-liquid chromatography.

Results and Discussion

The Limiting Rate of Metal-Catalyzed Autoxidation of Cumene

The effect of three metal decanoates on the rate of oxidation of cumene at 60°C was examined over a range of metal concentrations from 0.001 to 0.1M in Fig. 1.

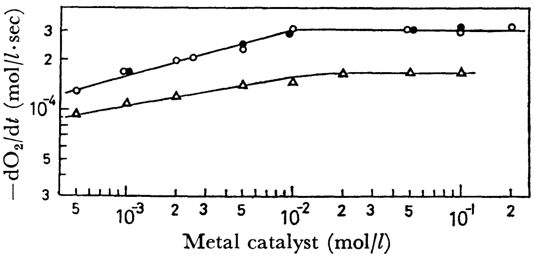

Fig. 1. The steady rate of oxidation of cumene as a function of metal decanoate concentration. ○ cobalt, ● manganese, △ copper.

As in the usual case, the cumene contained about 0.001M of hydroperoxide. In general, oxygen absorption proceeded linearly until several percent of cumene was consumed. The induction period of autoxidation was less than ten minutes and the metal catalysts were slowly deactivated during the oxidation as observed in the case of tetralin.

It can be seen that in the cobalt or manganese concentrations between 0.01 to 0.1M the measured maximum rate (ρ_m) reaches a limit of 3.1×10^{-4}M/sec, which is just over half the theoretical limit 6.0×10^{-4}M/sec. The theoretical value was calculated by the following equation, using the results of azobisisobutyronitrile initiated oxidation of cumene.

$$-dO_2/dt = k_p^2(RH)^2/2k_t \qquad (7)$$

ρ_m reaches a lower limit of 1.7×10^{-4}M/sec in the case of copper salt. This lower value might be due to the solubility as in the case of tetralin.[2)]

The rate of oxidation of cumene in acetic acid reaches a limit of 7.8×10^{-5}M/sec in an acetic acid — cumene mixture (1 : 1 by volume) as shown in Fig. 2 at cobalt concentrations above 0.05M. The limiting value after correcting $(RH)^2$ term of equation (7) will be 3.12×10^{-4}M/sec as in the case of neat cumene.

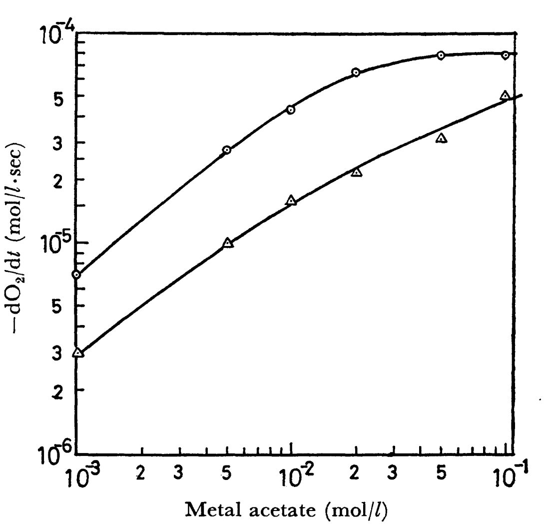

Fig. 2. The steady rate of oxidation of a 1 : 1 by volume cumene acetic acid mixture as a function of the metal acetate concentration. ○ cobalt, △ manganese.

Recently, it was suggested that the rate of oxidation depends on the dielectric function of solvent.[12)–14)] Therefore, the true rate of oxidation in acetic acid after correcting the dielectric function will be a little lower than 3.12×10^{-4}M/sec and probably around 2.5×10^{-4}M/sec according to the results of tetralin.[14)] The disaccordance between the experimental and the theoretical values might be due to the very fast induced decomposition of cumyl hydroperoxide by cumyloxy radical, because the ratio of cumyl alcohol to acetophenone in the oxidation products is higher than 1.7 (see Table 2). Recently, Hiatt and his co-workers,[16)] Howard and Ingold[15)] have shown that the chain length of the decomposition of tertiary hydroperoxide is as long as ten. If the induced decomposition of hydroperoxide by cumyloxy radical resulting from the metal catalyzed decomposition of hydroperoxide proceeds preferentially to hydrogen abstraction from cumene, the theoretical limiting rate will be $k_p^2(RH)^2/4k_t$, which is just half of the theoretical value and is in good agreement with the experimental values. The possibility of oxidation inhibition due to phenol can be ruled out, since we could not isolate any appreciable amount of acetone or phenol in the oxidation products.

The disaccordance between the theoretical and experimental rates of oxidation of neat tetralin[1)] was explained well by the effect of $(RH)^2$ term because the rate of oxidation of tetralin in acetic acid is in excellent agreement with the theoretical limiting rate.

The decomposition of cumyl hydroperoxide by cobalt salt at 2×10^{-4}M was of first order with respect to hydroperoxide, and the half life of 18 min

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12) D. G. Hendry and G. A. Russell, *J. Amer. Chem. Soc.*, **86**, 2368 (1964).

13) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044, 1250 (1964).

14) Y. Kamiya, This Bulletin, **38**, 2516 (1965).

15) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **46**, 2655 (1968).

16) R. Hiatt, T. Mill, K. C. Irwin and J. K. Castleman, *J. Org. Chem.*, **33**, 1421 (1968).

increased by a factor of one hundred, when acetic acid was used as the solvent instead of chlorobenzene.

These results correspond to the fact that the rate of oxidation in acetic acid reaches a limiting value at higher cobalt concentration than in the case of neat cumene.

In acetic acid, the manganese salt was a weak catalyst compared with cobalt as observed in the case of tetralin[2)] and ethylbenzene.[3)]

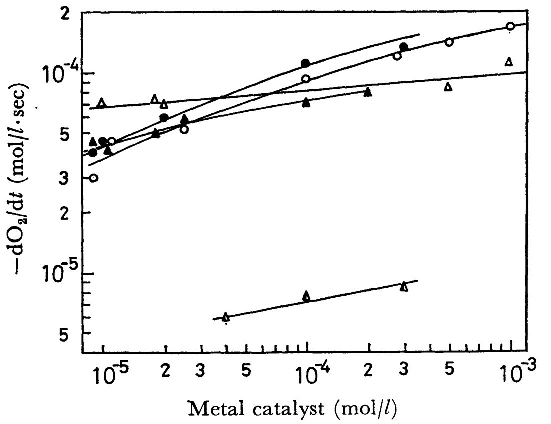


Fig. 3. The steady rate of oxidation of cumene as a function of metal decanoate or metal phthalocyanine concentrations at concentrations from 10^{-5} to 10^{-3} mol/l.
○ cobalt decanoate, △ copper decanoate, ● cobaltphthalocyanine, ◭ α-copper phthalocyanine, ▲ β-copper phthalocyanine

Metal-Catalysis by Phthalocyanines and Decanoates in the Autoxidation of Cumene. The rate of oxidation of cumene at metal concentration below 0.001 M is shown in Fig. 3. At metal concentration of 1×10^{-5} M, 0.05 M of cumyl hydroperoxide was added before the oxidation in order to reduce the induction period and to obtain a reproducible value of the rate of oxidation, since a metal catalyst was deactivated before reaching the maximum rate.

The chain length in the metal-catalyzed autoxidation of cumene was calculated to be 13 in the case of cobalt decanoate and 8 in the case of copper decanoate at the catalyst concentration of 1×10^{-5} M, using the results in Fig. 3 and the following equation obtained by the azobisisobutyronitrile initiated oxidation of cumene.

$$-dO_2/dt = 9 \times 10^{-4}(\mathrm{AIBN})^{1/2} \quad (8)$$

It seems peculiar that the rate of oxidation with copper becomes higher than with cobalt at low metal concentrations. The rate of decomposition of cumyl hydroperoxide with cobalt decanoate was higher than with copper decanoate by a factor of four at metal concentrations from 10^{-3} to 10^{-4} M, suggesting that cobalt gives a two fold higher rate of oxidation than copper.

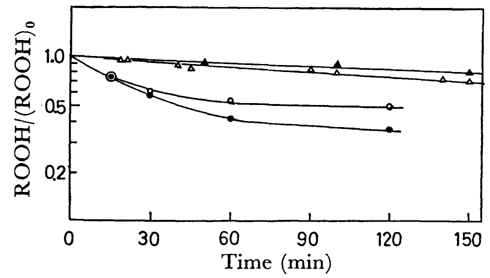


Fig. 4. The decomposition of cumyl hydroperoxide by metal decanoate or metal phthalocyanine at metal concentration of 6.3×10^{-5} mol/l in chlorobenzene.
$[\mathrm{ROOH}]_0$ 0.025 mol/l; ○ cobalt de canoate, △ copper decanoate, ● cobalt phthalocyanine, ▲ β-copper phthalocyanine.

However, the plots of hydroperoxide decomposition at catalyst concentration of 6.3×10^{-5} M (Fig. 4) indicate that cobalt catalysts are deactivated quickly at the beginning of hydroperoxide decomposition and copper compounds retain their activity for a longer time.

Cobalt phthalocyanine was deactivated more slowly than cobalt decanoate probably due to its stable structure, and it showed a little higher rate of oxidation than cobalt decanoate.

At the steady state of oxidation (after 30 to 60 min) the reactivity of copper decanoate will be equal to that of cobalt phthalocyanine according to Fig. 4.

The first order rate constant (k) of hydroperoxide decomposition increased by a factor of three in the case of copper decanoate when hydroperoxide concentration was increased from 0.025 to 0.125 M, while k remained constant in the case of cobalt decanoate.

Thus, it is not surprising to find that copper compounds give a higher rate of oxidation than the value expected from the rate of hydroperoxide decomposition in Fig. 4, since the concentration of hydroperoxide at the steady state of oxidation will reach a value higher than 0.1 M. The higher rate of oxidation by copper decanoate than by cobalt compounds at concentration of 1×10^{-5} M can be attributed to the higher rate of decomposition of hydroperoxide by copper decanoate.

The k value with β-CuPc was higher than with α-CuPc by a factor of sixty at metal concentration 6.3×10^{-5} M. It should be mentioned that α-CuPc, which is a very effective initiator in the autoxidation of α-methylstyrene[10)] by the addition mechanism, is exceptionally inactive for the decomposition of hydroperoxide.

For comparison, the autoxidation of tetralin in the presence of various catalysts is shown in Fig. 5. In this case β-CuPc is much more active than α-CuPc. From the hydroperoxide decomposition experiment by copper catalysts at initial hydroperoxide concentration 0.02 M and metal concentra-

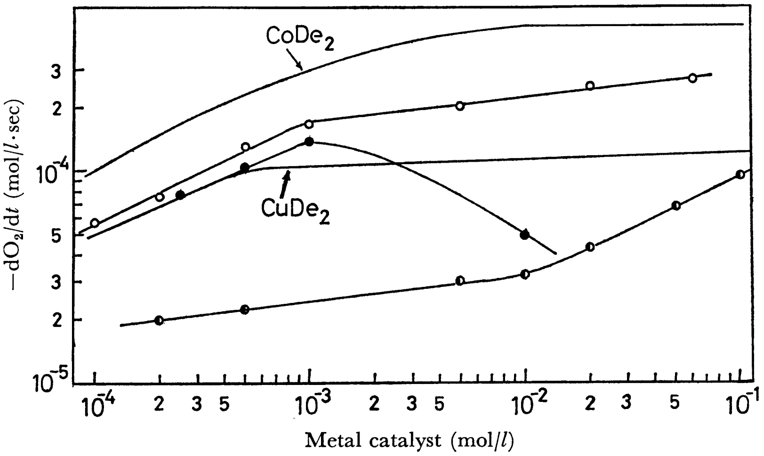


Fig. 5. The steady rate of oxidation of tetralin as a function of metal concentration at 50°C.

○ cobalt phthalocyanine, ◐ α-copper phthalocyanine, ● β-copper phthalocyanine

tion 0.001 M in chlorobenzene at 50°C, the half life of tetralyl hydroperoxide decomposition was found to be 80 min in the cases of CuDe$_2$ and β-CuPc and 1500 min in the case of α-CuPc. Thus, the rate of oxidation of tetralin is roughly proportional to the square root of the rate of hydroperoxide decomposition. Although the rate of oxidation with β-CuPc is a little higher than with CuDe$_2$ at concentration of 0.001 M, the two rates of oxidation at catalyst concentrations below 5×10^{-4} M coincide well as in the case of half lives of hydroperoxide decomposition.

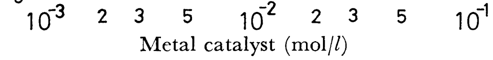


Fig. 6. The steady rate of oxidation of cumene as a function of metal phthalocyanine concentration at concentrations below 0.1 mol/l.

○ cobaltphthalo cyanine, △ α-copper phthalocyanine, □ oxygenat ed copper phthalocyanine

The activation of oxygen by CuPc and the direct oxidation by the oxygenated copper phthalocyanine (CuPcO) were further examined at high concentration of catalyst (Fig. 6). The rate of oxidation of cumene at metal concentrations from 10^{-4} to 10^{-2} M was entirely constant in the cases of CoPc, β-CuPc and CuPcO, but it gradually increased with the increase of metal concentrations above 0.01 M. The direct oxidation of cumene by the complex of metal phthalocyanine or by the oxygenated metal phthalocyanine might occur at high concentration of metal complex.

In conclusion, the results of hydroperoxide decomposition account for the relative rate of oxidation with various catalysts. The autoxidation of cumene catalyzed by CuPc should not involve the chain initiation step due to hydrogen abstraction from cumene by $(\text{CuPc})^{\delta+}\text{O}_2^{\delta-}$, since the effect of hydroperoxide decomposition is overwhelming. The reactivity of $(\text{CuPc})^{\delta+}\text{O}_2^{\delta-}$ is undoubtedly not so large as peroxy radical, although we found that copper phthalocyanine initiates the chain of autoxidation of α-methylstyrene.

According to Kropf,[5] the observed rate of oxidation of cumene by his copper phthalocyanine is about one-hundredth of our value by β-CuPc. The chain initiation due to copper phthalocyanine and oxygen will be about one–ten thousandth of the rate of radical production by the decomposition of hydroperoxide, even if his copper phthalocyanine could not decompose any amount of hydroperoxide. Therefore, production of radicals by the metal-catalyzed decomposition of hydroperoxide occurs predominantly as compared with hydrogen abstraction by copper phthalocyanine and oxygen.

A complex situation arizes from the fact that α-CuPc which is quite inactive for hydroperoxide decomposition can be gradually converted to β-CuPc in an aromatic solvent even at temperatures below 100°C. It was observed that α-CuPc, which was used in the autoxidation of α-methylstyrene at 60°C for 120 min, decomposed cumyl hydroperoxide with the rate as fast as that of CuDe$_2$, that is, the rate of decomposition of hydroperoxide by α-CuPc increases considerably in the course of reaction probably after isomerizing to β-CuPc or another active form of CuPc especially in the presence of peroxy radicals. Minkov[7] has also

Table 1. Oxidation products of cumene

Reaction conditions	Oxidation of neat cumene	Oxidation of cumene acetic acid mixture (1 : 1 by volume)	Decomposition of cumyl hydroperoxide of 0.08M in chlorobenzene
Metal catalyst	Cobalt and manganese decanoates from 0.001 to 0.1M	Cobalt and manganese acetate from 0.01 to 0.1M	Cobalt decanoate from 0.002 to 0.01M
Products distribution of cumene (mol %)			
α-Methylstyrene	3.3	1.7	2.0
Acetophenone	15.8	36.4	36.0
Cumyl alcohol	70.7	61.3	59.3
Dicumyl peroxide	10.2	2.5	2.7
The ratio of cumyl alcohol to acetophenone	4.5	1.7	1.64

pointed out that the activity of CuPc in the decomposition of hydroperoxide shows a maximum as the reaction proceeds.

Oxidation Products of Cumene. The oxidation products were cumyl alcohol, acetophenone, dicumyl peroxide, cumyl hydroperoxide and α-methylstyrene. No acetone or methyl alcohol were detected. Oxidation products other than hydroperoxide are shown in Table 1.

The ratio of alcohol to ketone is about 1.6, when cumyl hydroperoxide is decomposed in chlorobenzene by cobalt decanoate. However, autoxidation in acetic acid gives a value of about 1.7 and the ratio increases to 4.5 in the case of neat cumene. Since α-methylstyrene can be obtained from cumyl alcohol, the true ratio will be higher than the observed value.

The chain termination mechanism of cumyl peroxy radicals can be described as follows,[9)]

$$RO_2\cdot + RO_2\cdot \longrightarrow [ROOOOR] \longrightarrow ROOR + O_2$$

$$\searrow 2RO\cdot + O_2$$

$$RO\cdot \xrightarrow{O_2} CH_3O_2\cdot + C_6H_5COCH_3$$

$$CH_3O_2\cdot + RO_2\cdot \longrightarrow C_6H_5C(CH_3)_2OH + HCHO + O_2$$

When all alkoxy radicals formed by the decomposition of hydroperoxide due to metal catalysis result in cumyl alcohol, and all methyl peroxy radicals result in cumyl alcohol and formaldehyde after terminating with cumyl peroxy radical, the ratio of alcohol to ketone will be two. Thus, it can be concluded that some alkoxy radicals from the termination reaction in the solvent cage slip out of the cage and abstract hydrogen atom from hydroperoxide or cumene to yield alcohol.

If the solvent cage is composed of a viscous and inactive solvent for hydrogen abstraction, the probability of the alkoxy radical slipping out of the cage and abstracting hydrogen from the substrates will be decreased.

The effect of the amount of solvent was studied using chlorobenzene as a solvent (Table 2). As the solution is diluted with chlorobenzene, the ratio of alcohol to ketone decreases remarkably. Much lower ratio in acetic acid (Table 1) seems to indicate that the physical properties of solvent affects the strength of the cage.

Table 2. Effect of solvent on the ratio of alcohol to ketone in the autoxidation of cumene catalyzed by 0.02M cobalt decanoate

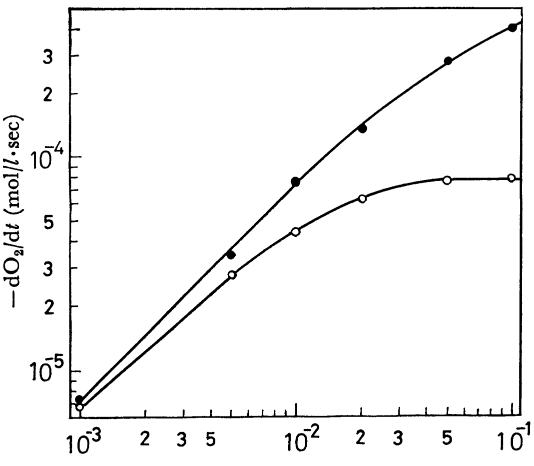
Cumene/chlorobenzene (volume/volume)	1/0	1/1	1/3	1/5
Cumyl alcohol/acetophenone (mol/mol)	4.5	2.7	1.94	1.67

The formation of alkoxy radical from the bimolecular termination of peroxy radicals gives two different effects on the rate of oxidation. The induced decomposition of hydroperoxide will cause a decrease in the rate of oxidation, since the initiation reaction by the decomposition of hydroperoxide will be retarded. On the other hand, the hydrogen abstraction from cumene will result in the increase in the rate of oxidation. We can not exactly evaluate these influences, since the rate constants of elementary steps are not known and the two reactions will proceed simultaneously.

However, the effect of alkoxy radical from the cage on the rate of oxidation of cumene may not be so large because the rate of oxidation of neat cumene is in excellent agreement with the rate in acetic acid solution after correcting $(RH)^2$ term. Even if the dielectric effect is corrected, the effect on the rate enhancement will probably be about 20% according to the results of tetralin oxidation.[14)]

The higher ratio of alcohol to ketone in the case of neat cumene can be attributed to the increase of dicumyl peroxide and to the decrease of acetophenone rather than to the decrease of cumyl alcohol. The bimolecular termination reaction of alkoxy radicals seems to be relatively fast.

Catalysis by Cobalt and Bromide Ions. In Fig. 7 the steady rate of oxidation of cumene is



Cobalt acetate (mol/l)

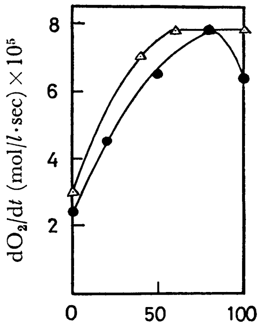
Fig. 7. The steady rate of oxidation of 1 : 1 by volume cumene: acetic acid mixture as a function of cobalt acetate concentration ○ in the presence or ● in the absence of sodium bromide.

plotted against the cobalt concentration in the presence and absence of sodium bromide. Two moles of sodium bromide per one mole of cobalt are used, since at this ratio the rate of oxidation has shown a limiting value as the amount of sodium bromide is varied.

The rate of oxidation of cumene in acetic acid reaches the limiting value 7.8×10^{-5}M/sec at 0.05M of cobalt. The rate of oxidation in the presence of sodium bromide tends to increase as the cobalt is increased. The difference of two rate curves due to the addition of sodium bromide to the solution is very small at cobalt 0.001M and is of first order with respect to cobalt concentration. The effect of bromide ion on the rate of oxidation of cumene is comparable as in tetralin[17] and not so remarkable as in *p*-xylene.[18] However, the steady concentration of cumyl hydroperoxide increased and the rate of decomposition of cumyl hydroperoxide decreased in the presence of bromide ion in contrast to the case of tetralin.[17]

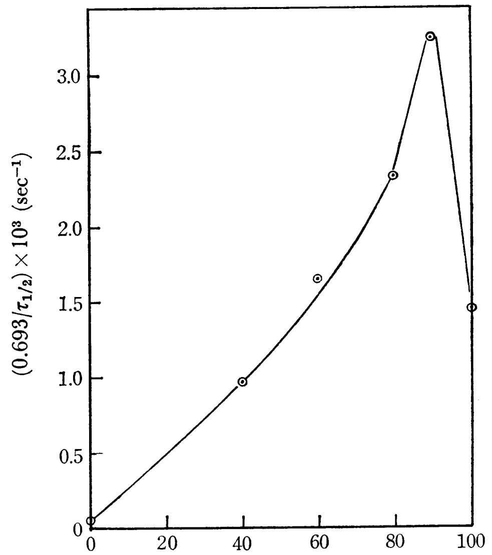
The Synergistic Effect Due to Metal Catalysts. A synergistic effect of metal catalyst was observed, *i.e.*, by replacing 20% of the cobalt acetate of 0.02M by manganese acetate an approximately 1.3 fold increase in the rate of oxidation of cumene was observed (Fig. 8).

However, the synergistic effect could not overcome the experimental limiting rate of oxidation. It is interesting that at total metal concentration of 0.05M no more synergistic effect can be observed as seen in Fig. 8.



Cobalt (mol%)

Fig. 8. The synergistic effect by cobalt and manganese acetates on the rate of oxidation of a 1 : 1 by volume cumene : acetic acid mixture at total metal concentration of ● 0.02 mol/l and △ 0.05 mol/l.



Cobalt (%)

Fig. 9. The synergistic effect of cobalt and manganese acetates on the decomposition of cumyl hydroperoxide in an acetic acid : chlorobenzene mixture (1 : 1 by volume) at total metal concentration of 0.01M. $\tau_{1/2}$ represents the half life of 0.05M hydroperoxide.

A synergistic effect was observed also in the rate of decomposition of cumyl hydroperoxide by metal acetate as shown in Fig. 9, corresponding to the result in which the rate of oxidation is of nearly half order with respect to the first order rate constant of hydroperoxide decomposition. Therefore, the rate enhancing effect by the mixing of metal catalysts can be attributed to the chain initiation step by the metal-catalyzed decomposition of cumyl hydroperoxide.

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

[18] Y. Kamiya, "Oxidation of Organic Compounds-II," Amer. Chem. Soc., Washington, D. C. (1968), p. 193.