Autoxidation of Aromatic Hydrocarbons Catalyzed with Cobaltic Acetate in Acetic Acid Solution. II. Oxidation of Ethylbenzene and Cumene[1)]

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The oxidation of ethylbenzene and cumene catalyzed with cobaltic acetate in acetic acid was studied kinetically in order to elucidate the reaction mechanism and the roles of cobaltic salt. The maximum absorption rate of oxygen as well as the maximum reduction rate of Co(III) in the oxidation of ethylbenzene or cumene were of first order with respect to the initial concentration of hydrocarbon, of inverse first order with respect to the initial concentration of Co(II), and of second order with respect to the initial concentration of Co(III). The kinetic equations are therefore just the same as in the case of toluene, but $d[Co(III)]/d[O_2]$ gave a quite different average value of 3.8, showing that almost no regeneration of Co(III) from Co(II) due to oxidation with peroxidic compounds occurred. Both rates were remarkably accelerated by the addition of sodium acetate and also influenced by a small amount of water. The order of oxygen absorption rate in oxidation was toluene>ethylbenzene> cumene in contrast to the order of hydrogen abstraction rate by peroxy radicals. The apparent activation energy for these hydrocarbons was found to be 10.1 kcal mol^{-1}.

Many papers have appeared on the mechanism of the initiation step in the autoxidation of ethylbenzene[1–3)] and cumene.[4–9)] The main role of transition metal salts established in the autoxidation of hydrocarbons with secondary and primary C–H bond is to decompose hydroperoxide[10–12)] into radicals by the following reactions.

$$M^{n+} + ROOH \longrightarrow M^{n+1} + RO\cdot + OH^-$$
$$M^{n+1} + ROOH \longrightarrow M^{n+} + ROO\cdot + H^+$$

However, another role of transition metal salts has been clarified recently, in which the hydrogen abstraction from hydrocarbon with a higher valence metal ion plays an important role in the reaction of methylbenzenes as follows.

$$M^{n+1} + RH \longrightarrow R\cdot + M^{n+} + H^+$$

We reported on the oxidation of toluene with cobaltic acetate either in the presence and the absence of oxygen and proposed that the reaction was initiated by an electron transfer equilibrium between cobaltic acetate and toluene.[13,14)]

The present kinetic study was undertaken in order to elucidate the reaction mechanism in the oxidation of ethylbenzene and cumene catalyzed with cobaltic acetate in acetic acid solution. The results were compared with those obtained in the oxidation of toluene.

Experimental

Materials. Ethylbenzene, cumene, benzene, and chlorobenzene were repeatedly shaken with concentrated sulphuric acid until no coloration was observed. They were then fractionally distilled after being washed with water and dried over calcium chloride. Acetic acid and cobaltous acetate were of reagent grade. Cobaltic acetate was prepared by the same method as in Part I[14)] and its concentration was determined by potentiometric titration.[13)] The amount of water in the solution was measured by Karl-Fischer titration. Ordinary reaction mixture containing 1.5—2.0M water was prepared unless otherwise stated.

Procedure. The oxidation apparatus and method were the same as in Part I.

Analysis. The solution after oxidation was poured into water of equal volume and extracted with ether. The extract was washed with aqueous sodium hydroxide and analyzed by gas chromatography with a Shimadzu model GC-20 with a 2.2 m column packed with D.O.P. on Celite 545; helium flow rate, 50 ml-min^{-1}, at 140°C. Analysis confirmed the formation of acetophenone and a small amount of α-phenylethanol and α-phenylethyl acetate in the oxidation of ethylbenzene. The main products in the oxidation of cumene were acetophenone, cumylalcohol and α-methylstyrene.

Results and Discussion

Oxidation of Cumene. Cumene can be easily oxidized with oxygen in acetic acid at 60°C, when cobaltic acetate is employed as a catalyst. Oxidation proceeded without induction period, the initial absorption rate of oxygen becoming the maximum rate of oxidation.

The initial oxidation rate and its rate constant in the oxidation of cumene are given in Table 1. The initial rate of oxidation was of first order with respect to the initial concentration of cumene, and of inverse first

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Table 1. Initial rate and rate constant in oxidation of cumene at 60°C, O_2: 1 atm

ϕ-CH(CH$_3$)$_2$ (M)	Co(III) (M)	Co(II) (M)	$-d[O_2]/dt$ (M/sec)	$k\times10^{-5}$ (l/M·sec)
0.083	0.134	0.035	8.60×10^{-7}	2.02
0.440	0.134	0.035	4.30×10^{-6}	1.90
0.830	0.134	0.035	8.80×10^{-6}	2.07
1.65	0.134	0.035	2.00×10^{-5}	2.36
				2.09
0.553	0.014	0.002	8.50×10^{-7}	1.47
0.553	0.029	0.004	1.80×10^{-6}	1.51
0.553	0.083	0.011	4.90×10^{-6}	1.41
0.553	0.168	0.022	1.02×10^{-5}	1.44
				1.46
0.553	0.168	0.022	1.20×10^{-6}	1.69
0.553	0.168	0.050	5.40×10^{-5}	1.73
0.553	0.168	0.096	2.90×10^{-5}	1.78
0.553	0.168	0.165	1.45×10^{-5}	1.53
				1.68

order with respect to the initial concentration of cobaltous ion. The initial rate also was of first order with respect to the total cobalt ion, when the molar ratio of cobaltic to total cobalt ions was kept constant. However, when the inverse first order dependence of the initial rate on the initial concentration of cobaltous ion is taken into account, the over-all reaction should be of second order with respect to cobaltic ion concentration. Although the rate constants present good accordance within each set of experiment, they show a considerable discrepancy between individual sets. This may be mainly due to the difference of water concentration in the course of Co(III) preparation, since water remarkably influences the initial rate of oxidation.

The initial absorption rate of oxygen can be expressed as follows.

$$-d[O_2]/dt = k[\phi\text{-}CH(CH_3)_2][Co(III)]^2[Co(II)]^{-1}$$

The initial reduction rate of Co(III) and its rate constant in the typical oxidation of cumene with cobaltic acetate in acetic acid at 60°C are given in Table 2. The result is similar to that in Table 1.

Thus, the initial reduction rate of Co(III) can be expressed as follows.

Table 2. Consumption rate of Co(III) and rate constants in oxidation of cumene, 60°C, O_2: 1 atm

ϕ-CH(CH$_3$)$_2$ (M)	Co(III) (M)	Co(II) (M)	$-d[Co(III)]/dt$ (M/sec)	$k'\times10^5$ (l/M·sec)
0.120	0.170	0.030	0.76×10^{-5}	6.57
0.240	0.170	0.030	1.98	8.56
0.360	0.170	0.030	2.66	7.67
0.480	0.170	0.030	3.40	7.35
				7.54
0.479	0.134	0.027	1.82×10^{-5}	5.71
0.479	0.134	0.050	0.98	5.69
0.479	0.134	0.077	0.67	5.99
0.479	0.134	0.128	0.36	5.36
				5.69

$$-d[Co(III)]/dt = k'[\phi\text{-}CH(CH_3)_2][Co(III)]^2[Co(II)]^{-1}$$

The reduction rate takes the value of 4.0×10^{-6} mol·l^{-1}·sec^{-1}, when cumene concentration is extrapolated to zero. This suggests that self-decomposition of Co(III) takes place in the early stage of reaction. Although it is considered that methyl radical (·CH$_3$) or carboxymethyl radical (·CH$_2$COOH) may be produced with self-decomposition of Co(III), they will not significantly contribute to the initial rate of oxidation and the initial reduction rate of Co(III) at higher concentration of cumene. In this case also there is an appreciable difference between rate constants of the two sets of experiment. This may be due to the concentration of water in the solution varies to some extent according to preparation condition of Co(III).

Table 3. Initial rate and rate constants in oxidation of ϕ-CH$_2$CH$_3$ at 60°C, O_2: 1 atm

ϕ-CH$_2$CH$_3$ (M)×10	Co(III) (M)×10	Co(II) (M)×10^3	$d[O_2]/dt$ (M/sec)	k (l/M·sec)
0.13	1.66	2.00	0.65×10^{-6}	3.63×10^{-5}
0.20	1.66	2.00	1.05	3.81
0.34	1.66	2.00	1.65	3.53
0.68	1.66	2.00	3.30	3.52
				3.62
6.79	1.71	15.9	0.38×10^{-5}	3.05×10^{-5}
6.79	1.71	8.48	0.90	3.85
6.79	1.71	2.92	2.60	3.83
				3.58
7.42	0.84	2.50	0.60×10^{-5}	2.87×10^{-5}
7.42	1.27	2.50	1.75	3.66
7.42	1.70	2.50	2.75	3.21
7.42	2.20	2.50	4.60	3.20
				3.24

Oxidation of Ethylbenzene. The initial rate of oxidation and its rate constant in the oxidation of ethylbenzene with cobaltic acetate in acetic acid at 60°C are given in Table 3. The absorption rate of oxygen can be expressed by a similar equation to that obtained in the oxidation of toluene and cumene:

$$-d[O_2]/dt = k''[\phi\text{-}CH_2CH_3][Co(III)]^2[Co(II)]^{-1}$$

The initial reduction rate of Co(III) in the oxidation of ethylbenzene can also be expressed by a similar equation to that obtained in the oxidation of toluene and cumene.

$$-d[Co(III)]/dt = k'''[\phi\text{-}CH_2CH_3][Co(III)]^2[Co(II)]^{-1}$$

Reaction Products. When cobaltic acetate was employed as a catalyst, the main products in the oxidation of cumene were acetophenone, cumyl alcohol and α-methylstyrene. The product distribution differs considerably from that obtained in the autoxidation of cumene, *viz.*, the molar ratio of acetophenone to (cumyl alcohol+α-methylstyrene) is about 1.2 (Fig. 1). However, the difference in the ratio of ketone to alcohol can be attributed to the effect of dilution.[12)]

Figure 2 shows a comparison of consumption curves of Co(III) under oxygen atmosphere with those under argon atmosphere in the oxidation of toluene, ethylbenzene, and cumene. The regeneration of Co(III)

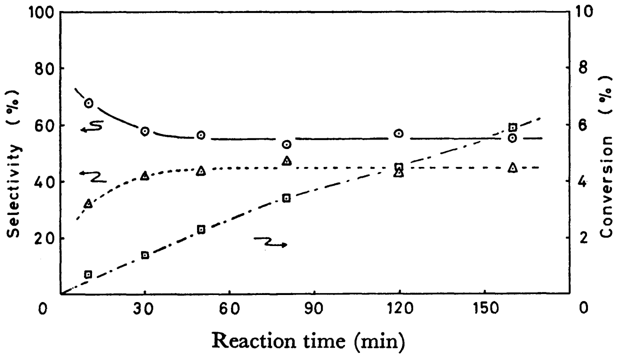

Fig. 1. Products distribution in oxidation of cumene
ϕ-CH(CH$_3$)$_2$: 0.553M, Co(III): 0.166M, Co(III): 0.017M, 60°C, O$_2$: 1 1 atm.
⊙: Acetophenone, ◬: Cumyl alcohol + α-Methylstyrene

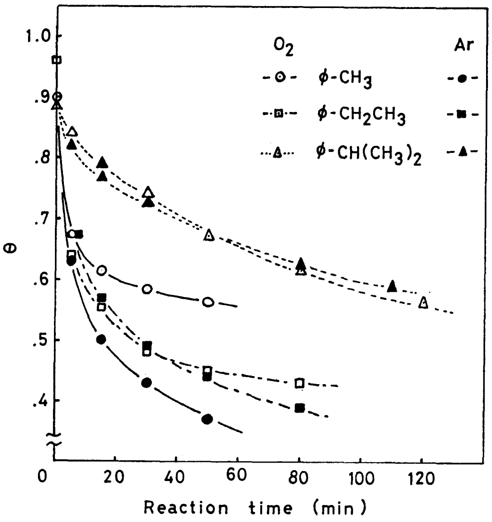

Fig. 2. Consumption curves of Co(III) in oxidn. of ϕ-CH$_3$, ϕ-CH$_2$CH$_3$ and ϕ-CH(CH$_3$)$_2$ at 60°C.

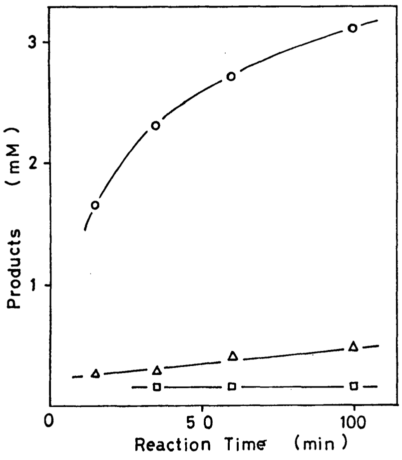

Fig. 3. Products distribution in Co(III) oxidn. of ϕ-CH$_2$CH$_3$.
ϕ-CH$_2$CH$_3$: 1.36M, Co(III): 0.19M, Co(II): 0.04M, 60°C, O$_2$: 1 atm.
○: ϕCOCH$_3$, △: ϕ-CH(OH)CH$_3$, □: ϕ-CH(OAc) CH$_3$

was not observed in the oxidation of ethylbenzene or cumene in contrast to toluene.

The main products in the oxidation of ethylbenzene with Co(III) were acetophenone, α-phenylethanol and α-phenylethyl acetate (Fig. 3). The salient point of product distribution is that the molar ratio of ketone to alcohol is large in comparison to that obtained in the autoxidation of ethylbenzene. This is probably due to the subsequent oxidation of α-phenylethanol and the reaction of peroxy radical with cobaltic acetate.

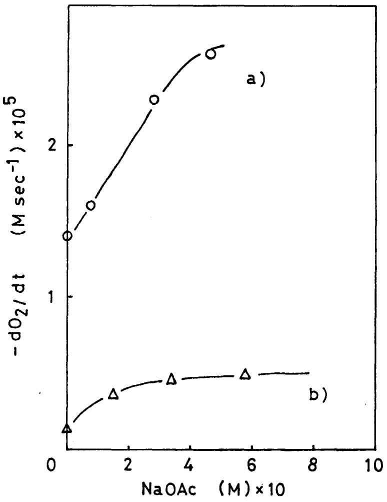

Fig. 4. Effect of NaOAc on initial rate
a) ϕ-CH$_2$CH$_3$: 1.26M, Co(III): 0.166M, Co(II): 0.017M.
b) ϕ-CH(CH$_3$)$_2$: 0.599M, Co(III): 0.153M, Co(II): 0.040M

Effect of Sodium Acetate. In the oxidation of cumene and ethylbenzene with cobaltic acetate in acetic acid, the initial rate of oxidation as well as the initial reduction rate of Co(III) were remarkably accelerated by the addition of sodium acetate (Fig. 4).

TABLE 4. SOLVENT EFFECT
Co(III): 0.106M, Co(II): 0.080M, 60°C

ϕ-CH$_2$CH$_3$ (ml)	AcOH (ml)	ϕ-Cl (ml)	ϕ-H (ml)	$-dO_2/dt$ (M·sec^{-1})
5.0	60	—	—	1.01×10^{-5}
5.0	45	15	—	1.57
5.0	30	30	—	2.45
5.0	30	—	30	1.78

This can be explained as follows. Since the dissociation constant of sodium acetate in acetic acid is relatively large (1.3×10^{-6}),[15] a cobaltic ion is easily coordinated with an extra acetate anion and forms an active cobalt ion with coordination number greater than three.[16,17]

Solvent Effect. A remarkable positive solvent effect is observed in oxidizing ethylbenzene with cobaltic acetate, when a part of acetic acid is replaced with benzene or chlorobenzene. The initial rate of oxidation increases linearly as the amount of benzene or chlorobenzene is increased (Table 4). This suggests that the solvation of acetic acid around Co(III) is relieved by the addition of neutral solvent and it becomes easy for cobaltic ion to interact with ethylbenzene and the initial rate of oxidation is enhanced

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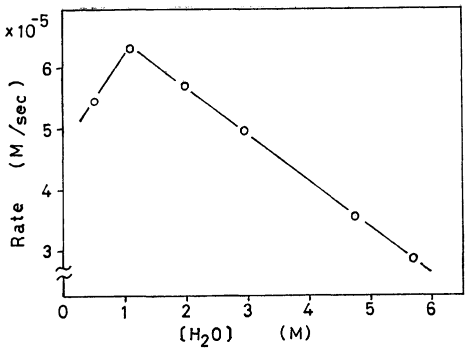

Fig. 5. Plots of initial rate *vs.* $[H_2O]_0$
ϕ-CH_2CH_3: 0.74M, Co(III): 0.21M, Co(II): 0.01M 60°C, O_2: 1 atm.

by the dilution of acetic acid.

When alkylbenzenes are oxidized with cobaltic acetate in acetic acid, water remarkably influences the initial rate of oxidation. The initial rate in the oxidation of ethylbenzene increases as water concentration increases and reaches the maximum value at water concentration of about 1.0 mol·l⁻¹ (Fig. 5). This can be explained as follows. The presence of a small amount of water makes the concentration of monohydroxide of cobaltic acetate increase which is more active than triacetate. When the concentration of water becomes very high, however, the deactivation effect of cobaltic ion with water will overcome the activation effect.

Effect of Reaction Temperature. The Arrhenius plot for the oxidation of toluene, ethylbenzene, and cumene with cobaltic acetate is shown in Fig. 6. The apparent activation energies (10.1 kcal·mol⁻¹) were found to be the same. The order of relative reactivities was toluene>ethylbenzene>cumene, a complete reverse of that expected from the C–H bond energy, *viz.*, the rate constant was profoundly affected in an inverse way to the case of oxidation by free radicals. The results are not explicable in terms of the C–H bond rupture process, but support the view that the electron transfer process is rate-determining.

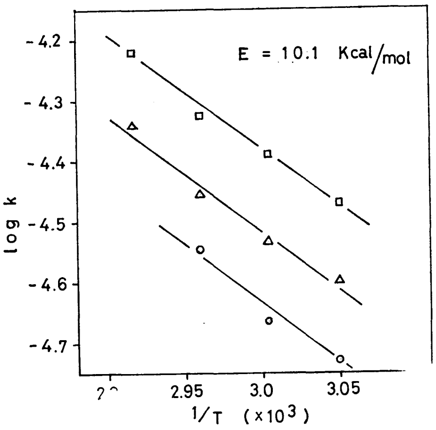

Fig. 6. Effect of reaction temp. on rate of aromatic hydrocarbon oxidn.
RH: 1.0M, Co(III): 0.13M. Co(II): 0.03M, O_2: 1 atm.
(—○—): ϕ-$CH(CH_3)_2$, (—△—): ϕ-CH_2CH_3, (—□—): ϕ-CH_3

Reaction Mechanism. We proposed that the active species of cobalt ion is a dimer of cobaltic ion or quadrivalent cobalt ion because the absorption rate of oxygen is of second order with respect to cobaltic ion and of inverse first order to cobaltous ion concentration.[14] We also postulated the following electron transfer equilibrium in the early stage of reaction.

$$\mathrm{Co(III)_2 + RH \rightleftharpoons [RH^+AcO^-Co(III)] + Co(II)}$$

$$\mathrm{[RH^+AcO^-Co(III)] \longrightarrow R\cdot + Co(III) + AcOH}$$

The electron transfer equilibrium can be applied to the oxidation of ethylbenzene or cumene. The following reactions will mainly contribute to the oxidation of ethylbenzene or cumene with cobaltic acetate in the early stage of reaction.

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

$$\mathrm{Co(III)_2 + RH} \overset{K_2}{\rightleftharpoons} \mathrm{[RH^+AcO^-Co(III)] + Co(II)} \tag{2}$$

$$\mathrm{[RH^+AcO^-Co(III)]} \xrightarrow{k_3} \mathrm{R\cdot + Co(III) + AcOH} \tag{3}$$

$$\mathrm{R\cdot + O_2} \xrightarrow{k_4} \mathrm{ROO\cdot} \tag{4}$$

$$\mathrm{ROO\cdot + Co(III)} \xrightarrow{k_5}$$

$$\text{ketone} + \mathrm{H^+(or\ CH_3^+) + Co(II)} + \frac{1}{2}\mathrm{O_2} \tag{5}$$

where R· is ϕ-$CHCH_3$ or ϕ-$C(CH_3)_2$ and ROO· is the corresponding peroxy radical. The difference in reactivities toward cobaltic acetate may be ascribed to that of the entropy decrease of the hydrocarbon in the transition state. When the rate determining step is reaction (3), the rate of oxygen absorption in the early stage of reaction can be expressed as follows.

$$-\mathrm{d[O_2]/d}t = \frac{1}{2}K_1K_2k_3\mathrm{[RH][Co(III)]^2[Co(II)]^{-1}}$$

The rate of Co(III) reduction in the early stage of reaction can be calculated as follows.

$$-\mathrm{d[Co(III)]/d}t = 2K_1K_2k_3\mathrm{[RH][Co(III)]^2[Co(II)]^{-1}}$$

Thus, the ratio of $\mathrm{d[Co(III)]/d[O_2]}$ is 4. The value is nearly equal to that obtained from Tables 1 and 2 and would be comparable with the value of 1.7 in the case of toluene, in which the regeneration of Co(III) by oxidation product takes place.