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# Catalysis of Manganese Salts in the Autoxidation of Cyclohexanone

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The rate of oxidation of cyclohexanone catalyzed by manganese salt increases remarkably in the presence of acetic acid, and is about one hundred times as high as the limiting rate of oxidation $k_p^2(\mathrm{RH})^2/2k_t$. However, manganese concentration does not affect the rate of oxidation much in a wide range. The oxidation of cyclohexanone by manganic ion should be the rate determining step, since the rate of oxidation, which is of first order in cyclohexanone but independent of manganous ion, corresponds to the rate of oxygen absorption of cyclohexanone with the same manganese concentration. The oxidation of cyclohexanone by manganic ion seems to proceed through enol intermediates, since the rate of oxidation increases in the presence of alkali acetates. The rate equation including enolization step and the subsequent oxidation of enol intermediate with manganic ion agrees with the experimental results. A remarkable synergistic effect of metal salts was observed in a mixture of manganese and cobalt. The oxidation products were also analyzed and discussed.

Although the autoxidation of cyclohexanone is an important process for the production of adipic acid and has been studied by many workers,[1] the role of metal catalysts in the autoxidation reaction is still not clear. The oxidation of cyclohexanone by metal ions was studied by Rocek and Riehl,[2] Best *et al.*[3] and Littler.[4,5] It was found that oxidation by V(V), Co(III), Ce(IV), and Mn(III) proceeds through direct oxidation, but that by Hg(II), Mn(VII), Tl(III), and $Br_2$ through enol intermediate.

The metal-catalyzed autoxidation of cyclohexanone shows a complicated behavior. (1) The rate of oxidation in an acidic solvent is much higher than that in a neutral one. (2) Although manganese salt is not so effective catalyst in acetic acid solution as cobalt salt, it shows the highest catalytic activity in the oxidation of cyclohexanone. (3) When a metal catalyst is used as a decomposer of hydroperoxide, the rate of oxidation of hydrocarbons does not exceed the limiting rate $k_p^2(\mathrm{RH})^2/2k_t$,[6] but that of cyclohexanone catalyzed by cobalt and manganese in acetic acid far exceeds the value of $k_p^2(\mathrm{RH})^2/2k_t$, where $k_p$ and $k_t$ represent the propagation and termination rate constants, respectively.

In a previous paper,[7] it was shown that the rate-determining step of the cobalt-catalyzed autoxidation of cyclohexanone in acetic acid is the oxidation of cyclohexanone by cobaltic ion. We have studied the effect of manganese catalyst on the autoxidation of cyclohexanone, since catalysis by manganese salt greatly differs from that by cobalt salt.

## Experimental

Cyclohexanone was fractionally distilled and kept in a brown glass bottle and in nitrogen atmosphere. Acetic acid was distilled in the presence of potassium permanganate and acetic anhydride.

*Manganic Acetate.*[8] A mixture of manganous acetate (303 g) and glacial acetic acid (4.4 kg) was boiled under reflux for 2 hr. Potassium permanganate (68.2 g) was then added, the mixture being stirred under reflux for 45 min and then allowed to cool while water (750 ml) was added dropwise. The crude $Mn(OAc)_3 \cdot 2H_2O$ was recrystallized from a mixture of glacial acetic acid and water.

*Oxidation of Cyclohexanone by Manganic Acetate in Nitrogen Atmosphere.* The reaction vessel, a *ca.* 60 ml flask with two necks, one at the top and the other at the side of the flask, was connected through a tygon tube to a vacuum line and a nitrogen reservoir. The solution was frozen with a dry ice-acetone solution and degassed repeatedly in the usual way, and the vessel was filled with nitrogen. After thermal equilibrium had been obtained, samples were withdrawn through the side neck at appropriate intervals under current of nitrogen. The volume of each sample was 5 ml. Determination of manganic acetate was carried out by potentiometric titration using ceric sulfate after adding an excess amount of ferrous ammonium sulfate.

*Determination of Reaction Products.* Cyclohexanone was oxidized under vigorous agitation in a three necked flask with oxygen inlet and outlet, and the oxidation products were analyzed by gas chromatography with a 3 m column of diethyleneglycol adipate after esterification with diazomethane. After cooling of outlet gas, carbon dioxide was absorbed by passing through an aqueous solution of sodium hydroxide and titrated.

The oxygen absorption apparatus has been described elsewhere.[6]

## Results and Discussion

*Rate of Oxidation of Cyclohexanone.* The steady rate of oxidation of neat cyclohexanone catalyzed by manganese decanoate as a function of catalyst concentration is given in Fig. 1. The rate of oxidation is of the order 0.7—0.8 with respect to manganese concentration and exceeds a little the limiting rate of

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[1] a) Fr. P. 1243571, Brit. P. 941662, Australian P. 61570. b) H. Masuda, K. Kobayashi, and N. Ohta, *Kogyo Kagaku Zasshi*, c) M. Ogawa, *ibid.*, **71**, 147 (1968). d) M. Ogawa, M. Kusunoki, and N. Kitabatake, *ibid.*, **70**, 1670 (1967).

[2] J. A. Rocek and Sr. A. Riehl, *J. Org. Chem.*, **32**, 3569 (1967).

[3] P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc*, **1962**, 822.

[4] J. S. Littler, *ibid.*, **1962**, 827.

[5] J. S. Littler, *ibid.*, **1962**, 822.

[6] a) Y. Kamiya, S. Beaton, F. A. Lafortune, and K. U. Ingold, *Can. J. Chem.*, **41**, 2020 (1963). b) Y. Kamiya, S. Beaton, F. A. Lafortune, and K. U. Ingold, *ibid.*, **41**, 2034 (1963). c) Y. Kamiya and K. U. Ingold, *ibid.*, **42**, 1027 (1964).

[7] Y. Kamiya, *Kogyo Kagaku Zasshi*,**74**, 1811 (1971).

[8] R. J. Andrulis, M. J. S. Dewar, D. R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966).

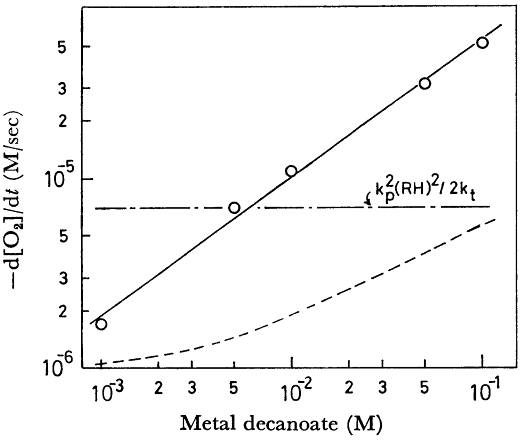

Fig. 1. The rate of oxidation of cyclohexanone as a function of manganese decanoate concentration at 60 °C. A broken line represents the rate of oxidation with cobalt decanoate

oxidation $k_p^2(RH)^2/2k_t$ $7\times10^{-6}$ M/sec calculated from azobisisobutyronitrile initiated autoxidation of cyclohexanone. This shows that manganese decanoate is more effective than cobalt decanoate as an oxidation catalyst of neat cyclohexanone.

When manganese acetate was used as a catalyst in acetic acid solution, the rate of oxidation of cyclohexanone became extremely high. For example, it was $4\times10^{-4}$ M/sec at manganese concentration of 0.02 M and 60 °C, and almost independent of catalyst concentration in contrast to the half order relation of cobalt acetate[7] (Fig. 2). A sudden decrease in the rate at manganese concentrations below $5\times10^{-4}$ M suggests a change of the rate determining step and also a slow regeneration of manganic ion by the oxidation of manganous ion due to the peroxidic intermediates as peracids.

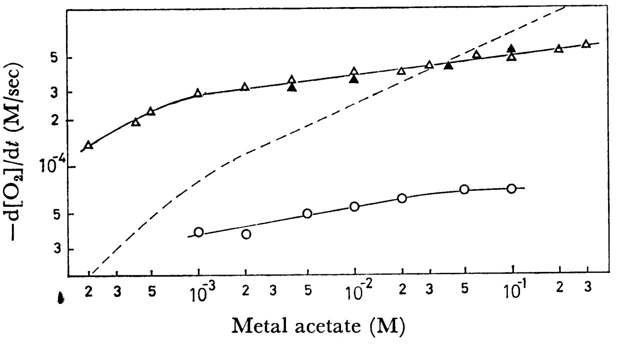

Fig. 2. The rate of oxidation of a 1: 1 mixture by volume of cyclohexanone and acetic acid as a function of metal acetate concentration.
△: manganous acetate at 60 °C, ▲: manganic acetate at 60 °C, ○: manganous acetate at 40 °C.
A broken line represents the rate of oxidation with cobalt acetate.

The rate of oxidation reached a steady state within a few minutes, the solution turning dark brown due to manganic ion. A portion of the solution in the steady state of oxidation was taken out and titrated potentiometrically to determine the concentration of manganic ion. Approximately 90% of the manganese ions was found to be manganic in the manganese concentration range 0.01—0.05 M.

The rate of oxidation catalyzed by pure manganic acetate is also shown in Fig. 2. There seems to be no difference between the catalysis by manganous and manganic acetates. This indicates that manganese ions rapidly reach a steady concentration in course of oxidation at manganese concentrations above 0.005 M.

The decomposition rate of hydroperoxide by manganese salt[6c] in acetic acid is usually slow as compared with that by cobalt. This corresponds to the fact that the rate of oxidation of tetralin,[5c] ethylbenzene,[9] and cumene[10] catalyzed by manganese acetate in acetic acid is much smaller than that catalyzed by cobalt acetate. In contrast, the decomposition of hydroperoxide by manganese salt does not seem to affect the rate of oxidation of cyclohexanone, since the actual rate of oxidation by manganese salt represents a similar value to that by cobalt salt, far exceeding the limiting rate.

The fact that the rate of oxidation exceeds the limiting rate of oxidation $k_p^2(RH)^2/2k_t$ by a factor of 100 indicates that the ordinary hydrogen abstraction step by peroxy radical plays only a minor role as explained by Walling,[11] since the chain length is nearly unity under the limiting rate conditions. If the rate of autoxidation $k_p(RH)(RO_2\cdot)$ increases one hundred times as fast as the limiting rate, the termination reaction should increase by a factor of ten thousands, and the oxidation should stop undoubtedly.

The important step of manganese-catalyzed autoxidation of cyclohexanone should be the oxidation of cyclohexanone due to manganic ion as in the case of cobalt acetate. However, the reaction mechanism by manganese catalyst seems to differ greatly from that by cobalt salt, since the rate of oxidation is almost independent of manganese concentration in a wide range of concentration above 0.001 M.

The rate of oxidation of cyclohexanone with manganese acetate was enhanced from $4.1\times10^{-4}$ M/sec to $1.15\times10^{-3}$, $9.9\times10^{-4}$, and $8.2\times10^{-4}$ M/sec in the presence of 0.5 M of lithium acetate, sodium acetate and potassium acetate, respectively. This effect seems to result from the enhancement of enolization rate of cyclohexanone. Lienhard and Wang[12] reported that sodium acetate and sodium pivalate increased the rate of enolization of cyclohexanone as acid and base. The effect of alkali acetate strongly supports the view that enol intermediate is involved in the rate-determining step of the oxidation of cyclohexanone catalyzed by manganese.

*Oxidation of Cyclohexanone by Manganic Acetate in Nitrogen Atmosphere.* Since the manganese ion in acetic acid solution during the course of oxidation is mostly manganic and radical formation by the manganese-catalyzed decomposition of hydroperoxide is not considered to be of significance, the oxidation of cyclohexanone by manganic ion seems to play an important role. The rate of Mn(III) reduction with Mn(III) of

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9) Y. Kamiya, *Kogyo Kagaku Zasshi*, **69**, 897 (1966).
10) Y. Kamiya, This Bulletin, **43**, 830 (1970).
11) C. Walling, *J. Am. Chem. Soc.*, **91**, 7590 (1969).
12) G. E. Lienhard and T. C. Wang, *ibid.*, **91**, 1146 (1969).

$9\times10^{-3}$ M and cyclohexanone of 4.83 M in acetic acid at 40 °C in the absence of oxygen was $5.2\times10^{-5}$ M/sec, which agrees with the value of $5.4\times10^{-5}$ M/sec, the rate of oxygen absorption of cyclohexanone with manganese acetate 0.01 M at 40 °C. Agreement of the two rates strongly support the view that the rate-determining step is the oxidation of cyclohexanone by Mn(III), since the molar ratio of oxygen molecule absorbed by oxidized cyclohexanone should be 1.0—1.5 according to oxidation products.

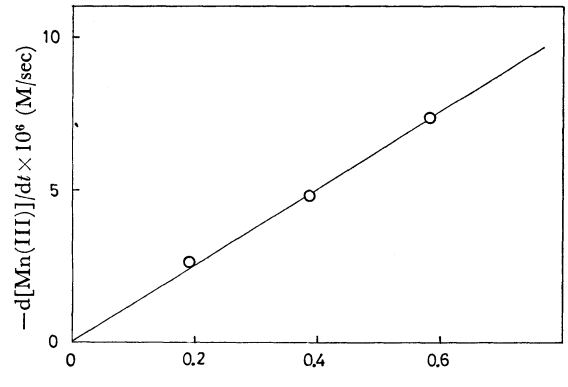


Fig. 3. The rate of reduction of manganic acetate with cyclohexanone as a function of cyclohexanone concentration in acetic acid at 40 °C. Initial manganic acetate 0.0285 M.

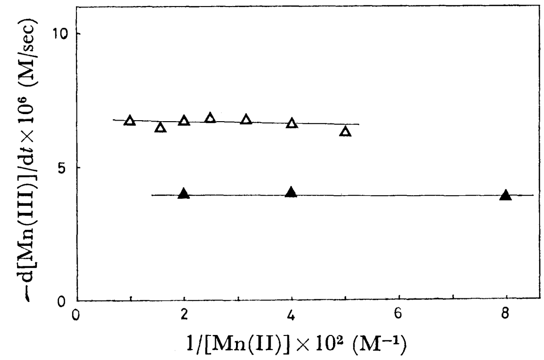


Fig. 4. The rate of reduction of manganic acetate with cyclohexanone as a function of manganous acetate in acetic acid at 40 °C.
Cyclohexanone 0.545 M, △: Mn(III) 0.02 M, ▲: Mn(III) 0.005 M.

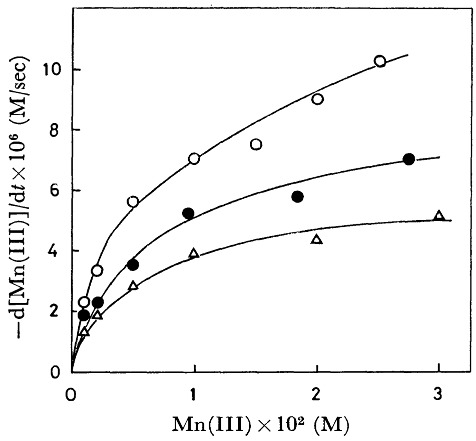


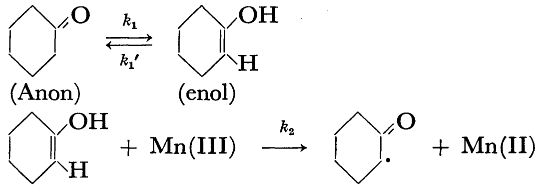
Fig. 5. The rate of reduction of manganic acetate with cyclohexanone as a function of manganic acetate concentration in acetic acid at 40 °C.
Cyclohexanone: ○ : 0.771 M, ● : 0.545 M, △ : 0.370 M.

Oxidation of cyclohexanone with manganic acetate under nitrogen atmosphere was studied under various conditions (Figs. 3, 4, and 5). The rate of reduction of Mn(III) was of first order with respect to cyclohexanone (Fig. 3) and independent of manganous ion (Fig. 4) in contrast to the case of cobalt salt.[7] The reduction of Mn(III) increased slowly with the increase of its concentration (Fig. 5).

There are several reasons for the rate determining step in the manganese-catalyzed autoxidation of cyclohexanone being the enolization of cyclohexanone and not the electron transfer step.

Den Hartog and Kooyman[13] confirmed that the enolization step of acetophenone was rate determining in the manganese-catalyzed autoxidation of acetophenone. There was no significant difference between the rates of oxidation of cyclohexanone by cobaltic and manganic acetates at 0.01 M, although the rate of oxidation of toluene by cobaltic acetate[14] was much higher than the rate by manganic acetate.[8] The rate of oxidation of cyclohexanone by manganic acetate was independent of manganous ion concentration and increased in the presence of alkali acetates.

When the oxidation of cyclohexanone by Mn(III) proceeds through enol intermediates, the reaction scheme and the rate of equation can be expressed as follows.



$$-\mathrm{d}[\mathrm{Mn(III)}]/\mathrm{d}t = k_1k_2[\mathrm{Mn(III)}][\mathrm{Anon}]/(k_1' + k_2[\mathrm{Mn(III)}]) \qquad (5)$$

$$[\mathrm{Anon}]/(-\mathrm{d}[\mathrm{Mn(III)}]/\mathrm{d}t) = (1/k_1) + k_1'/k_1k_2[\mathrm{Mn(III)}] \qquad (6)$$

A plot of [Anon]/(−d[Mn(III)]/d$t$) against 1/[Mn(III)] should give a straight line with an intercept equal to $1/k_1$ and a slope of $k_1'/k_1k_2$. The results

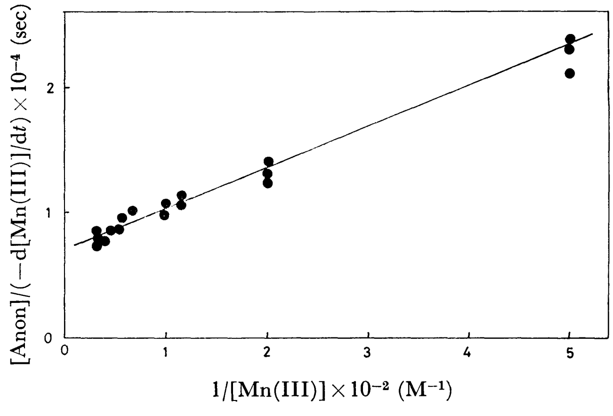


Fig. 6. [Anon]/(−d[Mn(III)]/d$t$) versus 1/[Mn(III)].

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[13] H. J. Den Hartog, E. C. Kooyman, *J. Catal.* **6**, 347 (1966).

[14] K.Sakota, Y. Kamiya, and N. Ohta, *Can. J. Chem.*, **47**, 387 (1969).

obtained in several cyclohexanone-acetic acid mixtures are plotted in this manner in Fig. 6. A straight line through the experimental points is consistent with an intercept of $7\times10^4$ sec as required for the value of $1/k_1$. Scattering of points might be mainly due to experimental error, with possible effects of other reactions.

The satisfactory linear correlation in Fig. 6 supports the enolization mechanism.

*Comparison of the Rate of Oxygen Absorption and the Rate of Reduction of Mn(III).* From the value of $k_1$ ($1.43\times10^{-5}$ sec$^{-1}$), the limiting rate of Mn(III) reduction at 4.83 M cyclohexanone and 40 °C was calculated to be $6.9\times10^{-5}$ M/sec.

The measured rate of oxygen absorption at 40 °C did not exceed the value of $6.8\times10^{-5}$ M/sec (Fig. 2). Thus, the maximum rate of oxygen absorption can be predicted by Eq. (5). There is no significant difference between the rate of reduction of Mn(III) and that of oxygen absorption at manganese concentrations above $5\times10^{-3}$ M, provided that the ratio of manganic to total manganese ions is kept 0.9 and the molar ratio of absorbed oxygen to reacted cyclohexanone 1—1.5.

The ratio of the rate of oxygen absorption to the rate of reduction of Mn(III) increases with decreasing manganese concentration and reaches 1.8 at $10^{-3}$ M manganese. This may be partly due to the participation of acylperoxy radical in the propagation step and also to a trace of oxygen remaining in the solution, since the regeneration of Mn(III) from the reaction of Mn(II) and peroxidic compounds would be affected even in the presence of $10^{-4}$ M of oxygen at manganese concentrations as low as $10^{-3}$ M.

*Synergistic Effect of Metal Acetates.* For the case in which one component is manganese acetate and the other a transition metal such as cobalt, the rate of oxidation was studied as a function of composition. A remarkable synergistic effect was observed in the mixture of manganese and cobalt as shown in Fig. 7. When the metal concentration is as low as $10^{-5}$ M, the synergistic effect was found to be more remarkable, since the rate of autoxidation by single component falls to values less than $10^{-5}$ M/sec.

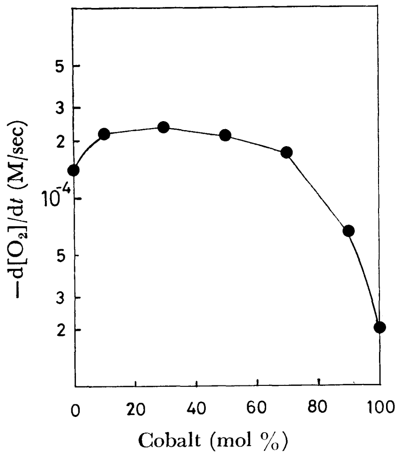

Fig. 7. The mixing effect of manganese with cobalt acetate at total concentration of $2\times10^{-4}$M on the oxidation of a 1: 1 mixture by volume of cyclohexanone and acetic acid at 60 °C.

In the case of cobalt acetate, the rate of oxidation of cyclohexanone can be expressed as $k[\mathrm{Co(III)}]^2[\mathrm{Anon}]/[\mathrm{Co(II)}]$ and the rate of oxygen absorption catalyzed by cobalt acetate in acetic acid is of about half order in total cobalt concentration. On the other hand, the manganese-catalyzed autoxidation showed a small dependence on catalyst concentration. The marked decrease in the rate of oxidation at low manganese concentration can be attributed mostly to the slow regeneration of Mn(III) by the oxidation of Mn(II) with peracids, since the rate of decomposition of peracids with manganese acetate in acetic acid is much smaller than that with cobalt acetate.

Thus, if cobalt is mixed with manganese at low catalyst concentrations, cobalt would take over the role of peroxide decomposition and the resulting cobaltic ion would oxidize manganous ion to manganic. As a result, the rate of oxidation catalyzed by a mixture of cobalt and manganese would assume the theoretical value represented by Eq. (5).

A similar synergistic effect was observed in the mixture of nickel and manganese acetates. This can also be explained in the same manner.

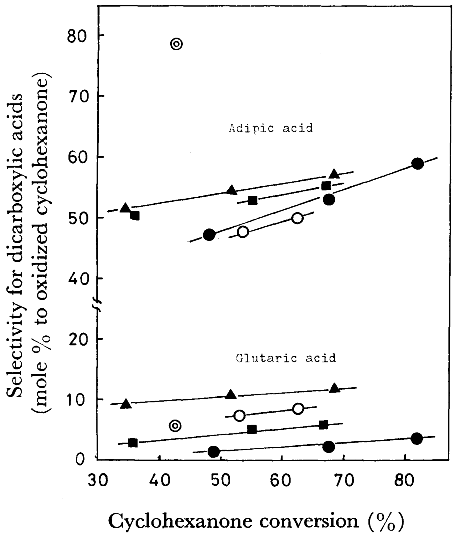

Fig. 8. The selectivities for adipic and glutaric acids in the oxidation of a 1: 1 mixture by volume of cyclohexanone and acetic acid as a function of cyclohexanone conversion with $10^{-3}$M metal acetates.

▲: Cobalt, ●: Manganese, ○: Cobalt/Manganese=1/1, ■: Manganese/Nickel 1/1, ◎: Manganese/Copper=1/1.

*Oxidation Products.* Selectivity to adipic and glutaric acids *versus* the conversion of cyclohexanone is given in Fig. 8. The selectivity for adipic acid increased gradually as the conversion increased and the highest value of 79% was obtained for all catalysts tested in the 1: 1 mixture of manganese and copper. The reason why the yield of adipic acid by Mn–Cu catalyst is considerably high can be attributed to the retardation effect of Cu(II) on the coupling reaction of alkyl radicals, since Cu(II) is known to oxidize alkyl radicals[15] and the rate of oxidation of cyclo-

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[15] J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, **90**, 4616 (1968).

hexanone catalyzed by $6.4 \times 10^{-4}$ M Mn decreased from $9.2 \times 10^{-5}$ to $5.2 \times 10^{-5}$ M/sec after 50% of Mn was replaced by Cu.

Cobalt showed a higher yield of glutaric acid than the other catalysts. This may be due to its activity[16] in the decarboxylation reaction of adipic acid. The ratio of carbon dioxide to glutaric acid was 1—1.5, and almost independent of cyclohexanone conversion at conversion 40—70%. The selectivity for adipaldehyde was 6—8% in the case of manganese catalyst but only 1—2% in the presence of cobalt acetate. It seems reasonable that cobalt is more effective in the oxidation of intermediate aldehydes than manganese.

The oxidation products described above can not explain the carbon distribution satisfactorily except for the products obtained by Mn–Cu. The balance may be mostly polymerized products such as 2-cyclohexan-1-yl cyclohexanone[2] and other intermediate products[1d,2] such as dione and oxycyclohexanone.

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[16] a) W. A. Waters, *Discuss. Faraday Soc.*, **46**, 158 (1969). b) H. B. Tinker, *J. Catal.* **19**, 237 (1970).