On the Critical Phenomena in the Decomposition of Hydroperoxides and in the Autoxidation of Cumene with Bis(acetylacetonato)manganese(II)

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The decomposition of 1-methyl-1-phenylethyl hydroperoxide and *t*-butyl hydroperoxide with Mn(II)(acac)$_2$ and the autoxidation of cumene with Mn(II)(acac)$_2$, Mn(III)(acac)$_3$, and $MnCO_3$ have been studied at 323 K. In the decomposition of the hydroperoxides with Mn(II)(acac)$_2$, the peroxyl radicals are observed only when the initial ratio of hydroperoxide to catalyst amount exceeds a certain value. The critical phenomenon is observed in the oxidation of cumene with Mn(II)(acac)$_2$ and also with $MnCO_3$. A scheme for the cause of the critical phenomena has been proposed.

It has been reported that, in the liquid phase oxidation of hydrocarbons with metal oxides, there is a critical amount of catalyst above which the reaction does not proceed.[1-10] A similar critical phnomenon was observed in the autoxidation with homogeneous catalysts.[11,12] Decrease of the oxidation rate at a high catalyst amount indicates that the solid acts as an inhibitor rather than as a catalyst. However, causes for the same substance having dual functions, *i.e.* it accelerates the oxidation rate at lower catalyst amount and inhibits the reaction at higher catalyst amount, and for the change from catalysis to inhibition occurring abruptly, have not been clarified.

As regards catalysis, it is accepted that the decomposition of the hydroperoxide on solid surface produces free radicals, which in turn, propagate the chain reactions in liquid phase.[1-10]

Interaction of hydroperoxide with surfaces also seems to cause the critical phenomena. Thus, a critical catalyst amount has been reported to depend on the initial concentration of the hydroperoxide.[1,3,7] Mukherjee and Graydon[1] found that there is a critical hydroperoxide to catalyst ratio, below which no reaction takes place in the oxidation of tetraline with Mn_2O_3. They assumed that there are two distinct sites on the catalyst, one preferentially adsorbing the hydroperoxide and the other taking part in the production of free radicals. When the amount of hydroperoxide is small, no reaction takes place, since all of it is consumed to saturate the inactive sites which do not contribute to radical formation.

The inhibiting action of the surface might depend also on the oxidation state of the metal cations. Manganese-catalyzed autoxidation was observed to start when Mn(II) was converted into Mn(III).[13] Inhibition of autoxidations by transition metals in low oxidation states such as Co(II) or Mn(II) was reported.[11,14-16] In cyclohexene oxidation with manganous heptanoate, Chalk and Smith[17] observed long induction periods, which do not terminate until sufficient hydroperoxide is formed to convert nearly all the manganous manganese into manganic state. The reaction of metal cations with peroxyl radicals has been postulated as one of the termination reactions also in the autoxidation with metal oxides.[7,10]

In the present work, we have found a critical phenomenon in the decomposition of hydroperoxides with bis(acetylacetonato)manganese(II), Mn(II)(acac)$_2$, and also in the oxidation of cumene with Mn(II)(acac)$_2$. No such phenomenon is observed in the oxidation with tris(acetylacetonato)manganese(III), Mn(III)(acac)$_3$, indicating the importance of the oxidation state of the cations for critical phenomena. The critical phenomenon in the oxidation and that in the hydroperoxide decomposition are closely related. A scheme for the cause of the critical phenomena is proposed. The critical phenomenon in the oxidation of cumene with $MnCO_3$ is also mentioned.

Experimental

Materials. Commercial cumene (reagent grade) was distilled and percolated through an activated alumina column three times prior to use in order to remove any trace of hydroperoxide. *t*-Butyl hydroperoxide and 1-methyl-1-phenylethylhydroperoxide(Nakarai Chem. Ltd.), were purified by vacuum distillation. Commercial Mn(II)(acac)$_2$, Mn(III)(acac)$_3$, and $MnCO_3$ were used.

Apparatus and Procedure. The apparatus has been described in detail.[18-20] Carbon tetrachloride was used as a solvent, since it is an inert solvent in autoxidation or hydroperoxide decomposition.[16-19] For example, the decay rate of 1-methyl-1-phenylethylperoxyl radical in CCl_4 was the same as that in cumene.[21] Measurements of the peroxyl radical concentration during the course of decomposition of hydroperoxide were performed as follows. The solvent (CCl_4 70 cm^3) and the catalyst (Mn(II)(acac)$_2$) were stirred in a flask and the part of the solution with the colloidal catalyst was circulated with use of a roller pump through the ESR cavity. The reaction was started by the addition of hydroperoxide (20—123 μl). ESR intensity of the peroxyl radicals was monitored with time by use of a JEOL-X-band spectrometer (JEOL-PE-1X) with 100 kHz magnetic modulation. The radical concentration was determined using 1,1-diphenyl-2-picrylhydrazyl in benzene as a reference.

The rates of oxygen absorption during the course of autoxidation of cumene with Mn(II)(acac)$_2$, Mn(III)(acac)$_3$, and $MnCO_3$ were measured with a gas burette or a gasometer. The radical concentration during the course of oxidation was determined in the same manner as above.

Results

Critical Phenomena in the Decomposition of Hydroperoxides by Mn(II)(acac)$_2$. The ESR spectrum of the

1-methyl-1-phenylethyl-peroxyl radical($RO_2\cdot$, $g=2.015 \pm 0.0002$) or the *t*-butylperoxyl ($BO_2\cdot$, $g=2.0144 \pm 0.0002$) was observed, when an amount of 1-methyl-1-phenylethyl hydroperoxide (ROOH) or *t*-butyl hydroperoxide (BOOH) exceeding a certain value was added to 70 cm^3 of CCl_4 solution containing 0.2 g of Mn(II)(acac)$_2$, indicating the decomposition of hydroperoxide. The radical concentration increased markedly with reaction time, reaching a maximum, then decreasing. Typical examples are shown in Fig. 1.

The maximum concentration of the peroxyl radicals, $[RO_2\cdot]_{max}$, are plotted against the initial concentration of the hydroperoxides in Fig. 2. For concentrations of the hydroperoxides lower than 4.0×10^{-3} M, no peroxyl radicals were observed. By a slight increase of hydroperoxide concentration above 4.0×10^{-3} M, the peroxyl radicals were observed, the maximum radical concentration increasing linearly with an increase in initial hydroperoxide concentration. It is evident that critical phenomenon exists in the decomposition of hydroperoxides. The critical concentration of the hydroperoxides is the same (4.0×10^{-3} M) for ROOH and BOOH, the critical ratio of hydroperoxide to Mn(II)(acac)$_2$ amount being 1.4×10^{-3} mol/g-Mn(II)(acac)$_2$.

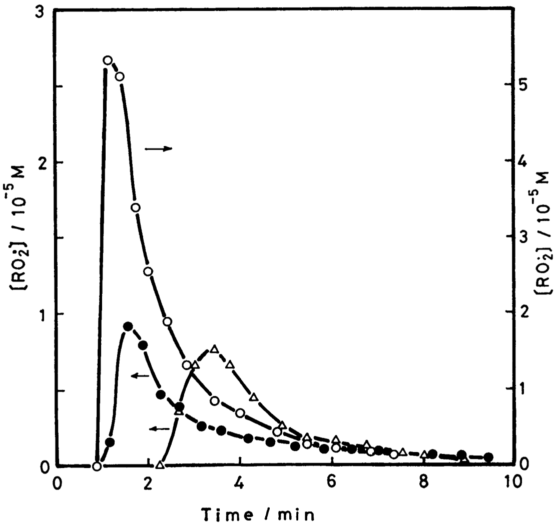

Fig. 1. Concentration of peroxyl radicals during the decomposition of *t*-butyl hydroperoxide and cumene hydroperoxide with Mn(II)(ffcac)$_2$ at 323 K plotted against reaction time; Mn(II)(acac)$_2$ 2.86 g l^{-1}, △ [BOOH] 4.47×10^{-3} M, ●[BOOH] 7.83×10^{-3} M, ○ [ROOH] 8.18×10^{-3} M.

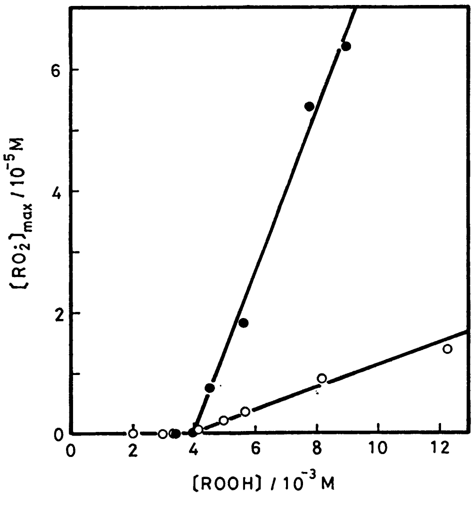

Fig. 2. Maximum concentration of peroxyl radicals during the decomposition of *t*-butyl hydroperoxide and cumene hydroperoxide with Mn(II)(acac)$_2$ at 323 K plotted against initial hydroperoxide concentration; Mn(II)(acac)$_2$ 2.86 g l^{-1}, solvent CCl_4, ● BOOH, ○ ROOH.

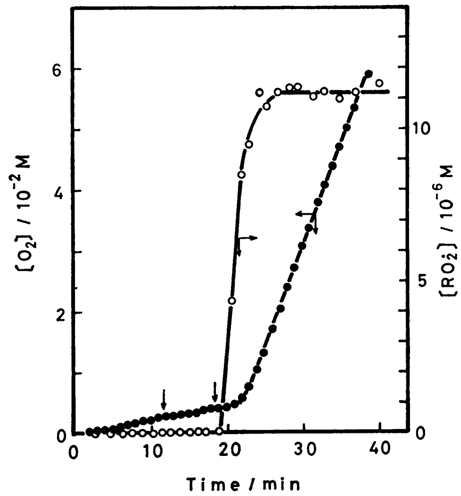

Fig. 3. Cumulative amount of oxygen absorbed and the concentration of cumylperoxyl radical during the autoxidation of cumene with Mn(II)(acac)$_2$ at 323 K plotted against reaction time; Mn(II)(acac)$_2$ 1.54 g l^{-1}, cumene 65 cm^3; Initial ROOH concentration is zero, 10 1 of ROOH was added at 12 min (↓) and another 10 1 of ROOH was added at 19 min (↓).

Critical Phenomena in the Autoxidation of Cumene with Mn(II)(acac)$_2$. In order to see whether the critical phenomenon is also observed in autoxidation with Mn-

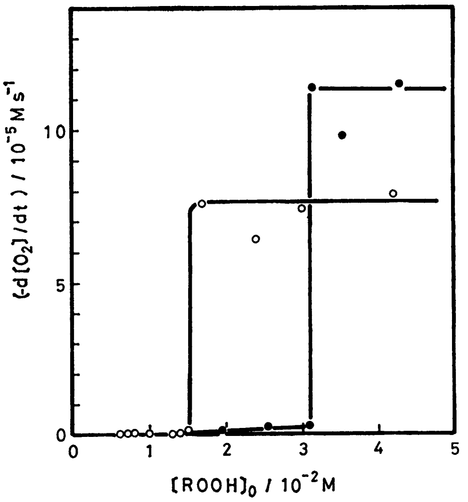

Fig. 4. Rate of oxygen absorption during the autoxidation of cumene with Mn(II)(acac)$_2$ at 323 K plotted against initial hydroperoxide concentration; Mn(II)(acac)$_2$; ○ 10.34 g l^{-1}, ● 20.7 g l^{-1}.

(II)(acac)$_2$, the autoxidation of cumene with Mn(II)(acac)$_2$ was studied at 323 K. As shown in Fig. 3, no peroxyl radicals were observed when no hydroperoxide was added, though a slow oxygen uptake was observed. Addition of 10 μl of ROOH caused no change in the situation. However, when another 10 μl of ROOH was added, peroxyl radicals were observed, the radical concentration and rate of oxygen absorption increasing markedly with time to reach a steady concentration and a steady rate, respectively.

Figure 4 shows the steady rate of oxygen absorption as a function of the initial hydroperoxide concentration. The rate of oxygen absorption is almost zero when the initial hydroperoxide concentrations are lower than 1.6×10^{-2} M and 3.1×10^{-2} M for 10.3 and 20.7 g l^{-1} of [Mn(II)(acac)$_2$], respectively. A slight increase in hydroperoxide concentration in excess of these values causes an abrupt increase in the oxidation rate, which does not change significantly by further increase in the hydroperoxide concentration (Fig. 4). The critical ratio of hydroperoxide to catalyst amount is 1.5×10^{-3} mol/g-Mn(II)(acac)$_2$.

It should be noted that the critical hydroperoxide concentration is doubled by doubling the amount of the catalyst, indicating that the parameter determining critical phenomenon is not hydroperoxide concentration but the ratio of the concentration to the catalyst amount, in agreement with the results of Mukherjee and Graydon,[1] and Neuberg *et al.*[3] This was confirmed also by examining the effect of catalyst amount on the rate of oxidation and on the concentration of peroxyl radical at a constant hydroperoxide concentration (1.56×10^{-2} M). The maximum rate of oxygen absorption and the maximum concentration of the peroxyl radical are plotted against the catalyst amount in Fig. 5. The rate of oxygen absorption increases with increases in the catalyst amount, reaching a constant value, and decreasing drastically above 12.1 g l^{-1} of Mn(II)(acac)$_2$. The critical ratio of hydroperoxide to catalyst amount is 1.3×10^{-3} mol/g-Mn(II)(acac)$_2$, which is very close to that given in Fig. 4.

It should be noted that the critical ratio of hydroperoxide to catalyst (1.3—1.5×10^{-3} mol/g) in cumene autoxidation with Mn(II)(acac)$_2$ is the same as that in the decomposition of hydroperoxides with the same catalyst (1.4×10^{-3} mol/g).

As shown in Fig. 5, the rate of oxygen absorption and radical concentration behave in exactly the same manner, *viz.*, the rate of oxygen absorption is proportional to the concentration of peroxyl radical. This indicates that oxygen is absorbed mainly by the elementary reactions, $R\cdot + O_2 \rightarrow RO_2\cdot$, and $RO_2\cdot + RH \rightarrow ROOH + R\cdot$.

Autoxidation of Cumene with Mn(III)(acac)$_3$. In order to find the effect of the oxidation state of manganese cation, the oxidation of cumene was studied with Mn(III)(acac)$_3$. The concentration of the peroxyl radical and the rate of oxygen absorption were measured simultaneously at 323 K. In the oxidation with Mn(III)(acac)$_3$, the reaction proceeds even when the initial hydroperoxide concentration is much lower than the critical concentration in the oxidation with Mn(II)(acac)$_2$. Figure 6 shows typical examples of the change in the rate of oxygen absorption and the peroxyl radical concentration with reaction time. When 4 μl of ROOH was added to 70 cm^3 of CCl$_4$ solution containing 0.60 g of Mn(III)(acac)$_3$, the peroxyl radical and the absorption of oxygen were observed after standing for 30 min. The hydroperoxide formed after prolonged standing might cause the reaction to proceed. When 150 μl of ROOH was added, the reaction proceeded immediately. In the case of Mn(II)(acac)$_2$, the reaction does not proceed when the initial ratio of hydroperoxide to catalyst amount is less than 1.5×10^{-3} mol/g-Mn(II)-

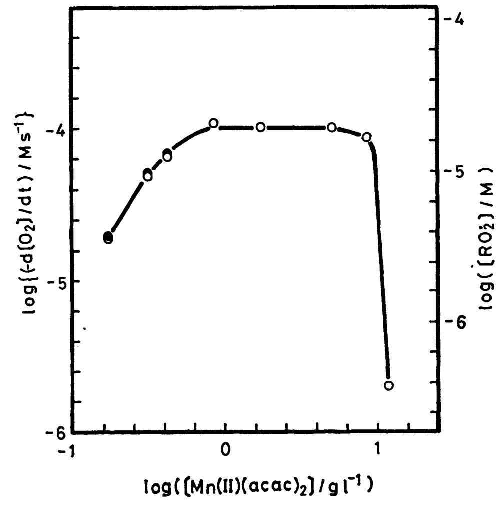

Fig. 5. The rate of oxygen absorption and the concentration of cumylperoxyl radical as a function of the catalyst weight to liquid volume ratio in the autoxidation of cumene with Mn(II)(acac)$_2$ at 323 K; ROOH 1.56×10^{-2} M, ● [RO$_2$-], ○ $-d[O_2]/dt$.

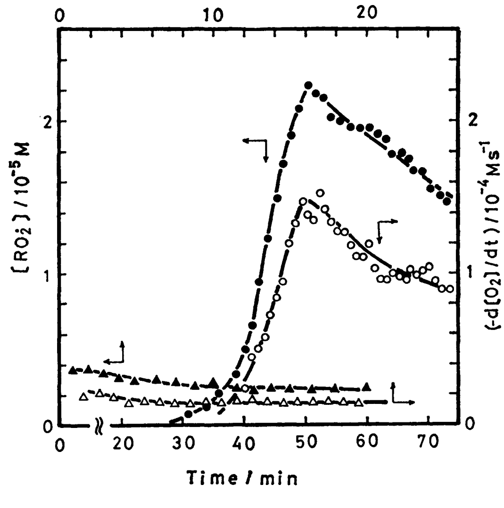

Fig. 6. Change in the rate of oxygen absorption and the concentration of cumylperoxyl radical with time in the autoxidation of cumene with Mn(III)(acac)$_3$ at 323 K. ○ ● Mn(III)(acac)$_3$ 8.57 g l^{-1}, ROOH 4.0×10^{-4} M, RH 7.18 M; △ ▲ Mn(III)(acac)$_3$ 0.17 g l^{-1}, ROOH 1.56×10^{-2} M, RH 7.18 M.

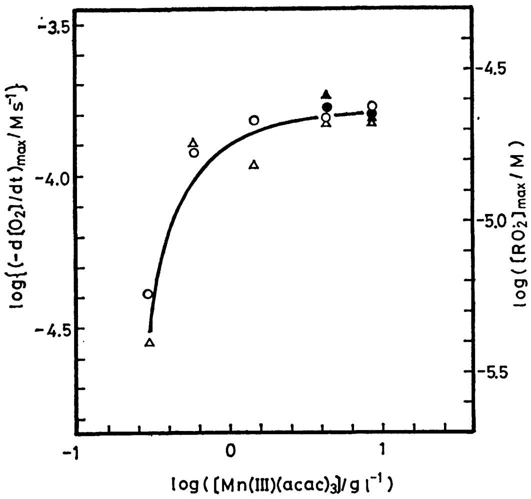

Fig. 7. The naximum rate of oxygen absorption and the maximum concentration of cumylperoxyl radical as a function of the catalyst weight to liquid volume ratio in the autoxidation of cumene with Mn(III)(acac)$_3$; $-d[O_2]/dt$: △ ROOH 4.0×10^{-4} M, ▲ ROOH 1.50×10^{-2} M; [RO$_2$]: ○ ROOH 4.0×10^{-4} M, ● ROOH 1.50×10^{-2} M.

(acac)$_2$; *e.g.*, ROOH 120 μl for Mn(II)(acac)$_2$ 0.60 g

The radical concentration and the rate of oxygen absorption increase with reaction time, reaching a maximum, then decreasing (Fig. 6). This might be due to the deactivation of catalyst. The effects of catalyst amount on the maximum rate of oxygen absorption and the maximum concentration of RO$_2$· are shown in Fig. 7. The rate of oxygen absorption and the radical concentration increase with increase in catalyst amount and reach a constant value, independent of the initial hydroperoxide concentration. As is the case of Mn(II)(acac)$_2$, the rate of oxygen absorption and the radical concentration behave in the same manner, showing that the rate of oxygen absorption is proportional to the radical concentration in the case of Mn(III)(acac)$_3$ as well.

ESR Spectra during Autoxidation of Cumene with Mn(II)(acac)$_2$ and Mn(III)(acac)$_3$. The ESR spectrum during the course of autoxidation of cumene with Mn(II)(acac)$_2$ was measured. When the concentration of the hydroperoxide is below the critical concentration, the broad signal due to Mn(II) is observed. When a sufficient amount of hydroperoxide is introduced to start the oxidation, the intensity due to Mn(II) decreases with time and becomes constant, a sharp signal due to peroxyl radical being observed. The essentially same ESR spectrum was observed during cumene oxidation with Mn(III)(acac)$_3$, indicating that the state of manganese ion is the same irrespective of the valency of the starting complexes, once oxidation is started.

Critical Phenomenon in the Autoxidation of Cumene by MnCO$_3$. The autoxidation of cumene by MnCO$_3$ was studied for 2.33×10^{-3} M of initial hydroperoxide concentration at 323 K. As shown in Fig. 8, the rate of oxygen absorption increases with an increase in the catalyst amount, the rate declining drastically at high catalyst amount. The critical ratio of hydroperoxide to catalyst amount is 2.1×10^{-5} mol/g-MnCO$_3$, much less than the value in the case of oxidation with Mn(II)(acac)$_2$.

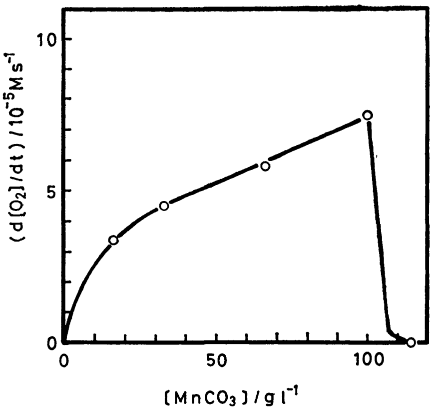

Fig. 8. Rate of oxygen absorption during the autoxidation of cumene by MnCO$_3$ at 323 K plotted against the ratio of catalyst weight to liquid volume; RH 7.18 M, ROOH 2.33×10^{-3} M.

Discussion

Results. The results in this study can be summarized as follows.

1. In the decomposition of ROOH and BOOH with Mn(II)(acac)$_2$ there is a critical ratio of hydroperoxide to catalyst amount (1.4×10^{-3} mol/g-Mn(II)(acac)$_2$) below which no peroxyl radicals are observed during the course of reaction.
2. In the autoxidation of cumene with Mn(II)(acac)$_2$, there is a critical ratio of hydroperoxide to catalyst amount below which the oxidation does not proceed, the ratio being the same as that found in the hydroperoxide decomposition.
3. In the autoxidation of cumene with Mn(III)(acac)$_3$, no critical phenomenon is observed.
4. The ESR signals due to manganese ion during the course of autoxidation of cumene with Mn(II)(acac)$_2$ are the same as those with Mn(III)(acac)$_3$.
5. In the autoxidation of cumene by MnCO$_3$, there is also a critical ratio of hydroperoxide to catalyst amount (2.1×10^{-5} mol/g-MnCO$_3$), the critical value being much smaller than that in the case of Mn(II)(acac)$_2$.

Reaction Mechanism. Agreement of critical ratios in the hydroperoxide decompositions and in cumene oxidation (observations 1 and 2) indicates that the critical phenomenon in the autoxidation is substantially identical to the critical phenomenon in the hydroperoxide decomposition. Inhibition of oxidation below a critical hydroperoxide concentration might be caused by the fact that the hydroperoxide decomposition gives no peroxyl radicals available for chain propagation.

From the results given in 3, we see that the Mn(II) and not Mn(III) species play an essential role in the appearance of the critical phenomena. 4 suggests that there is a redox interconversion between Mn(II) and Mn(III) during the course of reaction. The mechanism for the autoxidation of cumene with Mn(II)(acac)$_2$ and

Mn(III)(acac)$_3$ can be written as follows:

Initiation

$$\mathrm{ROOH} + \mathrm{Mn(II)} \xrightarrow{\text{fast}} \mathrm{RO}\cdot + \mathrm{Mn(III)} + \mathrm{OH}^- \qquad (1)$$

$$\mathrm{ROOH} + \mathrm{Mn(III)} \longrightarrow \mathrm{RO_2}\cdot + \mathrm{Mn(II)} + \mathrm{H} \qquad (2)$$

Propagation

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

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{RO_2}\cdot \qquad (4)$$

$$\mathrm{RO_2}\cdot + \mathrm{RO_2} \longrightarrow 2\mathrm{RO}\cdot + \mathrm{O_2} \qquad (5)$$

$$\mathrm{RO}\cdot + \mathrm{ROOH} \xrightarrow{\text{fast}} \mathrm{ROH} + \mathrm{RO_2}\cdot \qquad (6)$$

Termination

$$\mathrm{RO_2}\cdot + \mathrm{Mn(II)} \longrightarrow (\mathrm{RO_2}\cdot \cdots \mathrm{Mn(II)}) \longrightarrow \text{inactive product} \qquad (7)$$

$$\mathrm{RO_2}\cdot,\ \mathrm{RO}\cdot \longrightarrow \text{decay} \qquad (8)$$

The reaction mechanism is the same as that proposed for the cumene oxidation with PbO$_2$,[16] except for elementary Reactions 1, 2, and 7. The initiation Reactions 1 and 2 are accepted for homogeneous systems.[22,23] Reaction 7 is included to account for the inhibiting action of the catalyst. The radical scavenging action of the lower oxidation state of metal cation has been postulated by several authors,[7,11,14,16,17,24] and the rate constants for reactions of peroxyl radicals and the metal cations have been estimated.[15,25,26]

Origin of Critical Phenomena. In order to confirm the origin of the critical phenomena in oxidation and hydroperoxide decomposition, we should consider relative rates of elementary reactions. Reaction 1 is much faster than Reaction 2 in the manganese system.[23] Reaction 7 is much faster than Reaction 3, hydrogen abstraction from RH by RO$_2$. Thus, the rate constant for the reaction of cumylperoxyl radical with manganous cation is $4.3\times10^4\ \mathrm{M^{-1}\,s^{-1}}$ at 308 K,[15] while the rate constant for the reaction of the same radical and cumene is estimated to be 7.6 $\mathrm{M^{-1}\,s^{-1}}$ at the same temperature.[17] Thus, in the presence of sufficient amount of Mn(II), the peroxyl radicals formed by Reactions 1 and 6 are scavanged by Mn(II), the autoxidation being inhibited. Above the critical ratio of hydroperoxide to Mn(II) amount, most of Mn(II) species are converted into Mn(III) by Reaction 1 and the remaining ROOH molecules are converted into peroxyl radicals by Reaction 2 and the oxidation can proceed through Reactions 4 and 5. Under these conditions, Reaction 7 is negligible because of low concentration of Mn(II). For the same reason, no critical phenomena would be observed if Mn(III) is used as a catalyst from the beginning.

Reactions 1 and 7 are only known in the case of transition metal cations which have variable oxidation states, such as Co(II)/Co(III) and Mn(II)/Mn(III). The fact that critical phenomena in the autoxidation of hydrocarbons have been observed only with such transition metal ions[1-10] also supports the view that the cause of critical phenomena can be attributed to Reactions 1 and 7.

Elimination of the elementary Reactions 3 and 4 from the above oxidation mechanism should give the mechanism for the hydroperoxide decomposition.[19,27] Since the mechanisms of initiation and chain scavenging remain identical to those in the autoxidation, the origin of the critical phenomena both in the hydroperoxide decomposition and the autoxidation should be common. This explains why both critical phenomena occur at the same ratio of the hydroperoxide to catalyst amount.

The critical molar ratio of hydroperoxide to Mn(II), expected from Reactions 1 and 7, is unity. But the experimental critical ratio of hydroperoxide to Mn(II)(acac)$_2$ amount is 1.5×10^{-3} mol/g-Mn(II)(acac)$_2$, that is, the critical molar ratio is 0.38, smaller than unity, probably because of the fact that Mn(II)(acac)$_2$ is partly heterogeneous during the course of reaction.

The critical phenomenon in the autoxidation of cumene by MnCO$_3$ can be explained similarly. Since MnCO$_3$ is a heterogeneous catalyst, and only Mn(II) on the surface is available for the initiation, the effective Mn(II) species in MnCO$_3$ are much less than those in Mn(II)(acac)$_2$, resulting in a much smaller critical ratio of hydroperoxide to catalyst amount.

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