# Oxidation of 3,5-Di-*t*-butylcatechol Catalyzed by Metal Acetylacetonates in Organic Solvents

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The oxidation of 3,5-di-*t*-butylcatechol (3,5-DTBC) has been studied in organic solvents in the presence of metal acetylacetonates (M(acac)$_2$). The catalytic activity of M(acac)$_2$ decreased in the order M=Mn>Co>Ni≫Fe, and the product was 3,5-di-*t*-butyl-*o*-benzoquinone (3,5-DTBQ). The kinetic analysis has suggested a mechanism in which the radical chain reactions involving 3,5-di-*t*-butyl-*o*-benzosemiquinone (3,5-DTBSQ·) and hydroperoxyl radical (·OOH) are initiated by the reaction of 3,5-DTBC with the initially formed dioxygen metal complexes. Kinetic parameters for the complexation of molecular oxygen by Mn(acac)$_2$ and Co(acac)$_2$ were estimated: $\Delta H^{\neq}$(kJ mol$^{-1}$)=4.6±0.8 for Mn, 29.7±0.8 for Co; $\Delta S^{\neq}$(J mol$^{-1}$ K$^{-1}$)=−200±2 for Mn, −135±2 for Co.

There has been much interest recently in the study of the oxidation of catechol and the reversible absorption of oxygen by transition metal complexes, because both are related to biological phenomena which involve enzymes and hemoglobin. The oxidation of catechols is accompanied by the aromatic ring cleavage[1—4] or by the dehydrogenation to form *o*-benzoquinones.[3—9] The latter reaction has been catalyzed by enzymes,[5] aqueous bases,[4,6] metal ions in basic media,[4,7] metal oxides such as $PbO_2$ and $Ag_2O$,[8] and metal salts such as $Ag_2CO_3$,[9] but transition metal complexes have rarely been used as catalysts.[10] Recently, the formation of the dioxygen complex of cobalt(II) acetylacetonate, in which the metal-oxygen bond is very weak, has been proposed in the oxidation of cumene,[11] α-methylstyrene,[11] and 1-phenylethanol.[12] Thus, the dioxygen complex is expected to be an active species in the oxidation of catechol. We have studied the oxidation of 3,5-di-*t*-butylcatechol (3,5-DTBC) by metal acetylacetonates (M(acac)$_2$: M=Mn, Fe, Co, Ni, Cu) in order to determine the catalytic activity of these readily available complexes for the oxidation of catechol and to obtain information about the activation of oxygen by coordinating to metal complexes. 3,5-DTBC was used as reactant to avoid the solvolytic attack on the quinonoid nucleus,[4,6,13] and the reactions were performed in the organic solvents without base to avoid the complexity caused by the dissociation of the catechol to catechol anion. The coordination of catechol to the metal complex as mono- or dianion, which was proposed by Grinstead[4] or Martell,[7] will be neglected in the present conditions.

## Experimental

*Materials.* Metal acetylacetonates and 3,5-DTBC were recrystallized from chlorobenzene and heptane, respectively. 3,5-Di-*t*-butyl-*o*-benzoquinone (3,5-DTBQ) was prepared by the method of Grinstead[4] and recrystallized from 2,2,4-trimethylpentane. All the solvents were distilled before use.

*Manometric Study.* All the reactions were performed at 25 °C in a 50 cm$^3$ two-necked flask which was attached to an ordinary vacuum line system. The reaction was started by the addition of the 3,5-DTBC solution with an injection syringe through a serum cap to the catalyst solution, which was stirred magnetically in an oxygen atmosphere. The reaction was followed by measuring the oxygen absorption with a gas burette under a constant pressure. The yield of 3,5-DTBQ was determined spectrophotometrically.

*Spectroscopic Study.* The rate of the reaction (rate of the formation of 3,5-DTBQ) in acetone was measured spectrophotometrically on a JASCO UVIDEC-1 spectrophotometer with a 1 cm quartz cell in air. $\lambda_{max}$ and $\varepsilon$ of 3,5-DTBQ in acetone were 399 nm and $1.85\times10^3$ mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. The initial concentration of the dissolved oxygen was estimated by the use of the tabulated data.[15] ESR spectra were taken on a JEOL PE-2X spectrometer modified with a JEOL ES-SCXA gunn diode microwave unit.

## Results and Discussion

*Catalytic Activity.* Figure 1 shows the oxygen absorption curves in the oxidation of 3,5-DTBC by M(acac)$_2$ in acetonitrile. Oxygen was absorbed without an induction period by the manganese, cobalt, and nickel complexes, but Cu(acac)$_2$ exhibited a different mode of the oxygen absorption. This suggests that the mechanism for the former three complexes is

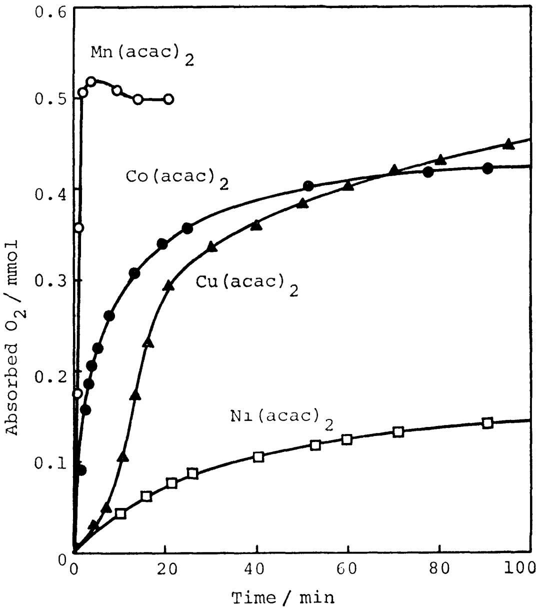


Fig. 1. Catalytic activity of M(acac)$_2$ in acetonitrile solvent at 25 °C under oxygen atmosphere. [M(acac)$_2$]$_0$=0.1 mmol; [3,5-DTBC]$_0$=1.0 mmol; total volume=10 cm$^3$.

different from that for $Cu(acac)_2$. The catalytic activity evaluated from the maximal rate of the oxygen absorption decreased in the order M=Mn>Co>Cu>Ni≫Fe(no reaction). This order is different from that reported for the oxidation of cumene and α-methylstyrene (Co>Mn>Ni).[11] The inactivity of $Fe(acac)_2$ is due to its ready conversion to an inactive Fe(III) species in the presence of oxygen.[16]

TABLE 1. CATALYTIC ACTIVITY AND SOLVENT EFFECT[a]

| Catalyst | Solvent | Reaction time (min) | Moles $O_2$ absorbed per mole 3,5-DTBC | Yield of 3,5-DTBQ (%) |
|---|---|---|---|---|
| non | Acetonitrile | 120 | 0 | 0 |
| $Mn(acac)_2$ | Acetonitrile | 5 | 0.50 | 95—100 |
| $Fe(acac)_2$ | Acetonitrile | 120 | 0 | 0 |
| $Co(acac)_2$ | Acetonitrile | 120 | 0.42 | 75—80 |
| $Ni(acac)_2$ | Acetonitrile | 180 | 0.23 | 40—45 |
| $Cu(acac)_2$ | Acetonitrile | 120 | 0.48 | 45—50 |
| $MnCl_2 \cdot 4H_2O$[b] | Acetonitrile | 120 | 0 | 0 |
| $FeCl_2 \cdot 4H_2O$ | Acetonitrile | 120 | 0.07 | 0 |
| $CoCl_2 \cdot 6H_2O$ | Acetonitrile | 120 | 0 | 0 |
| $NiCl_2 \cdot 6H_2O$ | Acetonitrile | 120 | 0 | 0 |
| $CuCl_2 \cdot 2H_2O$ | Acetonitrile | 120 | 0 | 0 |
| $Mn(OAc)_2 \cdot 4H_2O$ | Acetonitrile | 20 | 0.48 | 75—80 |
| $Co(OAc)_2 \cdot 4H_2O$ | Acetonitrile | 120 | 0.45 | 75—80 |
| $Ni(OAc)_2 \cdot 4H_2O$ | Acetonitrile | 180 | 0.24 | 40—45 |
| $Cu(OAc)_2 \cdot H_2O$ | Acetonitrile | 70 | 0.70 | 95—100 |
| $Mn(acac)_2$ | Acetone | 5 | 0.51 | 95—100 |
| $Mn(acac)_2$ | Benzene | 7 | 0.49 | 95—100 |
| $Mn(acac)_2$ | Methanol | 10 | 0.51 | 95—100 |

a) $[Catalyst]_0=0.1$ mmol; $[3,5\text{-DTBC}]_0=1.0$ mmol; total volume$=10$ $cm^3$ at 25 °C under oxygen atmosphere. b) The solution was somewhat heterogeneous.

The solvent effect was studied with $Mn(acac)_2$. As shown in Table 1, the rate decreased in the order: acetone≳acetonitrile>benzene>methanol, but the solvent effect was not so remarkable. Catalytic activity in organic solvent was also studied with some metal salts. As shown in Table 1, metal halides, which are active in $KHCO_3$ buffered aqueous methanol,[4] were not active. Metal carboxylates were active as metal acetylacetonates, but induction periods were clearly observed in the oxygen absorption curves, as in the case of $Cu(acac)_2$.

The oxidation product, which was isolated by ether extraction, was 3,5-DTBQ, and its yield was >95% in the case of $Mn(acac)_2$. The result that the maximal amount of the absorbed oxygen with $Mn(acac)_2$ was slightly greater than one-half of 3,5-DTBC (see Fig. 1) suggests a two-step reaction (Reactions 1 and 2) rather than the single step 3.

$$3,5\text{-DTBC} + O_2 \longrightarrow 3,5\text{-DTBQ} + H_2O_2 \qquad (1)$$

$$H_2O_2 \longrightarrow H_2O + 0.5O_2 \qquad (2)$$

$$3,5\text{-DTBC} + 0.5O_2 \longrightarrow 3,5\text{-DTBQ} + H_2O \qquad (3)$$

The formation of hydrogen peroxide was confirmed by iodometry and the blue color of potassium ferricyanide.[17] It was also observed that the complex catalyzed the rapid decomposition of hydrogen peroxide (Reaction 2).

*Kinetic and Spectroscopic Studies.* Kinetic studies were performed with $Mn(acac)_2$ and $Co(acac)_2$ in acetone, which was the most effective solvent for the oxidation. The reaction catalyzed by $Ni(acac)_2$ was too slow to be followed spectrophotometrically. Acetone was stable under the oxidation conditions, for no

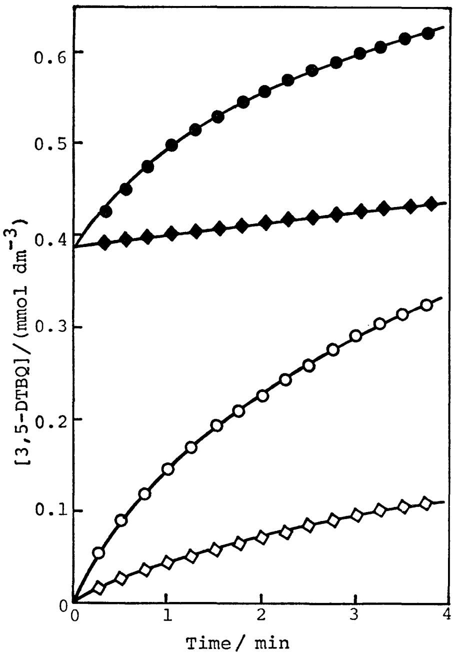


Fig. 2. The oxidation of 3,5-DTBC at 25 °C under air.
(○): $[Mn(acac)_2]_0=3.21\times10^{-5}$ mol $dm^{-3}$ and $[3,5\text{-DTBC}]_0=0.588$ mmol $dm^{-3}$. $r_0=2.30\times10^{-6}$ mol $dm^{-3}$ $s^{-1}$.
(◇): $[Co(acac)_2]_0=7.73\times10^{-5}$ mol $dm^{-3}$ and $[3,5\text{-DTBC}]_0=0.531$ mmol $dm^{-3}$. $r_0=3.11\times10^{-7}$ mol $dm^{-3}$ $s^{-1}$.
(●): $[Mn(acac)_2]_0=3.21\times10^{-5}$ mol $dm^{-3}$, $[3,5\text{-DTBC}]_0=0.588$ mmol $dm^{-3}$, and $[3,5\text{-DTBQ}]_0=0.380$ mmol $dm^{-3}$. $r_0=1.97\times10^{-6}$ mol $dm^{-3}$ $s^{-1}$.
(◆): $[Co(acac)_2]_0=7.73\times10^{-5}$ mol $dm^{-3}$, $[3,5\text{-DTBC}]_0=0.531$ mmol $dm^{-3}$, and $[3,5\text{-DTBQ}]_0=0.380$ mmol $dm^{-3}$. $r_0=0.79\times10^{-7}$ mol $dm^{-3}$ $s^{-1}$.

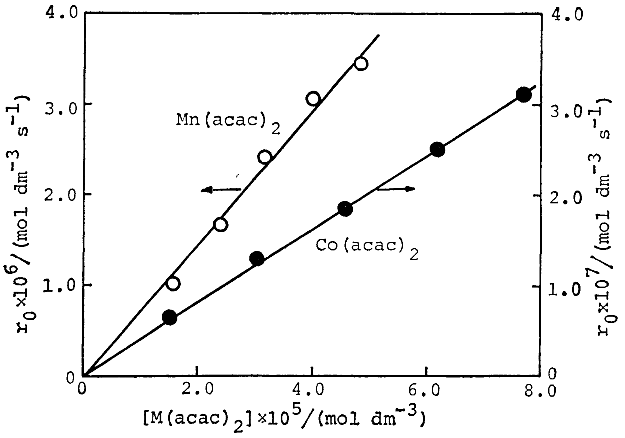


Fig. 3. Dependence of $r_0$ on the catalyst concentration at 25 °C under air.
(○): $[3,5\text{-DTBC}]_0=0.588$ mmol $dm^{-3}$.
(●): $[3,5\text{-DTBC}]_0=0.531$ mmol $dm^{-3}$.

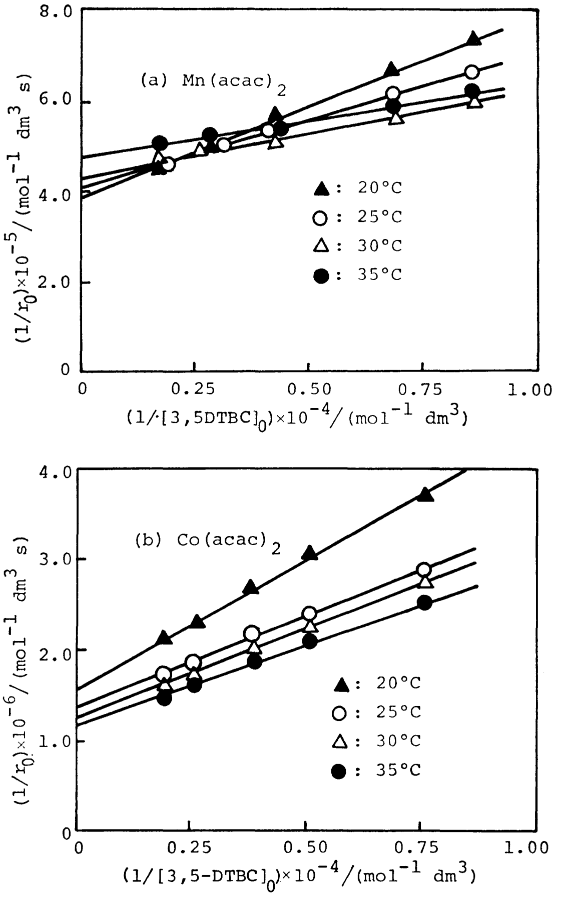


Fig. 4. Plots of $1/r_0$ *vs.* $1/[\text{3,5-DTBC}]_0$.
(a) $[\text{Mn(acac)}_2]_0=3.21\times10^{-5}$ mol dm$^{-3}$.
(b) $[\text{Co(acac)}_2]_0=7.71\times10^{-5}$ mol dm$^{-3}$.

oxidation product of acetone was detected by GLC in gaseous or liquid phase. A typical example of the oxidation of 3,5-DTBC is shown in Fig. 2. Figures 3 and 4 show the clear linear relations between the initial rate and catalyst concentration and between the reciprocals of the initial rate and of 3,5-DTBC concentration. As shown in Fig. 2, the addition of 3,5-DTBQ decreased the initial rate ($r_0$). Since Mn(III) and Co(III) species ($\lambda_{\max}=590$ nm (Mn), 595 nm (Co)) were formed by the addition of 3,5-DTBQ, the retardation may be attributed to the formation of these inactive species. Although Vásvari and Gál reported that Co(III) was formed in the initial stage of the oxidation of 1-phenylethanol catalyzed by Co(acac)$_2$,[13] the oxidation of the metal complexes was rather slow in the present condition and was affected by 3,5-DTBQ. Retardation by the addition of water, which was observed in the oxidation of acrylaldehyde[18] and tributylphosphine[19] by Co(acac)$_2$·2H$_2$O, was not observed even in the presence of $5.0\times10^{-4}$ mol dm$^{-3}$ of water. The effect of the oxygen concentration (oxygen pressure) on the initial rate was studied manometrically in the presence of high concentrations of 3,5-DTBC and catalysts; a first order dependence was observed, as shown in Fig. 5. We have tried to detect radical intermediates by the spin trapping method, as previously reported.[20] Double triplets were observed with 5,5-dimethyl-1-pyrroline 1-oxide in the reaction solution catalyzed by Mn(acac)$_2$: $a_N=14.6$ G (in acetone), 14.2 G (in benzene), $a_{\beta H}=16.6$ G, $g=2.0060$. The radical has not been assigned yet, but it may be a radical such as 3,5-di-*t*-butyl-*o*-benzosemiquinone (3,5-DTBSQ·) rather than the hydroxyl radical ($a_N=14.3$ G, $a_{\beta H}=11.7$ G, $g=2.0061$ in H$_2$O) or the hydroxyl radical ($a_N=15.3$ G, $a_{\beta H}=15.3$ G, $g=2.0060$ in H$_2$O).[21]

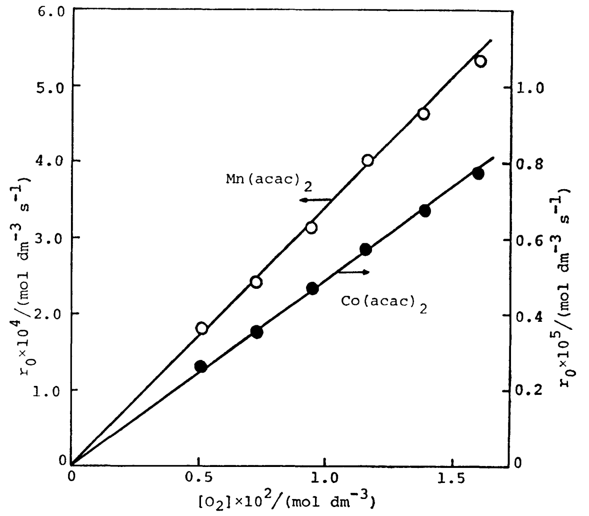
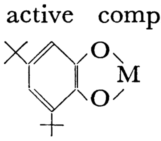
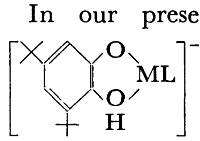


Fig. 5. Dependence of $r_0$ on the oxygen concentration at 25 °C.
$[\text{3,5-DTBC}]_0=0.1$ mol dm$^{-3}$.
(○): $[\text{Mn(acac)}_2]_0=1.25$ mmol dm$^{-3}$.
(●): $[\text{Co(acac)}_2]_0=2.50$ mmol dm$^{-3}$.
(The oxygen concentration was estimated by literature.[15])

*Reaction Mechanism.* In the studies of oxidation of catechol catalyzed by metal ions[4] or metal chelates,[7] aqueous methanol was used as a solvent, and the reaction was promoted in the basic media. The proposed mechanisms in these conditions involved the initial coordination of catechol dianion to metal ion (**1**) or of monoanion to metal chelate (**2**, L: 4-nitrocatechol or tetrabromocatechol),[7] followed by the reaction with oxygen. A ternary complex coordinated by oxygen and catechol anion has been proposed as an active complex.[4,7] In our present conditions, in organic solvents without base, the coordination of catechol to metal complexes as a mono- or dianion is improbable. This is reflected by the small solvent effect. We can expect that catechol itself coordinates to the metal complexes, but the coordination must be much weaker than that of anions in the basic aqueous media. In addition, the acac ligand initially occupies four coordination sites; this is less desirable for the coordination of catechol than the system by Martell,[7] in which a 1 : 1 ratio of metal ion and ligand was used to leave a maximum number of coordination sites open.



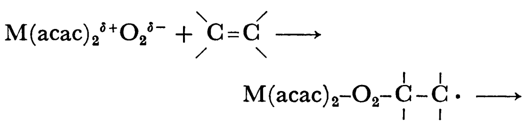
**1**



**2**

On the other hand, Kamiya has studied the oxidation of hydrocarbons (cumene, α-methylstyrene) by metal acetylacetonates, and proposed that the reaction was initiated by the activated oxygen molecule coordinated to metal acetylacetonates (M=Co(II), Mn(II)).[11)]

$$\mathrm{M(acac)_2 + O_2 \rightleftarrows M(acac)_2{}^{\delta+}O_2{}^{\delta-}}$$



Since the present reaction condition is similar to that suggested by Kamiya rather than those of Grinstead or Martell, it seems likely that the oxidation of 3,5-DTBC is initiated by a process similar to the oxidation of hydrocarbon rather than the processes proposed in the basic aqueous media. We propose here the following reaction sequences as a very probable mechanism; it well explains the kinetic results and the formation of hydrogen peroxide and a radical intermediate.

$$\mathrm{M(acac)_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M(acac)_2 \cdots O_2} \qquad (4)$$

$$\mathrm{M(acac)_2 \cdots O_2 + 3{,}5\text{-}DTBC \xrightarrow{k_2} M(acac)_2 + 3{,}5\text{-}DTBSQ\cdot + \cdot OOH} \qquad (5)$$

$$\mathrm{3{,}5\text{-}DTBC + \cdot OOH \xrightarrow{k_3} 3{,}5\text{-}DTBSQ\cdot + HOOH} \qquad (6)$$

$$\mathrm{3{,}5\text{-}DTBSQ\cdot + 3{,}5\text{-}DTBSQ\cdot \xrightarrow{k_4} 3{,}5\text{-}DTBQ + 3{,}5\text{-}DTBC} \qquad (7)$$

$$\mathrm{3{,}5\text{-}DTBSQ\cdot + \cdot OOH \xrightarrow{k_5} 3{,}5\text{-}DTBQ + HOOH} \qquad (8)$$

$$\mathrm{M(acac)_2 + 3{,}5\text{-}DTBQ \xrightarrow{k_6} Inactive\ species} \qquad (9)$$

$$\mathrm{M(acac)_2 + HOOH \xrightarrow{k_7} M(acac)_2 + H_2O + 0.5O_2} \qquad (10)$$

The high initial rate of oxidation without the induction period can be explained by the activation of oxygen by the formation of a weak metal-oxygen bond, followed by the abstraction of hydrogen from 3,5-DTBC to form 3,5-DTBSQ· and ·OOH. The Reactions 6 and 7 were assumed by reference to the autoxidation of hydrocarbon[22)] and the dismutation of 3,5-DTBSQ· anion.[6)] The possible termination reactions other than 7 are 8 and 11, but the latter may be neglected for a low concentration of

$$\mathrm{\cdot OOH + \cdot OOH \longrightarrow HOOH + O_2} \qquad (11)$$

the ·OOH radical compared with that of 3,5-DTBSQ·. Reactions 9 and 10 explain the retardation effect of 3,5-DTBQ and the decomposition of hydrogen peroxide, respectively.

In the initial period of the reaction, we can neglect Reactions 9 and 10. By applying the steady-state treatment for $\mathrm{M(acac)_2\cdots O_2}$, 3,5-DTBSQ·, and ·OOH (Eqs. 12—14), we obtain the rate equation 15 for the formation of 3,5-DTBQ:

$$\frac{\mathrm{d[M(acac)_2\cdots O_2]}}{\mathrm{d}t} \equiv 0 = k_1\mathrm{[M(acac)_2][O_2]} - k_{-1}\mathrm{[M(acac)_2\cdots O_2]} - k_2\mathrm{[M(acac)_2\cdots O_2][3{,}5\text{-}DTBC]} \qquad (12)$$

$$\frac{\mathrm{d[3{,}5\text{-}DTBSQ\cdot]}}{\mathrm{d}t} \equiv 0 = k_2\mathrm{[M(acac)_2\cdots O_2][3{,}5\text{-}DTBC]} + k_3\mathrm{[3{,}5\text{-}DTBC][\cdot OOH]} - 2k_4\mathrm{[3{,}5\text{-}DTBSQ\cdot]^2} - k_5\mathrm{[3{,}5\text{-}DTBSQ\cdot][\cdot OOH]} \qquad (13)$$

$$\frac{\mathrm{d[\cdot OOH]}}{\mathrm{d}t} \equiv 0 = k_2\mathrm{[M(acac)_2\cdots O_2][3{,}5\text{-}DTBC]} - k_3\mathrm{[3{,}5\text{-}DTBC][\cdot OOH]} - k_5\mathrm{[3{,}5\text{-}DTBSQ\cdot][\cdot OOH]} \qquad (14)$$

$$\frac{\mathrm{d[3{,}5\text{-}DTBQ]}}{\mathrm{d}t} = k_4\mathrm{[3{,}5\text{-}DTBSQ\cdot]^2} + k_5\mathrm{[3{,}5\text{-}DTBSQ\cdot][\cdot OOH]} = k_2\mathrm{[M(acac)_2\cdots O_2][3{,}5\text{-}DTBC]} \qquad (15)$$

Using the stoichiometric equation 16, we obtain Eq. 17:

$$\mathrm{[M(acac)_2] = [M(acac)_2]_0 - [M(acac)_2\cdots O_2]} \qquad (16)$$

$$\mathrm{[M(acac)_2\cdots O_2]} = \frac{k_1\mathrm{[M(acac)_2]_0[O_2]}}{k_1\mathrm{[O_2]} + k_{-1} + k_2\mathrm{[3{,}5\text{-}DTBC]}} \qquad (17)$$

Assuming $\mathrm{[3{,}5\text{-}DTBC] \simeq [3{,}5\text{-}DTBC]_0}$ and $\mathrm{[O_2] \simeq [O_2]_0}$, we obtain the equation for the initial rate of the formation of 3,5-DTBQ and its linearized form:

$$\left(\frac{\mathrm{d[3{,}5\text{-}DTBQ]}}{\mathrm{d}t}\right)_0 = r_0 = \frac{k_1k_2\mathrm{[3{,}5\text{-}DTBC]_0[O_2]_0[M(acac)_2]_0}}{k_1\mathrm{[O_2]_0} + k_{-1} + k_2\mathrm{[3{,}5\text{-}DTBC]_0}} \qquad (18)$$

$$1/r_0 = \frac{k_1\mathrm{[O_2]_0} + k_{-1}}{k_1k_2\mathrm{[M(acac)_2]_0[O_2]_0}}\left(\frac{1}{\mathrm{[3{,}5\text{-}DTBC]_0}}\right) + \frac{1}{k_1\mathrm{[M(acac)_2]_0[O_2]_0}} \qquad (19)$$

Eqs. 18 and 19 are consistent with the results shown in Figs. 3 and 4, respectively. If we ignore the pre-equilibrium (Eq. 4), the reactions of Eqs. 4 and 5 are described by Eq. 20.

$$\mathrm{M(acac)_2 + O_2 + 3{,}5\text{-}DTBC \xrightarrow{k} M(acac)_2 + 3{,}5\text{-}DTBSQ\cdot + \cdot OOH} \qquad (20)$$

In this case, the initial rate equation 21 is obtained by a similar steady-state treatment.

$$r_0 = k\mathrm{[M(acac)_2]_0[O_2]_0[3{,}5\text{-}DTBC]_0} \qquad (21)$$

Eq. 21 is not consistent with the results in Fig. 4, indicating that we can not neglect the pre-equilibrium.

The first order dependence of the rate on the oxygen concentration, as shown in Fig. 5, is consistent with the rate equation 18, because the rate equation 22 is derived by assuming $k_1\mathrm{[O_2]_0} + k_{-1} \ll k_2\mathrm{[3{,}5\text{-}DTBC]_0}$. This assumption

$$r_0 = k_1\mathrm{[M(acac)_2]_0[O_2]_0} \qquad (22)$$

is not unreasonable in the presence of a high concentration of 3,5-DTBC (about $10^3$ greater than the concentrations in the spectroscopic studies). We observed that the rate was independent of the concentration of 3,5-DTBC in the region of 0.1—0.3 mol dm$^{-3}$; this result supports our assumption.

Reaction 5 is the step of the abstraction of the hydrogen of catechol by the activated oxygen, and may proceed stepwise *via* a ternary complex, but the kinetic results are not enough to discriminate

$$\mathrm{M(acac)_2\cdots O_2 + 3,5\text{-}DTBC \rightleftharpoons M(acac)_2\cdots O_2(3,5\text{-}DTBC)}$$

$$\mathrm{M(acac)_2\cdots O_2(3,5\text{-}DTBC) \longrightarrow M(acac)_2 + 3,5\text{-}DTBSQ\cdot + \cdot OOH}$$

between a one-step and a two-step process. The coordination of 3,5-DTBC to the oxygen complex is not impossible, because acac can coordinate as a monodentate ligand, but the complex seems far less stable than the ternary complexes proposed by Grinstead[4)] or Martell.[7)] Vásvari and Gál has proposed the splitting of the O–O bond by the following reactions in the oxidation of 1-phenylethanol (ROH) with $\mathrm{Co(acac)_2}$,[12)] but the process

$$\mathrm{ROH\cdot Co(acac)_2\cdots O_2 + Co(acac)_2 \longrightarrow Co(acac)_2O\cdot + ROH\cdot Co(acac)_2\cdot O}$$

$$\mathrm{ROH\cdot Co(acac)_2O\cdot \longrightarrow Co(acac)_2OH(RO\cdot)}$$

$$\mathrm{Co(acac)_2O\cdot + ROH \longrightarrow Co(acac)_2OH(RO\cdot)}$$

is not consistent with the formation of hydrogen peroxide in the present system.

The reversible formation of a 1 : 1 dioxygen-transition metal complex and the reaction of the activated oxygen are of current interest. Many examples of a dioxygen cobalt complex have been found,[23)] and recently the formation of dioxygen complexes of manganese tetraphenylporphyrin[24)] and phthalocyanin[25)] have been reported. Thus, the formations of the dioxygen complexes of metal acetylacetonates are probable. The values of $k_1$ (Reaction 4) were estimated from the intercepts Fig. 4 (Table 2), or from the slopes in Fig. 5 (27.5 and 0.2 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for Mn and Co, respectively). The agreement of the values estimated in the different conditions was fairly good for $\mathrm{Mn(acac)_2}$, but rather poor for $\mathrm{Co(acac)_2}$. The smaller values obtained from Fig. 5 may be ascribed to the fact that the reaction was retarded by 3,5-DTBQ even in the initial stage, especially in the case of $\mathrm{Co(acac)_2}$. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for this step are given in Table 2, and the values for the cobalt complex are comparable to those of $\mathrm{[Co(Ph_2PCH{=}CHPPh_2)(O_2)]^+}$ ($\Delta H^{\ddagger}=14.2\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}=-117\ \mathrm{J\,mol^{-1}\,K^{-1}}$).[26)] The proposed mechanism is consistent with the order of the catalytic activity (Mn>Co>Ni), because it is expected that the low redox potential facilitates the electron transfer from metal to oxygen. The inactivity of $\mathrm{Fe(acac)_2}$ may be ascribed to the stabilization of a Fe(III) species rather than $\mathrm{Fe(acac)_2\cdots O_2}$ by the extreme electron transfer. We could not find any product formed by the aromatic ring cleavage, and this indicates that the activation of oxygen by coordination to $\mathrm{M(acac)_2}$ is not enough, compared with that of superoxide[3)] or singlet oxygen.[27)]

TABLE 2. KINETIC PARAMETERS OF $k_1$

| Catalyst[a)] | Temp (°C) | $1/(k_1 \times [\mathrm{M(acac)_2}] \times [\mathrm{O_2}])$[b)] | $k_1$ ($\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) | $\Delta H^{\ddagger}$ ($\mathrm{kJ\,mol^{-1}}$) | $\Delta S^{\ddagger}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$) |
|---|---|---|---|---|---|
| $\mathrm{Mn(acac)_2}$ | 20 | $3.96\times10^5$ | 29.9 | 4.6±0.8 | −200±2 |
| | 25 | $4.09\times10^5$ | 31.5 | | |
| | 30 | $4.33\times10^5$ | 33.0 | | |
| | 35 | $4.79\times10^5$ | 34.0 | | |
| $\mathrm{Co(acac)_2}$ | 20 | $1.55\times10^6$ | 3.17 | 29.7±0.8 | −135±2 |
| | 25 | $1.35\times10^6$ | 3.96 | | |
| | 30 | $1.20\times10^6$ | 4.95 | | |
| | 35 | $1.15\times10^6$ | 5.98 | | |

a) The concentrations of catalysts were same as those of Fig. 4. b) The concentrations of oxygen at 20, 25, 30, and 35 °C were estimated to be 2.63, 2.42, 2.18, and 1.88 $\mathrm{mmol\,dm^{-3}}$, respectively.[15)]

From the viewpoint of the potential use of the dioxygen metal complex as catalysts for the oxidation of organic substrates, this work has shown that metal acetylacetonates function as an efficient catalyst for the oxidation 3,5-DTBC. Mckillop and Ray[10)] have recently shown that $\mathrm{Co(acacene)(O_2)\cdot H_2O}$ catalyzes the oxidation of hydroquinones; $\mathrm{Co(acacene)(O_2)\cdot H_2O}$ was presumed to be an active species, but no mechanism has been proposed. The mechanism proposed here is a new radical mechanism for the oxidation of 3,5-DTBC which does not involve the redox of metal ion[4)] and is different from the ionic mechanism.[7)] We have not studied in detail the oxidation catalyzed by $\mathrm{Cu(acac)_2}$ and metal carboxylates, which may be explained by the most common pathway for catalysis by transition metal complexes involving the decomposition of peroxides.

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