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Ligand Effects of Amine Chelates in the Decomposition of 1,2,3,4-Tetrahydro-1-naphthyl Hydroperoxide Catalyzed by Cobalt(II) and Copper(II) Salts

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The ligand effects of 2,2′-bipyridine, ethylenediamine, and diethylenetriamine on the rate of decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide catalyzed by cobalt(II) decanoate and copper(II) decanoate in chlorobenzene were kinetically studied. The results were compared with the redox potentials measured in nonaqueous media and the spectral data of cobalt(II) and copper(II) complexes. It was found that the catalytic activity of Me(II) decanoate–ethylenediamine, or -diethylenetriamine complex (Me=Co, Cu) becomes maximum at 1/2 the molar ratio of ethylenediamine to Me(II), or at 1/3 that of diethylenetriamine to Me(II), and that further addition of these amines deactivates the catalysts. The activity of copper(II) decanoate increased from $k=0$ to $k=1.4\times10^{-3}$ s^{-1} on addition of 2,2′-bipyridine when the molar ratio of 2,2′-bipyridine to copper(II) decanoate was 0—4. No maximum activity was observed in copper(II) decanoate–2,2′-bipyridine system. A large excess of 2,2′-bipyridine, 150 times the quantity of copper(II) salt, did not decrease the decomposition rate in contrast to the case of the cobalt(II) decanoate–2,2′-bipyridine system. The difference in ligand effect of ethylenediamine, diethylenetriamine and 2,2′-bipyridine on cobalt(II) ion and copper(II) ion was discussed on the basis of the properties of these complexes.

The decomposition reaction of hydroperoxide catalyzed by transition metal complex, regarded as an important initiation reaction in autoxidation, has been extensively studied[1] during the last decade. Most of the studies afforded kinetic data presenting many kinds of reaction schemes and disclosing the outline of the reaction. However, no detailed account was given, and the relation between the structure and property of metal complex and its catalytic activity in the decomposition of hydroperoxide not being made clear. Clarification of this problem would be profitable not only for industrial chemistry but also for a new field of autoxidation in life science.

In a previous paper,[2] we reported the new finding of maximum activity in the decomposition reaction of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide catalyzed by cobalt(II) decanoate–2,2′-bipyridine in chlorobenzene, giving explanation on the basis of the change of redox potentials, spectral data and structural variations of catalysts. In this paper we report the ligand effect of 2,2′-bipyridine and aliphatic amines such as ethylenediamine, diethylenetriamine on cobalt(II) decanoate and copper(II) decanoate.

Experimental

Materials. Cobalt (II) decanoate ($CoDe_2$) and copper (II) decanoate ($CuDe_2$) were prepared by the conventional method[3] and used after being dried in a vacuum at 70 °C for 5 h. Elemental analyses were carried out on $CoDe_2$ and $CuDe_2$. Found: C, 58.2; H, 10.0%. Calcd for $CoDe_2[Co(C_{10}H_{19}O_2)_2]$: C, 59.8; H, 9.0%. Found: C, 58.0; H, 9.6%. Calcd for $CuDe_2[Cu(C_{10}H_{19}O_2)_2]$: C, 59.1; H, 9.4%. 1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide (THP) was prepared by the autoxidation of 1,2,3,4-tetrahydronaphthalene (tetralin) and recrystallized from heptane.[4] Ethylenediamine (en), diethylenetriamine (dien), 1,6-hexanediamine, 1,4-butanediamine, 2,2′-bipyridine (bpy) and 2,2′: 6′,2″-terpyridine (tpy) were purified before use. A mixed solution of the metal decanoate and the amine chelate were allowed to stand at room temperature for 15 h to equilibrate and then subjected to reactions and measurements.

Measurements. The decomposition of THP proceeded in chlorobenzene at 45 °C, the rate of decomposition being determined by iodometry. The redox potentials of catalysts were measured by cyclic voltammetry in dichloromethane at room temperature with use of tetrabutylammonium perchlorate as a supporting electrolyte. A saturated calomel electrode was used as a reference electrode. The concentration of complex was less than 10 mM. Infrared spectra were recorded as Nujol mulls on a JASCO-IRA 2 spectrophotometer. Details of experimental procedures were reported.[2]

Results and Discussion

Effect of Ethylenediamine and Diethylenetriamine on Cobalt(II) Salt. The effect of ethylenediamine and that of diethylenetriamine on the rate of the $CoDe_2$-catalyzed decomposition of THP in chlorobenzene are shown in Figs. 1 and 2, respectively. The rate of decomposition increases with the addition of the amines, maximum activities being found at the molar ratio $[en]/[CoDe_2]=$

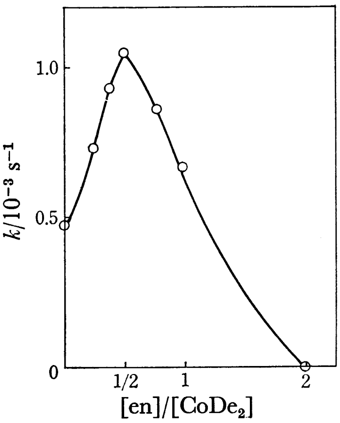

Fig. 1. Effect of ethylenediamine on the rate of decomposition of THP catalyzed by $CoDe_2$ in chlorobenzene at 45 °C.
$[CoDe_2]=2\times10^{-4}$ M, $[THP]=5\times10^{-2}$ M.

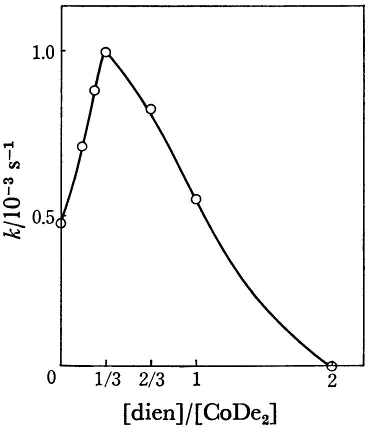

Fig. 2. Effect of diethylenetriamine on the rate of decomposition of THP catalyzed by CoDe$_2$ in chlorobenzene at 45 °C.
[CoDe$_2$]$=2\times10^{-4}$ M, [THP]$=5\times10^{-2}$ M.

1/2, [dien]/[CoDe$_2$]$=1/3$. The maximum value, almost the same in both systems, is one third of that of CoDe$_2$–bpy system. Unlike the case of the CoDe$_2$–bpy system, the CoDe$_2$ catalyst was deactivated by the amines at the raios [en]/[CoDe$_2$], [dien]/[CoDe$_2$] higher than 2.

The difference in activation of catalyst between the CoDe$_2$–bpy system and the CoDe$_2$–en, –dien systems can be attributed to the difference in electron donative force between 2,2′-bipyridine and two aliphatic amines; coordination of 2,2′-bipyridine having strong electron donative force causes an increase in the reductive force of cobalt(II) ion and weakening in the Co–O(decanoate) bond strength, resulting in facile coordination of hydroperoxide to the central cobalt(II) ion as well as the acceleration of cleavage of hydroperoxide molecule. Since ethylenediamine and diethylenetriamine do not have such a strong electron donative force as 2,2′-bipyridine, they can only change the reductive force of cobalt(II) ion moderately and not weaken the Co–O (decanoate) bond strength, resulting in smaller catalytic activities of the CoDe$_2$–en, –dien than that of the CoDe$_2$–bpy system. The IR data of the CoDe$_2$–en and CoDe$_2$–dien complexes given in Table 1 support our view. The shift of C–O stretching band to a higher wave number with an increase in the amount of 2,2′-bipyridine added as in the case of CoDe$_2$–bpy system shows the weakening in the Co–O(decanoate) bond strength. No shift of C–O stretching band upon the addition of ethylenediamine or diethylenetriamine suggests a very small effect due to the amines on the Co–O(decanoate) bond strength. The redox potentials of the CoDe$_2$–en complexes and the CoDe$_2$–dien complexes in dichloromethane or in *N,N*-dimethylformamide could not be obtained. No new C-T band or remarkable change in visible and ultraviolet spectra could be found.

Table 1. Infrared absorption bands and decomposition rates of THP for CoDe$_2$–en, CoDe$_2$–dien and CoDe$_2$–bpy complexes

Complex	C–O$_{\text{st.}}$, cm^{-1}	$k/10^{-3}$ s^{-1}
CoDe$_2$	1550	0.5
CoDe$_2$–en(1: 1/2)	1550	1.1
(1: 1)	1550	0.7
(1: 2)	1550	0.0
CoDe$_2$–dien(1: 1/3)	1550	1.1
(1: 2/3)	1550	0.9
(1: 1)	1550	0.5
(1: 2)	1550	0.0
CoDe$_2$–bpy(1: 1/2)	1570	3.7
(1: 1)	1590	1.3
(1: 2)	1595	1.3

The difference in the deactivation of catalyst between the CoDe$_2$–bpy complex and the CoDe$_2$–en, –dien complexes can be attributed to the difference in their steric factors. In the CoDe$_2$–bpy system, the steric hindrance makes it difficult for the second 2,2′-bipyridine to coordinate to a cobalt(II) ion. But in the CoDe$_2$–en, –dien systems, the steric hindrance of the amines smaller than that of 2,2′-bipyridine makes easier the coordination of the second ethylenediamine, diethylenetriamine to a cobalt(II) ion. Occupation of the coordination site by the amines may inevitably result in the deactivation of the CoDe$_2$ catalyst.

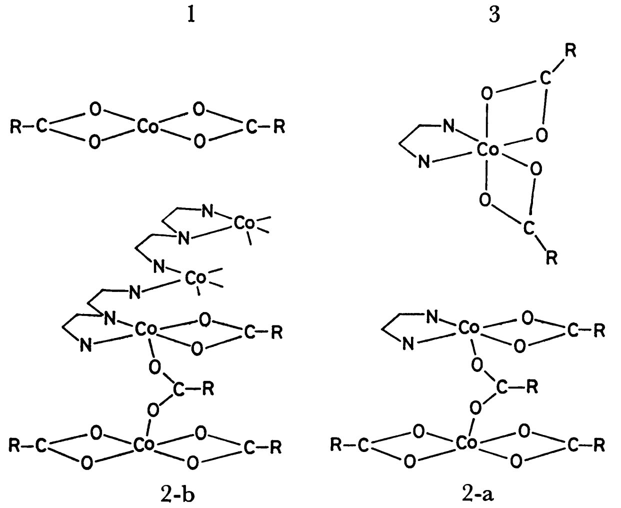

Fig. 3. Proposed structure of CoDe$_2$–en, –dien complexes.
1) CoDe$_2$, 2-a) CoDe$_2$–en (1: 1/2), 2-b) CoDe$_2$–dien (1: 1/3), 3) CoDe$_2$–en (1: 1).

The appearance of maximum suggests that the same structural variation[2)] as that of the CoDe$_2$–bpy system occurs. Figure 3 shows the proposed structures of CoDe$_2$–en, –dien complexes. CoDe$_2$ (Structure 1) has a lower activity, which can be attributed to its poor reductive force. CoDe$_2$–en (1: 1/2) or CoDe$_2$–dien (1: 1/3) (Structure 2-a, 2-b) has the highest activity. This structure has a vacant coordination site and an adequate reductive force. CoDe$_2$–en (1: 1) (Structure 3) shows relatively low activity, the structure having a strong reductive force but no vacant coordination site.

From the value of the ratio [Chelate]/[Metal] of maximum activity in CoDe$_2$–bpy, CoDe$_2$–en, and CoDe$_2$–dien systems, one metal to one N atom complex seems to have the highest activity. An exceptional case is the CoDe$_2$–2,2′: 6′,2″-terpyridine system. A maximum value was found at the ratio [tpy]/[$CoDe_2$] = 1/2 instead of 1/3. Steric difficulty would not allow all the pyridine rings to coordinate to a cobalt(II) ion.

Figure 4 shows the effect of the length of carbon chain in aliphatic amine on the rate of the $CoDe_2$–catalyzed decomposition of THP in chlorobenzene. The ability of activation or deactivation of the added amines decreases with an increase in the carbon number of the carbon chain. This can be explained by the fact that their chelate effect decrease with increase in the carbon number of the carbon chain; the decrease of the chelate effect would decrease the ability of activation and deactivation.

Effect of 2,2′-Bipyridine on Copper(II) Salt. The effect of 2,2′-bipyridine on the rate of the $CuDe_2$–catalyzed decomposition of THP in chlorobenzene is shown in Fig. 5. The catalytic activity of $CuDe_2$ increases monotonously with the addition of 2,2′-bipyridine, the activity curve becoming a gradual slope in the ratio [bpy]/[$CuDe_2$] higher than 1. The k value at [bpy]/[$CuDe_2$] = 1—2 is close to that of the $CoDe_2$–bpy complexes at [bpy]/[$CoDe_2$] = 1—2 (Table 2).

The redox potentials of $CuDe_2$–bpy complexes measured in dichloromethane by cyclic voltammetry are given in Table 2 with the values of $CoDe_2$–bpy complexes. The shift of redox potentials to the negative direction with the addition of 2,2′-bipyridine, a tendency similar to the case of $CoDe_2$–bpy system, will help to elucidate the increase in activity. The decomposition of hydroperoxide by copper(II) complex has been studied extensively.5) Some workers reported that the coordination of 2,2′-bipyridine to copper(II) ion increases the catalytic activity of copper(II) complex.6) The decomposition reaction of hydroperoxide by copper(II) ion proceeds with Cu(II)/Cu(I) redox reaction, the difficulty of reproduction of copper(I) ion giving new schemes differing from those of cobalt(II) and manganese(II) systems. The rate-determining step seems to be the decomposition process of the copper–

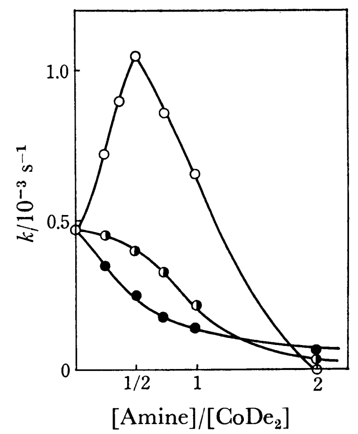

Fig. 4. Effect of aliphatic amines on the rate of decomposition of THP catalyzed by $CoDe_2$ in chlorobenzene at 45 °C.
(-●-) 1,6-Hexanediamine, (-◑-) 1,4-butanediamine, (-○-) ethylenediamine.
[$CoDe_2$] = 2×10^{-4} M, [THP] = 5×10^{-2} M.

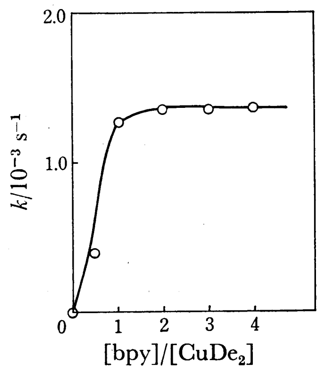

Fig. 5. Effect of 2,2′-bipyridine on the rate of decomposition of THP catalyzed by $CuDe_2$ in chlorobenzene at 45 °C.
[$CuDe_2$] = 2×10^{-4} M, [THP] = 5×10^{-2} M.

TABLE 2. COMPARISON OF VOLTAMMETRIC DATA WITH THE DECOMPOSITION RATES OF THP FOR $CuDe_2$–bpy AND $CoDe_2$–bpy COMPLEXES

Complex	Electrode reaction	$E_{1/2}$, V[a)]	$k/10^{-3}\ s^{-1}$
$CuDe_2$	Cu(II) + e ⟶ Cu(I)	−0.43[b)]	0.0
	Cu(I) − e ⟶ Cu(II)	−0.36[b)]	
$CuDe_2$–bpy (1 : 1/2)	Cu(II) + e ⟶ Cu(I)	−0.56	0.4
	Cu(I) − e ⟶ Cu(II)	−0.40	
(1 : 1)	Cu(II) + e ⟶ Cu(I)	−0.64	1.3
	Cu(I) − e ⟶ Cu(II)	−0.43	
(1 : 2)	Cu(II) + e ⟶ Cu(I)	−0.67	1.4
	Cu(I) − e ⟶ Cu(II)	−0.43	
$CoDe_2$	Co(II) − e ⟶ Co(III)	0.80	0.5
	Co(III) + e ⟶ Co(II)	0.84	
$CoDe_2$–bpy (1 : 1/2)	Co(II) − e ⟶ Co(III)	0.67	3.7
	Co(III) + e ⟶ Co(II)	0.70	
(1 : 1)	Co(II) − e ⟶ Co(III)	0.60	1.3
	Co(III) + e ⟶ Co(II)	0.63	
(1 : 2)	Co(II) − e ⟶ Co(III)	0.59	1.3
	Co(III) + e ⟶ Co(II)	0.59	

a) Potential sweep rate: 0.05 V/s. (V *vs.* SCE). b) Decanoic acid (10^{-3} M) added to raise the solubility of $CuDe_2$ to dichloromethane.

hydroperoxide complex. The redox force of copper ion might be the main factor of catalytic activity. The shift of redox potential to the negative direction shows an increase of reductive force of copper(I) ion which accelerates the cleavage of the hydroperoxide molecule, and also an increase of electron density of the copper ion which stabilizes[7] the copper–hydroperoxide complex. The increase in activity can be attributed to the change of the redox potential of catalyst.

The fact that the redox potential of copper(II) complexes is smaller than that of cobalt(II) complex is reasonable from their ionization potentials. The increase of catalytic activity upon the addition of 2,2′-bipyridine in the $CuDe_2$–bpy system or in the $CoDe_2$–bpy system can be explained by the change of their redox potentials. From a comparison of the activity of copper(II) complexes with that of cobalt(II) complexes, the small defference between the two activities can not be explained by the large difference between their redox potentials; the $CuDe_2$–bpy (1: 2) complex has almost the same activity as that of the $CoDe_2$–bpy (1: 2) complex, in spite of the large difference in the redox potential between the $CuDe_2$–bpy (1: 2) complex and the $CoDe_2$–bpy (1: 2) complex. This suggests that the $CuDe_2$–bpy system has a reaction mechanism differing from the $CoDe_2$–bpy system.

A maximum activity observed in the $CoDe_2$–bpy system[2] was absent in the $CuDe_2$–bpy system This is explained as follows: With an increase of added 2,2′-bipyridine the concentration of the inactive $CuDe_2$ may change to the active $CuDe_2$–bpy complex having a different structure from the five coordination $CoDe_2$–bpy (1: 1/2) type complex. Formation of the five coordination complex with 2,2′-bipyridine will be difficult for $CuDe_2$. In acetic acid, no catalytic activity was found on both $Cu(OAc)_2$ and $Cu(OAc)_2$–bpy (1: 1) complex.

The effect of a large amount of 2,2′-bipyridine on $CoDe_2$ and $CuDe_2$ is given in Table 3. The activity of $CoDe_2$ decreases to half the value of $CoDe_2$ with the addition of one hundred times of 2,2′-bipyridine. However, $CuDe_2$ could not be deactivated by the addition of one hundred fifty times of 2,2′-bipyridine. This can be explained by the difficult addition of three 2,2′-bipyridine to copper(II) ion. The $CuDe_2$–bpy (1: 1) complex has no absorption band in the 350 —400 nm region. However, C-T band ($\lambda_{max}=380$ nm) was found on the $CuDe_2$–bpy (1: 100) complex.

TABLE 3. DECOMPOSITION RATES OF THP FOR $CoDe_2$–bpy AND $CuDe_2$–bpy COMPLEXES IN CHLOROBENZENE AT 45 °C

Complex	$k/10^{-3}$ s^{-1}
$CoDe_2$	0.49
$CoDe_2$–bpy(1: 1)	1.32
(1: 50)	0.56
(1: 100)	0.28
(1: 150)	0.27
$CuDe_2$	0.00
$CuDe_2$–bpy(1: 1)	1.40
(1: 50)	0.91
(1: 100)	1.76
(1: 150)	1.78

[Metal]$=2\times10^{-4}$M, [THP]$=5\times10^{-2}$ M.

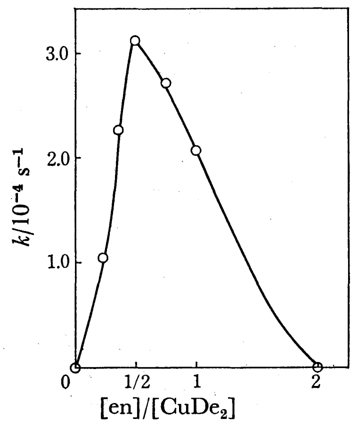

Fig. 6. Effect of ethylenediamine on the rate of decomposition of THP catalyzed by $CuDe_2$ in chlorobenzene at 45 °C.
[$CuDe_2$]$=2\times10^{-4}$ M, [THP]$=5\times10^{-2}$ M.

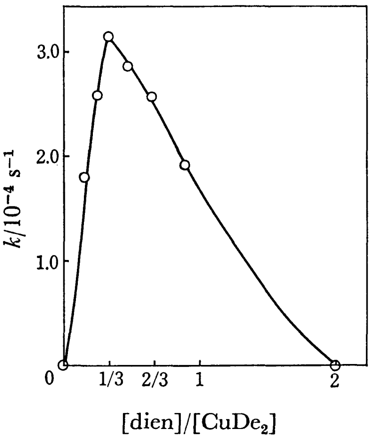

Fig. 7. Effect of diethylenetriamine on the rate of decomposition of THP catalyzed by $CuDe_2$ in chlorobenzene at 45 °C.
[$CuDe_2$]$=2\times10^{-4}$ M, [THP]$=5\times10^{-2}$ M.

Effect of Ethylenediamine and Diethylenetriamine on Copper(II) Salt. The effect of ethylenediamine and that of diethylenetriamine on the rate of the $CuDe_2$-catalyzed decomposition of THP in chlorobenzene are shown in Figs. 6 and 7, respectively. They show the same pattern as that of the $CoDe_2$–en and $CoDe_2$–dien systems. The rate increases with the addition of ethylenediamine or diethylenetriamine, the maximum activities being found at the ratio of [en]/[$CuDe_2$]$=1/2$ and [dien]/[$CuDe_2$]$=1/3$. $CuDe_2$ was deactivated by the amines at the ratio [en]/[$CuDe_2$], [dien]/[$CuDe_2$] higher than 2. The maximum values were one third of those of the $CoDe_2$–en, –dien systems. Appearance of a maximum in these systems suggests that the same structural variation occurs as in the $CoDe_2$–bpy system in $CuDe_2$–en, –dien systems. The order of maximum values is $CoDe_2$–bpy$>$$CoDe_2$–en, –dien$>$$CuDe_2$–en, –dien.

The following conclusions on the ligand effect were obtained from our results. 1) The catalytic activities of cobalt(II) ion and copper(II) ion in the deocmposition of THP change with the concentration of amine chelate added. 2) Aliphatic amine chelate acts as a deactivator and aromatic amine chelate as an activator. 3) In most cases a maximum activity was found at the molar ratio of [Chelate]/[Metal] = 1/(Number of N atom of chelate). 4) All the effects of chelate ligands can be explained in terms of the variation of structure or electrochemical and spectral property of catalyst.

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