Ligand Effects of 2,2′-Bipyridine in the Decomposition of 1,2,3,4-Tetrahydro-1-naphthyl Hydroperoxide Catalyzed by Cobalt(II) Salt

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The ligand effect of 2,2′-bipyridine on the rate of the decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide catalyzed by cobalt(II) decanoate in chlorobenzene was kinetically studied and compared with the redox potentials and the spectral data of cobalt(II) complexes. The activity of the anhydrous cobalt(II) decanoate increased by a factor of from three to seven by the addition of 2,2′-bipyridine when the molar ratio of 2,2′-bipyridine to cobalt was 0.25 to 2. It was found that the catalytic activity of the anhydrous cobalt(II) decanoate–2,2′-bipyridine complex shows a remarkable maximum value at the molar ratio of 2,2′-bipyridine to cobalt of 0.5. This novel finding can be explained on the basis of the redox potential measured by cyclic voltammetry in dichloromethane, the IR data, and the structure of the catalyst. The coordination of 2,2′-bipyridine causes the redox potential to change from 0.80—0.84 V to 0.60—0.64 V (*vs.* SCE) and also weakens the Co-O(decanoate) bond strength, resulting in a facile coordination of hydroperoxide to the cobalt ion as well as the acceleration of cleavage of hydroperoxide. The maximum activity was explained by the proposed structure of the cobalt(II) decanoate-2,2′-bipyridine (1 : 1/2) complex with a fairly low redox potential and a vacant coordination site.

The metal-catalyzed decomposition of alkyl hydroperoxide is the most common pathway of catalysis by transition-metal complexes in the autoxidation reaction. A catalytic cycle is possible *via* the following reduction oxidation reaction by two valency-state metal ions:

$$\mathrm{ROOH} + \mathrm{M}^{(n-1)+} \longrightarrow \mathrm{RO}\cdot + \mathrm{M}^{n+} + \mathrm{OH}^-$$

$$\mathrm{ROOH} + \mathrm{M}^{n+} \longrightarrow \mathrm{RO_2}\cdot + \mathrm{M}^{(n-1)+} + \mathrm{H}^+$$

Many kinetic investigations[1] of metal-catalyzed decomposition have been undertaken, but many points about the role of the metal are still obscure. A "ligand-effect" investigation must be one of the most valid probes to elucidate the role of the metal and also to serve as a gateway to many applications. Although, in some works[2] dealing with the kinetics of autoxidation, the fact of the activation or deactivation of a metal catalyst by a chelating agent has been mentioned, no systematic study has yet been presented.

The ligand effect in autoxidation seems to depend on the kind of metal, ligand and solvent, but it is hard to explain it because of its complexity. The difficulties derived from its complexity will be clarified only by the quantitative investigation of each factor affecting the catalytic activity. Not only a kinetic but also a structural study is needed to clarify the reaction mechanism. In this paper, we will report the interesting ligand effect of 2,2′-bipyridine in the cobalt salt-catalyzed decomposition of hydroperoxide.

Experimental

Materials. Cobalt(II) decanoate ($\mathrm{CoDe_2}$) was prepared according to the method of Heaton and Uri.[3] An aqueous solution of cobalt(II) sulfate was added to an aqueous solution of sodium decanoate. The resulting precipitate was washed with hot water and dried in two ways. The pink-colored catalyst, defined as the cobalt(II) decanoate (A) ($\mathrm{CoDe_2}$(A)), was air-dried at room temperature. The other, blue-colored catalyst, defined as the cobalt(II) decanoate (B) ($\mathrm{CoDe_2}$(B)), was obtained by drying under a vacuum at 70 °C for 5 h. Elemental analyses were carried out on both $\mathrm{CoDe_2}$(A) and $\mathrm{CoDe_2}$(B). Found: C, 54.6; H, 10.4%. Calcd for $\mathrm{CoDe_2}$(A) $[\mathrm{Co(C_{10}H_{19}O_2)_2\cdot 2H_2O}]$: C, 54.9; H, 10.0%. Found: C, 58.2; H, 10.0%. Calcd for $\mathrm{CoDe_2}$(B) $[\mathrm{Co(C_{10}H_{19}O_2)_2}]$: C, 59.8; H, 9.0%. 2,2′-Bipyridine (bpy) was further purified by recrystallization from heptane and dried under a vacuum at room temperature. Mixed solutions of cobalt(II) decanoate and 2,2′-bipyridine, a very strong chelating agents with a high stability constant,[4] were allowed to stand at room temperature for 15 h to equilibrate and then submitted to the reaction and other measurements. 1,2,3,4-Tetrahydro-1-naphthyl hydrperoxide (THP) was prepared by a modification of the conventional method.[5] After the autoxidation of 1,2,3,4-tetrahydronaphthalene (tetralin) initiated by azobisisobutyronitrile at 50 °C for 60 h, the oxidation products were concentrated by distillation under reduced pressure and then crystallized from a solution upon cooling to 0 °C. This crystal was recrystallized from heptane and then dried under a vacuum at room temperature. The purified hydroperoxide was confirmed to be 99.0% pure by iodometric titration. Dichloromethane was dried by calcium chloride and purified by repeated distillations. All the other chemicals were of a reagent grade.

Decomposition of THP. A 50-ml three-necked round-bottomed flask was filled with a solution (40 ml) containing a catalyst and maintained at the reaction temperature. Argon gas was introduced into the system to remove any dissolved oxygen. A solution of THP (10 ml) was prepared separately and heated to the reaction temperature. The reaction was started by the addition of all the THP solution. A certain portion of the solution (2 ml) was withdrawn from the reaction mixture at regular intervals and subjected to iodometric titration to determine the concentration of hydroperoxide. The decomposition products were analyzed by gas chromatography on a 3-m column packed with PEG-20M. The carrier gas was helium, and the column temperature was 200 °C.

Electrochemical and Spectral Measurements. Cyclic voltammetry was done using a potentiostat, a function generator, and a X-Y recorder. The electrode system consisted of a saturated calomel reference electrode (SCE), a platinum plate used as working electrode, and a platinum wire used as a counter electrode. Measurements were made at room temperature in a glass cell to which the reference electrode was connected with a double salt bridge. A solution of the complex (1—10 mM) was prepared by dissolving a weighed quantity in a measured volume of dichloromethane. As the supporting electrolyte tetrabutylammonium perchlorate was added to this solution, which was flushed with nitrogen for ten minutes prior to measurement. The visible and ultraviolet spectra were obtained in chlorobenzene using a Hitachi-124 spectrophotometer. The infrared spectra were obtained by the Nujol method using a JASCO-IRA 2 spectrophotometer.

Results

Effects of 2,2′-Bipyridine in Chlorobenzene. The effect of 2,2′-bipyridine on the rate of the $CoDe_2$-catalyzed decomposition of THP in chlorobenzene is shown in Fig. 1. The rate of decomposition was increased by the addition of 2,2′-bipyridine. The $CoDe_2$(A)–bpy complexes showed a monotonous increase in their activity, but surprisingly, the $CoDe_2$(B)–bpy complexes showed a maximum activity at the molar ratio of $[bpy]/[CoDe_2]=1/2$. Both $CoDe_2$(A)–bpy and $CoDe_2$(B)–bpy complexes showed almost the same activity at ratios of $[bpy]/[CoDe_2]$ higher than 1. Incidentally, the rate of the autoxidation of tetralin was increased by the addition of 2,2′-bipyridine and did not exceed the limiting rate. A large excess of 2,2′-bipyridine, one hundred times the quantity of $CoDe_2$(B), decreased the decomposition rate to half the value of $CoDe_2$(B) alone.

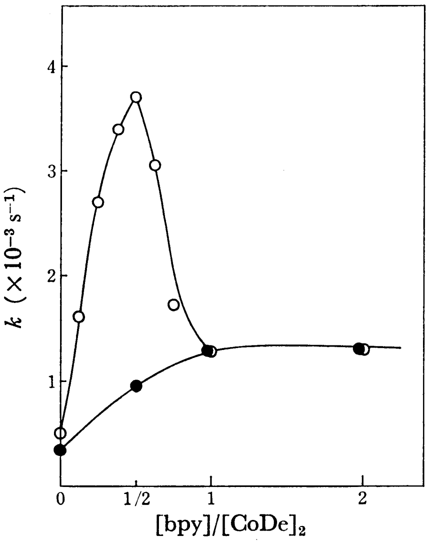

Fig. 1. Effect of 2,2′-biyridine on the rate of decomposition of THP catalyzed by $CoDe_2$ in chlorobenzene at 45 °C.
(-●-) $CoDe_2$(A), (-○-) $CoDe_2$(B), $[CoDe_2]=2\times10^{-4}$ M, $[THP]=5\times10^{-2}$ M.

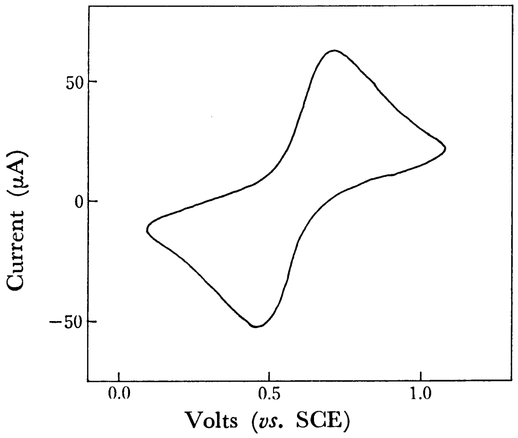

Fig. 2. Cyclic voltammogram of $CoDe_2$(B)-bpy(1: 1) in dichloromethane.
Scan rate was 0.05 V/s.

TABLE 1. COMPARISON OF THE VOLTAMMETRIC DATA WITH THE DECOMPOSITION RATES OF THP FOR $CoDe_2$-bpy COMPLEXES

Complex	Electrode reaction	$E_{1/2}$, V	k, 10^{-3} s^{-1}
$CoDe_2$(B)	Co(II) − e → Co(III)	0.80	0.5
	Co(III) + e → Co(II)	0.84	
$CoDe_2$(B)-bpy(1 : 1/2)	Co(II) − e → Co(III)	0.67	3.7
	Co(III) + e → Co(II)	0.70	
$CoDe_2$(B)-bpy(1 : 1)	Co(II) − e → Co(III)	0.60	1.3
	Co(III) + e → Co(II)	0.63	
$CoDe_2$(B)-bpy(1 : 2)	Co(II) − e → Co(III)	0.59	1.3
	Co(III) + e → Co(II)	0.59	

TABLE 2. INFRARED ABSORPTION BANDS AND DECOMPOSITION RATES OF THP FOR $CoDe_2$-bpy COMPLEXES

Complex	C-O st., cm^{-1}	k, $\times 10^{-3}$ s^{-1}
$CoDe_2$(B)	1550	0.5
$CoDe_2$(B)-bpy(1 : 1/2)	1570	3.7
$CoDe_2$(B)-bpy(1 : 1)	1590	1.3
$CoDe_2$(B)-bpy(1 : 2)	1595	1.3

The redox potentials of the $CoDe_2$(B)–bpy complexes, the determining factor for the activity of a catalyst in the redox reaction, were measured by cyclic voltammetry in dichloromethane. Table 1 shows the values of the redox potential and the decomposition rates for $CoDe_2$(B)–bpy complexes. The redox potential was shifted in the negative direction by the coordination of 2,2′-bipyridine. This shows that the reductive force of a cobalt(II) ion or the electron density on a cobalt(II) ion is increased by the coordination of 2,2′-bipyridine. Figure 2 shows the reversible change in the potential for anodic and cathodic sweeps of the Co(II)-Co(III) couple as established by cyclic voltammetry.

Table 2 shows the C–O stretching absorptions of the decanoate ligands of $CoDe_2$(B)–bpy complexes. The absorption peak shifts to a higher wave number with an increase in the amount of 2,2′-bipyridine added. This shows the increase in the double-bond character in the C–O bond. The C-T bands and d-d bands measured on $CoDe_2$(A)–bpy, and $CoDe_2$(B)–bpy complexes are shown in Table 3. The C-T band shifted to a longer wavelength, and the d-d band, to a shorter are, upon the addition of 2,2′-bipyridine. Both $CoDe_2$(A)–bpy and $CoDe_2$(B)–bpy complexes have shown the same absorption band at the $[bpy]/[CoDe_2]$ ratios of both 1 and 2.

As is shown in Fig. 3, product analysis⁶⁾ showed that the ratio of [C]/([C]+[D]) was about 0.29 for the $CoDe_2$(B) complex and about 0.39—0.45 for the $CoDe_2$(B)–bpy complexes; C and D are 1,2,3,4-tetrahydro-1-naphthol (α-tetralol) and 1,2,3,4-tetrahydro-1-naphthalenone (α-tetralone) respectively. The ratio of α-tetralol to α-tetralone was independent of the metal or hydroperoxide concentration.

TABLE 3. ULTRAVIOLET AND VISIBLE ABSORPTION BANDS OF $CoDe_2$-bpy COMPLEXES

Complex	d-d band, nm	(ε, l mol^{-1} cm^{-1})	C-T band, nm	(ε, l mol^{-1} cm^{-1})
$CoDe_2$(A)	526	(22.7)		
$CoDe_2$(A)-bpy(1 : 1/2)	522	(46.5)	361	(322)
$CoDe_2$(A)-bpy(1 : 1)	522	(41.8)	363	(569)
$CoDe_2$(A)-bpy(1 : 2)	520	(38.1)	365	(608)
$CoDe_2$(B)	526	(21.0)		
$CoDe_2$(B)-bpy(1 : 1/2)	522	(57.1)	355	(384)
$CoDe_2$(B)-bpy(1 : 1)	522	(50.7)	365	(560)
$CoDe_2$(B)-bpy(1 : 2)	520	(40.2)	365	(585)

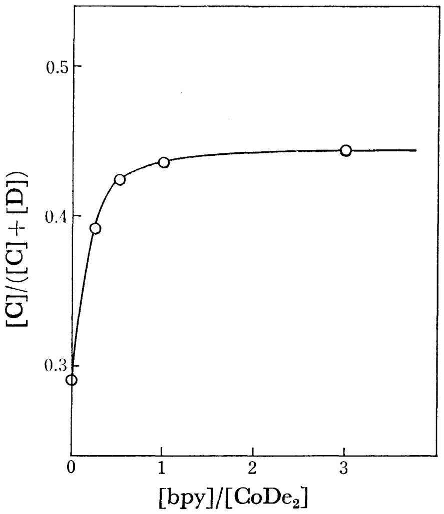

Fig. 3. Variation of [C]/([C]+[D]) in the decomposition of THP in chlorobenzene at 45 °C.
C: α-Tetralol, D: α-tetralone, [$CoDe_2$(B)] $= 2 \times 10^{-4}$ M, [THP] $= 5 \times 10^{-2}$ M.

TABLE 4. DECOMPOSITION RATES OF THP FOR $CoDe_2$-(bipyridine derivative) COMPLEXES IN CHLOROBENZENE AT 40 °C

Complex	k, $\times 10^{-4}$ s^{-1}
$CoDe_2$(B)-(2,2′-biquinoline)	3.5
$CoDe_2$(B)-(2,2′-bipyridine)	4.8
$CoDe_2$(B)-(6,6′-dimethyl-2,2′-bipyridine)	5.9
$CoDe_2$(B)-(4,4′-dimethyl-2,2′-bipuinoline)	6.5

[bipyridine derivative]/[$CoDe_2$] = 2,
[$CoDe_2$] $= 2 \times 10^{-4}$ M, [THP] $= 5 \times 10^{-2}$ M.

Table 4 shows the catalytic activities of the $CoDe_2$ (B)–bipyridine derivative complexes. These results show that the activity of a catalyst increases with an increase in the electron-donating property of the ligand; this supports the proposition that the increase in the electron density of the cobalt(II) ion causes an increase in the catalytic activity. The deviation of 6,6′-dimethyl-2,2′-bipyridine can be ascribed to the steric hindrance to the coordination to the cobalt(II) ion.

Effects of 2,2′-Bipyridine in Acids. Figure 4 shows the effect of 2,2′-bipyridine on the rate of the cobalt(II) acetate ($Co(OAc)_2$)-catalyzed decomposition of THP in acetic acid. Unlike the case of the decomposition in chlorobenzene, the decomposition rate in acetic acid decreased with an increase in the amount of 2,2′-bipyridine added. Similar reactions were carried out in various acid solvents as is shown in Table 5. The decomposition rate was decreased by the addition of 2,2′-bipyridine to all the solvents, suggesting that the inhibitive effect of 2,2′-bipyridine is independent of the strength of acids.

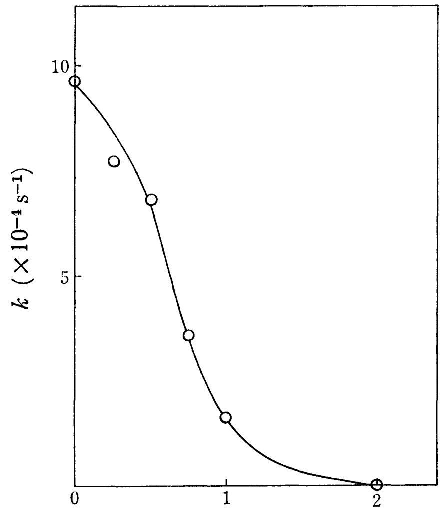

Fig. 4. Effect of 2,2′-bipyridine on the rate of decomposition of THP catalyzed by $Co(OAc)_2$ in acetic acid at 50 °C.
[$Co(OAc)_2$] $= 10^{-3}$ M, [THP] $= 5 \times 10^{-2}$ M.

TABLE 5. DECOMPOSITION RATE OF THP IN FATTY ACIDS[a)]

	k, $\times 10^{-4}$ s^{-1}	k_2, $\times 10^{-4}$ s^{-1}	k_2/k
Acetic acid(C_2)	0.89	0.18	0.20
Propionic acid(C_3)	1.35	0.35	0.26
Butyric acid(C_4)	2.00	0.68	0.34
Valeric acid(C_5)	3.08	1.08	0.35
Heptanoic acid(C_7)	5.83	1.94	0.33
Nonanoic acid(C_9)	7.61	2.21	0.29

a) k and k_2 are pseudo-first-order rate constants of the THP decomposition reactions by 10^{-3} M $Co(OAc)_2$ and 10^{-3} M $Co(OAc)_2$-bpy(1 : 1) respectively. [THP] $= 5 \times 10^{-2}$ M, temperature = 50 °C.

Discussion

Increase in Activity. It can be presumed that the redox potential of a catalyst is the most influential factor in hydroperoxide decomposition. The redox potentials of

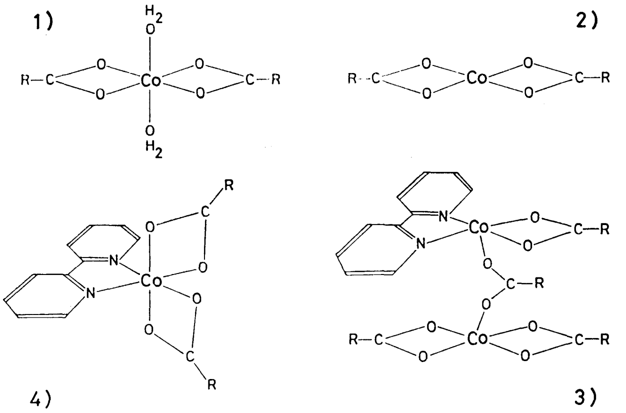

Fig. 5. Proposed structure of CoDe$_2$-bpy complexes. 1) CoDe$_2$(A), 2) CoDe$_2$(B), 3) CoDe$_2$(B)-bpy(1 : 1/2), 4) CoDe$_2$(B)-bpy(1 : 1).

metal ions were compared with the catalytic activity in oxidation reactions by Chalk and Smith,[7)] who reported that the redox potentials of metal ions in aqueous solution could not be correlated with the catlytic activity in non-polar media, though the values in absolute alcohol could be correlated fairly well.

As redox potentials are very sensitive to the ligand and the solvent, it is necessary to measure them in a similar non-polar solvent in order to make a comparison with the catalytic activities of the hydroperoxide decomposition in chlorobenzene. Recent progress in the field of electrochemistry in non-aqueous media[8)] enable us to measure the redox potentials of many complexes in various non-aqueous solvents. We measured the redox potentials of the CoDe$_2$(B)–bpy complexes in dichloromethane and compared them to their catalytic activities (Table 1). The catalytic activities seem to be correlated to their redox potentials except in the case of CoDe$_2$(B)–bpy(1:1/2). The increase in the activity upon the addition of 2,2′-bipyridine can be attributed to the change in the redox potential of the catalyst. Such a change in the redox potential of the cobalt ion by 2,2′-bipyridine will bring about two effects; one is the increase in the reductive force of the cobalt(II) ion, which accelerates the cleavage of the hydroperoxide molecule, while the other is the increase in the electron density on the cobalt(II) ion, which will stabilize the CoDe$_2$–hydroperoxide complex.

From the IR data (Table 2), another change was found in the first ligand decanoate, an increase in the double-bond character of the C–O bond. This suggests a weakening in the Co–O bond strength, which must bring about the facile coordination of the hydroperoxide molecule to the central cobalt(II) ion. The decomposition of hydroperoxide by the metal ion must take the pathway in which the coordination of hydroperoxide to the metal ion occurs. Then the facile coordination of hydroperoxide to the metal ion must lead to a higher decomposition rate.

Therefore, the increase in the rate of decomposition of hydroperoxide due to 2,2′-bipyridine can be ascribed to the change in the redox potential of the cobalt(II) ion and the weakening of the Co–O bond strength. The results of product analysis seem to indicate that there is a non-radical decomposition in the CoDe$_2$(B)–THP system and that the portion of radical decomposition increases upon the addition of 2,2′-bipyridine.

In acetic or other fatty acids, the effect of 2,2′-bipyridine was quite the reverse of that in chlorobenzene. The acid solvent may suppress the positive ligand effect; that is, there may be no weakening of the Co–O(acetate) bond strength in an acetic acid solvent. The 2,2′-bipyridine will just retard the decomposition of hydroperoxide by occupying the coordination site of the cobalt(II) ion.

Maximum Activity. The electrochemical and spectral data can not fully explain the maximum activity of the CoDe$_2$(B)–bpy(1:1/2). It can, however, be explained on the basis of the structural variation in the complexes. Figure 5 shows the proposed structure of these complexes. CoDe$_2$(A) (Structure 1) was pink and a six-coordination complex.[9)] The disappearance of the OH absorption at 3420 cm^{-1} and the weight decrease correspond to the loss of two coordinated H_2O molecules by drying Complex 1 under a vacuum at 70 °C for 5 h, leading inevitably to Structure 2. This is a four-coordination complex. The color change from pink to blue[10)] is consistent with the above structural change. From the spectral and electrochemical data and from the steric difficulties of 2,2′-bipyridine, it seems that CoDe$_2$–bpy(1:1) and CoDe$_2$–bpy(1:2) will take Structure 4. We propose Structure 3 for CoDe$_2$(B)–bpy(1:1/2), though a five-coordination complex with one vacant coordination site can not be excluded.

These catalytic activities can be explained according to these structures. The fact that the activities of CoDe$_2$(A) and CoDe$_2$(B) are lower than the others can be attributed to their weak reductive force because of no coordination of 2,2′-bipyridine. The slight difference in activity between CoDe$_2$(A) and CoDe$_2$(B) might be brought about by the two vacant coordination sites of CoDe$_2$(B). CoDe$_2$(B)–bpy(1:1/2) shows the highest activity of all the catalysts. This is explained by Structure 3 having a vacant coordination site and an adequate reductive force to cleave the hydroperoxide molecule. CoDe$_2$(A)–bpy (1:1/2) may not have the highest activity because of the coordinated H_2O molecule, which probably interferes with the coordination of the hydroperoxide molecule. The activity of CoDe$_2$(B)–bpy(1:1), which is between those of CoDe$_2$(B) and CoDe$_2$(B)–bpy(1:1/2), can be attributed to Structure 4, which may have a strong reductive force but no vacant coordination site. The fact that the activity is higher than that of CoDe$_2$(B) may be attributed to the strong reductive force, while the lower activity than CoDe$_2$(B)–bpy(1:1/2) may be attributable to the lack of any vacant coordination site. Judging from their spectral data, CoDe$_2$(A)–bpy(1:1) and CoDe$_2$(B)–bpy(1:1) must take the same structure; the data show a complete agreement with the results of catalytic activity.

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