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Effect of a Polymer Ligand on Oxidation of Thiophenol Catalyzed by Cobaloximes

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Synopsis. The oxidation mechanism of thiophenol catalyzed by cobaloximes was deduced by spectroscopic measurement of the oxidation rate at various concentrations of the reactants, the reaction being a Michaelis-Menten type reaction. Addition of polymer ligands such as poly(4-vinylpyridine) and 4-vinylpyridine-styrene copolymer, stabilizing the intermediate similar to a Michaelis complex, resulted in an increase in the oxidation rate under low substrate concentration.

Studies have been reported on the catalytic action of polymer metal complexes,[1] but few detailed investigations have been carried out because of the complicated structure of the complexes and intermediates. Polymer ligands or substrates coordinate with cobaloximes, only in an axial position, making it easy to analyze the reaction mechanism since the structures of the complex coordinated with a polymer ligand or a substrate are confined.

The oxidation reaction of thiophenol catalyzed by cobaloximes is mild and enables us to apply spectroscopic analysis. This report deals with the reaction mechanism as deduced from kinetic studies, discussion being given on the effect of the polymer ligand on the catalytic action of cobaloximes.

Experimental

Materials. Commercial $CoCl_2 \cdot 6H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, dimethylglyoxime ($dmgH_2$), pyridine (Py), thiophenol, and NaOH were used without further purification. Poly(4-vinylpyridine) (PVP) and 4-vinylpyridine-styrene copolymer (PPS) (styrene unit content 17%) were obtained by radical polymerization initiated by azobisisobutyronitrile purified by reprecipitation with ethyl acetate. The number-average molecular weights of PVP and PPS determined by the vapor pressure osmometry were 12800 and 18700, respectively. Methanol was distilled before use.

Preparation of Cobaloximes. $CoCl(dmgH)_2(Py)$ was prepared by the conventional method.[2] $CoCl(dmgH)_2(OH_2)$ was obtained through the reaction of 4.2 mmol NaOH in ethanol and aeration, and recrystallized from ethanol. Found: C, 28.0; N, 16.1; H, 4.8%. Calcd for $C_8H_{14}N_4O_4CoH_2OCl$: C, 28.0; N, 16.3; H, 4.7%.

Analysis of Oxidation Reaction. Air oxidation of thiophenol in alkaline methanol solution (containing 3×10^{-4} M NaOH) in the presence of cobaloximes gave diphenyl disulfide (DPS). An increase of absorbance at 310 nm, at which the difference of absorbance between the reactant and product (DPS) was large enough to detect a small change of the concentration of the product, gave the oxidation rate in a steady state under the addition of excess substrate using $CoCl(dmgH)_2(Py)$ as a catalyst. The rate was represented by the concentration of phenylthio radical produced per second. The formation of the Co(II) complex under an atmosphere of nitrogen accompanied by thiophenol oxidation and that of the air oxidation of the Co(II) complex were studied from a visible absorption spectral change. The relationsip between the oxidation rate and the added polymer ligand concentration was derived in a similar way using $CoCl(dmgH)_2(OH_2)$ as a catalyst and Py, PVP, and PPS as an axial ligand respectively. The concentration of the polymer ligand is indicated in 4VP unit mole per liter.

Results and Discussion

Reaction Mechanism of Thiophenol Oxidation. The following mechanisms were postulated for the thiol oxidation catalyzed by metals.[3]

$$\begin{gathered} M^{n+} + \text{thiophenol}^{-} \longrightarrow M^{(n-1)+} + \text{thiophenol}^{*} \\ M^{(n-1)+} \xrightarrow{O_2} M^{n+} \qquad 2\text{thiophenol}^{*} \longrightarrow \text{Pr} \end{gathered} \tag{1}$$

The oxidation rate determined by the measurement of oxygen uptake with Warburg's manometer was in agreement with that determined by spectroscopic measurement. This indicates that thiophenol was converted quantitatively into DPS in the present oxidation system.

The oxidation rate V is proportional to the catalyst concentration. The oxidation rate is proportional to the substrate concentration in the low substrate concentration range, approaching a certain value with increase in concentration (Fig. 1). This can be explained by assuming the existence of the intermediate complex consisting of a catalyst and a substrate. The linear relationship between the reciprocal of the oxidation rate, $1/V$, and that of the substrate concentration, $1/[S]$, suggests the following reaction mechanism, where $(Co) = Co(dmgH)_2XY$.

$$\begin{gathered} (Co^{III}) + C_6H_5\text{–}S^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Co^{III})\ C_6H_5\text{–}S^{-} \xrightarrow{k_2} \\ (Co^{II}) + C_6H_5\text{–}S^{*}, \qquad (Co^{II}) \xrightarrow{k_3} (Co^{III}), \\ 2C_6H_5\text{–}S^{*} \longrightarrow C_6H_5\text{–}S\text{–}S\text{–}C_6H_5 \end{gathered} \tag{2}$$

The change in visible spectra with time after the addition of the substrate to the solution containing $CoCl(dmgH)_2(Py)$ indicates the formation of the Co(II) complex with absorption maximum at 390 nm, reaching equilibrium after *ca.* 30 min. Reaction under nitrogen atmosphere is regarded to turn the Co(III) complex entirely into the Co(II) complex, causing an increase in the absorption at 390 nm about 1.5 times the equilibrium value in the air. The formation rate of Co(II) complex under nitrogen atmosphere at initial stage is proportional to the complex concentration. The decreasing rate in air of excess Co(II) complex formed by the thiophenol oxidation under a nitrogen atmosphere is also proportional to the complex concentration. These results strongly support the reaction mechanism describ-

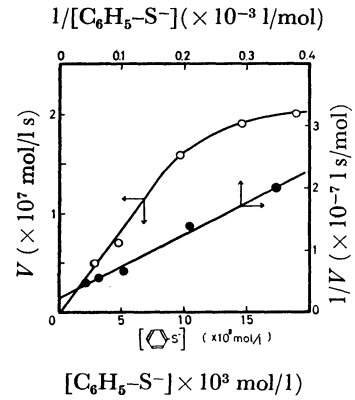

Fig. 1. Relationship between oxidation rate (*V*) and concentration of substrate ([C_6H_5–S^-]). [Co]$=3.16\times10^{-5}$ mol/l, [NaOH] $=3\times10^{-4}$ mol/l, solvent: methanol, at 22 °C.

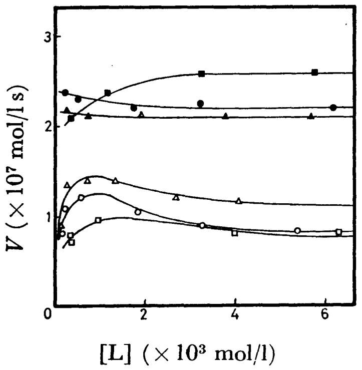

Fig. 2. Relationship between oxidation rate (*V*) and concentration of ligand ([L]). [Co]$=3.16\times10^{-5}$ mol/l, [NaOH] $=3\times10^{-4}$ mol/l, solvent: methanol, at 15 °C, [C_6H_5–S^-]$=3.25\times10^{-3}$ mol/l for ○, △, □, and 3.25×10^{-2} mol/l for ●, ▲, ■, L=Py: □, ■, PVP: △, ▲, and PPS: ○, ●.

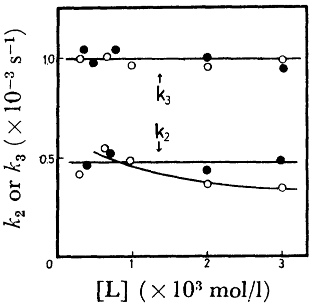

Fig. 3. Values of k_2 and k_3. [Co]$=3.16\times10^{-5}$ mol/l, [C_6H_5–S^-]$=3.25\times10^{-2}$ mol/l, [NaOH] $=3\times10^{-4}$ mol/l, solvent: methanol, at 15 °C, L=Py: ● or PVP: ○.

ed in Eq. 2. Equation 2 leads to the following equation for the oxidation rate at steady state.

$$1/V = [A + B/[C_6H_5\text{-}S^-]]/[Co]$$
$$A = (k_2+k_3)/k_2k_3, \quad B = (k_{-1}+k_2)/k_1k_2,$$
$$V = d[C_6H_5\text{-}S^*]/dt \tag{3}$$

This equation represents the linear relationship between $1/V$ and $1/[C_6H_5\text{–}S^-]$ as shown in Fig. 1. The rate constants k_2 and k_3 can be determined by spectroscopic measurements of the Co(II) complex formation under nitrogen atmosphere and of the decrease of the Co(II) complex in air, respectively.

Effect of Polymer Ligand. Variations in the thiophenol oxidation rate with the ligand concentration, using $CoCl(dmgH)_2(OH_2)$ as a catalyst and Py, PVP, and PPS as an axial ligand are shown in Fig. 2.

The oxidation rate-ligand concentration curves obtained in lower thiophenol concentration have a maximum. The formation constant *K* of $CoCl(dmgH)_2(OH_2)$ with PPS is about 1×10^5 in *N,N*-dimethylformamide.[4] If we consider the formation constant in methanol to be almost the same as that in *N,N*-dimethylformamide, almost all the complexes have a ligand at the ligand concentration of the maximum point. The coordination of the axial ligand makes the complex more active as a oxidation catalyst.

The oxidation of thiophenol by $Co\cdot O_2$ complexes scarcely occurs in this system since one axial position of the catalyst,[5] where O_2 should coordinate, is occupied by a ligand such as Py or PVP.

In higher substrate concentration, for which the second term of Eq. 3 is negligible, only the value of *A*, *i.e.*, $(k_2+k_3)/k_2k_3$, determines the oxidation rate *V*. Figure 3 shows that the k_2 value of the Py system is larger than that of the polymer system, though k_3 value has almost the same value in both systems. This causes the Py system to have a larger oxidation rate than that of polymer systems. In the polymer system the k_2 value decreases with increase in ligand concentration. This can be explained in terms of steric hindrance by the polymer chain which prevents elimination of the substrates activated by the complex in polymer domain. The decrease in k_2 value with increase in the ligand concentration is in line with the decrease in the oxidation rate of the polymer system shown in Fig. 2.

Under conditions of the lower substrate concentration, where the second term in Eq. 3 is not negligible, the oxidation rate *V* is affected by the value of *B*. The faster oxidation rate in the polymer system under the lower substrate concentration indicates that *B* has a smaller value in the polymer systems than in the Py system. This is because the polymer domain stabilizes the reaction intermediate complex, and prevents the substrate from elimination, thus making k_{-1} value decrease.

It is concluded that the addition of polymer ligands can raise the oxidation activity of the catalyst at a lower substrate concentration region.

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