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The Silver(I) Ion-catalyzed Oxidation of Ethylenediaminetetraacetatocobaltate(II) by the Peroxodisulfate Ion

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Synopsis. A spectrophotometric study of the silver(I) ion-catalyzed oxidation of the ethylenediaminetetraacetatocobaltate(II) (Co^{II}-edta) peroxodisulfate ion ($S_2O_8^{2-}$) was carried out in acidic media. The rate is independent of the concentration of Co^{II}-edta, but first-order-dependent with respect to the concentrations of $S_2O_8^{2-}$ and Ag(I) in the $1.67\times10^{-2}-7.25\times10^{-2}$ M and $2.00\times10^{-3}-2.26\times10^{-2}$ M ranges respectively.

Recently, kinetic studies of the oxidation reaction of nitrilopolyacetatocobaltate(II) with various oxidants have been carried out.[1-4] The present authors found that the rate of the oxidation of Co^{II}-edta by $S_2O_8^{2-}$ is first-order-dependent on the concentration of $S_2O_8^{2-}$, but is independent of the Co^{II}-edta concentration for $Co^{II}(bpy)_3^{2+}$ oxidation; however, the rate is dependent on the concentrations of both $Co^{II}(bpy)_3^{2+}$ and $S_2O_8^{2-}$. Such a difference in rate law between Co^{II}-edta and $Co(bpy)_3^{2+}$ must come from the difference in charge on the cobalt(II) complexes.[5] In this note, the mechanism of the silver(I) ion-catalyzed oxidation of Co^{II}-edta[6] by $S_2O_8^{2-}$ and also the effect of other ions on the rate will be reported.

Experimental

Materials. A cobalt(II) perchlorate solution was prepared by dissolving cobalt carbonate into a slight excess of perchloric acid. This cobalt(II) solution was standardized by titration with a disodium dihydrogenethylenediaminetetraacetate (Na_2H_2edta) solution. The working solution was prepared by dilution with redistilled water.

Standard solutions of Na_2H_2 edta were prepared by dissolving known quantities of disodium dihydrogenethylenediaminetetraacetate dihydrate into redistilled water. Standard solutions of potassium peroxodisulfate were prepared by dissolving known quantities of the reagent into redistilled water. The peroxodisulfate ion solution was prepared just before use to avoid any decomposition. The standard solutions of silver(I) nitrate were prepared by dissolving silver nitrate into 0.01 M perchloric acid. These silver(I) solutions were standardized by the Volhard method. The adjustment of the pH of the solution was made by adding an acetate buffer solution. The ionic strengths of the solutions of Co^{II}-edta were adjusted to 0.50 by the addition of sodium perchlorate.

Procedure for the Measurement of the Reaction Rate. For the preparation of Co^{II}-edta solutions, the concentration of Na_2H_2edta was kept at three times that of the cobalt(II) ion. The solutions of $S_2O_8^{2-}$, the acetate buffer, Co^{II}-edta, and the silver(I) ion were each thermostated at 25 °C. In each experiment, $S_2O_8^{2-}$, acetate buffer, and Co^{II}-edta solutions were pipetted into a 50-ml measuring flask. Then the silver(I) ion solution was added to the solution. A portion of the solution was transferred into a 1-cm cell placed in a thermostated cell compartment of a Hitachi EPS-3-type spectrophotometer. The time dependence on the variation in the absorbance of the solution was measured at 540 nm. All the kinetic measurements were carried out in a large excess of the $S_2O_8^{2-}$ concentration to that of Co^{II}-edta.

Results and Discussion

Kinetics of the Silver(I) Ion-catalyzed Oxidation of Co^{II}-edta by $S_2O_8^{2-}$. The rate of the oxidation of Co^{II}-edta by $S_2O_8^{2-}$ in the absence of silver(I) ions was slow, as was shown in a previous paper.[5] In the present work, however, it was found that the silver(I) ions catalyze the oxidation of Co^{II}-edta by $S_2O_8^{2-}$. The oxidation product was characterized spectrophotometrically as $Co^{III}(edta)^-$. It was confirmed spectrophotometrically that one mole of $S_2O_8^{2-}$ oxidizes two moles of Co^{II}-edta in the presence of silver(I) ions when there is a large excess of Co^{II}-edta relative to the concentration of $S_2O_8^{2-}$. However, the attempt to confirm the stoichiometry in the presence of a large excess of $S_2O_8^{2-}$ to Co^{II}-edta was unsuccessful.

As is shown in Fig. 1, the plot of the absorbance vs. the time shows a straight line up to a 95% reaction. This behavior indicates that the oxidation rate is zero-order with respect to the Co^{II}-edta concentration. It was ascertained that no oxidation rate changes with the variation in the Co^{II}-edta concentration (Table 1).

In order to examine the effect of the $S_2O_8^{2-}$ concentration on the rate, the reaction was carried out at five different initial concentrations of $S_2O_8^{2-}$. As is shown in Fig. 2, the plot of the apparent rate *vs.* the $S_2O_8^{2-}$ concentration shows a straight line. Furthermore, it was confirmed that the oxidation rates were first-order with respect to the silver(I) ion concentration (Fig. 3). The rate law for this reaction is represented by Eq. 1:

$$\frac{d[Co^{III}(edta)^-]}{dt} = k_{obsd}[Ag(I)][S_2O_8^{2-}], \qquad (1)$$

where k_{obsd} is the second-order rate constant at a given pH value.

The effect of the pH on the oxidation rate was investigated over the pH range from 3.50 to 5.00 (Fig.

Table 1. The kinetic data for the silver(I) ion-catalyzed oxidation of Co^{II}-edta by peroxodisulfate

Concentration of Co^{II}-edta (10^{-3} M)	Rate[a] (10^{-6} M s^{-1})
1.5	6.4
2.5	6.3
4.0	6.4
7.5	6.4
10.0	6.3

a) $[Ag(I)]=8.0\times10^{-3}$ M, $[S_2O_8^{2-}]=8.57\times10^{-2}$ M, pH 3.60, I=0.50, 25 °C.

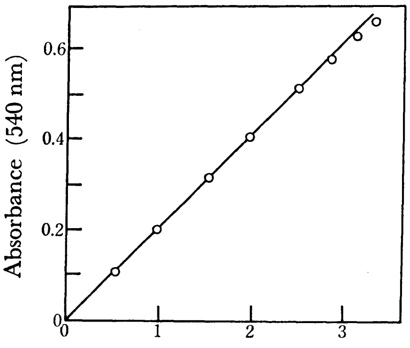

Fig. 1. A typical kinetic run of the reaction between Co^{II}-edta and peroxodisulfate ions in the presence of silver(I) ions at pH 3.60, 25 °C, and I=0.50 ($NaClO_4$).
$[Co^{II}\text{-edta}]=2.08\times10^{-3}$ M, $[S_2O_8{}^{2-}]=8.57\times10^{-2}$ M, $[Ag(I)]=1.35\times10^{-2}$ M.

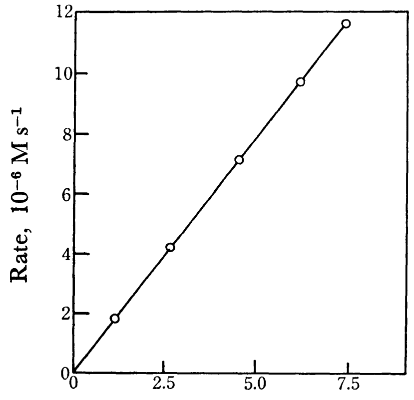

Fig. 2. Apparent rate *vs.* $[S_2O_8{}^{2-}]$ at pH 3.60, 25 °C, and I=0.50($NaClO_4$).
$[Co^{II}\text{-edta}]=2.08\times10^{-3}$ M, $[Ag(I)]=1.67\times10^{-2}$ M.

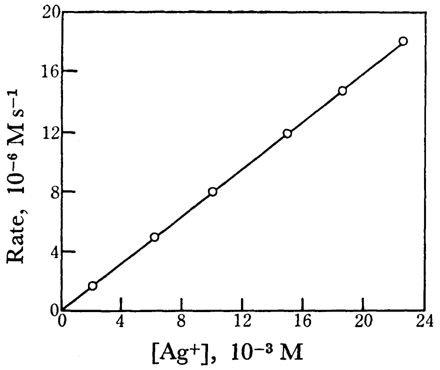

Fig. 3. Apparent rate *vs.* [Ag(I)] at pH 3.60, 25 °C, and I=0.50 ($NaClO_4$).
$[Co^{II}\text{-edta}]=2.08\times10^{-3}$ M, $[S_2O_8{}^{2-}]=8.57\times10^{-2}$ M.

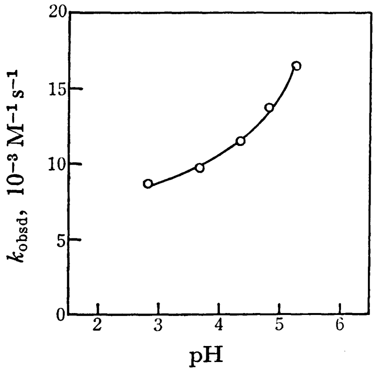

Fig. 4. The relation between the observed second-order rate constant and pH.
$[Co^{II}\text{-edta}]=2.08\times10^{-3}$ M, $[S_2O_8{}^{2-}]=8.57\times10^{-2}$ M, $[Ag(I)]=1.67\times10^{-2}$ M, 25 °C, and I=0.50 ($NaClO_4$).

4). The rate constant increases with an increase in the pH. No detailed explanations of the effect of the hydrogen ions on the rate could be given. The effect of the Na_2H_2edta concentration on the rate was not observed over the range of $1.40\times10^{-3}-7.54\times10^{-3}$ M.

The rate-determining step in the silver(I) ion-catalyzed oxidation reaction of Co^{II}-edta by $S_2O_8{}^{2-}$ must be the reaction between the silver(I) ion and $S_2O_8{}^{2-}$, since the oxidation rate is first-order with respect to the concentrations of both $S_2O_8{}^{2-}$ and silver(I) ions. The path for the oxidation of Co^{II}-edta may be represented by Eqs. 2, 3, 4, and 5:

$$Ag(I) + S_2O_8{}^{2-} \xrightarrow{\text{slow}} Ag(II) + SO_4{}^{2-} + SO_4{}^{\overline{\cdot}}, \qquad (2)$$

$$Ag(I) + SO_4{}^{\overline{\cdot}} \xrightarrow{\text{fast}} Ag(II) + SO_4{}^{2-}, \qquad (3)$$

$$Co^{II}\text{-edta} + SO_4{}^{\overline{\cdot}} \xrightarrow{\text{fast}} Co^{III}(edta)^- + SO_4{}^{2-}, \qquad (4)$$

$$Co^{II}\text{-edta} + Ag(II) \xrightarrow{\text{fast}} Co^{III}(edta)^- + Ag(I). \qquad (5)$$

The effects of the other ions on the silver(I) ion-catalyzed oxidation of Co^{II}-edta by $S_2O_8{}^{2-}$ were also examined. In the presence of 250 ppm Ag(I), the Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Mo(VI), and W(VI) metal ions did not affect the rate at a concentration of 200 ppm, but at the same concentration the Ni^{2+}, Mn^{2+}, and Cu^{2+} metal ions increase the rate by more than 40% of the rate in the presence of the silver(I) ions.

This reaction may be applied to the determination of the concentration of the silver(I) ions, since the rate of the oxidation reaction of Co^{II}-edta is first-order-dependent on the silver(I) ions over the range of 108 to 400 ppm (Fig. 3).

References

1) D. H. Huchital and R. G. Hodges, *Inorg. Chem.*, **12**, 998, 1004 (1973).

2) H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **47**, 1426 (1974).

3) R. G. Wilkins and R. E. Yelin, *J. Am. Chem. Soc.*, **92**, 1191 (1970).

4) K. Ohashi, A. Onuma, K. Yamamoto, and Y. Kurimura, *Nippon Kagaku Zasshi*, **92**, 51 (1971).

5) K. Ohashi, M. Matsuzawa, E. Hamano, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 2440 (1976).

6) The equilibrium constant ($K=[Co^{II}(Hedta)(H_2O)^-]/[Co^{II}(edta)^{2-}][H^+]$) is $10^{3.1}$ M^{-1} at 20 °C and I=0.10.[7] The Co^{II}-edta complex exists as $Co^{II}(Hedta)(H_2O)^-$ and $Co^{II}(edta)^{2-}$ in the pH range from 3.50 to 5.36. The formula of Co^{II}-edta used in this paper represents a mixture of $Co^{II}(edta)^{2-}$ and $Co^{II}(Hedta)(H_2O)^-$.

7) G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).