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The Kinetic Study of the Oxidation Reaction of the Tris(2,2′-bipyridine)cobalt(II) Ion and the Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetatocobaltate(II) Ion by the Peroxodisulfate Ion

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The kinetics of the oxidation of Co^{II}–EDTA and $Co^{II}(bpy)_3^{2+}$ by the peroxodisulfate ion ($S_2O_8^{2-}$) in acidic media have been studied spectrophotometrically; EDTA and bpy represent ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid and 2,2′-bipyridine respectively. The stoichiometry of the reactions of Co^{II}–EDTA with the peroxodisulfate ion was $2Co^{II}\text{–EDTA}+S_2O_8^{2-}=2Co^{III}(edta)^-+2SO_4^{2-}$. The rate for the oxidation of Co^{II}–EDTA by the peroxodisulfate ion is independent of the concentration of Co^{II}–EDTA, but first-order dependent with respect to the peroxodisulfate-ion concentration. The rate law is $d[Co^{III}(edta)^-]/dt=2k[S_2O_8^{2-}]$. The rate-determining step must be the decomposition of $S_2O_8^{2-}$ into $2SO_4^{\cdot-}$. The first-order rate constant, the activation enthalpy, and the activation entropy are $5.5\times10^{-8}\ s^{-1}$, 24 kcal mol^{-1}, and −12 eu respectively at pH 3.60, 25 °C, and $I=0.50$ ($NaClO_4$). Two moles of $Co^{II}(bpy)_3^{2+}$ are oxidized by one mole of the peroxodisulfate ion. For the oxidation of $Co^{II}(bpy)_3^{2+}$, the following reaction path and rate law were proposed:

$$Co^{II}(bpy)_3^{2+} + S_3O_8^{2-} \overset{K_e}{\rightleftarrows} [Co^{II}(bpy)_3^{2+}\cdot S_2O_8^{2-}] \xrightarrow{k} Co^{III}(bpy)_3^{3+} + SO_4^{2-} + SO_4^{\cdot-}$$

$$Co^{II}(bpy)_3^{2+} + SO_4^{\cdot-} \xrightarrow{\text{fast}} Co^{III}(bpy)_3^{3+} + SO_4^{2-}$$

$$\frac{d[Co^{III}(bpy)_3^{3+}]}{dt} = \left\{\frac{2k\cdot K_e}{1+K_e[S_2O_8^{2-}]}\right\}[S_2O_8^{2-}][Co^{II}(bpy)_3^{2+}]_T$$

At pH 3.60, 25 °C, and $I=0.50$ (Na_2SO_4), the rate constant, k, and the equilibrium constant, K_e, are 0.53 s^{-1} and 5.6 M^{-1} respectively. The difference in the rate law and mechanism between Co^{II}–EDTA and $Co^{II}(bpy)_3^{2+}$ may come from the difference in charge on the cobalt(II) complexes.

A large number of investigations have been done in the field of the oxidation of metal ions,$^{1-3)}$ metal complexes,$^{4-6)}$ and various organic compounds$^{7,8)}$ by the peroxodisulfate ion. The rate for the oxidation reactions of positively charged metal complexes such as $Fe^{II}(bpy)_3^{2+}$ 4) and $Os^{II}(bpy)_3^{2+}$ 6) by the peroxodisulfate ion is first-order dependent on the concentrations of the peroxodisulfate ion and also the metal complex. These have, however, been few of the oxidation reaction of the negatively charged metal complex by the peroxodisulfate ion. Recently, studies of the kinetics of the oxidation reaction of Co^{II}–EDTA using various oxidizing agents, for example, $Fe^{III}(CN)_6^{3-}$,$^{9,10)}$ $Fe^{III}(bpy)_3^{3+}$,$^{11)}$ $Fe^{III}(phen)_3^{3+}$,$^{11)}$ and Mn^{III}–EDTA$^{11)}$ have been carried out. Previously, the present authors have reported the kinetics of the oxidation reaction of the nitrilopolyacetate–cobalt(II) ion by chromic acid ($HCrO_4^-$) in acidic media, and suggested that the oxidation reaction proceeds through an inner-sphere mechanism.$^{12)}$

The present kinetic study of the oxidation reactions of Co^{II}–EDTA and $Co^{II}(bpy)_3^{2+}$ with the peroxodisulfate ion was carried out spectrophotometrically in order to obtain information on the behavior of the negatively and positively charged cobalt(II) complexes toward the oxidant.

Experimental

Materials. The Co^{II}–EDTA solution was prepared by adding an equivalent amount of an Na_2H_2edta solution to a cobalt(II) solution. For the preparation of the $Co^{II}(bpy)_3^{2+}$ solution, the concentration of 2,2′-bipyridine was kept at ten times that of the cobalt(II) ion.

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 adjustment of the pH of the solution was made by adding the acetate buffer solution. The ionic strengths of the solutions of Co^{II}–EDTA and $Co^{II}(bpy)_3^{2+}$ were adjusted to 0.50 by the addition of sodium perchlorate and sodium sulfate respectively.

All the other chemicals were of a reagent grade.

Measurement of the Reaction Rate. The solutions of potassium peroxodisulfate, the acetate buffer, and Co^{II}–EDTA were thermostated at a desired temperature. In each experiment, portions of these solutions were pipeted into a flask, the peroxodisulfate being added last to the solution containing Co^{II}–EDTA, and the time was counted from its addition. A portion of the solution was transferred into a 1 cm cell placed in a thermostated cell compartment of a Hitachi Model EPS-3-type spectrophotometer. The variation in the absorbance of the solution was measured at 540 nm.

The kinetic-measurements for $Co^{II}(bpy)_3^{2+}$ were performed at 420 nm by the stopped-flow technique using a Hitachi EPS-1-type rapid-scan spectrophotometer. The solution of $Co^{II}(bpy)_3^{2+}$ and the peroxodisulfate ion was thermostated at 25 °C before the initiation of the reaction.

All the kinetic experiments were carried out under the condition of a large excess of the peroxodisulfate-ion concentration with respect to the Co^{II}–EDTA and $Co^{II}(bpy)_3^{2+}$ concentration.

Results and Discussion

The Oxidation Reaction of Co^{II}–EDTA with $S_2O_8^{2-}$. Figure 1 shows the absorption spectral change of the Co^{II}–EDTA$^{13)}$ solution upon the addition of a large excess of the peroxodisulfate ion under the conditions of pH 3.60 and 50 °C. The oxidation product, $Co^{III}(edta)^-$ was characterized spectrophotometrically. The stoichiometry for the oxidation of Co^{II}–EDTA by the

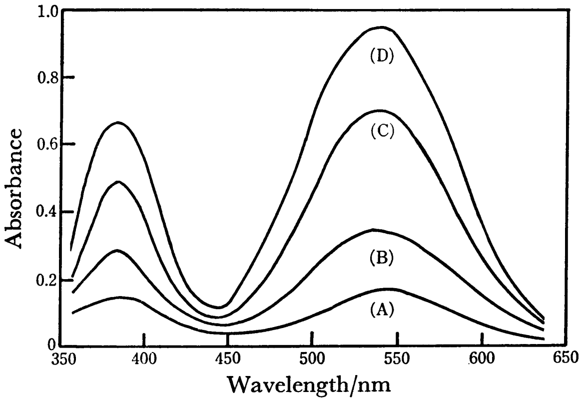

Fig. 1. Absorption spectral change of the Co^{II}-EDTA solution with the addition of peroxodisulfate ion solution at pH 3.60, 50 °C, and I=0.50 (NaClO$_4$).
(A) 2.0 h, (B) 4.5 h, (C) 10.0 h, (D) 13.5 h after the addition of peroxodisulfate ion.
[Co^{II}-EDTA]=3.08×10^{-3} M, [S$_2$O$_8^{2-}$]=3.68×10^{-2} M.

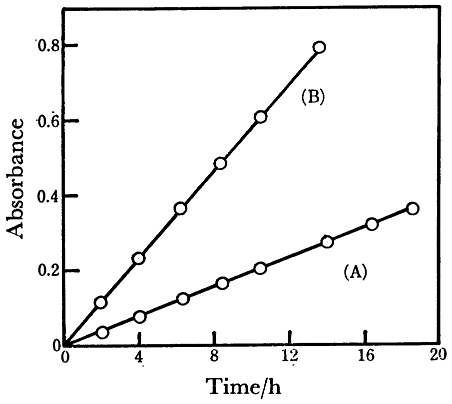

Fig. 2. Typical kinetic runs of the reaction between Co^{II}-EDTA and peroxodisulfate ion at 540 nm, pH 3.60, 40 °C, and I=0.50 (NaClO$_4$).
[Co^{II}-EDTA]=3.08×10^{-3} M.
(A) [S$_2$O$_8^{2-}$]=8.65×10^{-3} M, (B) [S$_2$O$_8^{2-}$]=2.89×10^{-2} M.

peroxodisulfate ion was confirmed spectrophotometrically as follows:

$$2\mathrm{Co^{II}\text{-}EDTA} + \mathrm{S_2O_8^{2-}} = 2\mathrm{Co^{III}(edta)^-} + 2\mathrm{SO_4^{2-}}$$

The plots of the absorbance *vs.* the time show a straight line for 80% of the whole reaction (Fig. 2). This behavior of the change in the absorbance with the time indicates that the oxidation rate is zero-order with respect to the Co^{II}-EDTA concentration. The kinetic data are shown in Table 1.

Table 1. Kinetic data for the oxidation of Co^{II}-EDTA by the peroxodisulfate ion

Concentration of Co^{II}-EDTA (10^{-3}M)	Rate$^{a)}$ (10^{-6} M s^{-1})
2.0	1.2
4.0	1.2
5.0	1.2
7.4	1.3
10.0	1.2

a) [S$_2$O$_8^{2-}$]=8.65×10^{-2} M, pH 3.60, 50 °C, I=0.50.

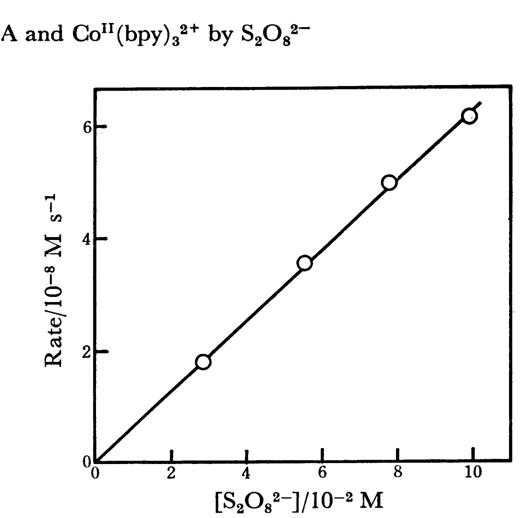

Fig. 3. Plot of the apparent rate for the peroxodisulfate oxidation of Co^{II}-EDTA *vs.* [S$_2$O$_8^{2-}$] at pH 3.60, 40 °C, and I=0.50 (NaClO$_4$).
[Co^{II}-EDTA]=3.02×10^{-3} M.

In order to determine the effect of the peroxodisulfate-ion concentration on the rate, the reaction was carried out at four different initial concentrations of the peroxodisulfate ion. As is shown in Fig. 3, the plot of the apparent rate *vs.* the peroxodisulfate-ion concentration shows a straight line (Fig. 3). The rate law for the oxidation reaction of Co^{II}-EDTA with the peroxodisulfate ion is represented by Eq. 1:

$$\frac{d[\mathrm{Co^{III}(edta)^-}]}{dt} = 2k[\mathrm{S_2O_8^{2-}}] \qquad (1)$$

where k is the first-order rate constant at a given pH value. The determination of the rate constants was performed in the temperature range from 50 °C to 75 °C. The rate constant at 25 °C was obtained by the extrapolation of the Arrhenius plots. The values of the rate constant at 25 °C and 75 °C, and of the activation enthalpy and entropy, are summarized in Table 2.

The effect of the pH on the oxidation rate was investigated in the pH range from 3.50 to 5.36. Table 3

Table 2. The rate constants, equilibrium constant, and activation parameters for the peroxodisulfate oxidation of Co^{II}-EDTA and Co^{II}(bpy)$_3^{2+}$

Complex ion	Rate constant (s^{-1})	K_e (M^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)
Co^{II}-EDTA	5.5×10^{-8} $^{a)}$ 2.3×10^{-5} $^{b)}$	—	24	−12
Co^{II}(bpy)$_3^{2+}$	0.53$^{c)}$	5.6	—	—

a) pH 3.60, 25 °C, I=0.50. b) pH 3.60, 75 °C, I=0.50. c) pH 3.60, 25 °C, I=0.50.

Table 3. The rate constants for the peroxodisulfate oxidation of Co^{II}-EDTA at various pHs

pH	Rate constant$^{a)}$ (s^{-1})
3.50	1.1×10^{-6}
4.10	1.0×10^{-6}
5.36	9.8×10^{-7}

a) at 50 °C and I=0.50.

shows the first-order rate constant at various pH values. The rate constant increases with a decrease in the pH value, but the variation in the rate constant is negligibly small.

The rate-determining step in the oxidation reaction of Co^{II}–EDTA with the peroxodisulfate ion must be homolytic fission into two sulfate radicals, since the oxidation rate is first-order with respect to the peroxodisulfate-ion concentration and is independent of the Co^{II}–EDTA concentration. The path for the oxidation of Co^{II}–EDTA may be represented by Eqs. 2 and 3:

$$S_2O_8^{2-} \xrightarrow{\text{slow}} 2SO_4^{\cdot-} \quad (2)$$

$$\text{Co}^{II}\text{-EDTA} + SO_4^{\cdot-} \xrightarrow{\text{fast}} \text{Co}^{III}(\text{edta})^- + SO_4^{2-} \quad (3)$$

Kolthoff and Miller[15] investigated the kinetics of the decomposition reaction of the peroxodisulfate ion in an acidic solution. They demonstrated that the rate law for the decomposition reaction was of the form:

$$-\text{d}[S_2O_8^{2-}]/\text{d}t = k_1[S_2O_8^{2-}] + k_2[S_2O_8^{2-}][H^+]$$

and that the contribution of the second term could be neglected above pH 2.0.

The values of the rate constant and the activation parameters of the peroxodisulfate-ion oxidation of Co^{II}–EDTA are different from those of the auto-decomposition reaction.[15] No detailed explanations of the differences in the effect of the hydrogen ion, the rate constant, and the activation parameters between the peroxodisulfate-ion oxidation reaction of Co^{II}–EDTA and the auto-decomposition reaction of the peroxodisulfate ion can be given.

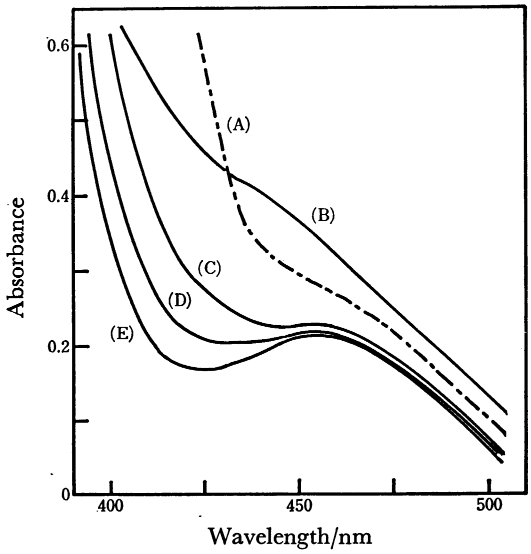

Fig. 4. Absorption spectra of the species related to the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion.
(A) Spectrum of Co^{II}(bpy)$_3^{2+}$ solution in the pH range from 3.10 to 6.50.
(B) Spectrum obtained for the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion at pH 6.50 after the completion of the reaction.
(C) Spectrum obtained for the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion at pH 5.50 after the completion of the reaction.
(D) Spectrum obtained for the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion at pH 4.03 after the completion of the reaction.
(E) Spectrum obtained for the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion in the pH range from 3.10 to 3.60 after the completion of the reaction.
[Co^{II}(bpy)$_3^{2+}$]=3.00×10^{-3} M, [S$_2$O$_8^{2-}$]=3.00×10^{-2} M.

The Oxidation of Co^{II}(bpy)$_3^{2+}$ by S$_2$O$_8^{2-}$. Figure 4 shows the change in the absorption spectra with the pH of the solution, which was obtained for the reaction of Co^{II}(bpy)$_3^{2+}$ with the peroxodisulfate ion. Curve E, which was obtained in the pH range from 3.10 to 3.60, coincides with the absorption spectrum of Co^{III}(bpy)$_3^{3+}$. However, the absorption spectra of the products obtained above pH 3.60 do not coincide with that of Co^{III}(bpy)$_3^{3+}$. Consequently, the kinetic measurements of the oxidation reaction were carried out at pH 3.60. The oxidation product obtained above pH 3.60 was not characterized.

The stoichiometry for the reaction of Co^{II}(bpy)$_3^{2+}$ with the peroxodisulfate ion was examined spectrophotometrically. If two moles of Co^{II}(bpy)$_3^{2+}$ are oxidized by one mol of the peroxodisulfate ion under an excess of the Co^{II}(bpy)$_3^{2+}$ concentration with respect to the peroxodisulfate-ion concentration, the absorbance (*D*) at a given wavelength after the completion of the reaction is shown by Eq. 4:

$$D = \varepsilon_{\text{Co}^{II}(\text{bpy})_3^{2+}}([\text{Co}^{II}(\text{bpy})_3^{2+}] - 2[S_2O_8^{2-}]) + 2\varepsilon_{\text{Co}^{III}(\text{bpy})_3^{3+}}[S_2O_8^{2-}] \quad (4)$$

where $\varepsilon_{\text{Co}^{III}(\text{bpy})_3^{3+}}$ and $\varepsilon_{\text{Co}^{II}(\text{bpy})_3^{2+}}$ denote the molar extinction coefficients of Co^{III}(bpy)$_3^{3+}$ and Co^{II}(bpy)$_3^{2+}$ respectively. At 420 nm, $\varepsilon_{\text{Co}^{III}(\text{bpy})_3^{3+}}$ and $\varepsilon_{\text{Co}^{II}(\text{bpy})_3^{2+}}$ are 61.0 and 157.0 respectively. At [Co^{II}(bpy)$_3^{2+}$]=4.50×10^{-3} M, Eq. 4 can be rewritten as Eq. 5:

$$D = 0.707 - 192[S_2O_8^{2-}] \quad (5)$$

Figure 5 shows the plots of the absorbance *vs.* [S$_2$O$_8^{2-}$] at pH 3.60. The values of the intercept and slope are 0.702 and −188 respectively. This result illustrates that the overall reaction can be represented as follows:

$$2\text{Co}^{II}(\text{bpy})_3^{2+} + S_2O_8^{2-} = 2\text{Co}^{III}(\text{bpy})_3^{3+} + 2SO_4^{2-}$$

The plots of log ($A_t - A_\infty$) *vs.* the time show a straight

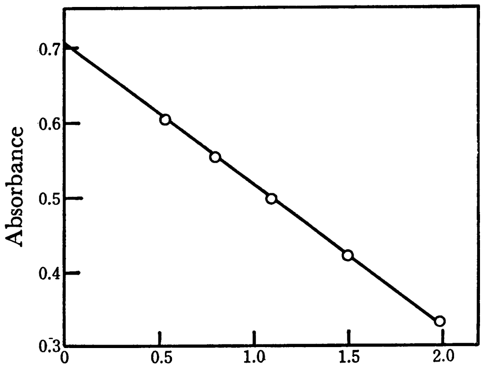

Fig. 5. Plot of the absorbance *vs.* [S$_2$O$_8^{2-}$] for the reaction of Co^{II}(bpy)$_3^{2+}$ with peroxodisulfate ion. The measurements of absorbance were made at pH 3.60, 25 °C, and 420 nm.
[Co^{II}(bpy)$_3^{2+}$]=4.50×10^{-3} M.

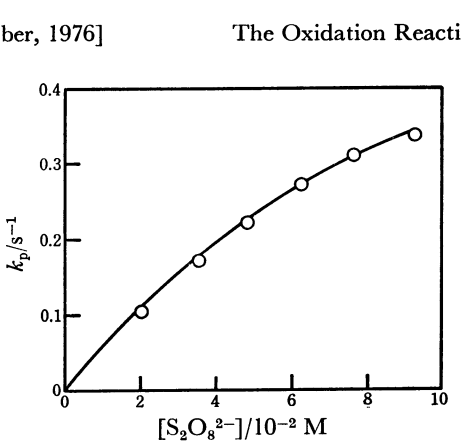

Fig. 6. Plot of the pseudo-first-order rate constant *vs.* $[S_2O_8^{2-}]$ at pH 3.60, 25 °C, and $I=0.50$ (Na_2SO_4). $[Co^{II}(bpy)_3^{2+}]=3.00\times10^{-3}$ M.

line for at least 80% of the whole reaction, where A_t is the absorbance at time t and A_∞, the absorbance after all the $Co^{II}(bpy)_3^{2+}$ has been oxidized to $Co^{III}(bpy)_3^{3+}$. This indicates that the rate of the oxidation of $Co^{II}(bpy)_3^{2+}$ by the peroxodisulfate ion is first-order-dependent on the concentration of $Co^{II}(bpy)_3^{2+}$. As is shown in Fig. 6, the relation between the apparent pseudo-first-order rate constants, k_p, which were evaluated from the slope of the log (A_t-A_∞) *vs.* time plots, and the concentrations of the peroxodisulfate ion is not linear. This result seems to be compatible with the existence of a pre-equilibrium between the $Co^{II}(bpy)_3^{2+}$ and $S_2O_8^{2-}$ to form an ion-pair, which then undergoes decomposition to give $Co^{III}(bpy)_3^{3+}$ and the sulfate radical ion. The reaction paths may be represented as follows:

$$Co^{II}(bpy)_3^{2+} + S_2O_8^{2-} \overset{K_e}{\rightleftharpoons} [Co^{II}(bpy)_3^{2+}\cdot S_2O_8^{2-}] \xrightarrow{k} Co^{III}(bpy)_3^{3+} + SO_4^{\cdot-} + SO_4^{2-} \quad (6)$$

followed by

$$Co^{II}(bpy)_3^{2+} + SO_4^{\cdot-} \xrightarrow{\text{fast}} Co^{III}(bpy)_3^{3+} + SO_4^{2-} \quad (7)$$

No effect of the pH on the rate of the oxidation could be found in the pH range from 3.1 to 3.6. The ion-pair formation between metal complexes and the peroxodisulfate ion has been reported on the basis of the kinetic data of the oxidation reaction.[16] Furthermore, for the oxidation of $Fe^{II}(bpy)_3^{2+}$ by the peroxodisulfate ion, ion-pair formation as an intermediate was postulated.[11] The rate law for the peroxodisulfate oxidation of $Co^{II}(bpy)_3^{2+}$ is represented by Eq. 8:

$$\frac{d[Co^{III}(bpy)_3^{3+}]}{dt} = \left\{\frac{2k\cdot K_e}{1+K_e[S_2O_8^{2-}]}\right\}[S_2O_8^{2-}][Co^{II}(bpy)_3^{2+}]_T \quad (8)$$

where k and K_e are the first-order rate constant and the equilibrium constant ($K_e=[Co^{II}(bpy)_3^{2+}\cdot S_2O_8^{2-}]/[Co^{II}(bpy)_3^{2+}][S_2O_8^{2-}]$) for Reaction 6 respectively, and where $[Co^{II}(bpy)_3^{2+}]_T$ is the total concentration of the tris(2,2′-bipyridine)cobalt(II) ion. The reciprocal of the observed second-order rate constant is shown by Eq. 9:

$$\frac{1}{k_{obsd}} = \frac{1}{2k\cdot K_e} + \frac{1}{2k}[S_2O_8^{2-}] \quad (9)$$

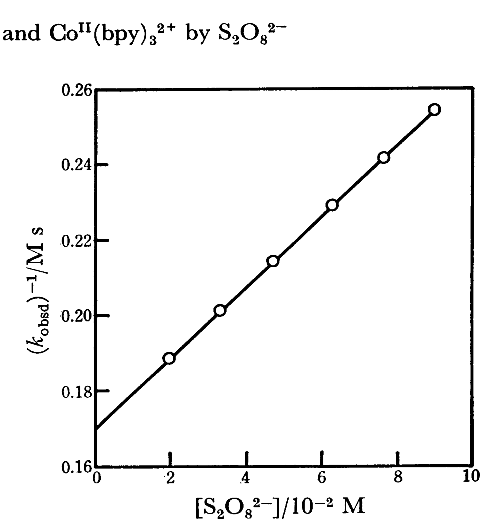

Fig. 7. Plot of the inverse of the observed second-order rate constant *vs.* $[S_2O_8^{2-}]$ at pH 3.60, 25 °C, and $I=0.50$ (Na_2SO_4). $[Co^{II}(bpy)_3^{2+}]=3.00\times10^{-3}$ M.

The plot of $1/k_{obsd}$ *vs.* $[S_2O_8^{2-}]$ shows a straight line (Fig. 7). The linear plot is consistent with the occurrence of the reaction of 6 and 7. The values of k and K_e are listed in Table 2.

It seems likely that the oxidation reaction of $Co^{II}(bpy)_3^{2+}$ with the peroxodisulfate ion would proceed through an outer-sphere mechanism, since the oxidation product is $Co^{III}(bpy)_3^{3+}$.

The standard oxidation-reduction potentials for the $Co^{II}(bpy)_3^{2+}$–$Co^{III}(bpy)_3^{3+}$ couple and the $Co^{II}(edta)^{2-}$–$Co^{III}(edta)^{-}$ couple are 0.37 V[17] and −0.37 V[18] respectively. With regard to the standard oxidation-reduction potential, the rate for the oxidation of $Co^{II}(bpy)_3^{2+}$ by the peroxodisulfate ion is expected to be smaller than that for the oxidation of Co^{II}–EDTA by the peroxodisulfate ion. As is shown in Table 2, however, reactivity of $Co^{II}(bpy)_3^{2+}$ against the peroxodisulfate ion was found to be much larger than that of Co^{II}–EDTA. The differences in reactivity and in rate law between $Co^{II}(bpy)_3^{2+}$ and Co^{II}–EDTA may come from the difference in the charge on the cobalt(II) complexes.

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13) The equilibrium constant ($K=[\mathrm{Co^{II}(Hedta)(H_2O)^-}]/[\mathrm{Co^{II}(edta)^{2-}}][\mathrm{H^+}]$) is $10^{3.1}$ $\mathrm{M^{-1}}$ at 20 °C and $I=0.10$.[14] $\mathrm{Co^{II}}$-EDTA complex exists as $\mathrm{Co^{II}(Hedta)(H_2O)^-}$ and $\mathrm{Co^{II}(edta)^{2-}}$ in the pH range from 3.50 to 5.36. The formula of $\mathrm{Co^{II}}$-EDTA used in this paper represents the mixture of $\mathrm{Co^{II}(edta)^{2-}}$ and $\mathrm{Co^{II}(Hedta)(H_2O)^-}$.

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