July, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **60**, *2367—2372 (1987)* 2367

# Light-induced Electron-transfer Reactions. 5. Kinetics of the Oxidation of Ethylenediaminetetraacetatocobaltate(II) Complexes by Peroxodisulfate Ion, Induced by Irradiation with Visible Light of Aqueous Solutions Containing Tris(2,2′-bipyridine)ruthenium(II) Ion

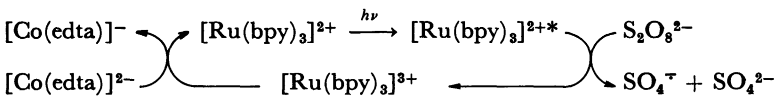
Suzuko Nishida and Masaru Kimura*
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

(Received November 4, 1986)

The oxidation reaction of ethylenediaminetetraacetatocobaltate(II) ($[Co(edta)]^{2-}$) by peroxodisulfate ion ($S_2O_8^{2-}$) is greatly accelerated by irradiation with visible light of aqueous solutions containing tris(2,2′-bipyridine)ruthenium(II) ion ($[Ru(bpy)_3]^{2+}$). The overall reaction is $2[Co(edta)]^{2-}+S_2O_8^{2-} \rightarrow 2[Co(edta)]^{-}+2SO_4^{2-}$. The $[Ru(bpy)_3]^{2+}$ ion acts as a photosensitizer and -catalyst for this reaction, and the mechanism consists of a chain reaction being initiated by the quenching reaction of the photoexcited ruthenium(II) complex ion ($[Ru(bpy)_3]^{2+*}$) by $S_2O_8^{2-}$ ion. The mechanism of the reaction is presented to account for the results obtained.

There has been much interest in the photoinduced electron-transfer reactions containing $[Ru(bpy)_3]^{2+}$ from viewpoints of solar energy conversion.[1-3] In order to produce oxygen by the water photolysis, it is generally required to combine oxidative quenching reactions with redox catalytic steps with solid catalysts such as $RuO_2$, $RuO_2 \cdot xH_2O$, and $IrO_2$. Peroxodisulfate ion ($S_2O_8^{2-}$) is one of the most useful oxidative quenchers because $S_2O_8^{2-}$ decomposes to two sulfate ions upon photoreduction and thus, the reverse electron-transfer reaction can be completely prevented. Actually, there have been several reports using $S_2O_8^{2-}$ for the production of oxygen from water by use of $[Ru(bpy)_3]^{2+}$ as a photocatalyst.[4-13]

The photoexcited ruthenium(II) complex ($[Ru(bpy)_3]^{2+*}$), is quenched rapidly by the peroxodisulfate ion, generating $[Ru(bpy)_3]^{3+}$, $SO_4^{\cdot -}$, and $SO_4^{2-}$.[4] Both the species $[Ru(bpy)_3]^{3+}$ and $SO_4^{\cdot -}$ are strong oxidants and are able to oxidize various compounds. Thus, it is possible to design various kinds of light-induced oxidation reactions by using the peroxodisulfate ion containing $[Ru(bpy)_3]^{2+}$ as a photocatalyst. In previous works,[14,15] we studied the light-induced oxidation reactions of oxalate ions and formate ions by the peroxodisulfate ion. The present paper describes an experiment for the light-induced electron-transfer reaction between $[Co(edta)]^{2-}$($edta^{4-}$=ethylenediaminetetraacetate ion) and $S_2O_8^{2-}$ by employing $[Ru(bpy)_3]^{2+}$ as a photo-catalyst. This reaction hardly proceeded in the absence of $[Ru(bpy)_3]^{2+}$ under the conditions in the present paper and we demonstrate that the proposed scheme (v.i.) operates well in solutions over the pH range 1.9—7.0. Proposed scheme:



Hereafter, we use the abbreviation EDTA for all the forms of $H_4edta$, $H_3edta^-$, $H_2edta^{2-}$, $Hedta^{3-}$, and $edta^{4-}$.

## Experimental

**Chemicals.** $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ and $K[Co(edta)] \cdot 2H_2O$ were prepared as described in the literature[16] and recrystallized twice from redistilled water. Reagent grade potassium peroxodisulfate (Wako Pure Chemicals Co.) was recrystallized twice from redistilled water and dried at room temperature in a vacuum desiccator. Sodium perchlorate used for adjusting ionic strength was recrystallized twice from redistilled water. Disodium dihydrogen ethylenediaminetetraacetate ($Na_2H_2edta$), cobalt sulfate($CoSO_4 \cdot 7H_2O$), and other chemicals were of guaranteed-reagent grade and used without further purification. Redistilled water was prepared from deionized water first by successive distillation from alkaline permanganate solution and then without addition of any reagents in a glass still.

**Procedures.** The reaction vessel was a colorless glass bottle (capacity 0.5 $dm^3$, diameter 80 mm, thickness 1 mm with 10 mm neck) and was placed in a thermostatted water bath made of colorless glass (2×3×3 $dm^3$, thickness 6 mm). Unless otherwise stated, the sample solution was irradiated with light from two 100-W tungsten lamps that were placed 3 dm to the right- and left-hand sides to the center of the reaction vessel. Irradiation was continued throughout the reaction. Oxygen was removed by bubbling pure nitrogen gas through the solution. Aliquot samples were withdrawn at appropriate times and mixed with a cation-exchange resin (Dowex 50W-X8, 200—400 mesh, hydrogen form, washed well with distilled water) in order to remove $[Ru(bpy)_3]^{2+}$ from the reaction solution and to stop the reaction. After filtration, the concentration of $[Co(edta)]^-$ formed was determined spectrophotometrically by using the maximum molar absorption coefficient 295 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 536 nm. The concentration of the peroxodisulfate ion remaining was determined polarographically at 0.1 V vs. SCE in a solution of 0.01 mol dm$^{-3}$ perchloric acid, 0.1 mol dm$^{-3}$ sodium perchlorate and 0.01% gelatine at 25 °C.

It was confirmed from the difference spectra between the reaction solution and the filtrate after removing $[Ru(bpy)_3]^{2+}$ with the cation-exchange resin (see above) that the concentration of $[Ru(bpy)_3]^{2+}$ maintained constant in the presence of $[Co(edta)]^{2-}$. The concentrations of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ in the absence of $[Co(edta)]^{2-}$ were determined from the measurements of absorbance by using the values of molar absorption coefficients (dm$^3$ mol$^{-1}$ cm$^{-1}$) $1.1\times10^4$ and $3.3\times10^3$ at 420 nm, respectively, and $1.4\times10^4$ and $2.8\times10^2$ at 452 nm, respectively.[17] The Stern-Volmer plots were obtained from measurements of the luminescence of $[Ru(bpy)_3]^{2+*}$ by using a Hitachi 850 spectrofluorometer at an excitation energy of 452 nm after removing oxygen by bubbling pure argon gas through the solution.

## Results and Discussion

As seen in Fig. 1, when the solutions containing $[Ru(bpy)_3]^{2+}$, $[Co(edta)]^{2-}$, and $S_2O_8^{2-}$ were irradiated with visible light, the concentration of $S_2O_8^{2-}$ decreased and that of $[Co(edta)]^-$ increased with the irradiation time ($t$). Both the kinetic curves in plots of $[S_2O_8^{2-}]$ vs. $t$ and $[[Co(edta)]^-]$ vs. $t$ were not influenced by the ratio of $[Co(II)]_{added}/[EDTA]_{added}$ over the range 1—3, but were seriously influenced at the ratio of 0.1.

**Stoichiometry.** When the light-induced reaction proceeded to large extent under the conditions $[Co(II)]_{added} \geq [EDTA]_{added}$, the concentrations of $[Co(edta)]^-$ and $S_2O_8^{2-}$ were determined. The ratio of $[[Co(edta)]^-]_{formed}/[S_2O_8^{2-}]_{decomposed}$ was $2.0\pm0.1$ as an average of 7 runs. This indicates that the stoichiometry ( and the overall reaction) is expressed by Eq. 1.

$$2[Co(edta)]^{2-} + S_2O_8^{2-} \longrightarrow 2[Co(edta)]^- + 2SO_4^{2-} \quad (1)$$

(in the case of $[Co(II)]_{added} \geq [EDTA]_{added}$)

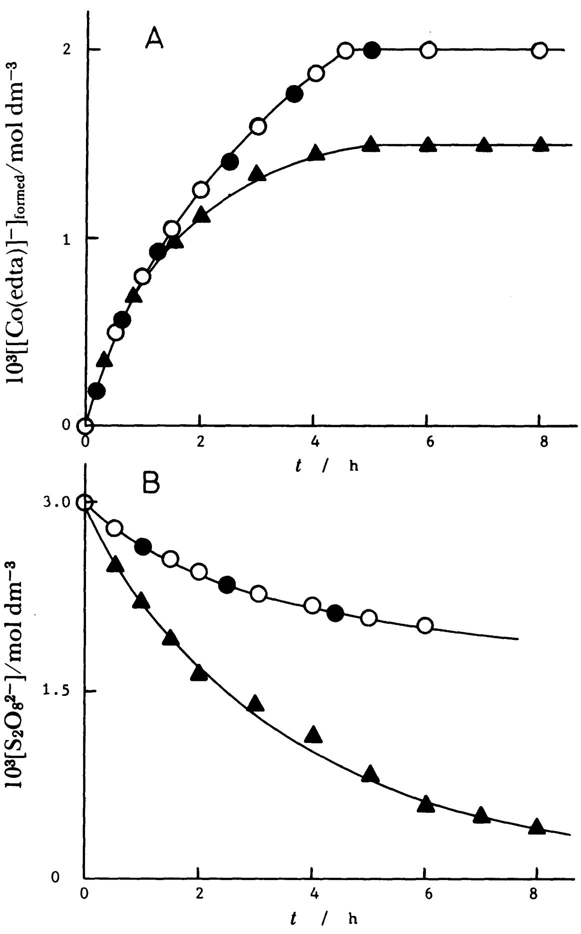


Fig. 1. Plots of $[[Co(edta)]^-]$ vs. $t$ (A) and $[S_2O_8^{2-}]$ vs. $t$ (B). Initial concentrations of $CoSO_4$ and EDTA are, respectively, 0.006 and 0.002 (-○-), 0.002 and 0.002 (-●-), and 0.002 and 0.020 mol dm$^{-3}$ (-▲-), and those of $K_2S_2O_8$ and $[Ru(bpy)_3]Cl_2$ are 0.003 and $5\times10^{-5}$ mol dm$^{-3}$, respectively. Reaction solution was irradiated with two 100-W tungsten lamps and saturated with nitrogen gas. pH 4.6. 30 °C. $\mu$= 0.1 mol dm$^{-3}$.

On the other hand, when the concentration of cobalt(II) ion added was less than that of EDTA, the decomposition rate of $S_2O_8^{2-}$ became much faster, while the formation rate of $[Co(edta)]^-$ did not change so much. At the ratio $[Co(II)]_{added}/[EDTA]_{added}=0.1$, the rate of decomposition of $S_2O_8^{2-}$ became almost two times faster than that at the ratios of 1—3 (see the plots ▲ in Fig. 1). After the results and mechanisms of reaction under the conditions of $[Co(II)]_{added}=[EDTA]_{added}$ are presented, we discuss such behavior under the conditions of $[Co(II)]_{added} \ll [EDTA]_{added}$. As stated before, the concentration of $[Ru(bpy)_3]^{2+}$ remained constant during the reaction. However, after all the $[Co(edta)]^{2-}$ ion was oxidized to the $[Co(edta)]^-$ ion, the $[Ru(bpy)_3]^{2+}$ concentration began to decrease accompanying the formation of $[Ru(bpy)_3]^{3+}$. This fact is given in Fig. 2. After the complete change of $[Co(edta)]^{2-}$ to $[Co(edta)]^-$ the latter concentration remained constant, but the concentrations of $[Ru(bpy)_3]^{2+}$ as well as $[Ru(bpy)_3]^{3+}$ decreased gradually. The $[Ru(bpy)_3]^{3+}$ ion oxidizes slowly water, and some of $[Ru(bpy)_3]^{3+}$ appears to dissociate in such a solution without any reductants[3] and the dissociated bipyridine may be oxidized by the $SO_4^{\cdot-}$ radical.

**Effect of Hydrogen Ion Concentration.** The effect of the hydrogen ion concentration on the reaction rates ($[S_2O_8^{2-}]$ vs. $t$ and $[[Co(edta)]^-]$ vs. $t$) was examined over the pH range 1.1—7.0 under the conditions of the plots● in Fig. 1. The rate of the reaction was independent of the hydrogen ion concentrations over the pH range 1.9—7.0, and at pH 1.1, the rate of the reaction became very slow, because $[Co(edta)]^{2-}$ in solution could dissociate to large extent at such a strong acidity.[18] Hereafter, all the experiments were carried out at pH 4.6.

**Effect of Concentrations of Reactants, $[Co(edta)]^{2-}$ and $S_2O_8^{2-}$.** Under the conditions of plots ● in Fig. 1, i.e., $[Co(II)]_{added}=[EDTA]_{added}$, the rates of the reaction $-d[S_2O_8^{2-}]/dt$ and $d[[Co(edta)]^-]/dt$ were independent of the initial concentrations of $[Co(edta)]^{2-}$ over the range 0.001—0.005 mol dm$^{-3}$, and were, however, dependent on those of peroxodisulfate ion. The initial rate of the reaction $\Delta[[Co(edta)]^-]_i/\Delta t(=V_i)$ was determined at various concentrations of $S_2O_8^{2-}$, and the reciprocal $V_i$ was plotted against the reciprocal of the initial concentration of $S_2O_8^{2-}$. As seen in Fig. 3, the plots of $V_i^{-1}$ vs. $[S_2O_8^{2-}]_i^{-1}$ showed a straight line with an intercept, and the slope of the plot was dependent on the ionic strength($\mu$).

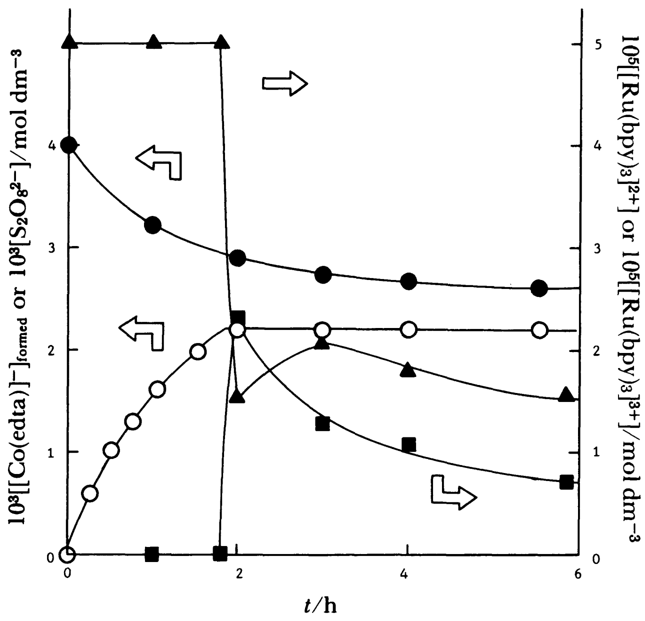


Fig. 2. Variations of the reactants' concentrations against reaction time. Plots ●, ○, ▲, and ■ indicate the variations of concentrations of $S_2O_8^{2-}$, $[Co(edta)]^-$, $[Ru(bpy)_3]^{2+}$, and $[Ru(bpy)_3]^{3+}$, respectively. Initial concentrations are 0.004 mol dm$^{-3}$ in $K_2S_2O_8$, $2.2\times10^{-3}$ mol dm$^{-3}$ in $Na_2[Co(edta)]$, and $5\times10^{-5}$ mol dm$^{-3}$ in $[Ru(bpy)_3]Cl_2$. Reaction solution was irradiated with four 100-W tungsten lamps. $\mu$=0.03 mol dm$^{-3}$. Other conditions are the same as in Fig. 1.

Thus the empirical rate law can be written as follows.

$$V_i^{-1} = \left(\frac{\Delta[[Co(edta)]^-]_i}{\Delta t}\right)^{-1} = \left(-\frac{2\Delta[S_2O_8^{2-}]_i}{\Delta t}\right)^{-1}$$
$$= \alpha + \beta[S_2O_8^{2-}]_i^{-1} \tag{2}$$

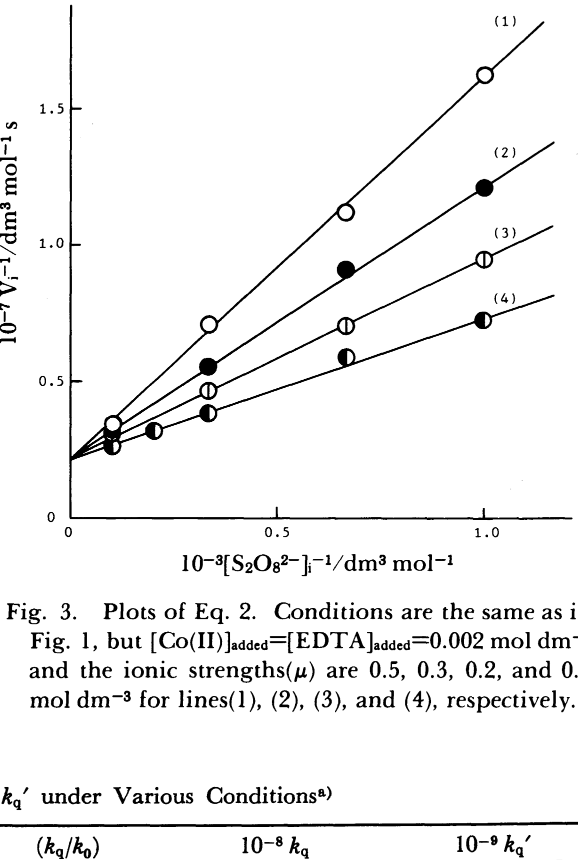


Fig. 3. Plots of Eq. 2. Conditions are the same as in Fig. 1, but $[Co(II)]_{added}=[EDTA]_{added}$=0.002 mol dm$^{-3}$ and the ionic strengths($\mu$) are 0.5, 0.3, 0.2, and 0.1 mol dm$^{-3}$ for lines(1), (2), (3), and (4), respectively.

Table 1. Values of $\alpha$, $\beta$, $k_q/k_0$, $k_q$, and $k_q'$ under Various Conditions[a]

| Temp<br>°C | $\mu$<br>mol dm$^{-3}$ | $10^{-6}\ \alpha$<br>dm$^3$ mol$^{-1}$ s | $10^{-3}\ \beta$<br>s | $(k_q/k_0)$<br>dm$^3$ mol$^{-1}$ | $10^{-8}\ k_q$<br>dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^{-9}\ k_q'$<br>dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 30 | 0.1 | 2.13 | 5.13 | 416 | 6.30 7.00[b] | 2.94[c] |
| 30 | 0.2 | 2.32 | 7.08 | 328 | 4.97 4.77[b] | 2.50[c] |
| 30 | 0.3 | 2.30 | 9.82 | 234 | 3.55 3.26[b] | 2.27[c] |
| 30 | 0.5 | 2.14 | 14.0 | 153 | 2.32 2.02[b] | 2.18[c] |
| 10 | 0.1 | 2.00 | 5.01 | 381 | | |
| 20 | 0.1 | 2.00 | 5.15 | 386 | | |
| 40 | 0.1 | 2.11 | 5.94 | 355 | | |
| | | Av. 2.13±0.11 | | | | |

a) Conditions are as in Fig. 3. The $k_q$ and $k_q'$ values are calculated by using $\tau_0=660$ ns and $k_0=\tau_0^{-1}=1.52\times10^6 s^{-1}$.[20] b) Values obtained from the Stern-Volmer plots of the quenching of the luminescence from $[Ru(bpy)_3]^{2+*}$ by $S_2O_8^{2-}$(see Ref. 14)). c) Values obtained from the Stern-Volmer plots of the quenching of the luminescence from $[Ru(bpy)_3]^{2+*}$ by $[Co(edta)]^-$ : the Stern-Volmer constants $K_{sv}$ were $1.94\times10^3$, $1.65\times10^3$, $1.50\times10^3$, and $1.44\times10^3$ dm$^3$ mol$^{-1}$ for ionic strengths 0.1, 0.2, 0.3, and 0.5 mol dm$^{-3}$, respectively.

The values of $\alpha$ and $\beta$ in Eq. 2 obtained at various temperatures and ionic strengths are given in Table 1 together with the rate constants.

**Effect of Incident Light.** No appreciable formation of $[\mathrm{Co(edta)}]^-$ and no appreciable decomposition of $S_2O_8^{2-}$ were found in the dark under the conditions given. It was found that the formation rate of $[\mathrm{Co(edta)}]^-$(or twofold decomposition rate of $S_2O_8^{2-}$) was proportional to the number of lamps used: $V_i$ in Eq. 2 was $1.18\times10^{-7}$, $2.27\times10^{-7}$, $3.50\times10^{-7}$, and $4.86\times10^{-7}$ mol dm$^{-3}$s$^{-1}$ at the number of lamps of 1, 2, 3, and 4, respectively.

**Effect of Concentration of Photocatalyst.** The initial rate ($V_i$ in Eq. 2) increased with concentrations of $[\mathrm{Ru(bpy)_3}]^{2+}$ and then reached a limiting value (see Fig. 4). This behavior is thought to be due to the change of the amount of light absorbed according to the concentation change of photo-catalyst $[\mathrm{Ru(bpy)_3}]^{2+}$ and is accounted for by Eq. 3.

$$I_a = I_0(1-\exp(-A[[\mathrm{Ru(bpy)_3}]^{2+}])), \tag{3}$$

where $I_0$ is the intensity of the incident light, $I_a$ is the amount of light absorbed by $[\mathrm{Ru(bpy)_3}]^{2+}$, and $A$ is an empirical constant comprising the length of the light path and the molar absorption coefficient of $[\mathrm{Ru(bpy)_3}]^{2+}$.

The rate of reaction ($V_i$) is proportional to $I_a$ (see Eq. 10), and thus, a curve shown in Fig. 4 coincides with the expression of Eq. 3.

**Mechanisms of the Reaction.** The following mechanism of the reaction is presented to account for the results obtained.

$$[\mathrm{Ru(bpy)_3}]^{2+} + h\nu \xrightarrow{I_a}$$

$$[\mathrm{Ru(bpy)_3}]^{2+*} \xrightarrow{k_0} \left\{ \begin{array}{l} \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + h\nu'(\text{emission}) \\ \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \Delta(\text{thermal energy}) \end{array} \right. \tag{4}$$

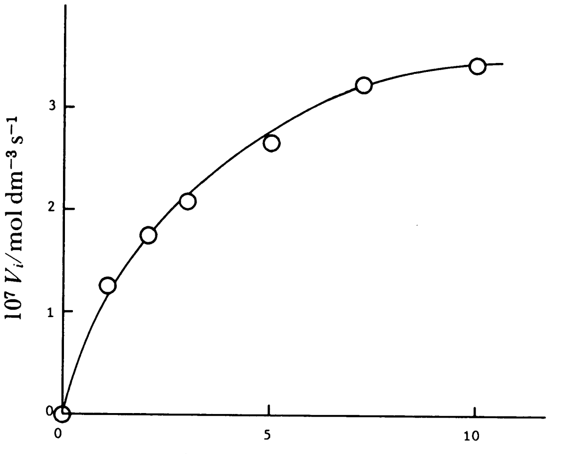


Fig. 4. Effect of the $[\mathrm{Ru(bpy)_3}]^{2+}$ ion concentration on the reaction rate. Conditions as in Fig. 1, but $[\mathrm{Co(II)}]_{\mathrm{added}}=[\mathrm{EDTA}]_{\mathrm{added}}=0.002$ mol dm$^{-3}$.

$$[\mathrm{Ru(bpy)_3}]^{2+*} + S_2O_8^{2-} \xrightarrow{k_q} [\mathrm{Ru(bpy)_3}]^{3+} + SO_4^{\bar{\cdot}} + SO_4^{2-} \tag{5}$$

$$[\mathrm{Ru(bpy)_3}]^{2+} + SO_4^{\bar{\cdot}} \xrightarrow{k_1} [\mathrm{Ru(bpy)_3}]^{3+} + SO_4^{2-} \tag{6}$$

$$[\mathrm{Co(edta)}]^{2-} + SO_4^{\bar{\cdot}} \xrightarrow{k_2} [\mathrm{Co(edta)}]^{-} + SO_4^{2-} \tag{7}$$

$$[\mathrm{Co(edta)}]^{2-} + [\mathrm{Ru(bpy)_3}]^{3+} \xrightarrow{k_3} [\mathrm{Co(edta)}]^{-} + [\mathrm{Ru(bpy)_3}]^{2+} \tag{8}$$

$$[\mathrm{Ru(bpy)_3}]^{2+*} + [\mathrm{Co(edta)}]^{-} \xrightarrow{k_q'} [\mathrm{Ru(bpy)_3}]^{3+} + [\mathrm{Co(edta)}]^{2-} \tag{9}$$

Assuming the steady state concentrations of $SO_4^{\bar{\cdot}}$, $[\mathrm{Ru(bpy)_3}]^{3+}$, and $[\mathrm{Ru(bpy)_3}]^{2+*}$, the following rate law is obtained.

$$\frac{d[[\mathrm{Co(edta)}]^-]}{dt} = \frac{2k_qI_a\phi[S_2O_8^{2-}]}{k_0 + k_q[S_2O_8^{2-}] + k_q'[[\mathrm{Co(edta)}]^-]}, \tag{10}$$

where $\phi$ is the formation efficiency of the excited species, $I_a$ is the amount of light absorbed by $[\mathrm{Ru(bpy)_3}]^{2+}$ (see Eq. 3) and $I_a\phi$ corresponds to the formation rate of $[\mathrm{Ru(bpy)_3}]^{2+*}$. Reaction 9 and the term $k_q'[[\mathrm{Co(edta)}]^-]$ in Eq. 10 might be negligible at least for the initial period of the reaction, and thus, the following rate law can be applied under such conditions.

$$V_i^{-1} = \frac{1}{2I_a\phi} + \frac{k_0}{2I_a\phi k_q}[S_2O_8^{2-}]_i^{-1} \tag{11}$$

Equation 11 is equivalent to Eq. 2 obtained empirically, and is in agreement with all the results. The $\alpha$ and $\beta$ values in Eq. 2 correspond to $(2I_a\phi)^{-1}$ and $k_0/(2I_a\phi k_q)$, respectively, and thus, the values of $k_q/k_0$ were obtained from the plots of $V_i^{-1}$ vs. $[S_2O_8^{2-}]_i^{-1}$. It is to be noted that the reaction rate of the light-induced reaction was hardly dependent on temperature. The values of $k_q/k_0$ were almost independent of the temperature of solution, and thus, the activation energy of the quenching reaction($E_q$) is almost equal to that of the nonradiative quenching of the photoexcited species($E_0$=10.6 kJ mol$^{-1}$ for $k_0$-path in Eq. 4[21]). The quenching rate constants $k_q'$ and $k_q$ were determined by the measurements of the luminescence of $[\mathrm{Ru(bpy)_3}]^{2+*}$ in solutions of various concentrations of $[\mathrm{Co(edta)}]^-$ and $S_2O_8^{2-}$. The $k_q$ values determined by using Eq. 11 were in good agreement with those determined by the measurements of quenching luminescence. This fact supports the validity of the mechanism and the rate law proposed.

**Confirmation of Rate Law (Eq. 11).** The integral form of Eq. 10 is given by

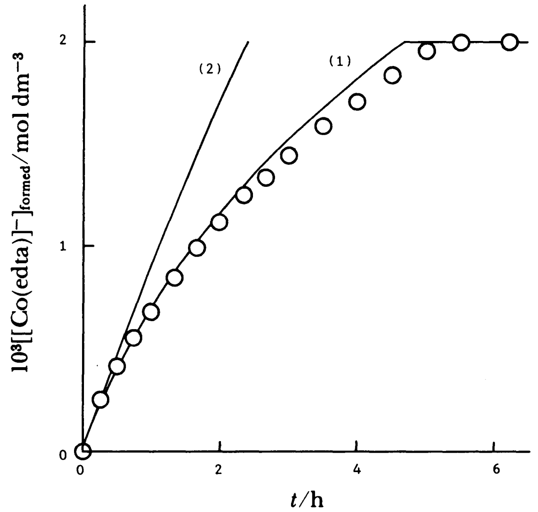


Fig. 5. Plots of Eq. 12. Conditions as in Fig. 1, but $[Co(II)]_{added}=[EDTA]_{added}=0.002$ mol dm$^{-3}$. The solid curve(1) indicates the calculated values using Eq. 12 and plots indicate the data obtained experimentally. Another solid curve(2) indicates the calculated values by using Eq. 12′.[22]

$$\left(\frac{1}{2}k_q-k_q'\right)[[Co(edta)]^-]_{t=t}-(k_0+2k_q'[S_2O_8{}^{2-}]_{t=0})\times \ln\frac{[S_2O_8{}^{2-}]_{t=t}}{[S_2O_8{}^{2-}]_{t=0}}=k_qI_a\phi t \qquad (12)$$

Using values of $k_q$, $k_q'$, $k_0$, and $I_a\phi$, we can calculate a curve of the plots $[[Co(edta)]^-]$ vs. $t$. The calculated curve was in good agreement with the data obtained experimentally (see curve(1) in Fig. 5). A slight deviation only near the completion of the reaction seems to be attributable to the inner-filter effect of $[Co(edta)]^-$ which is produced according to the progress of reaction time. It is to be noted that the calculated curve is greatly altered by neglecting the term $k_q'[[Co(edta)]^-]$ in Eq. 10 (compare curve(2) to curve(1) in Fig. 5), and that the validity of Eq. 11 is limited to the reaction time less than 20 minutes.

As stated before and seen in Fig. 1, under the conditions of $[Co(II)]_{added}/[EDTA]_{added}=0.1$, the formation rate of $[Co(edta)]^-$ decreased to a small extent, while the decomposition rate of $S_2O_8{}^{2-}$ was accelerated greatly. These facts may indicate the occurrence of the following reactions.

$$EDTA+[Ru(bpy)_3]^{3+}\longrightarrow EDTA^{\dot{+}}+[Ru(bpy)_3]^{2+} \qquad (13)$$

$$S_2O_8{}^{2-}+EDTA^{\dot{+}}\longrightarrow SO_4{}^{\dot{-}}+SO_4{}^{2-}+\text{products} \qquad (14)$$

$$EDTA+SO_4{}^{\dot{-}}\longrightarrow EDTA^{\dot{+}}+SO_4{}^{2-} \qquad (15)$$

Reaction 13 is a competitive reaction with reaction 8, and thus, the formation rate of $[Co(edta)]^-$ might have been decreased. Successively, the EDTA radicals will react with peroxodisulfate and thus, the rate of decomposition of $S_2O_8{}^{2-}$ can be greatly accelerated (the reaction mechanisms might become more complex).

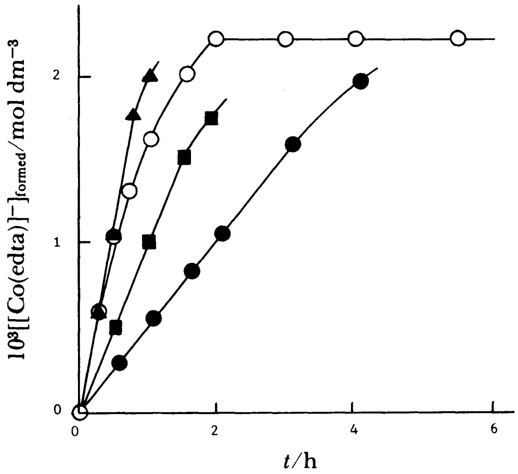


Fig. 6 Comparison with the silver(I) ion-catalyzed reaction. Plots ○ indicate the experimental data obtained under the same conditions as in Fig. 2. Plots ▲, ■, and ● indicate the silver(I) ion-catalyzed reaction. Conditions are $5\times10^{-3}$ mol dm$^{-3}$ in $AgClO_4$ and 30 °C (-▲-), $5\times10^{-3}$ mol dm$^{-3}$ in $AgClO_4$ and 20 °C (-■-), $1\times10^{-3}$ mol dm$^{-3}$ in $AgClO_4$ and 30 °C (-●-), and the other conditions are the same as in the plots ○.

It is known that the oxidation reactions by the peroxodisulfate ion are catalyzed by the silver(I) ion.[23] We have compared the light-induced reaction using $[Ru(bpy)_3]^{2+}$ as a catalyst with the silver(I) ion-catalyzed reaction (see Fig. 6). The reaction rate of the silver(I) ion-catalyzed reaction was dependent on the pH[23] as well as the temperature of the solution. On the other hand, the reaction rate of the light-induced reaction using $[Ru(bpy)_3]^{2+}$ as a photo-catalyst was little dependent on both temperature and pH over the range of pH 1.9—7.0. It may be also simply stated that the activity of the light-induced reaction under four lamps is almost 100 times larger than that of the silver(I) ion-catalyzed reaction under the same concentration of each catalyst.

## References

1) K. Kalyanasundaram, *Coord. Chem. Rev.*, **46**, 159 (1982).
2) N. Sutin, *J. Photochem.*, **10**, 19 (1979).
3) K. Kalyanasundaram, M. Grätzel, and E. Pelizzetti, *Coord. Chem. Rev.*, **69**, 57 (1986).
4) F. Bolletta, A. Juris, M. Maestri, and D. Sandrini, *Inorg. Chim. Acta*, **44**, L175 (1980).
5) M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel, and M. Grätzel, *Helv. Chim. Acta*, **62**, 1111 (1980).

6) M. Neumann-Spallart and K. Kalyanasundaram, *Ber. Bunsenges. Phys. Chem.*, **85**, 704 (1981).

7) J. N. Demas, *J. Chem. Educ.*, **60**, 803 (1983).

8) H. S. White, W. G. Becker, and A. J. Bard, *J. Phys. Chem.*, **88**, 1840 (1984).

9) G. Blondeel, A. Harriman, G. Porter, D. Arwin, and J. Kiwi, *J. Phys. Chem.*, **87**, 2629 (1983).

10) V. Ya Shafirovich and V. V. Strelets, *Nouv. J. Chim.*, **6**, 183 (1982).

11) D. H. M. W. Thewissen, N. Eeuwhorst-Reinten, K. Timmer, A. H. A. Tinnemans, and A. Mackor, *Recl. Trav. Chim. Pays-Bas.*, **101**, 79 (1982).

12) R. Humphry-Baker, J. Lilie, and M. Grätzel, *J. Am. Chem. Soc.*, **104**, 422 (1982).

13) N. K. Khannanov and V. Ya Shafirovich, *Dokl. Akad. Nauk. SSSR*, **260**, 1418 (1981).

14) M. Kimura and S. Nishida, *J. Chem. Soc., Dalton Trans.* **1985**, 355.

15) S. Nishida and M. Kimura, *J. Chem. Res. (S)*, **1986**, 336.

16) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 964 (1966); I. Fujita and H. Kobayashi, *Ber. Bunsunges. Phys. Chem.*, **76**, 115 (1972); T. Tachibana, M. Nakahara, and M. Shibata, "Shin Jikken Kagaku Koza 8," Maruzen, Tokyo (1977), pp. 1475 and 1533.

17) M. Kimura, M. Yamashita, and S. Nishida, *Inorg. Chem.*, **24**, 1527 (1985).

18) The equilibrium constants $K_{\mathrm{II}}$ (=[Co$^{\mathrm{II}}$(Hedta)(H$_2$O)$^-$]/[Co$^{\mathrm{II}}$(edta)$^{2-}$][H$^+$]) and $K_{\mathrm{III}}$(=[Co$^{\mathrm{III}}$(Hedta)(H$_2$O)]/[Co$^{\mathrm{III}}$(edta)$^-$][H$^+$]) are $10^{3.0}$ and $10^{2.98}$, respectively.[19] Thus, both [Co(Hedta)(H$_2$O)]$^-$ and [Co(Hedta)(H$_2$O)] will exist in strong acid solutions.

19) A. E. Martel and R. M. Smith, "Critical Stability Constant, Volume 1 : Amino Acid," PLENUM PRESS, New York and London (1974), p. 206.

20) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).

21) F. E. Lytle and D. H. Hercules, *J. Am. Chem. Soc.*, **91**, 253 (1969).

22) Assuming that reaction(9) is negligible, the integral form of Eq. 10 is:

$$\frac{1}{2}k_{\mathrm{q}}[[\mathrm{Co(edta)}]^-]_{t=t}-k_0\ln\frac{[\mathrm{S_2O_8}^{2-}]_{t=t}}{[\mathrm{S_2O_8}^{2-}]_{t=0}} = k_{\mathrm{q}}I_{\mathrm{a}}\phi t \qquad (12')$$

23) K. Ohashi and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 3049 (1977).