# Kinetic Studies on the Quenching Reaction of the Photo-Excited $[Ru(bpy)_3]^{2+}$ with $[Co(edta)]^-$ in the Presence of EDTA, CDTA, and $C_2O_4^{2-}$

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In the presence of a sacrificial donor (such as ethylenediaminetetraacetic acid, *trans*-1,2-cyclohexanediaminetetraacetic acid or oxalic acid in a deaerated aqueous solution) $[Co(edta)]^-$ is reduced to $[Co(edta)]^{2-}$ by quenching oxidatively the photo-excited $[Ru(bpy)_3]^{2+}$ ($[Ru(bpy)_3]^{2+*}$). The reduction rate for the $[Co(edta)]^-$ increases with an increase in the concentration of the sacrificial donor, and is kept constant at [EDTA] $\geqslant$ 0.03 mol dm$^{-3}$, [CDTA] $\geqslant$ 0.01 mol dm$^{-3}$, or $[C_2O_4^{2-}] \geqslant$ 0.07 mol dm$^{-3}$ at pH 4.6. The ratio $[[Co(edta)]^-]_{reacted}$ : $[EDTA]_{reacted}$ : $[[Co(edta)]^{2-}]_{formed}$ = 2 : 1 : 2 is obtained at pH 5.2. The reaction rates were examined as a function of the concentrations of $[Co(edta)]^-$ and $[Ru(bpy)_3]^{2+}$ as well as the pH, ionic strength, and temperature of the solution, and the intensity of the incident light. In the presence of oxygen, the decrease of $[Co(edta)]^-$ is greatly suppressed and the formation of the hydrogen peroxide is appreciable. The reaction mechanism is presented in order to account for the obtained results.

Various redox reactions induced by $[Ru(bpy)_3]^{2+}$ (bpy= 2,2'-bipyridine) or $[Ru(bpz)_3]^{2+}$ (bpz=2,2-bipyrazine) as a photocatalyst, i.e., hydrogen evolution from water decomposition[1-8] or the reduction of carbon dioxide to methane,[9,10] have been studied from the viewpoint of the photochemical conversion of solar energy. One of the major problems in the utilization of these complexes is that the energy-saving electron-transfer reactions are accompanied by very efficient reverse electron-transfer steps which regenerate the starting materials. A simple technique most often used to prevent a reverse electron-transfer reaction is the addition of a sacrificial donor, such as ethylenediaminetetraacetic acid or triethanolamine, into the reaction system. In this paper, the effects of such sacrificial donors as EDTA,[11] CDTA,[11] and $C_2O_4^{2-}$ are discussed concerning the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ with $[Co(edta)]^-$ in a deaerated aqueous solution.

## Experimental

**Chemicals.** $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ and $K[Co(edta)] \cdot 2H_2O$ were prepared and purified as described in the literature.[12] Disodiumdihydrogenethylenediaminetetraacetate ($Na_2[H_2edta]$) and other chemicals were of guaranteed reagent grade and were used without further purification. A solution containing CDTA was prepared by dissolving in a sodium hydroxide solution. The pH of the solution was continuously adjusted with acetic acid and sodium acetate. Deionized water was further distilled both with and without the addition of permanganate in a glass still.

**Procedures.** The procedures are essentially the same as those described in a previous paper.[13] The $[Co(edta)]^-$ concentration was determined spectrophotometrically after removing the $[Ru(bpy)_3]^{2+}$ by adding a cation-exchange resine (1 g) (Dowex 50W-X8, 200-400 mesh, hydrogen form, washed well with distilled water) into the solution. The total concentration of the EDTA remaining and the $[Co(edta)]^{2-}$ formed in the sample solution was determined by polarography at +0.3 V vs. SCE in a solution comprised 0.05 mol dm$^{-3}$ acetic acid, 0.05 mol dm$^{-3}$ sodium acetate, and 0.01% gelatin at 25 °C under a nitrogen atmosphere. Polarography was performed in the dark without removing the $[Ru(bpy)_3]^{2+}$, since the cation-exchange resin adsorbs some part of the EDTA. The amount of carbon dioxide formed during the reaction was measured by a method reported previously.[14] The rate constant of the redox reaction between $[Ru(bpy)_3]^{3+}$ and EDTA, CDTA, or $C_2O_4^{2-}$ was determined with a Union RA-401 stopped-flow spectrophotometer. A solution of $[Ru(bpy)_3]^{3+}$ was prepared by oxidizing $[Ru(bpy)_3]^{2+}$ with lead dioxide ($PbO_2$) in 0.5 mol dm$^{-3}$ sulfuric acid. After removing $PbO_2$ and $PbSO_4$ by filtration, the $[Ru(bpy)_3]^{3+}$ solution was used for the experiments.

## Results and Discussion

**Dependence of the Concentration of Sacrificial Donors.** No appreciable formation of $[Co(edta)]^{2-}$ was observed in the quenching of $[Ru(bpy)_3]^{2+*}$ with $[Co(edta)]^-$ in the absence of sacrificial agents. However, $[Co(edta)]^-$ decreased remarkably to produce $[Co(edta)]^{2-}$ upon the addition of sacrificial donors in a deaerated aqueous solution. As Fig. 1 shows, the initial rates for a decrease in the $[Co(edta)]^-$ concentration ($V_i$) increase with an increase in the concentration of the sacrificial donors and are kept constant at [EDTA] $\geqslant$ 0.03 mol dm$^{-3}$, [CDTA] $\geqslant$ 0.01 mol dm$^{-3}$, or $[C_2O_4^{2-}] \geqslant$ 0.07 mol dm$^{-3}$. This indicates that a reverse electron-transfer reaction between $[Ru(bpy)_3]^{3+}$ and $[Co(edta)]^{2-}$ competes with the reaction between $[Ru(bpy)_3]^{3+}$ and the sacrificial donor. It is noteworthy that the limiting rate with the excess EDTA is almost the same as that with CDTA, whereas is about 2 times as large as that with $C_2O_4^{2-}$. Otherwise (noted hereafter), the kinetic results observed with EDTA are presented in detail.

**Stoichiometry.** The stoichiometry of the reaction was examined in aqueous solutions containing $2\times10^{-3}$ mol dm$^{-3}$ K[Co(edta)] and $5\times10^{-5}$ mol dm$^{-3}$ $[Ru(bpy)_3]Cl_2$ at pH 5.2 and 25 °C. The ratio of $[[Co(edta)]^-]_{reacted}$ : $[EDTA]_{reacted}$ : $[[Co(edta)]^{2-}]_{formed}$ = 2 : 1 : 2 was always obtained, being independent of the initial EDTA con-

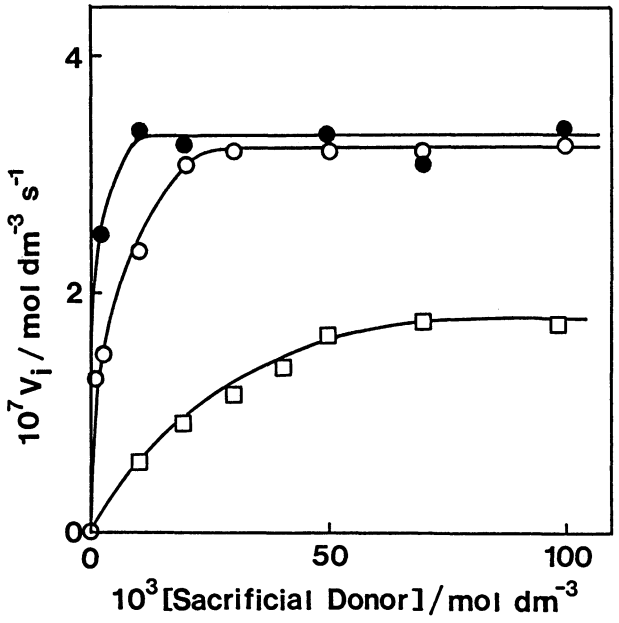


Fig. 1. Dependence of the $V_i$ on the concentration of the EDTA (○), CDTA (●), or $C_2O_4^{2-}$ (□) in deaerated aqueous solutions containing $2\times10^{-3}$ mol dm$^{-3}$ K[Co(edta)] and $5\times10^{-5}$ mol dm$^{-3}$ $[Ru(bpy)_3]Cl_2$ at pH 4.6 and 25 °C. Irradiation was done with four lamps.

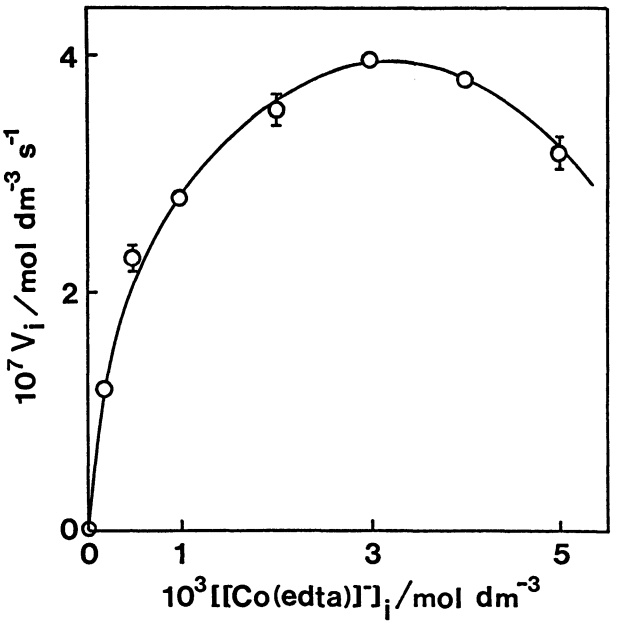


Fig. 2. Dependence of the $V_i$ on the initial concentration of the $[Co(edta)]^-$. Conditions are the same as in Fig. 1 except for 0.05 mol dm$^{-3}$ EDTA.

centration. Carbon dioxide was also formed in the solution; the amount produced per EDTA reacted was estimated to be 1.3—2.1. The concentration of $[Ru(bpy)_3]^{2+}$ was kept constant throughout the reaction. Thus, the stoichiometry of the photo-induced reaction can be expressed by

$$2[Co(edta)]^- + EDTA \rightarrow 2[Co(edta)]^{2-} + \text{products}(CO_2 \cdots). \quad (1)$$

**Dependence of the $[Co(edta)]^-$ Concentration.** Figure 2 indicates that $V_i$ in the presence of 0.05 mol dm$^{-3}$ EDTA increases with an increase in the initial concentrations of the $[Co(edta)]^-$ ($[[Co(edta)]^-]_i$), and has a maximum value at a $[Co(edta)]^-$ concentration of $3\times10^{-3}$ mol dm$^{-3}$. A similar result was obtained with 0.05 mol dm$^{-3}$ CDTA. Thus, the decrease of $V_i$ at $[[Co(edta)]^-]_i > 3\times10^{-3}$ mol dm$^{-3}$ is ascribed to an inner filter effect of $[Co(edta)]^-$ on the photoexcitation of $[Ru(bpy)_3]^{2+}$.

**Effect of Light Intensity and the $[Ru(bpy)_3]^{2+}$ Concentration.** The dependence of $V_i$ on the incident light intensity was examined in an aqueous solution containing 0.05 mol dm$^{-3}$ EDTA, $2\times10^{-3}$ mol dm$^{-3}$ K[Co(edta)], $5\times10^{-5}$ mol dm$^{-3}$ $[Ru(bpy)_3]Cl_2$, 0.05 mol dm$^{-3}$ acetic acid and 0.05 mol dm$^{-3}$ sodium acetate at 25 °C and pH 4.6. It was found that no appreciable formation of $[Co(edta)]^{2-}$ was observed in the dark and that $V_i$ increased in proportion to the number of the lamps irradiated. The dependence of $V_i$ on the $[Ru(bpy)_3]^{2+}$ concentration is presented in Fig. 3. With an increase

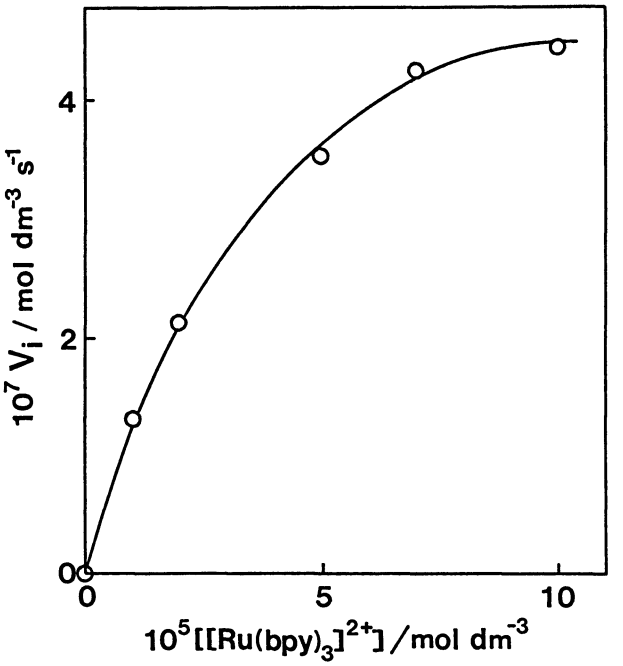


Fig. 3. Effect of the $[Ru(bpy)_3]^{2+}$ concentration. Conditions are the same as in Fig. 1 except for 0.02 mol dm$^{-3}$ EDTA and pH 5.2.

in the $[Ru(bpy)_3]^{2+}$ concentration, $V_i$ increases while approaching a limiting value. This finding as well as the linear relation between $V_i$ and the incident light intensity suggests that $V_i$ is proportional to the amount of light absorbed by $[Ru(bpy)_3]^{2+}$ ($I_a$), which is described by the Lambert–Beer equation:

$$I_a = I_0\{1 - \exp(-\alpha[[Ru(bpy)_3]^{2+}])\}. \quad (2)$$

Here, $I_0$ is the intensity of the incident light and $\alpha$ is a constant comprising an absorption coefficient and an optical path length.

**Effect of pH.** Figure 4 represents the pH effect on $V_i$, where the pH of the solution was adjusted with various concentrations of acetic acid and 0.05 mol dm$^{-3}$ sodium acetate. In this paper, the term "EDTA" is used to designate all of the forms of that substance, irrespective of the protonation states.[11] As the pH increases, smaller amounts of EDTA were required for a limiting rate. It is worth noting that the $V_i$ values under excess EDTA decrease with a decrease in pH.

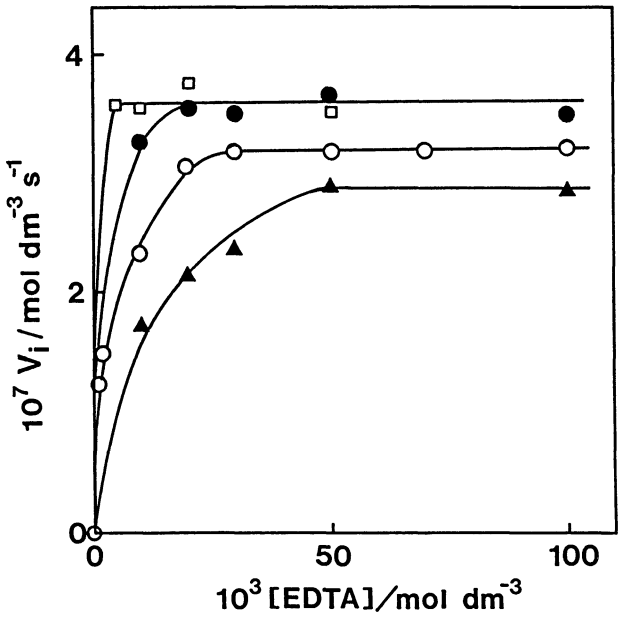


Fig. 4. Dependence of the $V_i$ on the concentration of the EDTA at pH 6.0 (□), 5.2 (●), 4.6 (○), and 4.0 (▲). Other conditions are the same as in Fig. 1.

**Effect of Ionic Strength and Temperature.** The effect of the ionic strength or solution temperature is shown in Figs. 5 and 6. It was found that the reaction rate for the reduction of $[Co(edta)]^-$ decreased as the ionic strength of the solution increased. This is explainable in terms of a reaction between oppositly charged ions (Eq. 5). The rate of the reaction also increases slightly with an increase in the solution temperature.

**Mechanism of Reaction.** It has been reported that oxidized EDTA ($EDTA_{OX}^+$) is rapidly deprotonated to form a reducing radical (EDTA').[15–19] The stability of the EDTA' is dependent on the solution pH. In an acidic medium, EDTA' decomposes due to acid-catalyzed decarboxylation.[18,19] Glyoxylic acid, formaldehyde, and carbon dioxide were identified as being the final products for the oxidation of EDTA.[20,21] Based on the above, the following reaction mechanism is proposed to account for the obtained results:

$$[Ru(bpy)_3]^{2+} + h\nu \longrightarrow [Ru(bpy)_3]^{2+*} \quad (3)$$

$$[Ru(bpy)_3]^{2+*} \xrightarrow{k_0} [Ru(bpy)_3]^{2+} + h\nu' \text{ or } \Delta \text{ (thermal energy)} \quad (4)$$

$$[Ru(bpy)_3]^{2+*} + [Co(edta)]^- \xrightarrow{k_q} [Ru(bpy)_3]^{3+} + [Co(edta)]^{2-} \quad (5)$$

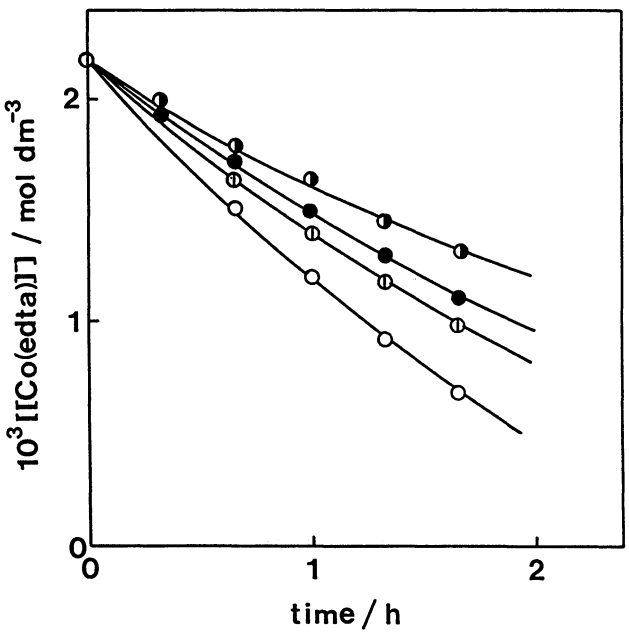


Fig. 5. Effect of the ionic strength. Conditions are the same as in Fig. 1 except for 0.02 mol dm$^{-3}$ EDTA and various ionic strength of 0.2 (○), 0.4 (◑), 0.6 (●), and 1.0 mol dm$^{-3}$ (◑).

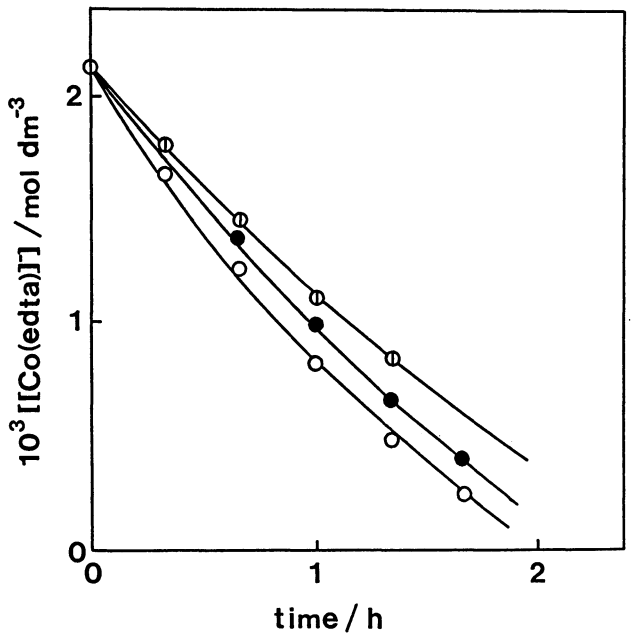


Fig. 6. Effect of temperature. Conditions are the same as in Fig. 1 except for 0.05 mol dm$^{-3}$ EDTA, pH 5.2 and temperature of 5 °C (◑), 15 °C (●), or 25 °C (○).

$$[Ru(bpy)_3]^{3+} + [Co(edta)]^{2-} \xrightarrow{k_1} [Ru(bpy)_3]^{2+} + [Co(edta)]^{-} \quad (6)$$

$$[Ru(bpy)_3]^{3+} + EDTA \xrightarrow{k_2} [Ru(bpy)_3]^{2+} + EDTA_{ox}^{+} \quad (7)$$

$$EDTA_{ox}^{+} \xrightarrow{k_3} EDTA' + H^{+} \text{ (deprotonation)} \quad (8)$$

$$EDTA' + [Co(edta)]^{-} \xrightarrow{k_4} [Co(edta)]^{2-} + \text{products } (CO_2 \cdots) \quad (9)$$

$$EDTA' \xrightarrow{k_5} \text{products (acid-catalyzed decarboxylation).} \quad (10)$$

Assuming a steady state concentration of the $[Ru(bpy)_3]^{2+*}$, $[Ru(bpy)_3]^{3+}$, $EDTA_{ox}^{+}$ and EDTA', the reaction rate is expressed by

$$-\frac{d[[Co(edta)]^{-}]}{dt} = \frac{k_q I_a \Phi [[Co(edta)]^{-}]}{k_0 + k_q [[Co(edta)]^{-}]} \times \frac{(1+\gamma)k_2[EDTA]}{k_1[[Co(edta)]^{2-}] + k_2[EDTA]}, \quad (11)$$

where $\Phi$ is the quantum yield for the excited species $[Ru(bpy)_3]^{2+*}$; thus, $I_a\Phi$ corresponds to the formation rate of $[Ru(bpy)_3]^{2+*}$, and the $\gamma$ value is defined as $k_4[EDTA'][[Co(edta)]^{-}]/\{k_4[EDTA'][[Co(edta)]^{-}] + k_5[EDTA']\}$ and is equal to unity if all of the EDTA' formed by reaction 8 reacts with $[Co(edta)]^{-}$. The second-order rate constant for reaction 6 has been estimated to be larger than $10^4\ dm^3\ mol^{-1}\ s^{-1}$. However, the reverse electron-transfer reaction between $[Ru(bpy)_3]^{3+}$ and $[Co(edta)]^{2-}$ in the solvent cage could take place quite rapidly, since no formation of $[Co(edta)]^{2-}$ was observed without adding a sacrificial donor.

In the presence of the excess EDTA, the relation $k_2[EDTA] \gg k_1[[Co(edta)]^{2-}]$ holds, and the reaction rate reduces to

$$-\frac{d[[Co(edta)]^{-}]}{dt} = \frac{(1+\gamma)k_q I_a \Phi [[Co(edta)]^{-}]}{k_0 + k_q [[Co(edta)]^{-}]}. \quad (12)$$

The obtained stoichiometry suggests that $\gamma$ is equal to unity and that the decomposition of the EDTA' (Eq. 10) does not occur at pH 5.2. With a decrease in pH, $\gamma$ decreases owing to reaction 10, and then the limiting rate observed at the excess EDTA decreases. Rate constant $k_2$ decreases with decreasing pH because of the protonation of EDTA. This is the reason why greater amounts of EDTA were required for the limiting rate at lower pH. Equation 12 indicates that the plot of $V_i^{-1}$ vs. $[[Co(edta)]^{-}]_i^{-1}$ should be a straight line with an intercept of $1/\{(1+\gamma)I_a\Phi\}$ and an intercept/slope ratio of $k_q/k_0$. Figure 7 shows such a treatment of the data at $[[Co(edta)]^{-}]_i \leq 3\times10^{-3}$ mol dm$^{-3}$ in Fig. 2. The values of $I_a\Phi$ and $k_q/k_0$ are calculated to be $2.4\times10^{-7}$ mol dm$^{-3}$ s$^{-1}$ and $1.38\times10^3$ dm$^3$ mol$^{-1}$, respectively. The latter value is almost the same as that estimated separately from the Stern–Volmer plot in the quenching experiment under the same conditions. This fact indicates the validity of the reaction mechanism and the proposed rate law. The $k_q$ value is estimated to be $2.1\times10^9\ dm^3\ mol^{-1}\ s^{-1}$ using a $k_0$ value of $1.52\times10^6\ s^{-1}$.[13] The small dependences of the reaction rate on the ionic strength and temperature suggest that both $k_q$ and $k_0$ have a similar dependence on them.

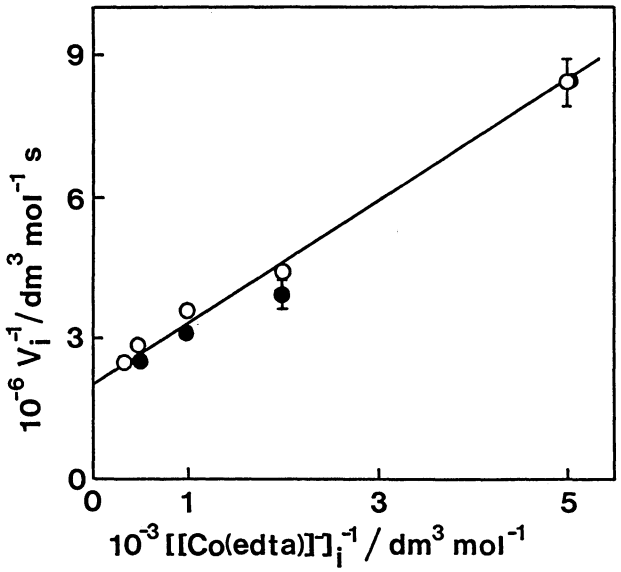


Fig. 7. Plots of $V_i^{-1}$ vs. $[[Co(edta)]^{-}]_i^{-1}$. Conditions are the same as in Fig. 1 except for 0.05 mol dm$^{-3}$ EDTA (○) or CDTA (●).

In the case of the CDTA or $C_2O_4^{2-}$ as a sacrificial donor, $[Ru(bpy)_3]^{3+}$ was reduced to $[Ru(bpy)_3]^{2+}$ according to the following reactions:

$$[Ru(bpy)_3]^{3+} + CDTA \xrightarrow{k_6} [Ru(bpy)_3]^{2+} + CDTA_{ox}^{+} \quad (13)$$

and

$$[Ru(bpy)_3]^{3+} + C_2O_4^{2-} \xrightarrow{k_7} [Ru(bpy)_3]^{2+} + C_2O_4^{-\cdot}. \quad (14)$$

The $k_2$, $k_6$, and $k_7$ were determined at pH 4.7 and 25 °C by the stopped-flow method to be $8.9\times10^3$, $1.7\times10^4$, and $1.7\times10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The reaction mechanism in the case of CDTA is supposed to be similar to that with EDTA, since the results obtained in the both systems were almost the same (Fig. 7). Smaller amounts of CDTA were required to be a limiting rate. This finding can be reasonably explained in terms of the $k_2$ and $k_6$ values. On the contrary, the dependence of $V_i$ on the $C_2O_4^{2-}$ concentration is different from that with EDTA or CDTA, as shown in Fig. 1. This might be due to a difference in the reactivity of the reducing radicals like EDTA' and $CO_2^{-\cdot}$, since the oxidized form of $C_2O_4^{2-}$ is known to decompose promptly to $CO_2^{-\cdot}$ and $CO_2$. If the $CO_2^{-\cdot}$ radical is consumed by a reaction with $[Ru(bpy)_3]^{3+}$ ($E^\circ$=1.26 V vs. NHE[1]), being not with $[Co(edta)]^{-}$ ($E^\circ$=0.37 V vs. NHE[22]), the reaction rate is derived as Eq. 16.

$$[Ru(bpy)_3]^{3+} + CO_2^{-\cdot} \longrightarrow [Ru(bpy)_3]^{2+} + CO_2 \quad (15)$$

$$-\frac{d[[Co(edta)]^-]}{dt}=\frac{k_q I_a \Phi[[Co(edta)]^-]}{k_0+k_q[[Co(edta)]^-]} \times\frac{2k_7[C_2O_4^{2-}]}{k_1[[Co(edta)]^{2-}]+2k_7[C_2O_4^{2-}]}. \quad (16)$$

A comparison of Eq. 16 to Eq. 11 at $\gamma=1$ indicates that the limiting rate in the case of excess $C_2O_4^{2-}$ is about half that with EDTA. This is consistent with the result shown in Fig. 1. The analogous reaction to Eq. 15, i.e., the reaction between EDTA′ and $[Ru(bpy)_3]^{3+}$ is also supposed to proceed. However, $[Ru(bpy)_3]^{3+}$ is reduced predominantly by EDTA since the EDTA′ radical reacts with $[Co(edta)]^-$ (Eq. 9). The finding that a $C_2O_4^{2-}$ concentration greater than 0.07 mol dm$^{-3}$ is needed to reach a limiting rate is not understandable, since the $k_7$ value is much greater than $k_2$ and $k_6$. This might be attributable to an interaction between $[Ru(bpy)_3]^{3+}$ and EDTA or CDTA. The equilibrium constant between $[Ru(bpy)_3]^{3+}$ and EDTA ions has been reported to be greater than 78 dm$^3$ mol$^{-1}$.[18]

The decrease rate of $[Co(edta)]^-$ is remarkably reduced in the presence of oxygen, with hydrogen peroxide being formed. The results obtained with EDTA as a sacrificial donor are presented in Fig. 8. The oxidative quenching of $[Ru(bpy)_3]^{2+*}$ with oxygen has been reported to be $5.5\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.[23] This indicates that the quenching rate with oxygen is comparable to that with $[Co(edta)]^-$ in aqueous solutions saturated with oxygen. Therefore, the $[Co(edta)]^{2-}$ produced by the quenching reaction is supposed to be reoxidized to $[Co(edta)]^-$ (Eq. 21). In fact, the formation of $[Co(edta)]^-$ was observed upon the addition of $[Co(edta)]^{2-}$, instead of $[Co(edta)]^-$, into the solution.

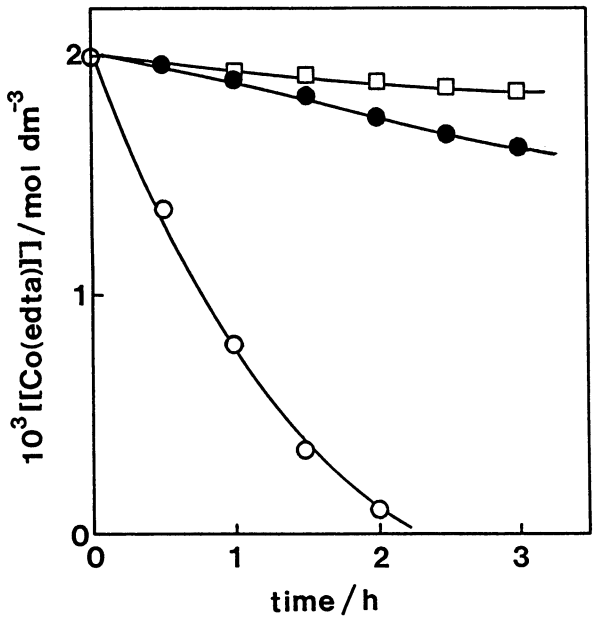


Fig. 8. Effect of oxygen. Conditions are the same as in Fig. 1 except for 0.01 mol dm$^{-3}$ EDTA at pH 5.2 in an aqueous solution saturated with $O_2$ (□), air (●), or $N_2$ (○).

$$[Ru(bpy)_3]^{2+*}+O_2 \longrightarrow [Ru(bpy)_3]^{3+}+O_2^{\cdot-} \quad (17)$$

$$O_2^{\cdot-}+H^+ \rightleftarrows HO_2^{\cdot} \quad (18)$$

$$[Ru(bpy)_3]^{3+}+HO_2^{\cdot} \longrightarrow [Ru(bpy)_3]^{2+}+O_2+H^+ \quad (19)$$

$$HO_2^{\cdot}+EDTA'+H^+ \longrightarrow H_2O_2+\text{products} \quad (20)$$

$$[Co(edta)]^{2-}+HO_2^{\cdot}+H^+ \longrightarrow [Co(edta)]^-+H_2O_2. \quad (21)$$

The drastic retardation effect of oxygen is obviously due to reactions 19—21.

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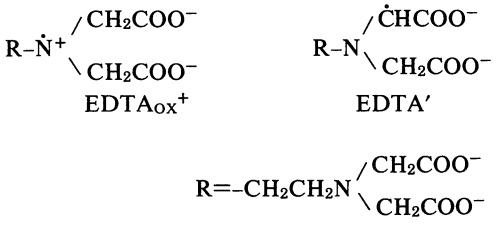
## References

1) K. Kalyanasundaram, *Coord. Chem. Rev.*, **46**, 159 (1982).
2) K. Kalyanasundaram, M. Grätzel, and E. Pelizzetti, *Coord. Chem. Rev.*, **69**, 57 (1986).
3) C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, **101**, 4815 (1979).
4) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 4781 (1975).
5) G. L. Gaines, Jr., *J. Phys. Chem.*, **83**, 3088 (1979).
6) K. Takuma, M. Kajiwara, and T. Matsuo, *Chem. Lett.*, **1977**, 1199.
7) J. K. Nagle, J. S. Bernstein, R. C. Young, and T. J. Meyer, *Inorg. Chem.*, **20**, 1760 (1981).
8) J. K. Nagle, R. C. Young, and T. J. Meyer, *Inorg. Chem.*, **16**, 3366 (1977).
9) R. Maidan and I. Willner, *J. Am. Chem. Soc.*, **108**, 8100 (1986).
10) I. Willner, R. Maidan, D. Mandler, H. Dürr, G. Dörr, and K. Zengerle, *J. Am. Chem. Soc.*, **109**, 6080 (1987).
11) Although the abbreviation EDTA or CDTA is generally for $H_4$edta or $H_4$cdta, we use, in this paper, for all the forms of $H_4$edta, $H_3$edta$^-$, $H_2$edta$^{2-}$, Hedta$^{3-}$, and edta$^{4-}$, or $H_4$cdta, $H_3$cdta$^-$, $H_2$cdta$^{2-}$, Hcdta$^{3-}$, and cdta$^{4-}$, respectively.
12) S. Nishida and M. Kimura, *Bull. Chem. Soc. Jpn.*, **60**, 2367 (1987).
13) M. Kimura, M. Yamashita, and S. Nishida, *Inorg. Chem.*, **24**, 1527 (1985).
14) M. Kimura and S. Nishida, *J. Chem. Soc., Dalton Trans.*, **1985**, 355.
15) $EDTA_{ox}^+$ and EDTA′ have been identified as follows by P. Keller, A. Moradpour, E. Amouyal, and H. B. Kagan (*Nouv. J. Chim.*, **4**, 377 (1980)), although the carboxyl groups are protonated, being dependent on pH of the solution.




16) M. Z. Hoffman, D. R. Prasad, G. Jones, II, and V. Malba, *J. Am. Chem. Soc.*, **105**, 6360 (1983).

17) K. Mandal and M. Z. Hoffman, *J. Phys. Chem.*, **88**, 185 (1984).
18) K. Mandal and M. Z. Hoffman, *J. Phys. Chem.*, **88**, 5632 (1984).
19) Q. G. Mulazzani, M. Venturi, and M. Z. Hoffman, *J. Phys. Chem.*, **89**, 722 (1985).
20) D. Miller and G. McLendon, *Inorg. Chem.*, **20**, 950 (1981).
21) E. Amouyal and B. Zidler, *Isr. J. Chem.*, **22**, 117 (1982).
22) N. Tanaka and H. Ogino, *Bull. Chem. Soc. Jpn.*, **38**, 1054 (1965).
23) J.R. Darwent and K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, **77**, 373 (1981).