

Light-induced Electron-transfer Reactions. Part 2. Kinetics of the Intra-molecular Redox Decomposition of Tris(oxalato)-cobaltate(III) by Irradiation with Visible Light of Aqueous Solution Containing Tris(2,2'-bipyridine)ruthenium(II) Ion

MASARU KIMURA*, TAKAKO YAMASHITA and SUZUKO NISHIDA

Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan

Received February 28, 1984

The rate of the intra-molecular redox decomposition of the tris(oxalato)cobaltate(III) ion $[\text{Co}(\text{Ox})_3]^{3-}$ is greatly accelerated by irradiation with visible light of aqueous acidic solutions containing the tris(2,2'-bipyridine)ruthenium(II) ion $[\text{Ru}(\text{bpy})_3]^{2+}$. The rate of the light-induced reaction in hydrochloric acid with an acidity range 0.05–0.18 mol dm⁻³ is of zero-order with respect to the $[\text{Co}(\text{Ox})_3]^{3-}$ ion concentration and is proportional to the light-intensity irradiated and also essentially to the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration. Moreover, the rate is independent not only of the oxalate ion concentrations, but also of the acidity over the range 0.05–0.18 mol dm⁻³ hydrochloric acid. The ionic-strength dependence, as well as temperature dependence, were extremely small. The $[\text{Ru}(\text{bpy})_3]^{2+}$ concentration does not change during the occurrence of the reaction and the tris(2,2'-bipyridine)ruthenium(II) ion acts as a homogeneous catalyzer. However, a dramatic indication that the situation was rather different was found in the stronger acid solutions of 0.5 or 1.0 mol dm⁻³ hydrochloric acid, in which the $[\text{Ru}(\text{bpy})_3]^{2+}$ concentration decreased greatly immediately after the initiation of reaction and then increased up to the initial concentration. Such a decrease at the initial stage of the reaction disappeared by addition of oxalate before the start of the reaction. A chain mechanism of reaction is proposed to account for these results.

Introduction

In the previous study we reported on the hydrogen peroxide formation by the light-induced reactions of tris(2,2'-bipyridine)ruthenium(II) ion in an aqueous acidic solution containing oxalic acid, manganese(II), and molecular oxygen [1]. In the course of the study, it was found that the amount

of hydrogen peroxide formation increased greatly by addition of a little tris(oxalato)cobaltate(III) into the reaction mixture. Such an effect of the cobalt(III) complex was thought to be due to the additional formation of CO_2^- radical by the intra-molecular redox decomposition of $[\text{Co}(\text{Ox})_3]^{3-}$, where Ox indicates oxalate ion. In the present paper we propose the mechanisms of the decomposition reaction of the $[\text{Co}(\text{Ox})_3]^{3-}$ ion in the solution containing the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion with irradiation of visible light.

Demas and Adamson [2] have reported that the tris-oxalato complexes $[\text{Fe}(\text{Ox})_3]^{3-}$, $[\text{Cr}(\text{Ox})_3]^{3-}$ and $[\text{Co}(\text{Ox})_3]^{3-}$ were efficient quenchers of the emission from the triplet-excited state $[\text{*Ru}(\text{bpy})_3]^{2+}$ and that the quenching in the $[\text{Cr}(\text{Ox})_3]^{3-}$ and $[\text{Co}(\text{Ox})_3]^{3-}$ cases proceeded *via* an encounter mechanism at about the diffusion-controlled rate. They concluded that the $[\text{*Ru}(\text{bpy})_3]^{2+}$ sensitized the racemization of d- $[\text{Cr}(\text{Ox})_3]^{3-}$, probably through energy-transfer, and sensitized the redox decomposition of $[\text{Co}(\text{Ox})_3]^{3-}$ through electron-transfer. The redox decomposition of $[\text{Fe}(\text{Ox})_3]^{3-}$ was not appreciably sensitized, the net reaction being one of quenching only.

The sensitized decomposition of $[\text{Co}(\text{Ox})_3]^{3-}$ is most interesting and appears to be the most complex in mechanism of the three cases. The investigation by Demas and Adamson was made by a quenching study only, based on the measurements of emission intensity and of the life-time [2]. We believe that the kinetic studies are important and necessary for the $[\text{Co}(\text{Ox})_3]^{3-}$ case. In the present paper, we report on the kinetic studies of the $[\text{Ru}(\text{bpy})_3]^{2+}$ -sensitized decomposition reaction of $[\text{Co}(\text{Ox})_3]^{3-}$ under various conditions.

Experimental

Chemicals

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was prepared as described in the literature [3] and recrystallized twice. The

*Author to whom correspondence should be addressed.

purified product had an absorption coefficient of $1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 452 nm, which was identical with that reported in the literature [4]. The $[\text{Ru}(\text{bpy})_3]^{3+}$ solution was prepared by oxidizing $[\text{Ru}(\text{bpy})_3]^{2+}$ with lead(IV) dioxide in 1 mol dm^{-3} sulphuric acid solution and then by removing the unchanged lead(IV) dioxide and lead(II) sulphate. The $\text{K}_3[\text{Co}(\text{Ox})_3] \cdot 3\text{H}_2\text{O}$ was prepared as described in the literature [5, 6] and recrystallized twice. All other chemicals used were of guaranteed reagent grade. Deionized water was further distilled in a glass still.

Procedure

Pure nitrogen gas was bubbled through the reaction solution to remove oxygen dissolved. The reaction vessel was a colourless glass bottle (5 dl; diameter 70 mm, thickness 1 mm, with 10 mm neck) and was placed in the thermostatted water in a cubic bath of colourless glass ($2 \times 3 \times 3 \text{ dm}^3$, thickness 6 mm). Unless otherwise stated, the sample solution was irradiated with visible light by using 100-W tungsten lamps, two of which were placed 3 dm to the right- and left-hand sides of the centre of the reaction vessel. The irradiation continued throughout the reaction. Aliquot samples were withdrawn at appropriate times and mixed with cation-exchange resin (Dowex 50W-X8, 200–400 mesh, hydrogen form of Wako Pure Chemical Co., washed well with distilled water) in order to remove the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion from the reacting solution and to stop the reaction. After filtration, the absorbance due to the $[\text{Co}(\text{Ox})_3]^{3-}$ ion in solution was measured at 423 nm. The $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration was determined by the measurements of absorbance at 452 nm after removal of the $[\text{Co}(\text{Ox})_3]^{3-}$ ion with anion-exchange resin (Dowex 1-X8, 50–100 mesh, Cl-form of Wako Pure Chemical Co., washed well with distilled water).

Results and Discussion

Stoichiometry

When the reaction had to a large extent run to completion, the concentrations of $[\text{Co}(\text{Ox})_3]^{3-}$ remaining and of the oxalate ion released were determined; the oxalate ion concentration was determined by titration with permanganate after addition of some manganese(II) sulphate. The results showed that the molar concentration of the oxalate ion released was, as an average of 8 runs, (2.5 ± 0.1) -fold that of the $[\text{Co}(\text{Ox})_3]^{3-}$ ion decomposed. Thus, the stoichiometric equation is written as follows:

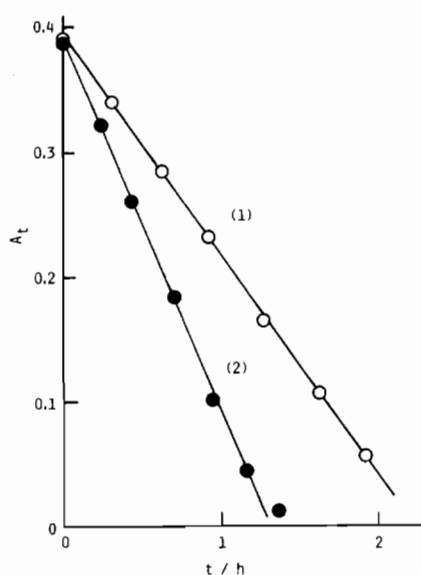
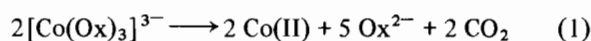


Fig. 1. Plots of A_t vs. t . Conditions: $5 \times 10^{-5} \text{ mol dm}^{-3}$ in $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $2 \times 10^{-3} \text{ mol dm}^{-3}$ in $\text{K}_3[\text{Co}(\text{Ox})_3]$, 0.1 mol dm^{-3} in HCl , an ionic strength of 0.2 mol dm^{-3} , nitrogen gas saturated, and 25°C . Lines (1) and (2) indicate the results of irradiation of visible light with two and four lamps respectively.

Kinetics of Reaction

The rate of decomposition of $[\text{Co}(\text{Ox})_3]^{3-}$ was accelerated by the presence of a little $[\text{Ru}(\text{bpy})_3]^{2+}$ with irradiation of visible light. The plots of decrease of the absorbance of $[\text{Co}(\text{Ox})_3]^{3-}$ (A_t) against time of reaction were linear over 90% of the whole reaction (Fig. 1). This indicates that the reaction rate is zero-order with respect to the $[\text{Co}(\text{Ox})_3]^{3-}$ ion concentration and is not influenced by the oxalate ion which is released according to the progress of reaction. This fact was obtained in all the kinetic runs over the acidity range $0.05\text{--}0.2 \text{ mol dm}^{-3}$. Therefore, the kinetic expression is described as follows:

$$-d[\text{Co}(\text{Ox})_3]^{3-}/dt = \text{constant} \equiv \phi \quad (2)$$

and thus,

$$A_t = -\phi \epsilon t + A_0 \quad (2')$$

where ϵ indicates the molar absorption coefficient of $[\text{Co}(\text{Ox})_3]^{3-}$, i.e., $199.5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 423 nm; A_t and A_0 indicate the molar absorbance of $[\text{Co}(\text{Ox})_3]^{3-}$ at reaction time t and zero, respectively. The $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration was maintained constant during the reaction, acting as a light-sensitized catalyzer.

Effect of Light Intensity

As seen in Fig. 2, the rate of the induced reaction increased in proportion to the number of lamps

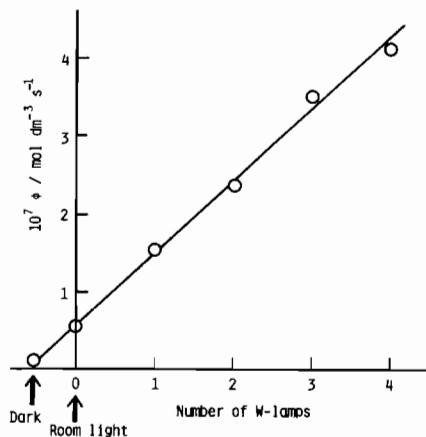


Fig. 2. Effect of light intensity. Conditions as in Fig. 1. For the dark reaction, the reaction vessel was covered with black plastic adhesive tape.

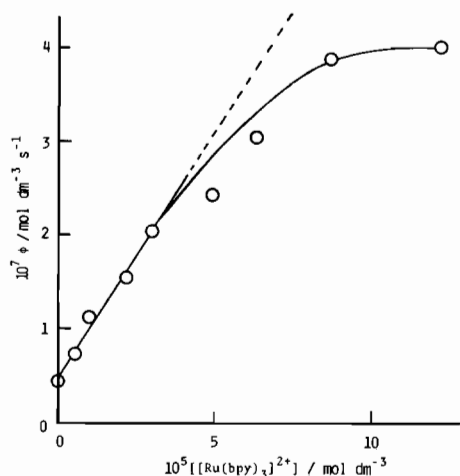


Fig. 3. Effect of concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$. Conditions as in line (1) in Fig. 1, except for the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentrations.

irradiated, the rate being so slow in the dark that it could be neglected.

Effect of $[\text{Ru}(\text{bpy})_3]^{2+}$ Concentration

The rate of reaction ϕ increased with increasing the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration, and appeared to be rectilinear in plots of ϕ vs. $[\text{Ru}(\text{bpy})_3]^{2+}$ at the range $0-3 \times 10^{-5} \text{ mol dm}^{-3}$ and then approached a limiting value (Fig. 3). This fact could be interpreted by eqn. 3:

$$I_{\text{abs}} = I_0 (1 - 10^{-\alpha c}) \quad (3)$$

where I_0 indicates the light intensity irradiated; α indicates an empirical constant; c is the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion concentration. When αc is less than 0.1, I_{abs} is approximately proportional to c , and is cons-

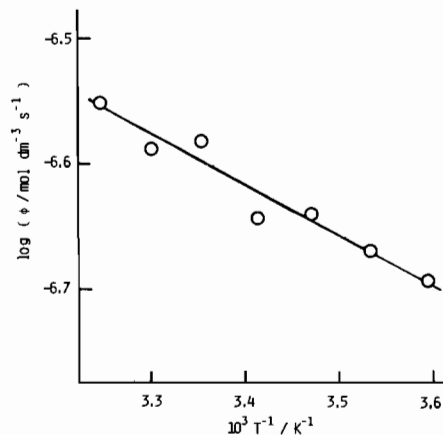


Fig. 4. Arrhenius plots of $\log \phi$ vs. T^{-1} . Conditions as in line (1) in Fig. 1.

stant at αc larger than 2. The curve in Fig. 3 would be attributable to the change of I_{abs} with the change of c . The I_{abs} corresponds to the rate of formation of the excited species $[\text{*Ru}(\text{bpy})_3]^{2+}$ in eqn. 4.

Effect of Oxalate Ion Concentration

ϕ was 2.3×10^{-7} , 2.4×10^{-7} , 2.4×10^{-7} , and $2.3 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ in 0, 0.001, 0.002, and 0.01 mol dm^{-3} sodium oxalate under conditions as (1) in Fig. 1, respectively. Thus, the rate of reaction is indifferent to the oxalate ion concentration. This fact is consistent with the facts that (1) no induction period is found in plots of A_t vs. t , and (2) the plots are rectilinear over the whole range of reaction (see Fig. 1).

Temperature Dependence

The temperature dependence of the reaction rate was examined over the range $5-35^\circ\text{C}$. Arrhenius plots are given in Fig. 4 from which the activation energy is evaluated to be $8 \pm 1 \text{ kJ mol}^{-1}$. The temperature dependence is extraordinarily small. Incidentally, the activation energy for the thermal decomposition of $[\text{Co}(\text{Ox})_3]^{3-}$ in the dark was determined to be $122 \pm 4 \text{ kJ mol}^{-1}$ at the same acidity conditions as in Fig. 4. Therefore, the value is about 15-fold of the activation energy for the light-sensitized reaction.

Effect of Ionic Strength

The rate of reaction ϕ was 2.5×10^{-7} , 2.3×10^{-7} , 2.3×10^{-7} , 2.2×10^{-7} , 2.3×10^{-7} , and $2.1 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ at the ionic strengths 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 mol dm^{-3} under conditions as (1) in Fig. 1, respectively. The plots of $\log \phi$ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$ were linear with a slope of -0.24 . Such a small effect of the ionic strength as well as the small temperature dependence are concerned with mechanisms of reaction (*v. i.*).

TABLE I. Effect of the Hydrogen Ion Concentration on the Reaction Rate ϕ in eqn. 2.^a

| [HCl] _{added} , mol dm ⁻³ | 10 ⁷ ϕ , mol dm ⁻³ s ⁻¹ | | 10 ⁷ ϕ_{corr} , mol dm ⁻³ s ⁻¹ |
|---|---|-------------------|---|
| 0.047 | 2.20 | 0.28 ^b | 1.92 ^c |
| 0.095 | 2.32 | 0.48 ^b | 1.84 ^c |
| 0.142 | 2.42 | 0.57 ^b | 1.85 ^c |
| 0.176 | 2.60 | 0.67 ^b | 1.93 ^c |
| 0.475 ^d | 0.80 | 0.65 ^b | 0.15 ^c |
| 0.95 ^d | 1.09 | 0.97 ^b | 0.12 ^c |

^aConditions as in (1) in Fig. 1. ^bValues in the absence of [Ru(bpy)₃]²⁺. ^cValues corrected. ^dIonic strength of 1.0 mol dm⁻³.

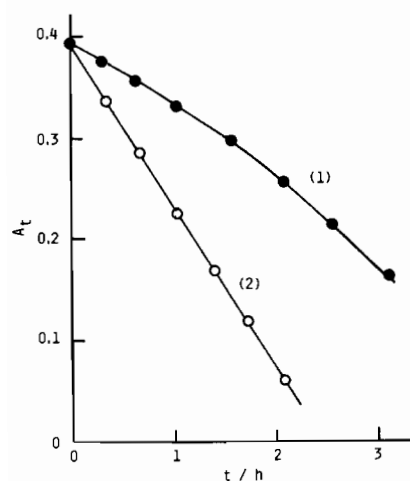


Fig. 5. Plots of A_t vs. t under strong acidity conditions. Conditions as in line (1) in Fig. 1, except for 0.475 mol dm⁻³ in HCl at an ionic strength of 1.0 mol dm⁻³. Curve 1 indicates the results without addition of oxalic acid, and line 2 indicates those with addition of oxalic acid of 0.1 mol dm⁻³ before to start the reaction.

Effect of Hydrogen Ion Concentration

When the hydrochloric acid concentration was varied over the range 0.047–0.176 mol dm⁻³, the rate of reaction increased slightly with an increase of acidity. However, such an increase was attributable to the unsensitized reaction. Namely, when the rate of reaction in the absence of [Ru(bpy)₃]²⁺ was subtracted from that in the presence of [Ru(bpy)₃]²⁺, the rate of the net sensitized reaction (ϕ_{corr}) appeared to be indifferent to the acidity (Table I).

On the other hand, a dramatic change appeared at the stronger acidities of 0.475 and 0.95 mol dm⁻³ in HCl (Table I, Figs. 5 and 6). The net sensitized reaction became less than 10% of the general sensitized reaction. Moreover, plots of A_t vs. t were not yet linear, becoming faster according to the progress of the reaction (see (1) in Fig. 5). The rate of reaction was accelerated by addition of oxalate ion, the plots becoming linear on further addition. Further,

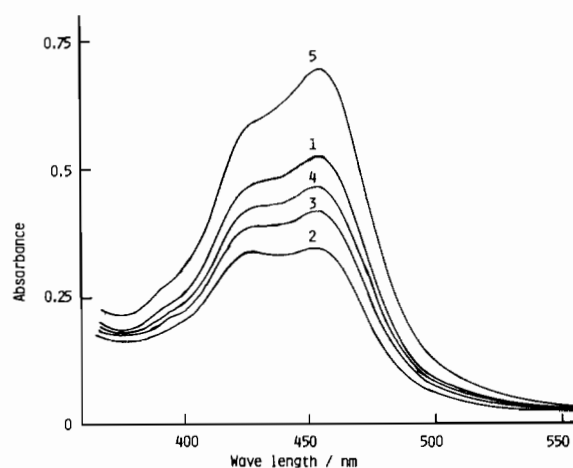


Fig. 6. Absorption spectra of [Ru(bpy)₃]²⁺ at certain times of reaction. Conditions as in line (1) in Fig. 5. The spectra 1, 2, 3, 4, and 5 are those at 0, 0.6, 1.5, 2.1, and 4 hours of reaction time, respectively, where 0 hr means the time when the [Co(Ox)₃]³⁻ ion was removed immediately after initiation of reaction.

the [Ru(bpy)₃]²⁺ concentration decreased to a large extent at the very early stage of the reaction and then increased again with time to reach the initial concentration (Fig. 6). Such a decrease of [Ru(bpy)₃]²⁺ was not appreciable in the presence of oxalic acid at more than 0.02 mol dm⁻³, the spectra being identical with (5) in Fig. 6.

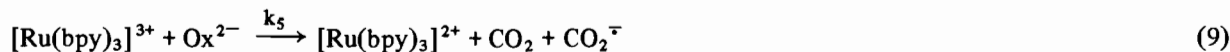
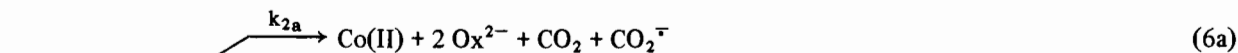
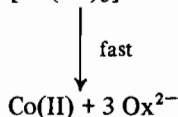
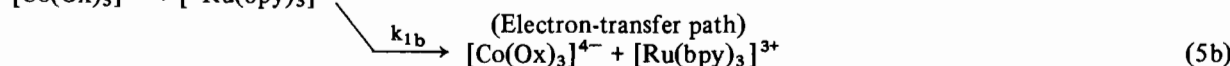
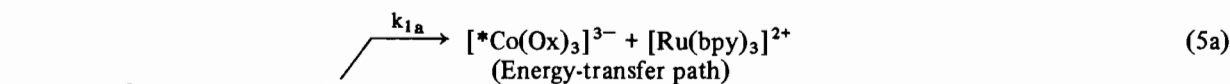
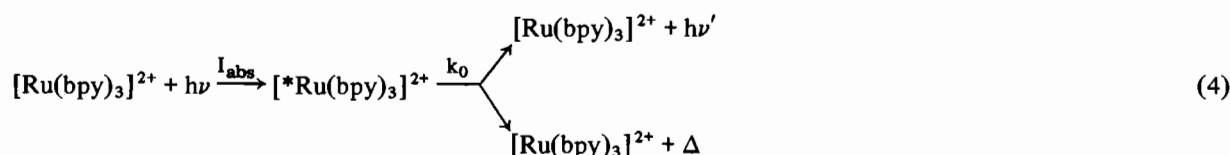
Rate of Reaction of [Ru(bpy)₃]³⁺ with Water and with Oxalate Ion

The rate of reaction between [Ru(bpy)₃]³⁺ and water was measured by following the increase of the absorbance at 452 nm due to the [Ru(bpy)₃]²⁺ ion. Plots of $\ln(A_\infty - A_t)$ vs. t were linear at least up to the half-life time which was 2 and 4 hours at 30 °C in 0.01 and 0.1 mol dm⁻³ in sulphuric acid, respectively, and the rate constant k_6 in eqn. 10 was 1×10^{-4} and 5×10^{-5} s⁻¹, respectively. The rate of reduction of [Ru(bpy)₃]³⁺ by oxalate ion was measured by using a Union RA-401 stopped-flow

spectrophotometer. Plots of $\ln(A_\infty - A_t)$ vs. t under the pseudo first-order conditions were linear at least up to the half-life time, and the rate constant k_5 in eqn. 9 was 6.4×10^3 and $1.1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C in 0.006 and 0.02 mol dm^{-3} in sulphuric acid, respectively. Consequently, the rate of reaction of $[\text{Ru}(\text{bpy})_3]^{3+}$ with the medium water and with oxalate ion is relatively slow and dependent on the acidity, decreasing with an increase of acidity.

Mechanisms of Reaction

The following mechanisms of reaction are presented to account for the results obtained.



Rates of reactions 9 and 10 were so slow that they could be neglected, and the assumption of steady-state concentrations for $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Co}(\text{Ox})_3]^{3-}$, $[\text{Ru}(\text{bpy})_3]^{3+}$, and CO_2^- in reactions (4)–(7) leads to eqn. 11 under conditions of $k_0 \ll (k_{1a} + k_{1b})[[\text{Co}(\text{Ox})_3]^{3-}]$.

$$-\frac{d[[\text{Co}(\text{Ox})_3]^{3-}]}{dt} = I_{\text{abs}} \left\{ 1 - \frac{k_{1a}k_{2b}}{(k_{1a} + k_{1b})(k_{2a} + k_{2b})} \right\} \quad (11)$$

The stoichiometry which is obtained from eqns. 4–7 is identical with eqn. 1 and is in agreement with the empirical stoichiometry. Equation 11 is consistent with all the results obtained. The extraordinarily small dependence of the rate on temperature as well as on ionic strength could be also understood by eqn. 11. In a limiting case where the electron-transfer path is negligible, *i.e.*, $k_{1b} \ll k_{1a}$, the right-hand side of eqn. 11 is $I_{\text{abs}}k_{2a}/(k_{2a} + k_{2b})$ which contains only the unimolecular rate constants and thus should be independent of temperature as well as of ionic strength. In the case that the electron-transfer path is predominant, *i.e.*, $k_{1a} \ll k_{1b}$, eqn. 12 can hold, see below.

$$-d[[\text{Co}(\text{Ox})_3]^{3-}]/dt = I_{\text{abs}} \quad (12)$$

This case is the most simple one, and the rate of reaction should be dependent only on the light absorbed. If only the electron-transfer path occurred, reaction 9 should be fast enough. Otherwise, the rate of reaction should be dependent on the oxalate ion concentration, and moreover, the $[\text{Ru}(\text{bpy})_3]^{3+}$ species should accumulate with the progress of reaction. The production of the $[\text{Ru}(\text{bpy})_3]^{3+}$ ion was found only under the strong acidity conditions, but became

unappreciable by sufficient addition of oxalate ion (see Fig. 6). This fact indicates clearly the occurrence of the electron-transfer path as well as that of reaction 9 under such conditions. The energy-transfer path could not directly be observed, but was supported by the kinetic results.

References

- 1 M. Kimura and S. Doi, *J. Chem. Soc., Dalton Trans.*, 37 (1983).
- 2 J. N. Demas and A. Adamson, *J. Am. Chem. Soc.*, 95, 5159 (1973).
- 3 'Shin Jikken-Kagaku Koza 8', eds. T. Tachibana, M. Nakahara and M. Shibata, Japan Chemical Society, 1975, p. 1475; R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 5, 964 (1966); I. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, 76, 115 (1972).
- 4 P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, 77, 1823 (1973).
- 5 S. P. L. Sørensen, *Z. Anorg. Allg. Chem.*, 11, 1 (1896).
- 6 J. C. Bailar, Jr. and E. M. Jones, *Inorg. Synth.*, 1, 35 (1939).