Light-induced Electron-transfer Reactions. Part 3.[†] Kinetics of the Oxidation Reaction of Oxalate Ion by Peroxidisulphate Ion, induced by Irradiation with Visible Light of an Aqueous Solution containing Tris(2,2′-bipyridine)-ruthenium(II)[‡]

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

---

The rate of the oxidation reaction of the oxalate ion to carbon dioxide by the peroxodisulphate ion ($S_2O_8^{2-}$) is greatly accelerated by irradiation with visible light of aqueous solutions containing tris(2,2′-bipyridine)ruthenium(II) ion, $[Ru(bipy)_3]^{2+}$, as a photo-sensitizer and catalyst. The mechanism constitutes a chain reaction initiated by the reaction between the photo-excited complex $[{}^*Ru(bipy)_3]^{2+}$ and $S_2O_8^{2-}$. The results are accounted for by a mechanism described by equations (i)—(v). The rate of reaction is given by equation (vi). The mechanism of reaction and the rate law were verified, and the bimolecular quenching constants k_q were determined by kinetic experiments under various conditions.

$$[Ru(bipy)_3]^{2+} + h\nu \xrightarrow{I_a} [{}^*Ru(bipy)_3]^{2+} \xrightarrow{k_0} [Ru(bipy)_3]^{2+} + h\nu' + \Delta \qquad (i)$$

$$[{}^*Ru(bipy)_3]^{2+} + S_2O_8^{2-} \xrightarrow{k_q} [Ru(bipy)_3]^{3+} + SO_4^{\cdot -} + SO_4^{2-} \qquad (ii)$$

$$C_2O_4^{2-} + SO_4^{\cdot -} \longrightarrow CO_2^{\cdot -} + CO_2 + SO_4^{2-} \qquad (iii)$$

$$[Ru(bipy)_3]^{3+} + CO_2^{\cdot -} \longrightarrow [Ru(bipy)_3]^{2+} + CO_2 \qquad (iv)$$

$$SO_4^{\cdot -} + CO_2^{\cdot -} \longrightarrow SO_4^{2-} + CO_2 \qquad (v)$$

$$-d[S_2O_8^{2-}]/dt = \frac{k_q I_a \Phi [S_2O_8^{2-}]}{k_0 + k_q [S_2O_8^{2-}]} \qquad (vi)$$

The peroxodisulphate system with tris(2,2′-bipyridine)-ruthenium(II) ion, $[Ru(bipy)_3]^{2+}$, is of interest in the context of model solar-energy conversion systems as well as regards pure photochemistry aspects. Demas[1] has indicated that the photochemistry of the peroxodisulphate system has many merits, and in the present case this appears to be the most promising simple chemical method of investigation. The photochemical reaction between $[Ru(bipy)_3]^{2+}$ and peroxodisulphate ion, $S_2O_8^{2-}$, has been examined previously.[2–5] The oxidative quenching of the photo-excited $[{}^*Ru(bipy)_3]^{2+}$ by $S_2O_8^{2-}$ generates $[Ru(bipy)_3]^{3+}$, $SO_4^{\cdot -}$, and SO_4^{2-}. Both the species $[Ru(bipy)_3]^{3+}$ and $SO_4^{\cdot -}$ are strong oxidants and able to oxidize oxalate ion if it is present in the reacting solution. Thus the oxidation reaction between oxalate and peroxodisulphate, which is induced by irradiation with visible light of an aqueous solution containing $[Ru(bipy)_3]^{2+}$ ion, can be investigated. The overall reaction can be written as in equation (1). The reaction (1) hardly occurred without catalysts, but proceeded at a moderate rate on irradiation with visible light of solutions containing the $[Ru(bipy)_3]^{2+}$ ion as a sensitizer and catalyst. In this paper, detailed kinetic studies of the light-induced reaction (1) are made and mechanisms are presented to account for the results obtained.

$$C_2O_4^{2-} + S_2O_8^{2-} \longrightarrow 2\,CO_2 + 2\,SO_4^{2-} \qquad (1)$$

Experimental

Chemicals.—$[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ was prepared as described in the literature[6] and recrystallized twice. Reagent grade potassium peroxodisulphate (Wako Pure Chemicals Co.) was recrystallized twice from redistilled water and dried at room temperature in a vacuum desiccator. The sodium perchlorate used for adjusting ionic strength was recrystallized twice from redistilled water. All other chemicals used were of reagent grade. Redistilled water was prepared from anion–cation exchange resin water first by successive distillation from alkaline permanganate solution and finally without addition of any reagents in a glass still. Redistilled water was used also for washing the glassware.

Procedure.—The reaction vessel (a colourless glass bottle: capacity 500 cm³, diameter 70 mm, thickness 1 mm, neck 10 mm) was placed in a thermostatted water-bath (colourless glass: 20 × 30 × 30 cm, thickness 6 mm). Unless otherwise stated, the sample was irradiated with visible light from 100-W tungsten lamps which were placed 30 cm to the right- and left-hand sides of the centre of the reaction vessel. Irradiation was continued throughout the reaction. Oxygen dissolved in the solutions was removed by bubbling through pure nitrogen gas. Aliquot samples were withdrawn at appropriate times and mixed with cation-exchange resin (Dowex 50W-X8: 200—400 mesh, hydrogen form, washed well with distilled water) in order to remove the $[Ru(bipy)_3]^{2+}$ ion from the reacting solution and to stop the reaction. After filtration, the concentration of the peroxodisulphate ion remaining was determined by polarography at 0.15 V *vs.* s.c.e. (saturated calomel electrode) in a

---

[†] Part 2, M. Kimura, T. Yamashita, and S. Nishida, *Inorg. Chim. Acta*, in the press.

[‡] *Non-S.I. unit employed:* 1 einstein = 1 mol of photons.

solution of 0.01 mol dm^{-3} perchloric acid, 0.1 mol dm^{-3} sodium perchlorate, and 0.01% gelatine at 25 °C. The concentration of $[Ru(bipy)_3]^{2+}$ was determined spectrophotometrically using the molar absorption coefficient of 1.4×10^4 dm^3 mol^{-1} cm^{-1} at 452 nm. The luminescence of $[{}^*Ru(bipy)_3]^{2+}$ was measured by using a Hitachi model 850 spectrofluorometer at an excitation energy of 452 nm: the oxygen dissolved in the $[Ru(bipy)_3]^{2+}$ solution was removed by bubbling through pure argon gas.

Results

Under the conditions employed, the concentration of $[Ru(bipy)_3]^{2+}$ remained constant during the reaction. This indicates that the tris(2,2'-bipyridine)ruthenium(II) ion acts as a catalyst in the chain reaction.

Stoicheiometry.—The stoicheiometry for the light-induced reaction was determined after removal of $[Ru(bipy)_3]^{2+}$ near completion of the reaction. The concentration of peroxodisulphate ion was determined polarographically. The concentration of oxalate ion was determined, after addition of some manganese(II) sulphate, by titration with a standard permanganate solution. The result was $[S_2O_8^{2-}]_{reacted}/[C_2O_4^{2-}]_{reacted} = 1.01$. The concentration of carbon dioxide produced due to the reaction in acidic solution was determined by transport using the passage of nitrogen gas through the solution to a separate bottle containing a solution of 0.1 mol dm^{-3} $BaCl_2$ and 0.5 mol dm^{-3} NaOH, in order to precipitate all the carbon dioxide as $BaCO_3$. The amount of $BaCO_3$ was weighed after filtration and drying at 110 °C. The result was $[CO_2]_{formed}/[S_2O_8^{2-}]_{reacted} = 1.95$. These two results show that the concentration of $S_2O_8^{2-}$ reacted is equivalent to that of $C_2O_4^{2-}$ reacted, and half the molar concentration of CO_2 formed. Thus, the stoicheiometry is as in equation (1).

Reaction Order and Rate Law.—The initial rate of reaction (v_i) was determined at varied concentrations of the oxalate and peroxodisulphate ions under the given conditions in the presence of $[Ru(bipy)_3]^{2+}$ with irradiation of visible light. The rate was independent of the oxalate concentration in the range 0.002—0.05 mol dm^{-3}. The relationship of v_i with $[S_2O_8^{2-}]_i$ is given in Figure 1: the plot of v_i^{-1} *vs.* $[S_2O_8^{2-}]_i^{-1}$ was rectilinear, having an intercept. Therefore, the empirical rate law is represented by equation (2), where α and β correspond to

$$v_i^{-1} = \alpha + \beta[S_2O_8^{2-}]_i^{-1} \qquad (2)$$

the intercept and slope, respectively, in plots of v_i^{-1} *vs.* $[S_2O_8]_i^{-1}$, and equation (2) is equivalent to equations (10) and (10') given later.

Effect of Light Intensity.—The rate of reaction was found to be proportional to the irradiated light intensity. A plot of v_i *vs.* number of lamps used is shown in Figure 2.

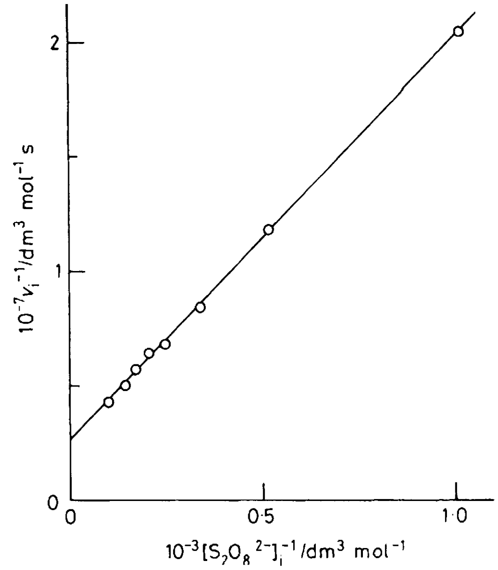

Figure 1. An example of a plot of v_i^{-1} *vs.* $[S_2O_8^{2-}]_i^{-1}$ (potassium peroxodisulphate). Conditions: 5×10^{-5} mol dm^{-3} $[Ru(bipy)_3]Cl_2$, 0.004 mol dm^{-3} sodium oxalate, $\mu = 0.5$ mol dm^{-3} $(Na[ClO_4])$, nitrogen-gas saturated, 30 °C, irradiated by light from two tungsten lamps

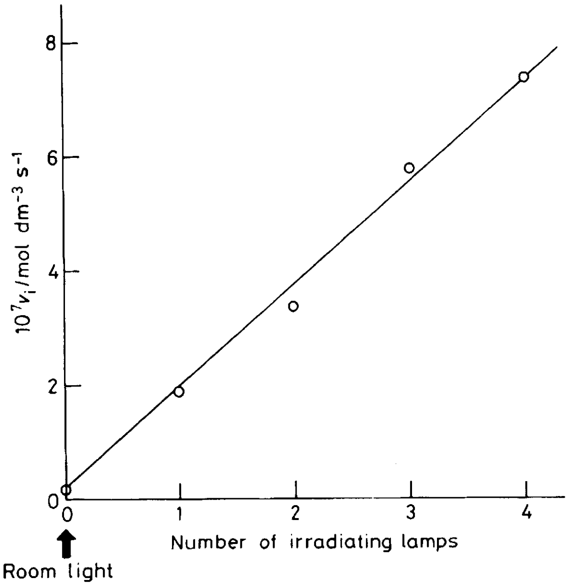

Figure 2. Effect of light intensity (v_i *vs.* number of lamps). Conditions as in Figure 1: except for 0.004 mol dm^{-3} potassium peroxodisulphate. No appreciable decrease of $[S_2O_8^{2-}]$ was found in the dark under the conditions

Effect of Concentration of $[Ru(bipy)_3]^{2+}$.—The concentration of $[Ru(bipy)_3]^{2+}$ was unchanged during the light-induced reaction. The rate of reaction appeared to be, within experimental error, proportional to the concentration of $[Ru(bipy)_3]^{2+}$ in the range 0 to *ca.* 5×10^{-6} mol dm^{-3}, and then deviated from the straight line. Such a deviation may be due to the change of the efficiency of the absorbed-light intensity according to the change of the concentration of $[Ru(bipy)_3]^{2+}$. The absorbed-light intensity (I_a) is given by equation (3), where I_0 is the intensity of the irradiated light; γ is

$$I_a = I_0(1 - \exp\{-\gamma[Ru(bipy)_3{}^{2+}]\}) \qquad (3)$$

an empirical constant combining the length of the light path and the molar absorption coefficient of $[Ru(bipy)_3]^{2+}$. If the values of I_0 and γ are assumed to be 5.9×10^{-7} einstein s^{-1} dm^{-3} and 2.7×10^4 dm^3 mol^{-1}, respectively, I_a can be calculated using equation (3). The calculated values are in good agreement with the observed ones which are obtained by measurements of the reaction rate [see equation (10') below, where Φ is assumed to be 1 mol $einstein^{-1}$]. Both values are given in Figure 3.

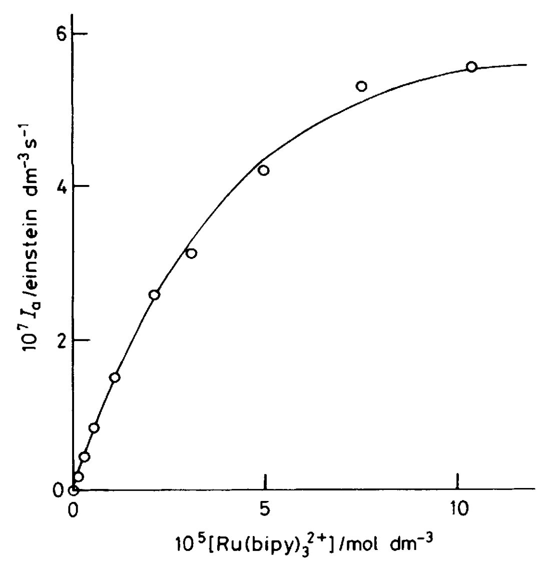

Figure 3. I_a *vs.* concentration of $[Ru(bipy)_3]^{2+}$. Conditions as in Figure 1: except for 0.004 mol dm^{-3} potassium peroxodisulphate, $\mu = 0.024$ mol dm^{-3}. (○) Experimental results obtained using equation (10′) in which Φ is assumed to be unity; (———) calculated using equation (3)

Table. Effect of ionic strength (μ) and temperature[a]

Temp. (°C)	μ/mol dm^{-3}	$10^{-6}\alpha$/ dm^3 mol^{-1} s	$10^{-3}\beta$/s	$10^{-8} k_q$/ dm^3 mol^{-1} s^{-1}	
30	0.042	2.6_0	3.24	12.2	
30	0.05	2.2_4	4.25	8.0	9.4[b]
30	0.1	2.4_5	5.33	6.9_6	7.0[b]
30	0.2	2.5_1	7.37	5.2	4.8[b]
30	0.3	2.6_6	9.60	4.2	3.3[b]
30	0.4	2.4_1	13.8	2.7	2.4[b]
30	0.5	2.6_3	17.4	2.3	2.0[b]
10	0.05	2.4_0	4.43	—	
15	0.05	2.2_4	4.51	—	
20	0.05	2.2_5	4.06	—	
40	0.05	2.2_2	4.20	—	
		(av. 2.4 ± 0.2)			

[a] Conditions as in Figure 1, except for variation of ionic strength and temperature. [b] Values obtained by the determination of the Stern–Volmer constant K_{sv} with measurements of the luminescence of $[{}^*Ru(bipy)_3]^{2+}$; the values of K_{sv} were 620, 462, 315, 215, 160, and 133 dm^3 mol^{-1} at ionic strengths of 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 mol dm^{-3}, respectively.

Effect of Hydrogen Ion Concentration.—The initial rates of reaction under the conditions of Figure 1 but with 4×10^{-3} mol dm^{-3} peroxodisulphate were 1.48×10^{-7}, 1.41×10^{-7}, 1.46×10^{-7}, 1.30×10^{-7}, and 1.32×10^{-7} mol dm^{-3} s^{-1} in 0, 0.05, 0.1, 0.15, and 0.2 mol dm^{-3} perchloric acid, respectively. Thus, the rate of the light-induced reaction would be essentially independent of acidity over the range 0—0.2 mol dm^{-3} $HClO_4$.

Effect of Ionic Strength.—The effect of ionic strength (μ) was examined over the range 0.042—0.5 mol dm^{-3}. The empirical constants α and β in equation (2) were determined under various ionic strengths (Table). The α value corresponds to $(I_a\Phi)^{-1}$ and is virtually independent of the ionic strength, as to be expected. The β value corresponds to $k_0/(k_q I_a \Phi)$ and is dependent on the ionic strength.

Temperature Dependence.—The effect of temperature on the rate was examined over the range 10—40 °C. Both α and β in equation (2) were virtually independent of the temperature of the reacting solution (Table). This could be due to the character of α and β which correspond to $(I_a\Phi)^{-1}$ and $k_0/(k_q I_a \Phi)$, respectively. The temperature dependence of β would be counter-balanced by the temperature dependences of k_0 and k_q.

Discussion

The following mechanism of reaction given below [equations (4)—(9)] is postulated to account for the results obtained. The overall reaction is essentially the same as reaction (1).

$$[Ru(bipy)_3]^{2+} + h\nu \xrightarrow{I_a} [{}^*Ru(bipy)_3]^{2+} \quad (4)$$

$$[{}^*Ru(bipy)_3]^{2+} \xrightarrow{k_0} \begin{cases} [Ru(bipy)_3]^{2+} + h\nu' \text{(emission)} \\ [Ru(bipy)_3]^{2+} + \Delta \text{(thermal energy)} \end{cases} \quad (5)$$

$$[{}^*Ru(bipy)_3]^{2+} + S_2O_8^{2-} \xrightarrow{k_q} [Ru(bipy)_3]^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (6)$$

$$C_2O_4^{2-} + SO_4^{\bullet -} \xrightarrow{k_1} CO_2^{\bullet -} + CO_2 + SO_4^{2-} \quad (7)$$

$$[Ru(bipy)_3]^{3+} + CO_2^{\bullet -} \xrightarrow{k_2} [Ru(bipy)_3]^{2+} + CO_2 \quad (8)$$

$$SO_4^{\bullet -} + CO_2^{\bullet -} \xrightarrow{k_3} SO_4^{2-} + CO_2 \text{ (termination)} \quad (9)$$

Reactions (4)—(9) constitute a chain reaction in which the photo-excitation reaction (4) and the quenching reaction (6) are the initiating reactions. The rate of the decrease of the peroxodisulphate ion concentration is described by equations (10) and (10′), where the term $I_a\Phi$ corresponds to the formation rate of $[{}^*Ru(bipy)_3]^{2+}$; I_a indicates the absorbed light intensity, and Φ the efficiency of formation for the excited species.

$$-d[S_2O_8^{2-}]/dt = k_q[{}^*Ru(bipy)_3^{2+}][S_2O_8^{2-}] = \frac{k_q I_a \Phi [S_2O_8^{2-}]}{k_0 + k_q[S_2O_8^{2-}]} \quad (10)$$

$$v_i = \frac{k_q I_a \Phi [S_2O_8^{2-}]_i}{k_0 + k_q[S_2O_8^{2-}]_i} \quad (10')$$

Equation (10′) is equivalent to the empirical rate law equation (2). Using the empirical parameters α and β, the relationship between $[S_2O_8^{2-}]$ and t could be obtained by means of equation (11), which is an integral form of equation (10);

$$\alpha\left([S_2O_8^{2-}]_i - [S_2O_8^{2-}]\right) + \beta \ln\left(\frac{[S_2O_8^{2-}]_i}{[S_2O_8^{2-}]}\right) = t \quad (11)$$

$[S_2O_8^{2-}]_i$ and $[S_2O_8^{2-}]$ indicate concentrations of peroxodisulphate ion at $t = 0$ and $t = t$, respectively. The calculated curve is given in Figure 4 together with the data obtained experimentally. The calculated curve is in good agreement with the experimental data. This indicates the validity of the rate law of equations (2) and (10).

The oxidation reaction of $C_2O_4^{2-}$ by $[Ru(bipy)_3]^{3+}$ [equation (12)] is a competing reaction to reactions (7) and (8).

$$C_2O_4^{2-} + [Ru(bipy)_3]^{3+} \xrightarrow{k_{12}} CO_2^{\bullet -} + CO_2 + [Ru(bipy)_3]^{2+} \quad (12)$$

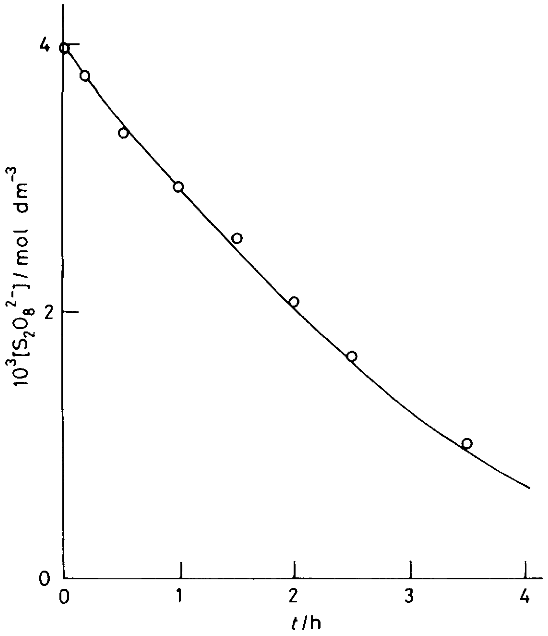

Figure 4. Plots of $[S_2O_8^{2-}]$ *vs.* *t* of equation (11). Calculated using equation (11) with $\alpha = 2.60 \times 10^6$ dm^3 mol^{-1}s and $\beta = 3.24 \times 10^3$s at $\mu = 0.042$ mol dm^{-3} at 30 °C (Table); (○) experimental data obtained under corresponding conditions

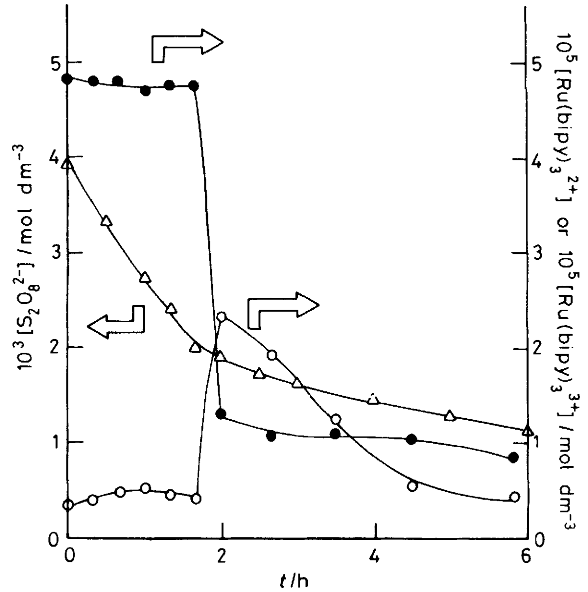

Figure 5. Variations of concentrations of $S_2O_8^{2-}$ (△), $[Ru(bipy)_3]^{2+}$ (●), and $[Ru(bipy)_3]^{3+}$ (○). Initial concentrations: 0.002 mol dm^{-3} sodium oxalate, 0.004 mol dm^{-3} potassium peroxodisulphate, and 5.2×10^{-5} mol dm^{-3} $[Ru(bipy)_3]Cl_2$. Other conditions are as in Figure 1

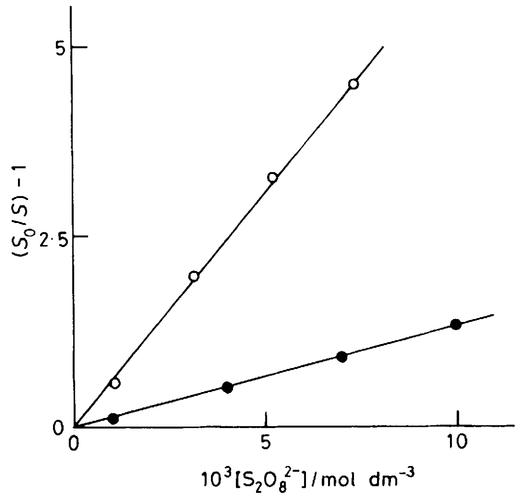

Figure 6. Examples of the Stern–Volmer plot. Conditions as in Figure 1: except $\mu = 0.05$ mol dm^{-3} (○) and 0.5 mol dm^{-3} (●). S_0 and S indicate the signal intensity of luminescence of $[{*}Ru(bipy)_3]^{2+}$ without and with the quencher $S_2O_8^{2-}$, respectively

Although reaction (12) has been studied previously,[7] the rate constant has not been reported. Thus we determined the rate constant of reaction (12) using a stopped-flow spectrophotometer;* the $CO_2^{\cdot -}$ is rapidly consumed according to reaction (8). The rate of reaction (12) was extremely dependent on acidity, decreasing with an increase of the hydrogen ion concentration in the reacting solution; *e.g.*, the rate constant $2k_{12}$ was 1.1×10^3 and 6.4×10^3 dm^3 mol^{-1} s^{-1} at 25 °C in 0.02 and 0.006 mol dm^{-3} sulphuric acid, respectively. On the contrary, the rate of the light-induced reaction was virtually independent of acidity. Therefore, the reaction (12) could not occur in the light-induced reaction scheme of equations (4)—(9). If the reaction (12) could participate in the scheme of reaction, the rate of the light-induced reaction should be dependent not only on the oxalate ion concentration, but also on acidity. However, the experimental results show that the rate of the light-induced reaction is virtually independent not only of the oxalate ion concentration, but also of acidity. When all the oxalate ions are exhausted by the reaction, the reactions (7)—(9) should disappear from the scheme of reaction; thus, the concentration of $[Ru(bipy)_3]^{3+}$ began to increase at that time, being due to the occurrence of reaction (13). This behaviour is

$$[Ru(bipy)_3]^{2+} + SO_4^{\cdot -} \xrightarrow{k_{13}} [Ru(bipy)_3]^{3+} + SO_4^{2-} \quad (13)$$

illustrated in Figure 5. The reaction (13) is a competing reaction to reaction (7), and the rate constant has been reported as $k_{13} \geqslant 10^9$ dm^3 mol^{-1} s^{-1}.[3] The existence of the radical ions in the reacting solution was confirmed.† As can be seen in Figure 5, the $[Ru(bipy)_3]^{3+}$ ion concentration increased once and then decreased, due to reaction with the H_2O solvent. It is noted that the total concentration of $[Ru(bipy)_3]^{2+}$ plus $[Ru(bipy)_3]^{3+}$ also decreased according to the decrease of the latter species after the expiration of oxalate ion. This may be caused by the reaction of $[Ru(bipy)_3]^{3+}$ and/or the dissociated bipyridine with the powerfully oxidizing $SO_4^{\cdot -}$ radical.

The bimolecular quenching constant k_q was evaluated using the relationship $\alpha/\beta = k_q/k_0$ with $k_0 = 1.52 \times 10^6$ s^{-1}, where

---

* The solution of $[Ru(bipy)_3]^{3+}$ was prepared by oxidizing $[Ru(bipy)_3]^{2+}$ with PbO_2 in 0.05 mol dm^{-3} sulphuric acid. Immediately after removal of PbO_2 and $PbSO_4$ by filtration, the $[Ru(bipy)_3]^{3+}$ solution was used for the kinetic runs carried out with a Union RA-401 stopped-flow spectrometer.

† When either a monomer of acrylonitrile or acrylamide was added into the reacting solution, the white sediment of poly(acrylonitrile) or the colourless jelly due to the poly(acrylamide) was observed obviously to indicate the existence of the radical species.

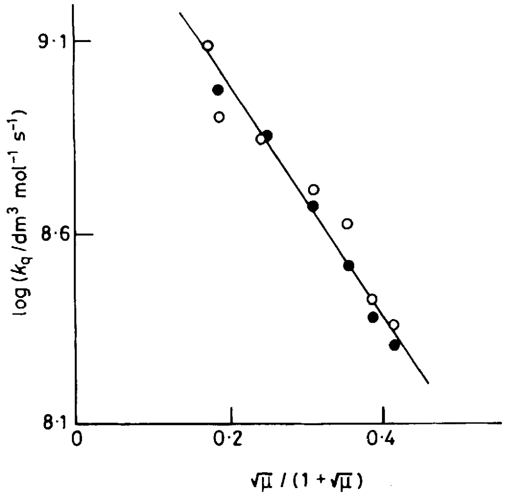

Figure 7. Plots of log k_q *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$. (○) Obtained from the kinetics' runs using the equations (2) and (10′); (●) obtained by measurements of luminescence of [*Ru(bipy)$_3$]$^{2+}$ quenched by the the $S_2O_8^{2-}$ ion

$k_0 = \tau_0^{-1}$ and $\tau_0 = 660$ ns.[8] The values of k_q evaluated were in good agreement with those determined by measurements of the luminescence of [*Ru(bipy)$_3$]$^{2+}$, the quenching experiments of [*Ru(bipy)$_3$]$^{2+}$ by $S_2O_8^{2-}$ being made using an excitation energy of 452 nm (see Table). Examples of the Stern–Volmer plot are given in Figure 6. The plots of log k_q *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$ were rectilinear with a slope of -3.0 (see Figure 7). The ionic-strength dependence of k_q is thought to be somewhat smaller than that expected for the charge products. This may be due to the counter-balancing effect of the first and third steps in reaction scheme (14). Assuming the steady-state concentrations for the intermediate species, equation (15) can be obtained. When $k_{-2} \gg k_3$, equation (16) holds. The electron-transfer steps of K_2 are reversible in a solvent cage and the K_2 term should be indifferent to the ionic strength. Thus, the K_1 and k_3 terms only are dependent on the ionic strength. The terms K_1 and k_3 correspond to ion-association and ion-dissociation, respectively, and the dependence of ionic strength on them may be counter-balanced. Consequently, the ionic strength dependence of k_q could be smaller than that expected for the charge products of [*Ru(bipy)$_3$]$^{2+}$ and $S_2O_8^{2-}$. The quenching constant k_q has been reported to be 5.33×10^8 dm^3 mol^{-1} s^{-1} (no conditions were given),[2] and 8×10^8 dm^3 mol^{-1} s^{-1} in acetate buffer (pH 4.7, 0.1 mol dm^{-3}, temperature not given).[4] The experimental conditions are not exactly defined in the literature, and thus, they cannot be simply compared to the k_q values in the Table. We believe that our results (Table) are the most promising available at this time.

$$[{}^*\mathrm{Ru(bipy)_3}]^{2+} + S_2O_8^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [{}^*\mathrm{Ru(bipy)_3}]^{2+}\cdot S_2O_8^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Ru(bipy)_3}]^{3+}\cdot S_2O_8^{3-} \xrightarrow{k_3} [\mathrm{Ru(bipy)_3}]^{3+} + SO_4^{2-} + SO_4^{\bullet -} \quad (14)$$

$$k_q = \frac{k_1k_2k_3}{(k_{-1} + k_2)(k_{-2} + k_3) - k_2k_{-2}} \quad (15)$$

$$k_q = (k_1/k_{-1})(k_2/k_{-2})k_3 = K_1K_2k_3 \quad (16)$$

References

1 J. N. Demas, *J. Chem. Educ.*, 1983, **60**, 803.
2 F. Bolletta, A. Juris, M. Maestri, and D. Sandrini, *Inorg. Chim. Acta*, 1980, **44**, L175.
3 R. H-Baker, J. Lilie, and M. Grätzel, *J. Am. Chem. Soc.*, 1982, **104**, 422.
4 M. N-Spallart, K. Kalyanasundaram, C. Grätzel, and M. Grätzel, *Helv. Chim. Acta*, 1980, **63**, 1111.
5 D. H. M. W. Thewissen, M. Eeuwhorst-Reinten, K. Timmer, A. H. A. Tinnemans, and A. Mackor, *Recl. Trav. Chim. Pays-Bas.*, 1982, **101**, 79.
6 'Shin Jikken Kagaku Koza 8,' eds. T. Tachibana, M. Nakahara, and M. Shibata, Japanese Chemical Society, Maruzen, Tokyo, 1975, p. 1475; R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 964; I. Fujita and H. Kobayashi, *Ber Bunsenges. Phys. Chem.*,1972, **76**, 115.
7 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 512.
8 J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, 1973, **95**, 5159.

Received 26*th March* 1984; *Paper* 4/495