Kinetic Studies of Electron-Transfer Reactions Induced by the Reductive Quenching of Tris(2,2′-bipyrazine)ruthenium(II)

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The oxidation reaction of the oxalate ion ($C_2O_4^{2-}$) by the peroxodisulfate ion ($S_2O_8^{2-}$) is greatly accelerated by irradiation with visible light in an aqueous solution containing tris(2,2′-bipyrazine)ruthenium(II) ($[Ru(bpz)_3]^{2+}$). The mechanism constitutes a chain reaction initiated by a reductive quenching of photoexcited $[Ru(bpz)_3]^{2+}$ with $C_2O_4^{2-}$. The rate of reaction increases with an increase of the $[Ru(bpz)_3]^{2+}$ concentration or incident light intensity. On the other hand, the reaction rate hardly depends not only on the concentrations of $C_2O_4^{2-}$ and $S_2O_8^{2-}$, but also on the ionic strength and temperature. The $[Ru(bpz)_3]^{2+}$ acts as a photo-catalyst, although the absorption spectra of the reaction solution are slightly changed during the photoreaction. An analysis of the absorption spectra by a graphic method indicates that another absorbing species than $[Ru(bpz)_3]^{2+}$ is formed in the reaction solution. Such a complex has no photocatalytic effect for the redox reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$. The concentration of the produced complex is always coincident with ca. 0.7% of that of the $S_2O_8^{2-}$ reacted. The reaction mechanism and rate law are clarified to account for the results obtained.

Tris(2,2′-bipyridine)ruthenium(II)($[Ru(bpy)_3]^{2+}$) and its derivatives have been extensively investigated from the viewpoint of the solar energy conversion.[1–9] Recently, the analogous tris(2,2′-bipyrazine)ruthenium(II) ion ($[Ru(bpz)_3]^{2+}$) has attracted the attention of many researchers.[10–15] The photochemical properties of $[Ru(bpz)_3]^{2+}$ are similar to those of the $[Ru(bpy)_3]^{2+}$. A salient feature of the former is that the excited state lifetime is longer than that of the latter and that the standard redox potentials are more positive by ca. 0.5 V than those of the corresponding couples for ($[Ru(bpy)_3]^{2+}$), respectively.[16–19] As a result, the photo-excited ruthenium(II) complex ($[Ru(bpz)_3]^{2+*}$) is a stronger oxidant, but poorer reductant, than $[Ru(bpy)_3]^{2+*}$. The $[Ru(bpz)_3]^{2+*}$ has been reported to be reductively quenched with an oxalate ion and ethylenediaminetetraacetic acid (EDTA) in an aqueous solution; the anodic photocurrent obtained in the photoelectrochemical system was attributable to the oxidation of $[Ru(bpz)_3]^{+}$ produced by the quenching reaction.[20–22] As far as the $[Ru(bpy)_3]^{2+}$ is concerned, only a few reductive quenchers, such as Eu^{2+} and ascorbate ion, are known in aqueous solutions.

Various photo-induced electron-transfer reactions with $[Ru(bpy)_3]^{2+}$ as a photocatalyst have been studied kinetically in order to clarify the reaction mechanisms. On the other hand, there have been few kinetic studies on photoreactions with $[Ru(bpz)_3]^{2+}$, except for a reaction system consisting of methylviologen (MV^{2+}), a sacrificial donor (such as EDTA and triethanolamine (TEOA)) and colloidal metal redox catalysts.[12,16,17] In such a system, the $[Ru(bpz)_3]^{2+*}$ is quenched reductively by EDTA or TEOA; the resulting $[Ru(bpz)_3]^{+}$ reacts with MV^{2+} to produce $MV^{+\cdot}$ and, subsequently, $MV^{+\cdot}$ reduces water in the presence of a catalyst. The quantum yield of the $MV^{+\cdot}$ formation by $[Ru(bpz)_3]^{2+}$ is reported to be nearly 100%, while that by $[Ru(bpy)_3]^{2+}$ is only 20% under similar photochemical conditions.

We previously studied the electron-transfer reaction between oxalate and peroxodisulfate induced by photo-excited $[Ru(bpy)_3]^{2+}$.[23] This reaction was initiated by the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ by $S_2O_8^{2-}$.

In this paper we present a kinetic study of the photo-induced electron-transfer reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$ by using $[Ru(bpz)_3]^{2+}$ as a photocatalyst. Several remarkable differences between the $[Ru(bpy)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ systems are: (1) the photo-induced reaction is initiated by the oxidative quenching reaction of $[Ru(bpy)_3]^{2+*}$ by the $S_2O_8^{2-}$, while by the reductive quenching of $[Ru(bpz)_3]^{2+*}$ by the $C_2O_4^{2-}$; (2) the ligand-substitution reaction for $[Ru(bpy)_3]^{2+}$ does not occur at all, but that for $[Ru(bpz)_3]^{2+}$ occurs to produce the bis(2,2′-bipyrazine)ruthenium(II) complex. The photochemical stability of the ruthenium(II) complex is an important problem concerning utilization as a photosensitizer and -catalyst. This paper also proposes that the ligand-substitution product of $[Ru(bpz)_3]^{2+}$ is inactive for a photo-catalyzed reaction between $C_2O_4^{2-}$ and $S_2O_8^{2-}$.

Experimental

$[Ru(bpz)_3]Cl_3 \cdot 3.5H_2O$ was prepared and purified as described in the literature.[24,25] Ruthenium trichloride and 2,2′-bipyrazine were purchased from Wako Pure Chemical Co. and Aldrich, respectively. The other chemicals used were of guaranteed reagent grade and were used without further purification. Unless otherwise stated, each sample solution was irradiated with visible light from two 100-W tungsten lamps placed 3 dm to the right- and left-hand sides from the center of the reaction vessel. Oxygen dissolved in the solutions was removed by bubbling through pure nitrogen gas. The concentration of $S_2O_8^{2-}$ remaining in the solution was determined as reported previously,[23] except that the amount of cation exchange resin (Dowex 50W-X8, 200—400 mesh, hydrogen form, washed well with distilled water) to remove the $[Ru(bpz)_3]^{2+}$ was twice as much as that for $[Ru(bpy)_3]^{2+}$. The measurement of the spectral changes in a deaerated solution was carried out by using a Shimadzu digital double beam spectrophotometer (UV-200S).

Results

Dependence of the Reaction Rate on the Concentrations of $S_2O_8^{2-}$, $C_2O_4^{2-}$, and $[Ru(bpz)_3]^{2+}$, Light Intensity, Ionic Strength, and Temperature. Plots of the $S_2O_8^{2-}$ concentration against the reaction time are shown in Fig. 1 under the conditions of 5×10^{-5} mol dm^{-3} $[Ru(bpz)_3]Cl_2$, 0.04 mol dm^{-3} $Na_2C_2O_4$, 30 °C, and an ionic strength of 0.4 mol dm^{-3}. The decomposition rate of $S_2O_8^{2-}$ is almost independent of the $S_2O_8^{2-}$ concentration, and decreases gradually with an increase of the reaction time. Such a time-profile is attributable to the concentration change of $[Ru(bpz)_3]^{2+}$ as a photocatalyst (mentioned later). The plots of $[S_2O_8^{2-}]$ vs. t are also independent of the $C_2O_4^{2-}$ concentrations over the range 0.04—0.055 mol dm^{-3}. On the other hand, the decomposition rate of $S_2O_8^{2-}$ increases with an increase of $[Ru(bpz)_3]^{2+}$ concentration or intensity of the incident light as shown in Figs. 2 and 3. The electron-transfer reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$ hardly proceeds without either of $[Ru(bpz)_3]^{2+}$ or visible light. The dependences of the reaction rate on the ionic strength and temperature were also examined over the range 0.2—0.5 mol dm^{-3} and 20—40 °C, respectively. It is found that the ionic strength as well as temperature of the reaction solution have little effect on the reaction rate. The kinetic studies were carried out in a neutral solution, although the pH of the solution increases after $S_2O_8^{2-}$ is completely exhausted by the photoreaction. This fact is attributed to water reduction with $[Ru(bpz)_3]^{+}$ (see Eq. 10).

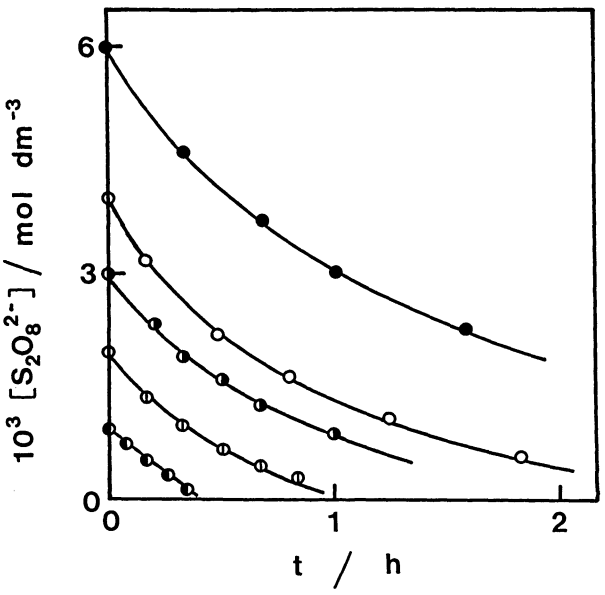

Fig. 1. Plots of $[S_2O_8^{2-}]$ vs. t obtained in the deaerated solution containing 4×10^{-2} mol dm^{-3} $Na_2C_2O_4$ and 5×10^{-5} mol dm^{-3} $[Ru(bpz)_3]Cl_2$ at an ionic strength of 0.4 mol dm^{-3} and 30 °C. Irradiation was done with two lamps. Initial concentrations of $S_2O_8^{2-}$ are (●) 6×10^{-3}, (○) 4×10^{-3}, (◑) 3×10^{-3}, (◔) 2×10^{-3}, and (◐) 1×10^{-3} mol dm^{-3}.

Spectral Change of the Reaction. The typical spectral changes obtained by the irradiation of the reaction solution are presented in Fig. 4. The absorption spectrum at t=0 coincides with that of $[Ru(bpz)_3]^{2+}$. The absorption band of $[Ru(bpz)_3]^{2+}$ at 442 nm decreased with the irradiation time, while new bands appeared at around 380 and 480 nm. Two isosbestic points were

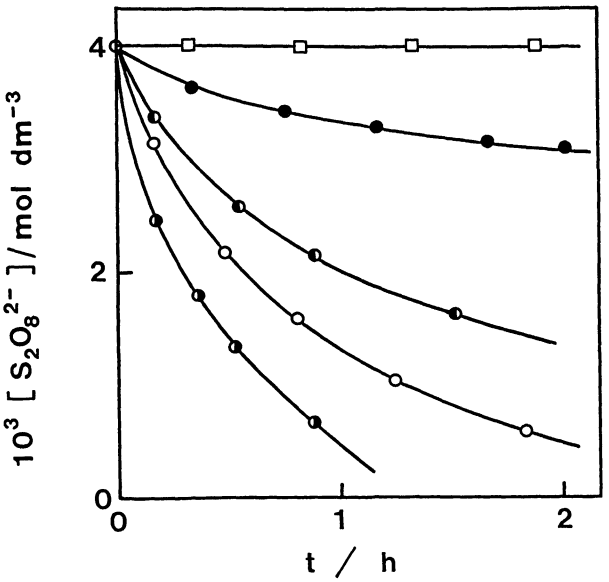

Fig. 2. Effect of the $[Ru(bpz)_3]^{2+}$ ion concentration. Initial concentrations of $[Ru(bpz)_3]Cl_2$ are (□) 0, (●) 1.1×10^{-5}, (◐) 3.1×10^{-5}, (○) 5×10^{-5}, and (◑) 7.7×10^{-5} mol dm^{-3}. Other conditions are the same as in the plots ○ in Fig. 1.

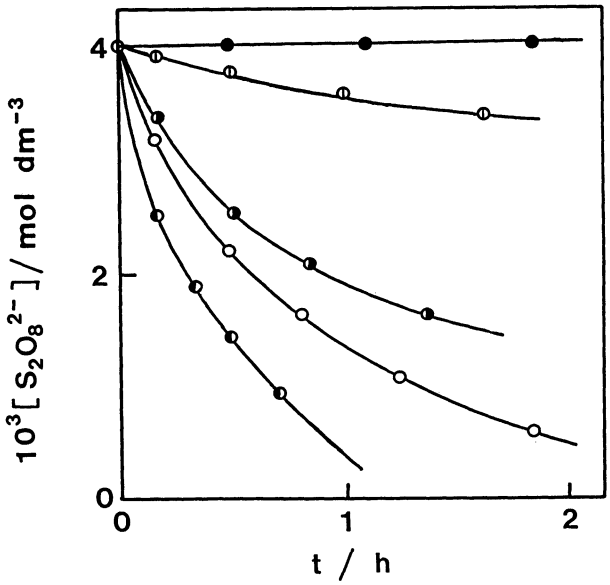

Fig. 3. Effect of the incident light intensity. Conditions:(●) dark, (◔) room light, (◑) 1 lamp, (○) 2 lamps, and (◐) 4 lamps. Other conditions are the same as in the plots ○ in Fig. 1.

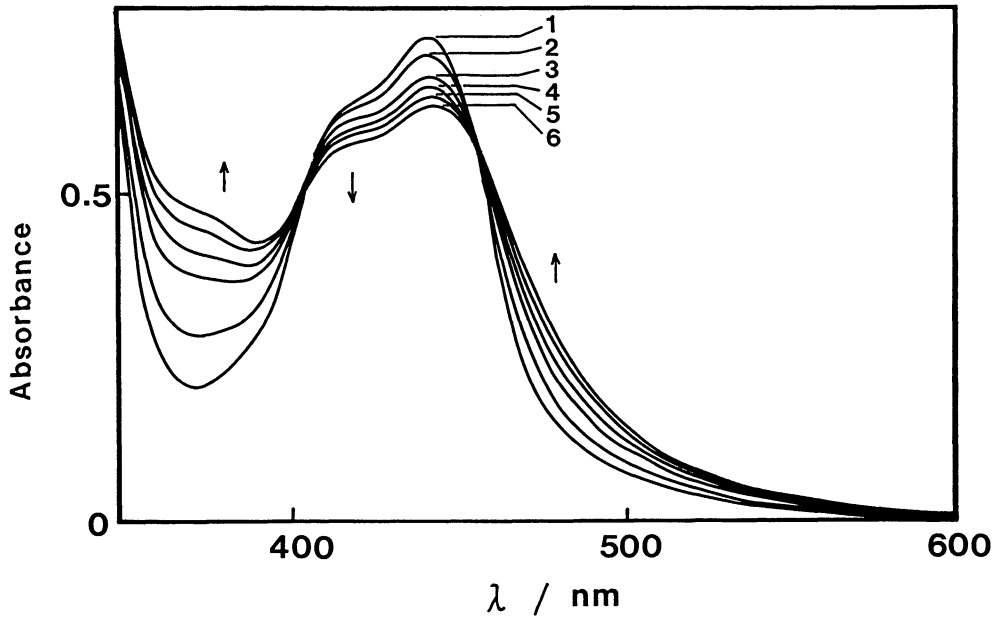

Fig. 4. Spectral change of the solution. Conditions are the same as in the plots O in Fig. 1. Reaction time: (1) 0, (2) 10 min, (3) 28 min, (4) 48 min, (5) 72 min, and (6) 108 min.

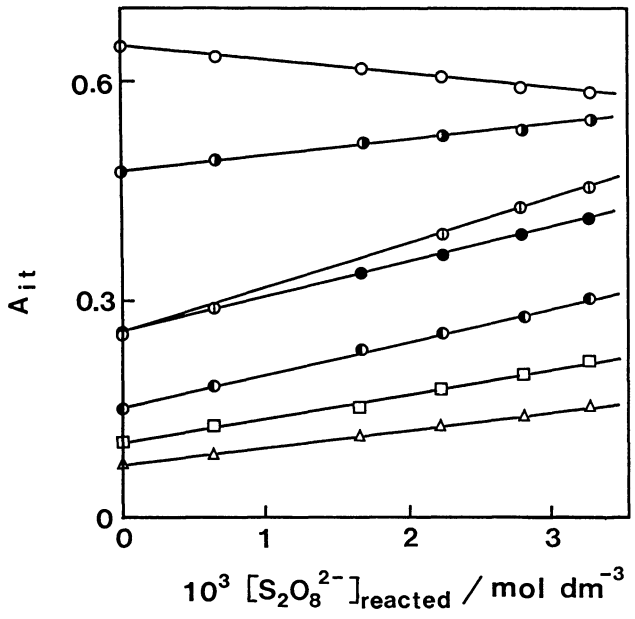

Fig. 5. Plots of A_{it} vs. $[S_2O_8^{2-}]_{reacted}$. Conditions are the same as in Fig. 4. The data are taken at wavelength of (⊙) 380 nm, (○) 420 nm, (◑) 460 nm, (●) 470 nm, (◐) 480 nm, (□) 490 nm, and (△) 500 nm.

observed at 407 and 456 nm. The absorption spectra of $[Ru(bpz)_3]^{2+}$ were not recovered, even if the solution was saturated with air. Figure 5 indicates that plots of A_{it} vs. $[S_2O_8^{2-}]_{reacted}$ are rectilinear; an intercept where A_{it} indicates absorbance at a given wavelength, i, and reaction time, t; $[S_2O_8^{2-}]_{reacted}$ represents the concentration of $S_2O_8^{2-}$ consumed up to $t=t$.

$$A_{it} = a_i + b_i[S_2O_8^{2-}]_{reacted} \quad (1)$$

The intercept, a_i, is the absorbance at a wavelength i and $t=0$. The b_i value varies with the wavelength, whereas it is independent of other experimental factors, such as the initial concentrations of $S_2O_8^{2-}$, $C_2O_4^{2-}$,, and $[Ru(bpz)_3]^{2+}$, light intensity, ionic strength, and temperature. The b_i values are estimated to be 67.9±6.3, −21.8±2.2, 19.9±3.3, 46.3±3.2, 44.7±2.4, 33.8±2.0, and 24.4±1.9, at 380 nm, 420 nm, 460 nm, 470 nm, 480 nm, 490 nm, and 500 nm, respectively.

Quenching Reaction of $[Ru(bpz)_3]^{2+*}$ with $C_2O_4^{2-}$ and $S_2O_8^{2-}$. The quenching rate constants (k_q) of $[Ru(bpz)_3]^{2+*}$ with $C_2O_4^{2-}$ or $S_2O_8^{2-}$ were evaluated from quenching experiments using an unbuffered neutral solution. The Stern–Volmer plots are linear and the k_q values, respectively, 7.2×10^6 and 3.3×10^6 dm^3 mol^{-1} s^{-1} for $C_2O_4^{2-}$ and $S_2O_8^{2-}$ at an ionic strength of 0.4 mol dm^{-3}. Figure 6 depicts the spectral change of a deaerated $[Ru(bpz)_3]^{2+}$ solution containing $C_2O_4^{2-}$ under continuous irradiation. An absorbance at 442 nm decreases the new bands at 420 and 470 nm. The observed absorption spectra did not change along with air saturation in the solution. A similar absorption spectrum has been reported from a flash photolysis of a deaerated solution containing $[Ru(bpz)_3]^{2+}$ and EDTA.[26]

Discussion

The photoexcited $[Ru(bpz)_3]^{2+}$ is quenched reductively by $C_2O_4^{2-}$ and oxidatively by $S_2O_8^{2-}$ with quenching-rate constants of 7.2×10^6 and 3.3×10^6 dm^3 mol^{-1} s^{-1}, respectively. Under the experimental conditions investigated, the concentrations of $C_2O_4^{2-}$ are always ten-

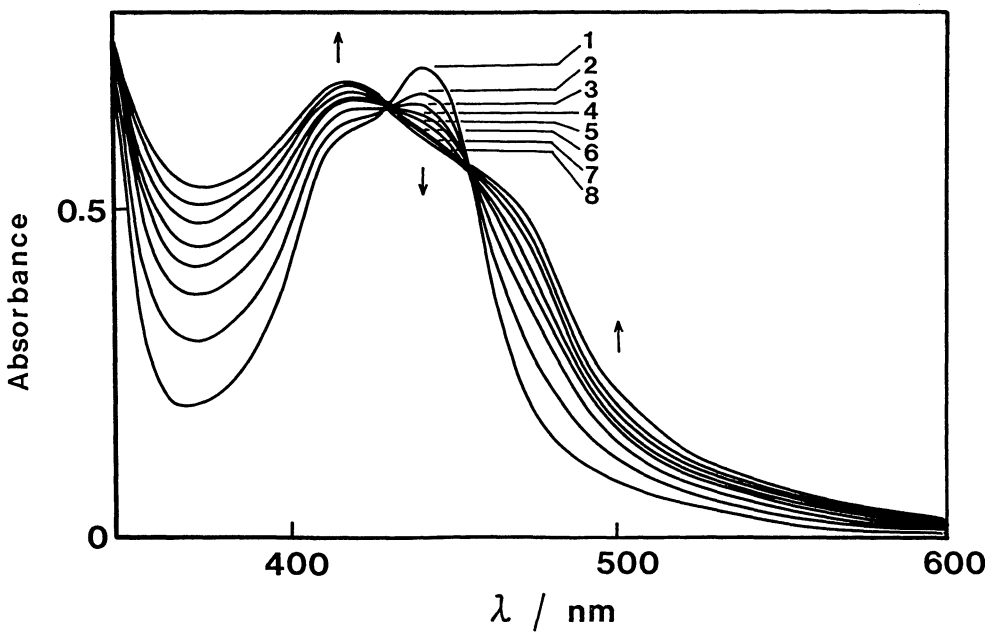

Fig. 6. Spectral change in the reductive quenching reaction of $[Ru(bpz)_3]^{2+*}$ with $C_2O_4^{2-}$. Conditions are the same as in Fig. 1 without an addition of $S_2O_8^{2-}$. Reaction time: (1) 0, (2) 5 min, (3) 10 min, (4) 15 min, (5) 21 min, (6) 30 min, (7) 40 min, and (8) 60 min.

times as much as those of $S_2O_8^{2-}$. Thus, it is most likely that reductive quenching proceeds predominantly in the present system.

The following reaction mechanism is assumed to account for the results obtained:

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

$$[Ru(bpz)_3]^{2+*} \xrightarrow{k_0} [Ru(bpz)_3]^{2+} + h\nu' \text{ or } \Delta\,(\text{thermal energy}), \quad (3)$$

$$[Ru(bpz)_3]^{2+*} + C_2O_4^{2-} \xrightarrow{k_q} [Ru(bpz)_3]^{+} + CO_2^{\cdot-} + CO_2, \quad (4)$$

$$[Ru(bpz)_3]^{2+*} + CO_2^{\cdot-} \longrightarrow [Ru(bpz)_3]^{+} + CO_2, \quad (5)$$

$$S_2O_8^{2-} + [Ru(bpz)_3]^{+} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} + [Ru(bpz)_3]^{2+}, \quad (6)$$

and

$$SO_4^{\cdot-} + [Ru(bpz)_3]^{+} \longrightarrow SO_4^{2-} + [Ru(bpz)_3]^{2+}. \quad (7)$$

Assuming a steady state concentration for $[Ru(bpz)_3]^{+}$, $SO_4^{\cdot-}$, and $CO_4^{\cdot-}$ radicals, the following reaction rate is obtained:

$$-d[S_2O_8^{2-}]/dt = \frac{k_q I_a \Phi [C_2O_4^{2-}]}{k_0 + k_q [C_2O_4^{2-}]}, \quad (8)$$

Here, I_a is the amount of light absorbed, Φ the quantum yield for the formation of $[Ru(bpz)_3]^{2+*}$ and $I_a\Phi$ corresponds to the formation rate of $[Ru(bpz)_3]^{2+*}$. The I_a can be rewritten as Eq. 9 with an incident light intensity of I_0, and an empirical constant, γ, comprising the molar absorption coefficient of $[Ru(bpz)_3]^{2+}$ and the length of the light path:

$$I_a = I_0(1-\exp(-\gamma[[Ru(bpz)_3]^{2+}])). \quad (9)$$

The rate law (Eq. 8) suggests that the reaction rate is independent of the $S_2O_8^{2-}$ concentration and is dependent on the incident light intensity and the $[Ru(bpz)_3]^{2+}$ concentration. This is coincident with all of the experimental results. Equation 8 also indicates that the reaction rate should depend on the $C_2O_4^{2-}$ concentration. However, the reaction rate observed was almost independent of the $C_2O_4^{2-}$ concentration within the range 0.04—0.055 mol dm^{-3}. The value of $k_q[C_2O_4^{2-}]$ is comparable within such a concentration range to that of k_0 which is estimated to be 9.6×10^5 s^{-1} from the lifetime of $[Ru(bpz)_3]^{2+*}$. The right-hand side of Eq. 8 is rewritten as $I_a\Phi\{1-k_0/(k_0+k_q[C_2O_4^{2-}])\}$; the value of $k_0/(k_0+k_q[C_2O_4^{2-}])$ changes little when the concentration varies by at most 1.5 times as much. Thus, if we were to examine the dependence of the reaction rate on the $C_2O_4^{2-}$ concentration over a wider concentration range, a dependence like that shown in Eq. 8 might be obtained. In fact, however, in the lower concentrations of $C_2O_4^{2-}$, the oxidative quenching of $S_2O_8^{2-}$ for $[Ru(bpz)_3]^{2+*}$ should be considered in the reaction mechanism, while at higher concentrations of $C_2O_4^{2-}$, the dark redox reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$ proceeds considerably. According to Eq. 8, the $S_2O_8^{2-}$ decreases linearly with the reaction time under excess concentrations of $C_2O_4^{2-}$. However, as described later, some $[Ru(bpz)_3]^{2+}$ are transformed to an inert complex for the photoreaction, causing a decrease in the reaction rate with the reaction time. The reaction rate was independent of both the ionic strength and temperature of the solution. This finding is attributed to the fact

that the k_q- and k_0-paths have a similar dependence on the ionic strength and temperature. The latter means that the activation energies for both reaction paths are almost the same. The $[Ru(bpz)_3]^+$ is capable of reducing water when all the $S_2O_8^{2-}$ ions are exhausted by the reaction, which is responsible for an increase in the solution pH.

$$[Ru(bpz)_3]^+ + H_2O \longrightarrow [Ru(bpz)_3]^{2+} + 1/2\,H_2O + OH^- \quad (10)$$

Since the $SO_4^{\cdot-}$ radical is a strong oxidant, the following reactions can be considered:

$$SO_4^{\cdot-} + C_2O_4^{2-} \longrightarrow SO_4^{2-} + CO_4^{\cdot-} + CO_2, \quad (11)$$

$$SO_4^{\cdot-} + [Ru(bpz)_3]^{2+} \longrightarrow SO_4^{2-} + [Ru(bpz)_3]^{3+}, \quad (12)$$

and

$$[Ru(bpz)_3]^{3+} + C_2O_4^{2-} \longrightarrow [Ru(bpz)_3]^{2+} + CO^{\cdot-} + CO_2, \quad (13)$$

The $CO_2^{\cdot-}$ radicals produced by reactions 11 and 13 react with $[Ru(bpz)_3]^{2+}$ to form $[Ru(bpz)_3]^+$, which is subsequently oxidized by $S_2O_8^{2-}$ (see Eqs. 5 and 6). When reactions 11—13 could occur, the reaction rate should be dependent on the $S_2O_8^{2-}$ concentration; but being quite different from the obtained results, these reactions have been ruled out.

A graphical analysis has been developed regarding the change in the absorption spectra (Fig. 4) in order to determine the number of species in the solution. A plot of $A_{it}-A_{it'}$ vs. $A_{i't}-A_{i't'}$ gives a straight line through the origin only when two absorbing species exist in the solution.[27,28] From the results given in Fig. 7, we can conclude that another absorbing species (RuL) as well as $[Ru(bpz)_3]^{2+}$ is present in the solution. The following relationship is derived from Eq. 1:

$$\frac{[[Ru(bpz)_3]^{2+}]_{decreased}}{[S_2O_8^{2-}]_{reacted}} = \frac{[RuL]_{produced}}{[S_2O_8^{2-}]_{reacted}} = \frac{b_i}{\varepsilon_i' - \varepsilon_i}, \quad (14)$$

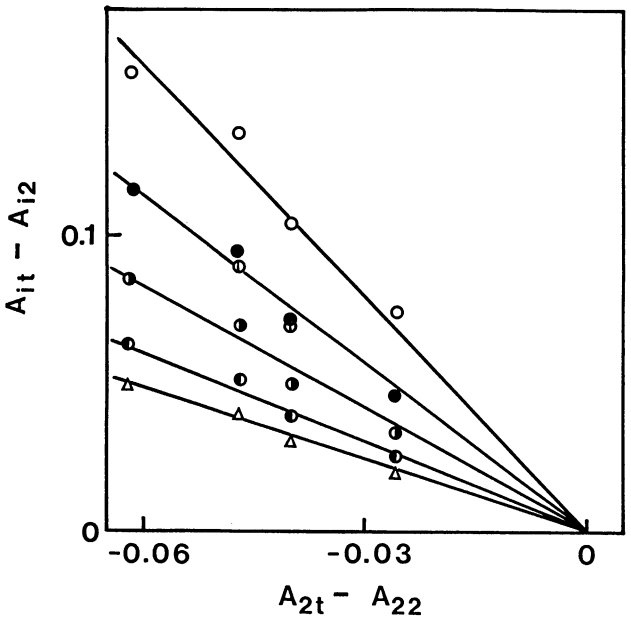

Fig. 7. A graphic method for two absorbing species. The data are taken from Fig. 4. The values of i and t correspond to the wavelength and reaction time, respectively. i=2:420 nm, t=2:10 min. (○) 380 nm, (△) 460 nm, (●) 470 nm, (⊙) 480 nm, (◑) 490 nm, (◐) 500 nm.

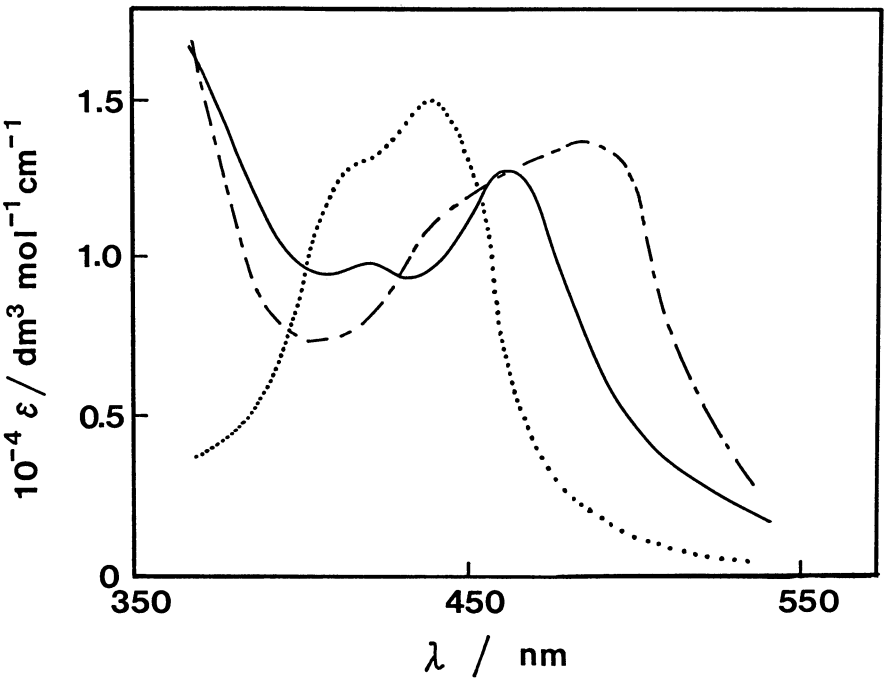

Fig. 8. Absorption spectra of $[Ru(bpz)_3]^{2+}$ (·····), $[Ru(bpz)_3]^+$ (—·—),[17] and RuL (——). The absorption spectra of RuL are calculated from the spectral data in Fig. 4.

where ε_i' indicates the molar absorption coefficient for RuL at wavelength i. Since the value of $b_i/(\varepsilon_i'-\varepsilon_i)$ must be constant for all observed wavelengths, the absorption spectra for RuL is represented in Fig. 8 from the spectral data in Fig. 4 and the b_i values obtained from the plots A_{it} vs. $[S_2O_8^{2-}]_{reacted}$ (Fig. 5). The b_i value was independent of any experimental conditions investigated and the $b_i/(\varepsilon_i'-\varepsilon_i)$ value was estimated to be 7×10^{-3}. Therefore, in the present reaction system, the amount of RuL formed always corresponds to ca. 0.7% of the $S_2O_8^{2-}$ reacted, suggesting that RuL has little photocatalytic effect on the photo-induced redox reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$. This causes a decrease in the reaction rate with an increase in the reaction time (as described in Fig. 1). The RuL might be a bis(bipyrazine)ruthenium(II) complex, such as $[Ru(bpz)_2(C_2O_4)]$, $[Ru(bpz)_2(CO_2)(H_2O)]^+$, or $[Ru(bpz)_2(SO_4)(H_2O)]^+$. The former two species are not likely to be formed, since the absorption spectra observed in the reaction solution are different from those obtained in the quenching reaction of $[Ru(bpz)_3]^{2+*}$ with $C_2O_4^{2-}$ (Fig. 6).

In conclusion, $[Ru(bpz)_3]^{2+}$ acts as a photocatalyst in a way similar to $[Ru(bpy)_3]^{2+}$ for a redox reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$. The reaction rate law is apparently similar with respect to the concentration of the quencher. However, the reaction mechanism is quite different, i.e., the initial step is the reductive quenching of $[Ru(bpz)_3]^{2+*}$ by $C_2O_4^{2-}$ for $[Ru(bpz)_3]^{2+}$ as a photocatalyst. Some $[Ru(bpz)_3]^{2+}$ is transformed to an inactive species for the photo-induced electron-transfer reactions. The stability of the ruthenium(II) complex during the photoreaction is a serious problem for the utilization of $[Ru(bpz)_3]^{2+}$, although $[Ru(bpz)_3]^{2+}$ has been described as a new photo-catalyst.

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