Generation of Anodic and Cathodic Currents based on Photoexcited Tris(2,2′-bipyrazine)ruthenium(II) in Aqueous Solutions

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Anodic and cathodic currents have been induced at an indium–tin oxide electrode by irradiation of aqueous solutions of tris(2,2′-bipyrazine)ruthenium(II) $[Ru(bipyz)_3]^{2+}$ containing ethylenediaminetetraacetic acid (H_4edta) and $S_2O_8^{2-}$, respectively. The anodic photocurrent is ascribed to reductive quenching of the photoexcited species $[{}^*Ru(bipyz)_3]^{2+}$ due to edta, as with $C_2O_4^{2-}$. On the other hand, the cathodic photocurrent is explained in terms of the oxidative quenching of $[{}^*Ru(bipyz)_3]^{2+}$ by $S_2O_8^{2-}$. A theoretical analysis is developed to account for the dependences of the photocurrents on applied potential, concentrations of $[Ru(bipyz)_3]^{2+}$, edta and $S_2O_8^{2-}$, pH and light intensity.

Tris(2,2′-bipyridine)ruthenium(II) $[Ru(bipy)_3]^{2+}$ is a promising material for conversion of solar energy into electric or chemical energy. The photoelectrochemical properties of the complex have been investigated intensively.[1–6] So far as we know, however, most of the studies are restricted to oxidative quenching of the photoexcited species $[{}^*Ru(bipy)_3]^{2+}$ in aqueous solutions, except for the reductive quenching reaction in acetonitrile reported by Cano-Yelo and Deronzier.[5]

The analogous tris(2,2′-bipyrazine)ruthenium(II) $[Ru(bipyz)_3]^{2+}$ has the following salient features: the lifetime of the excited state is fairly long and the standard redox potentials for $[Ru(bipyz)_3]^{2+}$ are *ca.* 0.5 V more positive than those of the corresponding couples for $[Ru(bipy)_3]^{2+}$.[7–15] Our previous paper[16] ascribed anodic photocurrents observed with an aqueous solution of $[Ru(bipyz)_3]^{2+}$ and $C_2O_4^{2-}$ to reductive quenching of $[{}^*Ru(bipyz)_3]^{2+}$ by $C_2O_4^{2-}$. Moreover, an analytical equation has been derived to describe the anodic photocurrents as functions of the quenching rate constant (k_q) for $[{}^*Ru(bipyz)_3]^{2+}$ by $C_2O_4^{2-}$, concentrations of $C_2O_4^{2-}$ and $[Ru(bipyz)_3]^{2+}$, etc.

In the present paper, we show that anodic and cathodic photocurrents observed with ethylenediaminetetraacetate (edta) and $S_2O_8^{2-}$ as quenchers are attributable to reductive and oxidative quenching of $[{}^*Ru(bipyz)_3]^{2+}$, respectively. In addition, the theoretical equation developed previously[16] is improved to explain the photocurrents observed with edta and $S_2O_8^{2-}$

Experimental

Chemicals.—The complex $[Ru(bipyz)_3]Cl_2{\cdot}3.5H_2O$ was prepared and purified as described in the literature.[17,18] Ruthenium trichloride and 2,2′-bipyrazine (bipyz) were purchased from Wako Pure Chemicals and Aldrich, respectively. Other chemicals were of guaranteed reagent grade and were used without further purification.

Procedures.—Electrochemical measurements were carried out on a Hokuto Denko HA-104 potentiostat/galvanostat and HB-107A function generator. Photocurrent measurements were performed in the three-electrode system with an indium–tin oxide working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference. Photoinduced potentials were measured with respect to the SCE in the two-electrode system. The light source was a 250 W tungsten–halogen lamp with a Toshiba KL-44 interference filter and V-44 colour filter. Solutions were illuminated through the indium–tin oxide electrode as described.[16] The intensity of the monochromatic light (440 nm) incident on this electrode was measured as 0.75 mW cm^{-2} with a calibrated Eppley thermopile comprising 16 junctions. Oxygen dissolved in sample solutions was removed by bubbling pure argon gas through them. All measurements were done at room temperature.

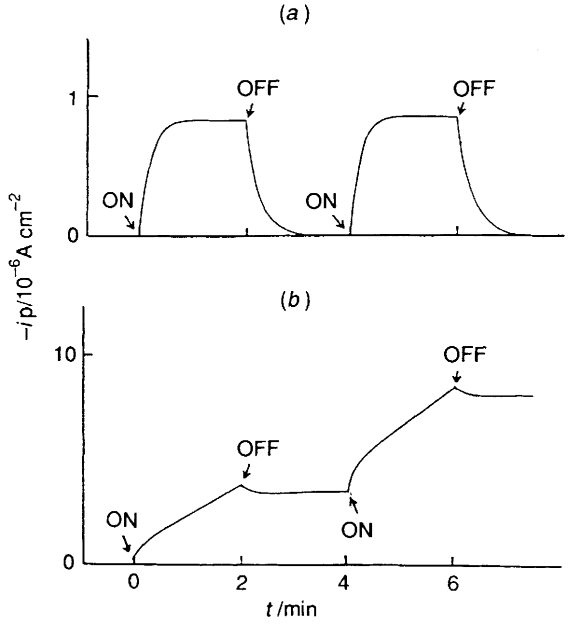

Fig. 1 Time dependence of the cathodic photocurrent obtained at the indium–tin oxide electrode in 0.1 mol dm^{-3} Na_2SO_4 solution containing 0.28 mmol dm^{-3} $[Ru(bipyz)_3]Cl_2$ and 20 mmol dm^{-3} $K_2S_2O_8$. The applied potentials were (*a*) +0.4 and (*b*) 0 V *vs.* SCE, respectively, and irradiation was done at 440 nm

Results and Discussion

Fig. 1 shows time profiles of photoinduced currents at the

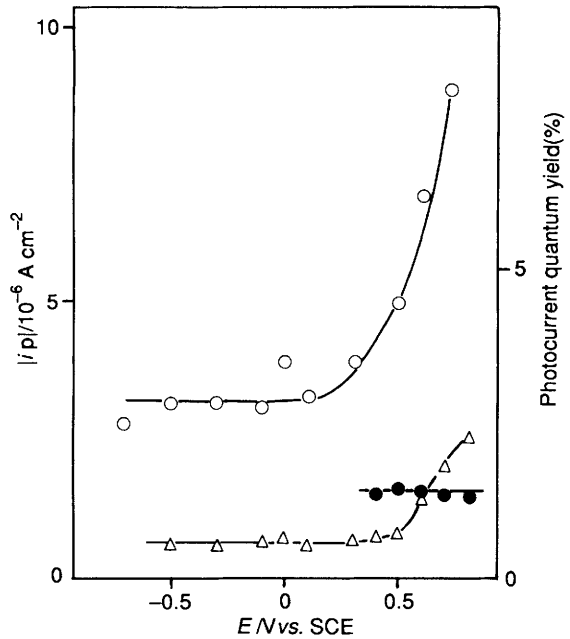

Fig. 2 Dependence of the anodic or cathodic photocurrent and the photocurrent quantum yield on the applied potential. The solution contained 0.1 mol dm^{-3} Na_2SO_4, 0.28 mmol dm^{-3} $[Ru(bipyz)_3]Cl_2$ and 40 mmol dm^{-3} (○) $Na_2C_2O_4$, (△) edta, or (●) $K_2S_2O_8$

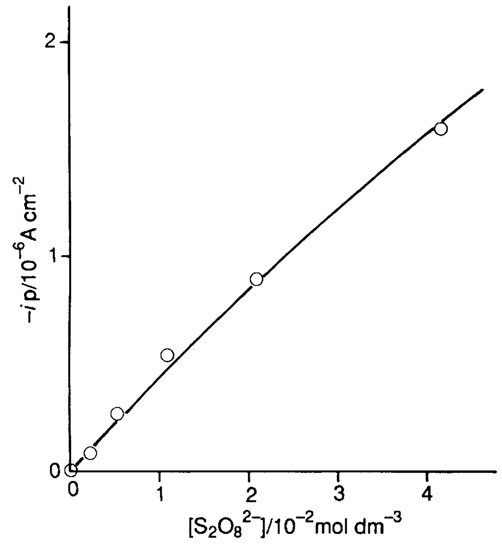

Fig. 3 Dependence of the cathodic photocurrent on the concentration of $S_2O_8^{2-}$ in an aqueous solution containing 0.28 mmol dm^{-3} $[Ru(bipyz)_3]Cl_2$ and 0.1 mol dm^{-3} Na_2SO_4. The solid curve was calculated using equation (14) with $k_q = 4 \times 10^6$ dm^3 mol^{-1} s^{-1} and $\gamma/k^{\frac{1}{2}} = 1.89$ s$^{\frac{1}{2}}$. The photocurrents were measured at +0.5 V *vs.* SCE

indium–tin oxide electrodes biased at +0.4 and 0 V *vs.* SCE in an aqueous solution containing $[Ru(bipyz)_3]^{2+}$ and $S_2O_8^{2-}$. Cathodic photocurrents are seen irrespective of the electrode potentials applied. However, the time response of the photocurrent depended on the applied potential, as typically shown in Fig. 1(*a*) and (*b*). When the applied potentials were more positive than +0.4 V the photocurrents became constant within about 20 s after irradiation and were kept constant for at least 20 min during the irradiation. Similar time dependences of the anodic photocurrents were observed with edta and $C_2O_4^{2-}$ in the potential range between −0.7 and +0.8 V. In contrast, the cathodic photocurrent for $S_2O_8^{2-}$ at potentials less positive than +0.3 V increased slowly and did not recover to the initial value even after the light was off. The irreversible change in the current was ascribed to some change in the surface of the indium–tin oxide electrode enhancing electrochemical reduction of $S_2O_8^{2-}$ in the dark. When the cathodic current for $S_2O_8^{2-}$ at this electrode in the dark was measured after irradiation the dark current was found to increase to 2–20 times that observed before irradiation. Such an effect was not observed with the $[Ru(bipy)_3]^{2+}$–$S_2O_8^{2-}$ system, showing that the phenomenon is specific to $[Ru(bipyz)_3]^{2+}$. Ghosh and Bard[19] have reported that electropolymerization of $[Ru(bipyz)_3]^{2+}$ takes place to form a film on a glassy carbon electrode in an acidic solution and then $[Ru(bipyz)_3]^{2+}$ is incorporated into the film. In the present study, however, no appreciable change in the electrode surface was detected visually and through measurement of a visible absorption spectrum of the electrode used under continuous irradiation for 20 min.

Fig. 2 depicts potential dependences of the photocurrent and the photocurrent quantum yield for $C_2O_4^{2-}$, edta and $S_2O_8^{2-}$ in neutral solutions. The anodic photocurrent for edta is almost constant in the range −0.4 to +0.3 V and increases with increasing potential more positive than +0.3 V, similarly to the anodic photocurrents for the $[Ru(bipyz)_3]^{2+}$–$C_2O_4^{2-}$ system. This current increase is ascribed to the reoxidation of hydrogen atoms or molecules produced in reaction (6) represented below.[16] Furthermore, photoinduced potentials for both systems were close to the redox potential of the $[Ru(bipyz)_3]^{+/2+}$ couple, suggesting that the anodic photocurrents originate from the electrochemical oxidation of $[Ru(bipyz)_3]^+$. On this basis, it is quite reasonable to assume that the mechanism of generation of the anodic photocurrent for edta is similar to that for $C_2O_4^{2-}$, *i.e.* edta reductively quenches $[^*Ru(bipyz)_3]^{2+}$ to $[Ru(bipyz)_3]^+$, which is subsequently oxidized at the electrode, equations (1)–(6) where $edta_{ox}^+$ denotes the oxidized form of

$$[Ru(bipyz)_3]^{2+} + h\nu \longrightarrow [^*Ru(bipyz)_3]^{2+} \quad (1)$$

$$[^*Ru(bipyz)_3]^{2+} \longrightarrow [Ru(bipyz)_3]^{2+} + h\nu' \text{ or } \Delta \text{ (thermal energy)} \quad (2)$$

$$[^*Ru(bipyz)_3]^{2+} + \text{edta} \longrightarrow [Ru(bipyz)_3]^{+} + \text{edta}_{ox}^{+} \quad (3)$$

$$\text{edta}_{ox}^{+} \longrightarrow H^+ + \text{edta}' \quad (4)$$

$$\text{edta}' + [Ru(bipyz)_3]^{2+} \longrightarrow [Ru(bipyz)_3]^{+} + \text{products} \quad (5)$$

$$[Ru(bipyz)_3]^{+} + H_3O^+ \text{ (or impurities)} \longrightarrow [Ru(bipyz)_3]^{2+} + \tfrac{1}{2}H_2 + H_2O \text{ (or products)} \quad (6)$$

$$[Ru(bipyz)_3]^{+} \longrightarrow [Ru(bipyz)_3]^{2+} + e^- \text{ (at the electrode)} \quad (7)$$

edta; edta′ produced by the deprotonation of $edta_{ox}^+$ is known to be a reducing agent.[20] as shown in Fig. 2, on the other hand, cathodic photocurrents for $S_2O_8^{2-}$ at potentials where no complication of a surface change in the electrode was involved were independent of the applied potentials. Hereafter, the cathodic photocurrents measured at +0.5 V *vs.* SCE were used for further investigation to clarify the mechanism of the photocurrent generation in the $[Ru(bipyz)_3]^{2+}$–$S_2O_8^{2-}$ system.

Fig. 3 shows the dependence of the photocurrent on the concentration of $S_2O_8^{2-}$ in 0.1 mol dm^{-3} Na_2SO_4 solution containing 0.28 mmol dm^{-3} $[Ru(bipyz)_3]Cl_2$. The photocurrent increases with the concentration of $S_2O_8^{2-}$ and is not observed without $S_2O_8^{2-}$. The solid curve in Fig. 3 was calculated by using equation (14) described later. At a fixed concentration of $K_2S_2O_8$, the photocurrent is in proportion to the concentration of $[Ru(bipyz)_3]^{2+}$ as shown in Fig. 4. Likewise, Fig. 5 indicates that the photocurrent increases almost linearly with the light intensity. With increasing light intensity, on the other hand, the photopotential became more positive. This may be attributable to the increase in concentration of the photogenerated species $[Ru(bipyz)_3]^{3+}$ at the electrode surface.

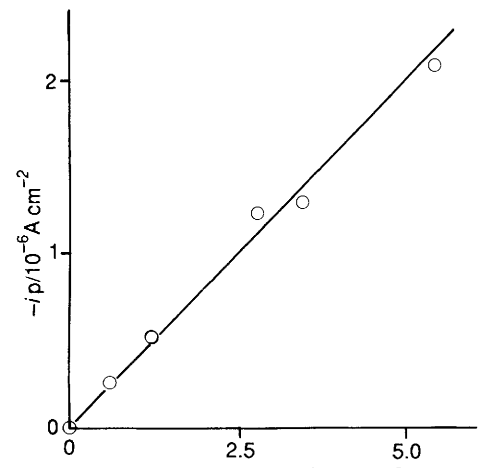

Fig. 4 Dependence of the cathodic photocurrent on the concentration of $[\mathrm{Ru(bipyz)_3}]^{2+}$. Conditions as in Fig. 3 except for 20 mmol dm^{-3} $K_2S_2O_8$

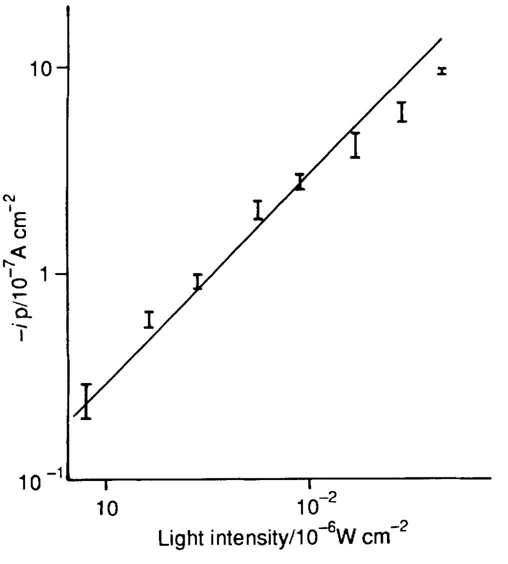

Fig. 5 Dependence of the cathodic photocurrent on the light intensity. Conditions as in Fig. 3 except for 20 mmol dm^{-3} $K_2S_2O_8$

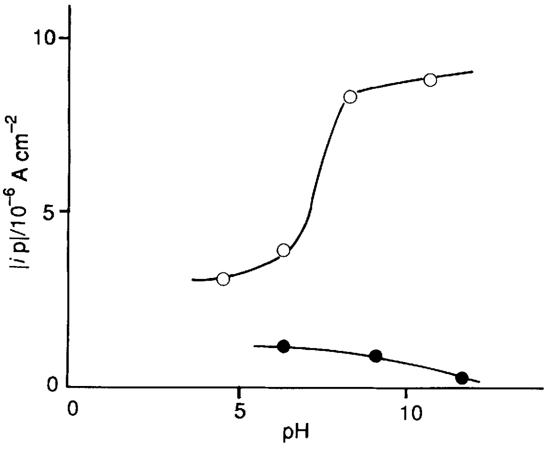

Fig. 6 Effect of pH on (●) the cathodic photocurrent obtained for $S_2O_8^{2-}$ at +0.5 V, or (○) the anodic photocurrent for $C_2O_4^{2-}$ at 0 V *vs.* SCE. Conditions as in Fig. 3 except for 20 mmol dm^{-3} $K_2S_2O_8$ and 40 mmol dm^{-3} $Na_2C_2O_4$

The effect of pH on the cathodic photocurrent for $S_2O_8^{2-}$ is shown in Fig. 6, where the pH dependence of the anodic photocurrent for $C_2O_4^{2-}$ is included for comparison. The cathodic photocurrent observed with $S_2O_8^{2-}$ decreases gradually as the pH increases, while the anodic photocurrent for $C_2O_4^{2-}$ increases strikingly at pH 6–8. The conspicuous difference in the pH effect between the two quenchers can be explained as below. The intermediate species $[\mathrm{Ru(bipyz)_3}]^{3+}$ and $[\mathrm{Ru(bipyz)_3}]^{+}$ produced by the oxidative and reductive quenching with $S_2O_8^{2-}$ and $C_2O_4^{2-}$ are strong oxidizing and reducing agents, respectively. Therefore, $[\mathrm{Ru(bipyz)_3}]^{3+}$ is likely to react with OH^- (or H_2O) in a basic (or neutral) solution to form $[\mathrm{Ru(bipyz)_3}]^{2+}$ prior to the reduction at the electrode surface. On the other hand, $[\mathrm{Ru(bipyz)_3}]^{+}$ can be oxidized by H_3O^+ in the vicinity of the electrode surface before the electrochemical oxidation takes place.

On this basis one can propose the reaction mechanism in equations (8)–(11) together with reactions (1) and (2) in order to account for the observed cathodic photocurrents. Reaction (9)

$$[{}^*\mathrm{Ru(bipyz)_3}]^{2+} + S_2O_8^{2-} \longrightarrow [\mathrm{Ru(bipyz)_3}]^{3+} + SO_4^{\bullet -} + SO_4^{2-} \quad (8)$$

$$[\mathrm{Ru(bipyz)_3}]^{2+} + SO_4^{\bullet -} \longrightarrow [\mathrm{Ru(bipyz)_3}]^{3+} + SO_4^{2-} \quad (9)$$

$$[\mathrm{Ru(bipyz)_3}]^{3+} + \tfrac{3}{2}H_2O\,(\text{or impurities}) \longrightarrow [\mathrm{Ru(bipyz)_3}]^{2+} + \tfrac{1}{4}O_2 + H_3O^+\,(\text{or products}) \quad (10)$$

$$[\mathrm{Ru(bipyz)_3}]^{3+} + e^- \longrightarrow [\mathrm{Ru(bipyz)_3}]^{2+}\,(\text{at the electrode}) \quad (11)$$

is deduced from the redox potentials for the couples of $SO_4^{\bullet -}$–SO_4^{2-} and $[\mathrm{Ru(bipyz)_3}]^{3+}$–$[\mathrm{Ru(bipyz)_3}]^{2+}$, *i.e.* $E(SO_4^{\bullet -}\text{–}SO_4^{2-}) > 3.4$ V *vs.* normal hydrogen electrode (NHE)[21] and $E\{[\mathrm{Ru(bipyz)_3}]^{3+}\text{–}[\mathrm{Ru(bipyz)_3}]^{2+}\} = 1.86$ V *vs.* SCE.[10] The pH dependence of the photocurrent shown in Fig. 6 indicates the occurrence of chemical reduction of $[\mathrm{Ru(bipyz)_3}]^{3+}$ to reproduce $[\mathrm{Ru(bipyz)_3}]^{2+}$. In the present work, unfortunately, no direct experimental evidence was found to support the oxygen evolution reaction (10) which is thermodynamically favourable.

Assuming a steady-state approximation with respect to the concentrations of $SO_4^{\bullet -}$, $[{}^*\mathrm{Ru(bipyz)_3}]^{2+}$ and $[\mathrm{Ru(bipyz)_3}]^{3+}$ in reactions (1), (2) and (8)–(11), equation (12) is obtainable in

$$D\frac{\partial^2[\mathrm{Ru(bipyz)_3}^{3+}]}{\partial x^2} + \gamma\alpha\psi I_o\{c_o - [\mathrm{Ru(bipyz)_3}^{3+}]\}\exp\{-\alpha(c_o - [\mathrm{Ru(bipyz)_3}^{3+}])x\} - k[\mathrm{Ru(bipyz)_3}^{3+}] = 0 \quad (12)$$

the same manner as described for the $[\mathrm{Ru(bipyz)_3}]^{2+}$–$C_2O_4^{2-}$ system,[16] where D is the diffusion coefficient of $[\mathrm{Ru(bipyz)_3}]^{3+}$, x the distance from the electrode surface, γ the quantum yield defined as the number of electroactive species, $[\mathrm{Ru(bipyz)_3}]^{3+}$, formed per photon absorbed, I_o the intensity of light incident at the electrode–electrolyte interface, c_o the initial concentration of added $[\mathrm{Ru(bipyz)_3}]^{2+}$ and k the pseudo-first-order rate constant for the reduction of $[\mathrm{Ru(bipyz)_3}]^{3+}$ with water or impurities. In addition, α is defined as 2.303 ε, where ε is a molar absorption coefficient of $[\mathrm{Ru(bipyz)_3}]^{2+}$ and ψ is $k_q[S_2O_8^{2-}]/(k_o + k_q[S_2O_8^{2-}])$. The γ value for the $[\mathrm{Ru(bipyz)_3}]^{2+}$–$C_2O_4^{2-}$ system has been reported to be 2, *i.e.* all the $CO_2^{\bullet -}$ radicals produced by the reductive quenching of $[{}^*\mathrm{Ru(bipyz)_3}]^{2+}$ by $C_2O_4^{2-}$ reduce $[\mathrm{Ru(bipyz)_3}]^{2+}$ to $[\mathrm{Ru(bipyz)_3}]^{+}$.[16] On the contrary, as an alternative to reaction (9), the $SO_4^{\bullet -}$ radical could oxidize the ligands of $[\mathrm{Ru(bipyz)_3}]^{2+}$ to yield bis(bipyrazine)ruthenium(II) complexes such as $[\mathrm{Ru(bipyz)_2(H_2O)_2}]^{2+}$ because it is a strong oxidant.[22] In the case that all of the $SO_4^{\bullet -}$ radicals react with $[\mathrm{Ru(bipyz)_3}]^{2+}$ to produce $[\mathrm{Ru(bipyz)_3}]^{3+}$, as expressed in equation (9), the value of γ should be equal to 2. The boundary condition of equation

(12) is defined by $[\mathrm{Ru(bipyz)_3}^{3+}] = 0$ for $x = 0$ and $x = \infty$. Hence, the solution of equation (12) is (13). In consequence, the

$$[\mathrm{Ru(bipyz)_3}^{3+}] = \frac{\alpha I_o \gamma \psi c_o}{k - \alpha^2 c_o^2 D}\{\exp(-\alpha c_o x) - \exp[-(k/D)^{\frac{1}{2}} x]\} \quad (13)$$

cathodic photocurrent (i_p) based on oxidative quenching with $S_2O_8^{2-}$ can be expressed as in equation (14) where F is the

$$i_p = -FAD\left(\frac{\partial[\mathrm{Ru(bipyz)_3}^{3+}]}{\partial x}\right)_{x=0} = -\frac{\gamma FA\alpha I_o c_o D^{\frac{1}{2}} k_q [S_2O_8^{2-}]}{k^{\frac{1}{2}}(k_o + k_q[S_2O_8^{2-}])} \quad (14)$$

Faraday constant and A is the surface area of the electrode contacting the electrolyte; k_o^{-1} is the lifetime of $[^*\mathrm{Ru(bipyz)_3}]^{2+}$, which has been reported to be 1.04 μs.[12] The D value for $[\mathrm{Ru(bipyz)_3}]^{3+}$ is assumed to be nearly equal to that $[(5.1 \pm 0.1) \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}]$ for $[\mathrm{Ru(bipyz)_3}]^{2+}$.[16] The photocurrents calculated by using equation (14) with $k_q = 4 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and $\gamma/k^{\frac{1}{2}} = 1.89\ \mathrm{s}^{\frac{1}{2}}$ are represented in Fig. 3, being a fair fit of those observed experimentally. The k_q value employed is in good agreement with the value of $3.4 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ obtained from Stern–Volmer plots for the quenching of $[^*\mathrm{Ru(bipyz)_3}]^{2+}$ by $S_2O_8^{2-}$ at an ionic strength of 0.4 mol dm^{-3}. These results support the proposed mechanism [reactions (8)–(11)]. There was no evidence in the absorption measurement to suggest degradation of $[\mathrm{Ru(bipyz)_3}]^{2+}$ to produce $[\mathrm{Ru(bipyz)_2(H_2O)_2}]^{2+}$ during the photoelectrochemical experiment. Hence, the γ value for the $S_2O_8^{2-}$ system is assumed to be 2 under the experimental conditions investigated. Introducing $\gamma = 2$ into $\gamma/k^{\frac{1}{2}} = 1.89\ \mathrm{s}^{\frac{1}{2}}$, the value of k for $[\mathrm{Ru(bipyz)_3}]^{3+}$ was evaluated to be 1.1 s^{-1}. This is comparable to the value for $[\mathrm{Ru(bipyz)_3}]^{+}$ obtained from measurements of the anodic photocurrents for the $[\mathrm{Ru(bipyz)_3}]^{2+}$–$C_2O_4^{2-}$ system in neutral solution.[16]

The mechanism of generation of the cathodic photocurrent for $S_2O_8^{2-}$ [equations (8)–(11)] is essentially the same as that of the anodic photocurrent for edta or $C_2O_4^{2-}$,[16] except for the difference in electroactive species to produce photocurrents and in the sign of the photocurrents. Equation (14) indicates that the magnitude of anodic or cathodic photocurrent depends on the values of k_q, k and γ. As shown in Fig. 2, the photocurrent obtained for $C_2O_4^{2-}$ is about twice that for $S_2O_8^{2-}$ in neutral solution. This is ascribed to the difference between the k_q values[16] of 8.2×10^6 and $3.4 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for $C_2O_4^{2-}$ and $S_2O_8^{2-}$, because the k value for $[\mathrm{Ru(bipyz)_3}]^{+}$ is comparable to that for $[\mathrm{Ru(bipyz)_3}]^{3+}$ and the γ values for both systems are almost equal to 2. The k_q value for edta is estimated from the Stern–Volmer plots to be $4.8 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, which is greater than that for $S_2O_8^{2-}$. Nevertheless, the photocurrent obtained for edta is smaller than that for $S_2O_8^{2-}$. This can be explained by the difference between the γ values for edta and $S_2O_8^{2-}$. The γ value for edta is dependent on pH because the reducing potentiality of the edta′ radical is remarkably dependent on the pH of the solution. For example, at pH 11 the rate constant for reduction of $[\mathrm{Ru(bipyz)_3}]^{2+}$ by edta′ is $4 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ and then the γ value becomes 2.[23] At pH 4.7, however, edta′ does not reduce $[\mathrm{Ru(bipyz)_3}]^{2+}$ at all which indicates $\gamma = 1$, because the bimolecular decay of edta′ occurs predominantly.[23] From equation (14) and k_q values for edta and $S_2O_8^{2-}$, it is deduced that the γ value for edta in the neutral solution investigated is unity, while that for $S_2O_8^{2-}$ is about 2. This accounts for the small photocurrents obtained for edta compared with $S_2O_8^{2-}$. In addition, the quantum yield of the cathodic photocurrent for the $[\mathrm{Ru(bipy)_3}]^{2+}$–$S_2O_8^{2-}$ system was about 30 times greater than that for the $[\mathrm{Ru(bipyz)_3}]^{2+}$–$S_2O_8^{2-}$ system. This is explained by the fact that the k_q value for the quenching of $[^*\mathrm{Ru(bipyz)_3}]^{2+}$ with $S_2O_8^{2-}$ is two orders of magnitude greater than that for $[^*\mathrm{Ru(bipyz)_3}]^{2+}$.[24]

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