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Kinetic Studies of the Reductive Quenching of Photoexcited Tris(2,2′-bipyrazine)ruthenium(II) by an Oxalate Ion in the Photoelectrochemical System

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The anodic photocurrent obtained at the irradiated ITO electrode in the Na_2SO_4 solution containing $[Ru(bpz)_3]Cl_2$ and $Na_2C_2O_4$ depends on the concentrations of the $[Ru(bpz)_3]^{2+}$ ion, hydrogen ion, and oxalate ion and on the light intensity. The photopotential is about −0.7 V versus SCE, which is cathodic enough for a hydrogen ion to be reduced. The quantum yield of photocurrent increases in proportion to the concentration of the $[Ru(bpz)_3]^{2+}$ ion and reaches about 10% at 1.2 mmol dm^{-3} $[Ru(bpz)_3]^{2+}$. The origin of the photocurrent and photopotential is explained by a quenching reaction of the photoexcited $[Ru(bpz)_3]^{2+}$ ($[Ru(bpz)_3]^{2+*}$) with an oxalate ion, followed by the electrochemical oxidation of the resulting $[Ru(bpz)_3]^{+}$ ion on the ITO electrode. The differential equations describing the concentrations of the chemical species concerned are solved analytically to yield a concentration profile of the electroactive species $[Ru(bpz)_3]^{+}$. The validity of the solution is confirmed by the photocurrent measurements under various conditions. The rate constant k_q for the quenching reaction of $[Ru(bpz)_3]^{2+*}$ with an oxalate ion is evaluated as 6.6×10^7 dm^3 mol^{-1} s^{-1}, which is almost consistent with the value of 8.2×10^6 dm^3 mol^{-1} s^{-1} determined in a previous photochemical study.

Introduction

The light-induced splitting of water into hydrogen and oxygen using the transition-metal complexes such as tris(2,2′-bipyridine)ruthenium(II) [($[Ru(bpy)_3]^{2+}$) ion is the subject of intensive investigations.[1-7] The $[Ru(bpy)_3]^{2+}$ ion excited by visible light produces highly oxidizing and reducing agents ($[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{+}$) via an oxidative and a reductive quenching reaction, respectively. However, the quantum yield for oxygen production by the oxidation of water by $[Ru(bpy)_3]^{3+}$ is rather low. The main reason is considered to be the difficulty in coupling the four-electron oxidation of water with the one-electron-transfer process of the photoredox species. The addition of noble-metal oxides such as RuO_2 and IrO_2 facilitates this coupling process,[5-7] but the production of oxygen from water has still remained a problem area.[8,9]

The reaction system most investigated for hydrogen production from water consists of $[Ru(bpy)_3]^{2+}$ as a sensitizer, methylviologen (MV^{2+}) as a mediator and triethanolamine or ethylenediaminetetraacetic acid as a sacrificial donor.[8-15] In such a system, the photoexcited $[Ru(bpy)_3]^{2+}$ ($[Ru(bpy)_3]^{2+*}$) is quenched by MV^{2+} oxidatively and subsequently $MV^{\bullet+}$ reduces water in the presence of platinum catalyst. However, there have been few studies for hydrogen evolution from water using the reducing potentiality of $[Ru(bpy)_3]^{+}$. Although most of the aromatic amines are good reductive quenchers in nonaqueous media, only a few reductants such as Eu^{2+} and ascorbate ion are known as reductive quenchers for $[Ru(bpy)_3]^{2+*}$ in aqueous solutions.[16-18]

Utilization of a photoelectrochemical cell with an electrode having a catalytic activity such as RuO_2 or Pt was also investigated for oxygen or hydrogen evolution.[19-22] These studies were focused on the practical use of the photochemical reactions and presented little information on their kinetics. On the other hand, Dressick et al.[23] have developed a theoretical treatment for the photocurrent observed with the photoelectrochemical cell based on the oxidative quenching reaction of $[Ru(bpy)_3]^{2+*}$ with MV^{2+} or $[Co(C_2O_4)_3]^{3-}$ in stirred solutions. Up to date, however, no theoretical treatment of the photocurrent due to the reductive quenching reaction of $[Ru(bpy)_3]^{2+*}$ has been reported, although the anodic photocurrent attributable to the generation of $[Ru(bpy)_3]^{+}$ has been observed in acetonitrile solutions.[24]

More recently, the analogous tris(2,2′-bipyrazine)ruthenium(II) ($[Ru(bpz)_3]^{2+}$) ion has attracted the attention of many researchers from the viewpoint of a conversion of solar energy into chemical energy, e.g. photoreduction of carbon dioxide to methane.[25,26] The photochemical properties of $[Ru(bpz)_3]^{2+}$ ion are similar to those of the $[Ru(bpy)_3]^{2+}$ ion. A salient feature of the former is that the lifetime of the excited state is longer than that of the latter. The standard redox potentials for $[Ru(bpz)_3]^{2+}$ are shifted by ca. 0.5 V more positive than those of the corresponding couples for $[Ru(bpy)_3]^{2+}$, respectively.[27-30] Various amines and methoxybenzene derivatives quench reductively the excited state of $[Ru(bpz)_3]^{2+}$ in acetonitrile solutions.[31] In an aqueous system, the

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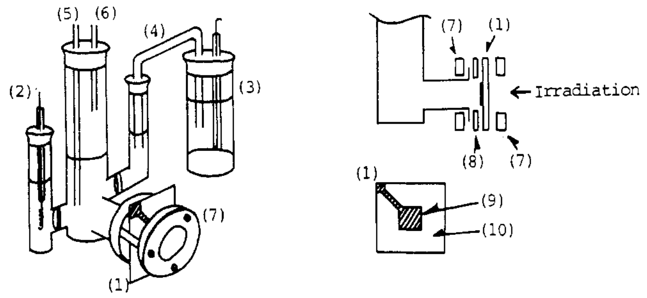

Figure 1. Photoelectrolysis cell: (1) ITO electrode; (2) Pt counter electrode; (3) SCE; (4) salt bridge; (5) inlet for argon gas; (6) outlet for argon gas; (7) Teflon O-ring; (8) silicone rubber O-ring; (9) ITO; (10) slide glass.

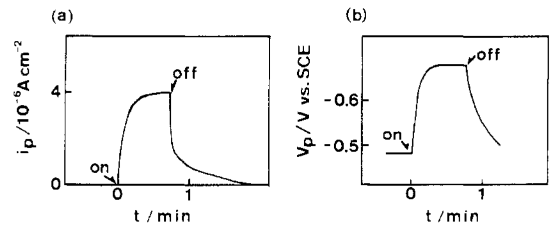

Figure 2. Time dependence of (a) the current and (b) the potential at the ITO electrode with and without illumination in 0.1 mol dm^{-3} Na_2SO_4 solution (pH 6.4) containing 0.32 mmol dm^{-3} $[Ru(bpz)_3]Cl_2$ and 40 mmol dm^{-3} $Na_2C_2O_4$. Illumination was done at 440 nm, and the photocurrent was measured at 0 V versus SCE.

oxidants of these organic compounds, produced by the one-electron-transfer reactions with $[Ru(bpz)_3]^{2+*}$, undergo further reactions such as dimerization or deprotonation. Meanwhile, it has been found that an oxalate ion quenches reductively $[Ru(bpz)_3]^{2+*}$ to yield $[Ru(bpz)_3]^+$ and carbon dioxide in an aqueous solution.[32]

In this paper, we describe the kinetic study of the reductive quenching reaction of $[Ru(bpz)_3]^{2+*}$ with an oxalate ion in the photoelectrochemical system. The photocurrent quantum yield of 10% is obtained without optimizing the reaction conditions.

Experimental Section

$[Ru(bpz)_3]Cl_2 \cdot 3.5H_2O$ was prepared and purified as described in the literature.[33,34] Ruthenium trichloride and 2,2'-bipyrazine (bpz) were purchased from Wako Pure Chemicals Co. and Aldrich, respectively. Other chemicals used were of guaranteed reagent grade and were used without further purification.

An indium-tin oxide (ITO) was purchased from Matsuzaki Sinku Co. and etched with aqua regia except for the area of 1 cm^2 used as the working electrode (Figure 1). A Pt wire was employed as the counter electrode and a saturated calomel electrode (SCE) as the reference in the three-electrode system. Measurements of photocurrent and photopotential were carried out by a Hokuto Denko HAB-151 potentiostat/galvanostat and a Takeda TR-8651 electrometer. A 500-W xenon lamp was used as a light source with a Toshiba KL-44 interference filter and an IRQ-80 cutoff filter. The intensity of the monochromatic light (440 nm) incident on an ITO electrode was 320 μW cm^{-2}, which was measured with a calibrated Eppley thermopile of 16 junctions. The irradiation was carried out from the back side of the ITO electrode to prevent the absorption of light due to $[Ru(bpz)_3]^{2+}$ ions in the solution. Oxygen dissolved in solutions was removed by bubbling pure argon gas through the solution. All experiments were done at room temperature.

Results and Discussion

No obvious photoresponse at the ITO electrode was observed in a Na_2SO_4 solution containing only $[Ru(bpz)_3]^{2+}$ ions. However, the current is strikingly enhanced in anodic direction by adding oxalate ions into the solution under illumination.

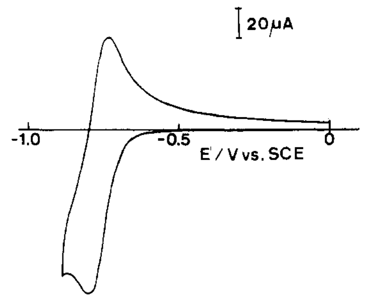

Figure 3. Cyclic voltammogram of 1 mmol dm^{-3} $[Ru(bpz)_3]Cl_2$ in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution at the ITO electrode (scan rate: 100 mV/s).

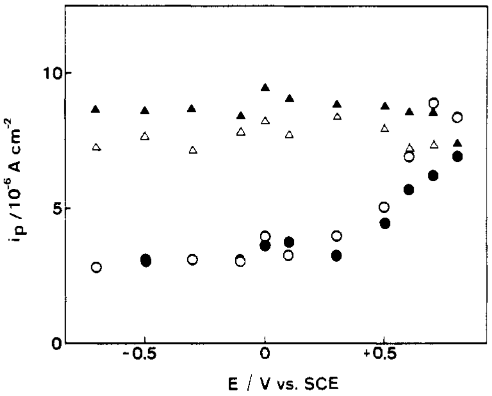

Figure 4. Dependence of the photocurrent on pH. Conditions are the same as in Figure 2 except for various hydrogen ion concentrations. pH = (●) 4.5, (○) 6.3, (△) 8.3, and (▲) 10.6.

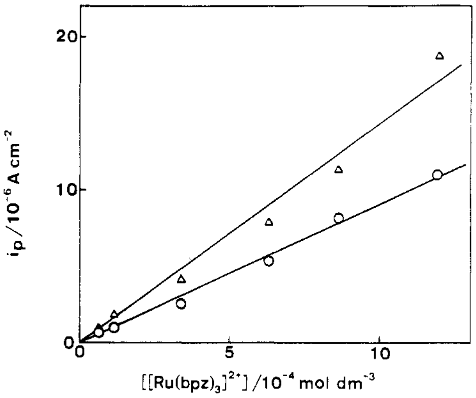

Figure 5. Dependence of the photocurrent on the $[Ru(bpz)_3]^{2+}$ ion concentration. Conditions are the same as in Figure 2. The ITO electrode was potentiostated at (○) 0 V and (△) +0.7 V versus SCE.

Figure 2 depicts the time dependence of the photocurrent (i_p) and photopotential (V_p) at the ITO electrode with and without illumination, where the photopotential is measured with respect to the SCE. The rising and falling of the photocurrent and photopotential correspond well to the illumination being turned on and off. It takes ca. 20 s for the photocurrent and photopotential to become stationary. This phenomenon is typical of a photogalvanic cell. The photopotential reaches a limiting value of ca. −0.7 V versus SCE, which is close to the redox potential of a $[Ru(bpz)_3]^{2+/+}$ couple obtained by cyclic voltammetry (Figure 3). This potential coincidence and the enhanced anodic photocurrent observed indicate that the $[Ru(bpz)_3]^+$ species are oxidized to $[Ru(bpz)_3]^{2+}$ at the ITO electrode, following the quenching reaction of $[Ru(bpz)_3]^{2+*}$ with oxalate ions. If we construct the photoelectrochemical cell as ITO/$[Ru(bpz)_3]Cl_2$, $Na_2C_2O_4$, Na_2SO_4/Pt, the ITO electrode would act as a photoanode and the counter electrode of platinum as a photocathode, where hydrogen ions are presumably reduced.

The effect of pH on the anodic photocurrent at varying potentials is shown in Figure 4. The photocurrents are almost independent of the applied potentials below +0.3 V versus SCE and increase with the increase in pH of the solution. The pH dependence of the photocurrents is attributed to the consumption

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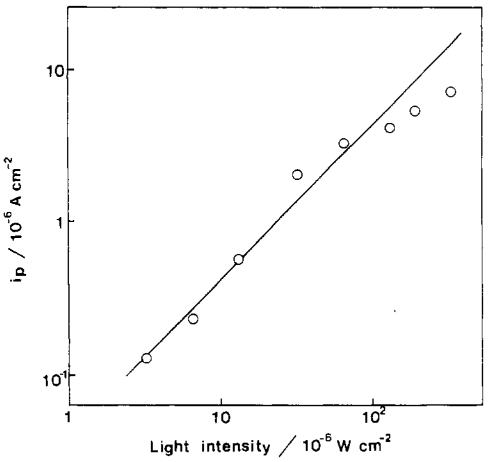


Figure 6. Dependence of the photocurrent on the incident light intensity. Conditions are the same as in Figure 2 except 0.88 mmol dm^{-3} $[Ru(bpz)_3]Cl_2$ was used.

of the $[Ru(bpz)_3]^+$ ion by its reaction with hydrogen ion since the $[Ru(bpz)_3]^+$ ion is a strong enough reducing agent for a hydrogen ion to be reduced. It should be noted here that the photocurrents at pH 4.5 and pH 6.3 are almost the same and tend to increase with the increase of the applied potential beyond +0.5 V versus SCE. These facts will be discussed later in more detail.

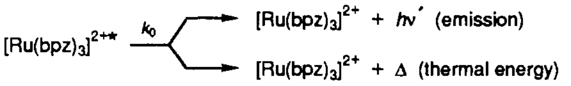
Figure 5 shows the dependence of the photocurrent on the concentration of $[Ru(bpz)_3]^{2+}$. It is found that the photocurrents are in proportion to the concentration of $[Ru(bpz)_3]^{2+}$ at potentials ranging from −0.7 to +0.8 V versus SCE.

The photocurrent quantum yield, which is defined as the number of electrons produced per photon absorbed by the $[Ru(bpz)_3]^{2+}$ ion, is proportional to the photocurrent and thus can be increased by an increase in the concentration of the $[Ru(bpz)_3]^{2+}$ and pH in the solution. In this work, we obtained the quantum yield of 10% without optimizing the conditions of the $[Ru(bpz)_3]^{2+}$ ion concentration and pH. This value is relatively high among the photogalvanic cells studied so far, in which the electroactive species have to diffuse to the electrode surface to generate the photocurrent.

As shown in Figure 6, the magnitude of the photocurrent depends on the intensity of light incident on the ITO electrode. The light exponent (γ) in $i_p \propto I_0^{\gamma}$ is equal to unity. At higher light intensities, the plots tend to deviate downward from the straight line. This might be ascribed to the disproportionation of $[Ru(bpz)_3]^+$.[1] On the other hand, the photopotential at the ITO electrode shifts to the positive direction with the decrease in the light intensity because of the decrease in the concentration of the photogenerated species $[Ru(bpz)_3]^+$ in the solution.

The following reaction mechanism is proposed to account for the results obtained.

$$[Ru(bpz)_3]^{2+} + h\nu \xrightarrow{I_{abs}} [Ru(bpz)_3]^{2+*} \quad (1)$$



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

(2)

$$C_2O_4^{2-} + [Ru(bpz)_3]^{2+*} \xrightarrow{k_q} CO_2^{\bullet -} + CO_2 + [Ru(bpz)_3]^+ \quad (3)$$

$$CO_2^{\bullet -} + [Ru(bpz)_3]^{2+} \xrightarrow{k_1} CO_2 + [Ru(bpz)_3]^+ \quad (4)$$

$$[Ru(bpz)_3]^+ + H_3O^+ \xrightarrow{k_2} [Ru(bpz)_3]^{2+} + \tfrac{1}{2}H_2 + H_2O \quad (5)$$

$$[Ru(bpz)_3]^+ \rightarrow [Ru(bpz)_3]^{2+} + e^- \text{ (at the ITO electrode)} \quad (6)$$

It is noticed here that Lever et al.[29] have shown that the pK_a value of the excited complex of $[Ru(bpz)_3]^{2+}$ is 2.0. In the present case, however, the protonation of the excited complex can be ruled out, because our experiments are carried out at pH greater than 4.5.

Assuming a steady-state approximation with respect to the concentrations of $[Ru(bpz)_3]^{2+*}$, $[Ru(bpz)_3]^+$ and $CO_2^{\bullet -}$, we obtain

$$\frac{\partial[[Ru(bpz)_3]^{2+*}]}{\partial t} = D^* \frac{\partial^2[[Ru(bpz)_3]^{2+*}]}{\partial x^2} + \left|\frac{\partial I}{\partial x}\right| - (k_0 + k_q[C_2O_4^{2-}])[[Ru(bpz)_3]^{2+*}] = 0 \quad (7)$$

$$\frac{\partial[[Ru(bpz)_3]^+]}{\partial t} = D\frac{\partial^2[[Ru(bpz)_3]^+]}{\partial x^2} + k_q[[Ru(bpz)_3]^{2+*}][C_2O_4^{2-}] + k_1[[Ru(bpz)_3]^{2+}][CO_2^{\bullet -}] - k_2[[Ru(bpz)_3]^+][H_3O^+] = 0 \quad (8)$$

$$\frac{\partial[CO_2^{\bullet -}]}{\partial t} = k_q[[Ru(bpz)_3]^{2+*}][C_2O_4^{2-}] - k_1[[Ru(bpz)_3]^{2+}][CO_2^{\bullet -}] = 0 \quad (9)$$

where D^* and D are the diffusion coefficients of $[Ru(bpz)_3]^{2+*}$ and $[Ru(bpz)_3]^+$, respectively, and I is the light intensity or more precisely the photon flux at a distance x from the surface of the ITO electrode. The $CO_2^{\bullet -}$ radical is a strong reducing agent, so that it is consumed rapidly according to reaction 4. Hence, the diffusion term of the $CO_2^{\bullet -}$ radical is neglected in eq 9.

The first term on the right-hand side of eq 7 represents the flux due to the diffusion of $[Ru(bpz)_3]^{2+*}$. The second term can be rewritten as

$$\partial I/\partial x = -\alpha[[Ru(bpz)_3]^{2+}]I \quad (10)$$

with $\alpha = 2.303\epsilon$, where ϵ is the molar extinction coefficient of the $[Ru(bpz)_3]^{2+}$ ion.

On the assumption that the excited species $[Ru(bpz)_3]^{2+*}$ are quenched rapidly according to reactions 2 and 3, the first term on the right-hand side of eq 7 is negligible, and then the concentration of $[Ru(bpz)_3]^{2+*}$ is given by

$$[[Ru(bpz)_3]^{2+*}] = \frac{\alpha[[Ru(bpz)_3]^{2+}]I}{k_0 + k_q[C_2O_4^{2-}]} \quad (11)$$

Combining eq 9 and 11 with eq 8, we obtain

$$D\frac{\partial^2[[Ru(bpz)_3]^+]}{\partial x^2} + \phi\alpha I[[Ru(bpz)_3]^{2+}] - k[[Ru(bpz)_3]^+] = 0 \quad (12)$$

where ϕ is $2k_q[C_2O_4^{2-}]/(k_0 + k_q[C_2O_4^{2-}])$ and k corresponds to $k_2[H_3O^+]$. The value of ϕ is kept constant, provided that oxalate ions are added in excess of $[Ru(bpz)_3]^{2+}$. Equation 12 is equivalent to the differential equation derived by Albery and Archer for the photogalvanic and photovoltaic systems.[35,36]

Substituting eq 13 (Lambert–Beer's law) and eq 14 into eq 12, one obtains eq 15, where I_0 is the intensity of light incident on

$$I = I_0 \exp(-\alpha[[Ru(bpz)_3]^{2+}]x) \quad (13)$$

$$[[Ru(bpz)_3]^+] + [[Ru(bpz)_3]^{2+}] = C_0 \quad (14)$$

$$D\frac{\partial^2[[Ru(bpz)_3]^+]}{\partial x^2} + \alpha I_0\phi(C_0 - [[Ru(bpz)_3]^+]) \times (\exp\{-\alpha(C_0 - [[Ru(bpz)_3]^+])x\}) - k[[Ru(bpz)_3]^+] = 0 \quad (15)$$

the ITO/electrolyte interface and C_0 is the initial concentration of added $[Ru(bpz)_3]^{2+}$.

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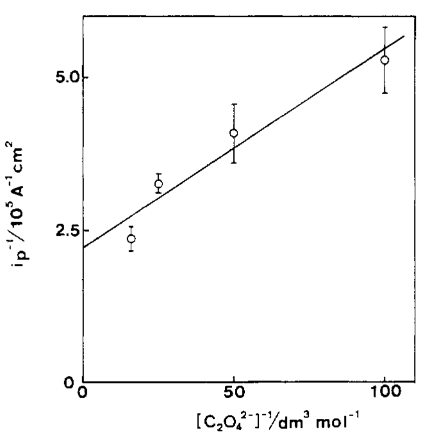

Figure 7. Plot of the reciprocal of photocurrent against that of concentration of $C_2O_4^{2-}$. Conditions are the same as in Figure 2. The straight line obtained from the least-squares method is represented as $i_p^{-1} = 2.21 \times 10^5 + 3.21 \times 10^3[C_2O_4^{2-}]^{-1}$ with a correlation coefficient of 0.91.

When the potential applied to the ITO electrode is positive and is more than the redox potential of $[Ru(bpz)_3]^{2+/+}$, where the surface concentration of $[Ru(bpz)_3]^+$ is negligibly small, eq 15 becomes

$$D\frac{\partial^2[[Ru(bpz)_3]^+]}{\partial x^2} + \alpha I_0 \phi C_0 \exp(-\alpha C_0 x) - k[[Ru(bpz)_3]^+] = 0 \quad (16)$$

The boundary condition of eq 16 is defined by $[[Ru(bpz)_3]^+] = 0$ for $x = 0$ and $x = \infty$. So, the solution of eq 16 is given as

$$[[Ru(bpz)_3]^+] = \frac{\alpha I_0 \phi C_0}{k - \alpha^2 C_0^2 D}[\exp(-\alpha C_0 x) - \exp(-\sqrt{k/D}x)] \quad (17)$$

Consequently, the photocurrent (i_p) can be expressed as

$$i_p = FAD\left(\frac{\partial[[Ru(bpz)_3]^+]}{\partial x}\right)_{x=0} = \frac{2FA\alpha I_0 C_0 \sqrt{D} k_q[C_2O_4^{2-}]}{(\sqrt{k} + \alpha C_0 \sqrt{D})(k_0 + k_q[C_2O_4^{2-}])} \quad (18)$$

where *F* is the Faraday constant and *A* is the surface area of the ITO electrode contacting the electrolyte. The diffusion coefficient *D* for $[Ru(bpz)_3]^+$ may be assumed to be nearly equal to that of $(5.1 \pm 0.1) \times 10^{-6}$ cm^2 s^{-1} for $[Ru(bpz)_3]^{2+}$ estimated by use of potential-step chronoamperometry and potential-sweep voltammetry in the present study. Equation 18 manifests the observed linear dependence of the photocurrent on the incident light (Figure 6).

The observed linear dependence of the photocurrent on the concentration of $[Ru(bpz)_3]^{2+}$ (Figure 5) suggests that the relationship $\sqrt{k} \gg \alpha C_0/D$ holds under the experimental conditions investigated. Therefore, eq 18 is rewritten as

$$\frac{1}{i_p} = \frac{\sqrt{k}}{2FA\alpha I_0 C_0 \sqrt{D}}\left(1 + \frac{k_0}{k_q[C_2O_4^{2-}]}\right) \quad (19)$$

Equation 19 indicates that the plot of i_p^{-1} versus $[C_2O_4^{2-}]^{-1}$ yields a straight line with a slope of $k_0\sqrt{k}/(2FA\alpha I_0 C_0 \sqrt{D} k_q)$ and the intercept of $\sqrt{k}/(2FA\alpha I_0 C_0 \sqrt{D})$. The observed value of i_p^{-1} is plotted as a function of $[C_2O_4^{2-}]^{-1}$ in Figure 7, where we can see a good correlation between them. The quenching rate constant k_q is evaluated to be 6.6×10^7 dm^3 mol^{-1} s^{-1} from the values of the slope and the intercept and $k_0 = \tau_0^{-1} = 9.62 \times 10^5$ s^{-1}.[28] The k_q value obtained is in fairly good agreement with the literature value of 8.2×10^6 dm^3 mol^{-1} s^{-1}.[32] This agreement also supports the validity of the proposed mechanism and some approximations employed. In addition, the value of 1.8 s^{-1} for the pseudo-first-order rate constant *k* evaluated from the intercept satisfies the inequality $\sqrt{k} \gg \alpha C_0 \sqrt{D}$.

As stated previously, the smaller photocurrent observed at the lower pH solution was qualitatively explainable by the consumption of $[Ru(bpz)_3]^+$ due to the reaction with hydrogen ion (eq 5). In view of the fact that the rate of reaction 5 is first-order with respect to the concentration of H_3O^+, however, the reasoning fails to explain the too small photocurrent difference between acidic and basic media together with no difference at pH 4.5 and pH 6.3 at potentials below +0.3 V versus SCE. This might be resolved by taking account of the following protonation reaction of $[Ru(bpz)_3]^+$:

$$[Ru(bpz)_3]^+ + H_3O^+ \rightarrow [Ru(bpz)_2(bpzH)]^{2+} + H_2O \quad (20)$$

According to Venturi et al.,[37] the lifetime of the protonated species is 20 s, which is longer than that of $[Ru(bpz)_3]^+$, and the oxidation potential of $[Ru(bpz)_2(bpzH)]^{2+}$ lies close to that of the unprotonated species. Therefore, if we assume that the rate constants of reactions 5 and 20 are comparable, $[Ru(bpz)_3]^{2+}$ and $[Ru(bpz)_2(bpzH)]^{2+}$ will be generated at almost the same rate independent of pH; most likely, the protonated species can reach the ITO surface to give anodic photocurrents. Cyclic voltammetry for the reduction of $[Ru(bpz)_3]^{2+}$ in a Na_2SO_4 solution showed that the magnitudes of kinetic currents[38] were independent of solution pH's below 6. It is noticed, furthermore, that the pseudo-first-order rate constant for the oxidation reaction of $[Ru(bpz)_3]^+$ evaluated by assuming only reaction 5 without regard to the contribution of reaction 20 to the kinetic current depended solely on the potential-sweep rates used, but was of the same order of magnitude as the *k* value obtained photoelectrochemically. Incidentally, the increase of the photocurrent with the increase of the applied potential beyond +0.5 V versus SCE in acidic media might be ascribed to the reoxidation of hydrogen atoms or molecules produced by the reaction of $[Ru(bpz)_3]^+$ with hydrogen ions at the ITO electrode. In the acidic solution of pH 4.5, it is known that a significant portion of the oxalate ions exist as a monoprotonated form. However, the quenching reaction rate constant k_q evaluated from the Stern–Volmer plots was independent of the solution pH in the range from 4 to 7. This fact suggests that the k_q values for the deprotonated and monoprotonated species of the oxalate ion are almost the same with each other.

In conclusion, it is found that the photocurrent increases with the increase in the concentrations of $[Ru(bpz)_3]^{2+}$ and oxalate ion, pH, and the light intensity. These results are interpreted in terms of the mechanism that involves the formation of $[Ru(bpz)_3]^+$ from the quenching reaction of $[Ru(bpz)_3]^{2+*}$ with $C_2O_4^{2-}$. The observed values of k_q and *k* are 6.6×10^7 dm^3 mol^{-1} s^{-1} and 1.8 s^{-1}, respectively. Cano-Yelo et al.[24] have also observed anodic photocurrents attributable to the formation of the $[Ru(bpy)_3]^+$ by the reductive quenching reaction of the $[Ru(bpy)_3]^{2+*}$ with a benzylthiolate in acetonitrile. They have reported that the photocurrent decays slowly 1 min after the start of irradiation because of some side reaction of $[Ru(bpy)_3]^+$. In the present study, the photocurrent remains constant for 20 min, at least. This fact and the fact that no appreciable change of the absorption spectra after the experiment occurs suggest that any side reaction does not occur in our reaction system. That no side reaction was found in our system might be ascribed in part to the reducing potentiality of the $[Ru(bpz)_3]^+$ being milder than that of the $[Ru(bpy)_3]^+$.

We obtained a photocurrent quantum yield of ca. 10% in our system, which can be increased further by optimization of experimental conditions. In the photogalvanic system, however, there is an essential problem, resisting the achievement of much higher photocurrent quantum yields, that the photogenerated $[Ru(bpz)_3]^+$ ions do not necessarily reach the ITO surface because of their

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reaction with hydrogen ions or impurities and/or the diffusion away of them from the ITO electrode. Research is currently in progress to improve the efficiencies by fixing $[Ru(bpz)_3]^{2+}$ and other chemicals in a Nafion membrane.

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Photoselection Studies of Mixed-Ligand Ruthenium(II) Complexes: $[RuL_2L']^{2+}$ Multiple-State Emission

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Comparison of photoselection spectra for tris $[RuL_3]^{2+}$ and mixed-ligand $[RuL_2L']^{2+}$ complexes as a function of temperature, solvent, excitation, and detection wavelength indicates that the large oscillations in the steady-state excitation polarization (SSExP) and steady-state emission polarization (SSEmP) spectra result from multiple-state emission of these materials. A type of heterogeneous solvation of the individual ligand chromophores creates the oscillating pattern and does result in the variation of the magnitude and wavelength of P_{max} with detection wavelength. A rough estimate of the magnitude of this heterogeneous solvation energy is obtained by comparison of tris and mixed-ligand complexes. The invariance with solvent of the P_{max} magnitude as well as earlier results verifies that the solvent heterogeneity effect is not the origin of the single ring charge localization.

Introduction

The photoselection spectra of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and other tris chelate ruthenium species have been important in the assignment of the lowest excited manifold of this series as spatially isolated localized orbital states, similar to those charge-transfer excited states of monomeric species such as $[Ru(bpy)(py)_4]^{2+}$ (py = pyridine).[1] Results obtained for mono chelate, tris chelate, and cis-configuration bis chelate complexes have been reported[1,2] with a variety of different solvents, ligands, and counterions.

The interchromophoric coupling (ICC) model presented, which rationalized the polarization results obtained for the complexes, is based upon the spin–orbit coupling (SOC) interactions of the lowest triplet state with a single manifold of mixed character. The model demonstrated that the complexes possess levels of both localized and delocalized spatial extent. The results of this analysis compared well with the experimental steady-state photoselection spectra.

In the work that led to the development of the interchromophoric coupling model, only complexes that were nearly exact mono, bis, or tris complexes were used. However, the model is also valid for molecules which do not fit this description. That is, the limiting values obtained for bis and tris complexes should not be found when the degeneracy of the ligand-localized states is lifted to some degree as in $[RuL_2L']^{2+}$, where L and L′ are bidentate diimine complexes. By use of the optical energies and electrochemical redox patterns of the parent $[RuL_3]^{2+}$ and $[RuL'_3]^{2+}$ complexes, predictions of the degeneracy or lack of degeneracy for mixed-ligand complexes as $[RuL_2L']^{2+}$ can be made.

This paper focuses upon details of both photoselection and luminescence spectra for these Ru(II) complexes synthesized with ligands that contain small perturbations in their π^* energy levels due to incorporation of substituent groups into the ligand. For example, the steady-state emission photoselection (SSEmP) of $[Ru(bpy)_2(pphen)](PF_6)_2$ (bpy = 2,2′-bipyridine; pphen = 4,7-diphenyl-9,10-phenanthroline) was done with excitation at P_{max}, while measuring the emission polarization as a function of emission wavelength gave large oscillations of P. Data for true tris complexes such as $[Ru(bpy)_3]^{2+}$ typically display such oscillations as well, though of much smaller magnitude than found in these mixed-ligand complexes. Thus, a similarity exists between the structure found in the emission photoselection of mixed-ligand species with near-degenerate chromophoric units and true tris complexes, though the effect is exaggerated in the former by the lack of any formal degeneracy. Therefore, this paper focuses upon the relationship between emitting oscillators in tris and mixed-ligand complexes that contain orbital π^* near-degeneracies. This is described in terms of the ICC model and indicates the extent of heterogeneous solvation found for tris complexes, a factor frequently cited by some to explain localization in dilute, disordered media.

Experimental Section

$[Ru(pphen)(mphen)_2](PF_6)_2$ (pphen = 4,7-diphenyl-1,10-phenanthroline; mphen = 4,7-dimethyl-1,10-phenanthroline), $[Ru(bpy)_2(pphen)](PF_6)_2$ (bpy = 2,2′-bipyridine), and $[Ru(bpy)(mphen)_2](PF_6)_2$ were prepared by R.L.B. and were available from previous studies.[2] $[Ru(tmbpy)_3](ClO_4)_2$ (tmbpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine), $[Ru(bpy)_3]Cl_2$, $[Ru(bpy)_2(pbpy)](PF_6)_2$, and $[Ru(pbpy)_3](PF_6)_2$ (pbpy = 4,4′-diphenylbipyridine) were available from previous studies. Purity was determined by the excitation independence of the emission energy and band shape.

Plastic samples were prepared by dissolving the complex in methyl methacrylate monomer. Addition of 2,2′-azobis[2-methylpropionitrile], an initiation agent, followed by evacuation and sealing of the samples in 7 mm o.d. glass cells and incubation at 60 °C for 1–5 days, produced hard clear plastic materials with minimal surface defects. The samples contracted during polymerization in a manner qualitatively similar to that found when alcoholic glasses are formed. Samples were brightly luminescent even at room temperature under interior fluorescent lighting. Samples were removed from the glass cells by cracking the cell.

Plastics were processed as follows. For only room-temperature studies, the sample was left untreated and was immersed in *m*-xylene for study. The primary reason for this was to ensure that mechanical working of the plastics did not affect the polarization properties of the guest materials. The liquid *m*-xylene was used, as it does not easily dissolve the plastics and possesses a refractive index close to that of the plastics themselves. Thus, a clear system was produced, with little indication of any surface scatter effects from the imperfect polymer. A second procedure utilized carborundum powder to polish the samples by using first a coarse grit for rough grinding, then a fine grit for a smooth finish.

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