Photoelectrochemical Production of Oxygen Based on Electron Transfer Quenching of Ru(2,2′-bipyridine)$_3^{2+*}$

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Summary A photoelectrochemical cell based on electron transfer quenching of the excited state Ru(2,2′-bipyridine)$_3^{2+*}$, in which visible photolysis gives both O_2 and an appreciable photocurrent is described.

We have earlier described the design of a photoelectrochemical cell based on the irreversible oxidative quenching of the excited state, Ru(bpy)$_3^{2+*}$ (bpy = 2,2′-bipyridine), by $Co(C_2O_4)_3^{3-}$ ($C_2O_4^{2-}$ is oxalate).[1] In the cell, the photochemical production of Ru(bpy)$_3^{3+}$ was coupled with oxidation of Fe^{2+}(aq.) to Fe^{3+}(aq.) in a second compartment which occurs with the production of appreciable photocurrents at efficiencies per photon which are relatively high.[1] With regard to the photochemical splitting of water, the experiment indicated that such photoelectrochemical cells have the distinct advantage of allowing the component half-reactions, $2H^+ + 2e^- \rightarrow H_2$ and $H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2$, to be studied separately and combined later to give a net cell. A photoelectrochemical cell which accomplishes the reduction step, $2H^+ + 2e^- \rightarrow H_2$, has recently been reported.[2] In an earlier report, Kobayashi, Furata, and Simamura described a photoelectrochemical cell in which oxygen was produced catalytically following oxidative quenching of Ru(bpy)$_3^{2+*}$ by $MeNC_5H_4C_5H_4NMe^{2+}$ (Paraquat) in the presence of O_2; however, the quantum efficiency per photon was low (0·005).[3] We describe here the operation of a cell in which the oxidation, $H_2O \rightarrow 2e^- + 2H^+ + 1/2O_2$, is driven with relatively high efficiency following visible photolysis.

The operation of the photoelectrochemical cell is illustrated by equations (1)—(4). Illumination of the cathode

$$\text{Cathode: } Ru(bpy)_3^{2+} + h\nu \rightarrow Ru(bpy)_3^{2+*} \tag{1}$$

$$Ru(bpy)_3^{2+*} + Co(C_2O_4)_3^{3-} + 6H^+ \rightarrow Ru(bpy)_3^{3+} + Co^{2+} + 3H_2C_2O_4 \tag{2}$$

$$Ru(bpy)_3^{3+} + e^- \xrightarrow{Pt} Ru(bpy)_3^{2+} \tag{3}$$

$$\text{Anode: } OH^- \xrightarrow{Pt} e^- + \tfrac{1}{2}H_2O \tag{4}$$

cell compartment results in excitation of Ru(bpy)$_3^{2+}$ (equation 1) followed by irreversible oxidative quenching of Ru(bpy)$_3^{2+*}$ by $Co(C_2O_4)_3^{3-}$.[4] The Ru(bpy)$_3^{3+}$ so formed is reduced at the Pt cathode (equation 3) regenerating Ru(bpy)$_3^{2+}$. Oxidizing equivalents are transferred to the anode where water is oxidized to oxygen (equation 4). The net cell reaction (equation 5) involves the photochemical oxidation of water by $Co(C_2O_4)_3^{3-}$.

$$4Co(C_2O_4)_3^{3-} + 2H_2O + 20H^+ \xrightarrow{4h\nu} 12H_2C_2O_4 + O_2 + 4Co^{2+} \qquad (5)$$

In a typical experiment, the anode (1 × 4 cm, 50 mesh Pt gauze electrode) compartment contained an aqueous 1·0 M NaOH–1·0 M Na_2SO_4 solution, and the cathode (1 × 4 cm, 50 mesh Pt gauze electrode located at the glass cell interface) compartment $K_3[Co(C_2O_4)_3]$ (9·3 × 10^{-3} M) and $[Ru(bpy)_3]Cl_2$ (4·0 × 10^{-3} M) in 1·0 M H_2SO_4, connected through an agar salt bridge. The anode solution was degassed with bubbling argon for 30 min prior to irradiation of the cathode compartment (436 nm) with a light intensity of 2·82 × 10^{-8} Einstein s^{-1}. A maximum current of 90 ± 2 μA was obtained which was stable for nearly 5 min. Further irradiation resulted in a slow decrease in current due to the competitive scavenging of the $Ru(bpy)_3^{3+}$ by oxalic acid released in equation (2). Nearly identical current characteristics (max. current = $103\pm2\,\mu$A) were noted when $Ru(bpy)_3^{2+}$ was replaced by 4·0 × 10^{-3} M $[Ru(phen)_3]Cl_2$ (phen = 1,10-phenanthroline). In both cases, $99\pm3\%$ of the appropriate Ru complex was recovered at the conclusion of the experiment demonstrating the stability of the cells. Sampling of the anode atmosphere by gas chromatography after 3787 s of photolysis showed the presence of 6·20 × 10^{-7} mol of O_2 as measured by gas chromatography. This value is in reasonable agreement with the value of 7·56 × 10^{-7} mol of O_2 expected based on the integrated current of 0·290 C. The results for the $Ru(phen)_3^{2+}$ cell (sampling at 3650 s; 7·78 × 10^{-7} mol of O_2 found *vs.* 8·79 × 10^{-7} mol of O_2 expected for 0·336 C) are comparable. We assume that the slightly lower values obtained by gas chromatography are attributable to a systematic error in the technique.

The total integrated current for the $Ru(bpy)_3^{2+}$ cell was used to calculate the quantum yield per photon for O_2 production. During the initial stages of the photolysis, the quantum efficiency (*ca.* 40%) was essentially the same as that for equation (2)[4] measured under the conditions described above. However, ϕ falls rapidly with photolysis time because, as oxalate is released, it reduces Ru^{III} competitively with diffusion to the electrode. After *ca.* 3 min, ϕ had fallen to *ca.* 3% and remained essentially constant for a further extended period (*ca.* 1 h) of photolysis.† We have made no attempt to measure the wavelength dependence of the cell since previous results have shown that the efficiency for production of $Ru(bpy)_3^{3+}$ in the $Ru(bpy)_3^{2+}/Co(C_2O_4)_3^{3-}$ cell is independent of wavelength throughout much of the visible region of the spectrum.[1]

The current response and photopotential of the cell were studied as a function of several variables. The current increased linearly with $Ru(bpy)_3^{2+}([Co(C_2O_4)_3^{3-}] = 9{\cdot}3 \times 10^{-3}\,\text{M})$. The photopotential of the cell varied with pOH as shown in equation (6). The observed slope of 11 ± 2 mV/decade is in fair agreement with the expected value of 14 mV/decade for an $n = 4e$ process.‡ A separate measurement of the photopotential developed by the cell under conditions of open-circuit operation (resistance $\geqslant 10\,\mathrm{M}\Omega$, $\imath < 10$ nA) gave a value of 0·81 ± 0·03 V. The expected thermodynamic value obtained from the half-reactions (7) and (8) is 0·86 V. The difference between the two values is not unexpected since an overvoltage is expected to exist for O_2 evolution at the anode,[5] and the steady-state concentrations of $Ru(bpy)_3^{2+}$, $Ru(bpy)_3^{3+}$, and O_2 are unknown under our photolytic conditions.

$$E/\text{mV} = 72 - (58/n)\text{pOH} \qquad (6)$$

$$Ru(bpy)_3^{3+} + e^- \rightarrow Ru(bpy)_3^{3+} \quad E^\circ\ (vs.\ \text{N.H.E.})\ 1{\cdot}26\ \text{V} \qquad (7)$$

$$40H^- \rightarrow 4e^- + 2H_2O + O_2 \qquad -0{\cdot}40\ \text{V} \qquad (8)$$

The experiments described here are of limited immediate practical value because of the nature of the oxidant (equation 5) and the pH difference between cell compartments. However, it should be emphasized that they point out a valid experimental approach to the problem of photochemically splitting water into H_2 and $\tfrac{1}{2}O_2$. If the excited state redox properties of $Ru(bpy)_3^{2+*}$ or a related system can be coupled to H_2 production in neutral or basic solution giving $Ru(bpy)_3^{3+}$, the photoelectrochemical approach provides a means for completing the catalytic cycle by giving both oxygen and an appreciable photocurrent. It is also worth noting that many substrates can be oxidized in the anode compartment and that related experiments may lead to useful photoelectrochemical synthesis cells.

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† The efficiency of 82% for the cell reported in ref. 1 was found to be incorrect upon more detailed analysis. The actual efficiency of this cell was 9 ± 1% for a 3 min photolysis period which compared favourably with the value of 7 ± 1% found in this investigation for an identical photolysis time.

‡ The experimental intercept of 72 ± 3 mV in the Nernst equation (6) is not identical with the expected theoretical thermodynamic potential of 860 mV because the measured photopotentials were not made under conditions of open-circuit operation That is, a non-zero current ($\imath$ = 90 μA) was flowing through the cell. An identical measurement using a potentiometer ($\imath$ < 5 nA) yields the value 0·81 ± 0·03 V.

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