Photoelectrochemical Production of Hydrogen from the Tris(2,2′-bipyridine)ruthenium–*NN′*-Dimethyl-4,4′-bipyridylium (Paraquat) System

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Summary A photoelectrochemical cell based on electron transfer quenching of the excited state $Ru(bpy)_3^{2+*}$ (bpy = 2,2′-bipyridine) is described in which visible photolysis gives both H_2 and an appreciable photocurrent.

In a recent communication we described the operation of a photoelectrochemical cell which was based on irreversible oxidative quenching of the excited state $Ru(bpy)_3^{2+*}$ by $Co(ox)_3^{3-}$ to give $Ru(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine; H_2ox = oxalic acid).[1] In the cell the oxidizing equivalents in $Ru(bpy)_3^{3+}$ were transferred to a second cell compartment giving a photocurrent and oxidation of Fe^{2+} to Fe^{3+}. In the previous communication, the point was made that such cells have potential value in photochemical synthesis or fuel cell applications. In particular, with regard to the photochemical splitting of water, they allow the component half-reactions, $2H^+ + 2e^- \longrightarrow H_2$ and $H_2O - 2e^- \longrightarrow 2H^+ + 1/2O_2$, to be studied separately and combined later as separate compartments in a net cell. We report here the operation of a photoelectrochemical cell in which H_2 is produced by visible photolysis with an efficiency which is high relative to other chemical systems[2–6] and which produces a significant photocurrent.

The system is based on an illuminated cell compartment in which excitation (equation 1) occurs followed by oxidative quenching of $Ru(bpy)_3^{2+*}$ by Paraquat (*NN′*-dimethyl-4,4′-bipyridylium; PQ^{2+}) which is known to give $Ru(bpy)_3^{3+}$ and PQ^+ (equation 2).[7] Although back electron transfer, $Ru(bpy)_3^{3+} + PQ^+ \longrightarrow Ru(bpy)_3^{2+} + PQ^{2+}$, would normally occur in such a cell, with added reductants like triethanolamine or cysteine, $Ru(bpy)_3^{3+}$ can be competitively scavenged (equations 3 and 4) and the concentration of PQ^+ builds up in the cell. The PQ^+ produced photochemically is then used to drive H_2 evolution in a second cell compartment at a platinized-Pt electrode (equations 5 and 6).

$$Ru(bpy)_3^{2+} + h\nu \longrightarrow Ru(bpy)_3^{2+*} \qquad (1)$$

$$Ru(bpy)_3^{2+*} + PQ^{2+} \longrightarrow Ru(bpy)_3^{3+} + PQ^+ \qquad (2)$$

$$Ru(bpy)_3^{3+} + D \rightarrow Ru(bpy)_3^{2+} + D^+ \qquad (3)$$

$$D^+ \longrightarrow \text{irreversible oxidation} \qquad (4)$$

$$PQ^+ - e^- \xrightarrow[\text{Pt}]{} PQ^{2+} \qquad (5)$$

$$H^+ + e^- \xrightarrow[\text{Pt}]{} 1/2H_2 \qquad (6)$$

The Figure shows a plot of the photocurrent *vs.* time for a photoelectrochemical cell with the following components: (a) in the cathode compartment (1 × 1 cm platinized Pt foil) 1 M HCl; (b) in the anode compartment (1 × 2 cm Pt gauze) $Ru(bipy)_3^{2+}$ (5×10^{-5} M), $(PQ^{2+})(ClO_4)_2$ (2×10^{-3} M), triethanolamine (TEOA) (0·4 M), and 0·1 M NaCl at an overall pH of 9; and (c) a salt bridge consisting of 0·1 M NaCl and saturated Na_3BO_3. The cell was irradiated at 436 nm with an intensity of $3{\cdot}8 \times 10^{-8}$ Einstein s^{-1}. Both the anode and cathode compartments were deaerated with argon. Operation of the cell could be maintained for 1 h with no noticeable change in current after the steady state value of 200 μA had been reached. In addition no observable decrease in absorbance of the solution containing

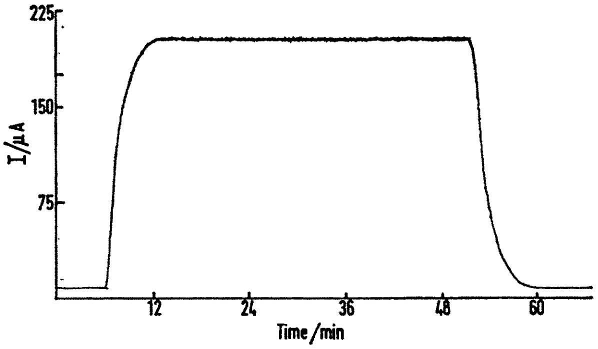

Figure. Plot of photocurrent *vs.* time for a cell with $[Ru(bipy)_3^{2+}] = 5 \times 10^{-5}$ M, $[PQ^{2+}] = 2 \times 10^{-3}$ M, [TEOA] = 0·4 M, pH 9 in 0·1 M aqueous NaCl. Both cell compartments were deaerated with argon.

$Ru(bpy)_3^{2+}$ was observed which could not be accounted for by diffusion between cell compartments showing the chemical stability of the system. After 37 min of photolysis the atmosphere in the cathode compartment was sampled and analysed for hydrogen gas by gas chromatography. At this point in the photolysis 3×10^{-6} mol of hydrogen were measured by g.l.c. while the theoretical amount, calculated from the total integrated current of 0·44 C, was $2{\cdot}3 \times 10^{-6}$ mol. The discrepancy between the g.l.c. and electrochemical values probably arises because of the uncertainty in the dead volume of the cathode compartment and we are currently making more accurate measurements. The quantum efficiency of the cell in terms of current produced per photon added to the system was calculated to be 5% based on the maximum steady state current but the intrinsic value may be higher since corrections for the amount of light absorbed were not made. From our previous results, the efficiency of the cell should be wavelength independent throughout the near-u.v. and much of the visible.[1]

The effects on the maximum cell current of variations in pH, $[Ru(bpy)_3^{2+}]$, and $[N(C_2H_4OH)_3]$ are all consistent with the scheme in equations(1)—(6). The dark current observed after photolysis and the response of the cell to changes in electrode surface area both suggest that the current drawn in the cell is limited by diffusion of PQ^+ to the electrode. We have investigated a series of electron donors such as piperidine, triethylamine, isopropylamine, diethyl thiocarbamate, and cysteine and although the cysteine and triethanolamine based cells have very similar current–concentration relationships, in the triethyl- and isopropyl-amine systems marked decomposition of $Ru(bpy)_3^{2+}$ occurs during the photolysis.

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