Visible-light-induced Oxidation of Water and of Chloride Ions in Photoelectrochemical Cells

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Summary The photoredox reaction between the complex RuL_3^{2+} (L = di-isopropyl 2,2'-bipyridine-4,4'-dicarboxylate) and $S_2O_8^{2-}$ has been used in a photoelectrochemical cell to demonstrate the visible-light-induced ($\lambda \geqslant 450$ nm) oxidation of water to give O_2 and of chloride ions to give Cl_2 in acidic solutions; the high redox-potential of the $RuL_3^{3+/2+}$ complex and the utilisation of a RuO_2-coated Ti anode enable these rather difficult oxidations to occur.

THERE are various approaches to the photochemical conversion and storage of solar energy and, of these, there has been considerable interest in the visible-light-induced photodecomposition of water to give molecular hydrogen and oxygen. Some success has been achieved[1,2] in schemes involving photoredox reactions combined with redox-catalysis steps (Scheme 1). Numerous studies have been

$$S + A \xrightarrow{h\nu} S^+ + A^- \quad (1)$$

$$4S^+ + 2H_2O \xrightarrow{\text{catalyst}} 4S + 4H^+ + O_2 \quad (2)$$

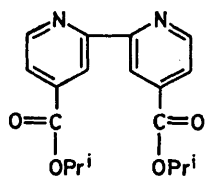
$$2A^- + 2H_2O \xrightarrow{\text{catalyst}} 2A + 2OH^- + H_2 \quad (3)$$

SCHEME 1.

S = sensitizer, A = acceptor relay.

reported which utilise $Ru(bpy)_3^{2+}$ (**1**) (bpy = 2,2′-bipyridine) as the sensitizer S, methyl viologen (MV^{2+}) as the acceptor relay A, and Pt- and RuO_2-based catalysts for the H_2 and O_2 evolution steps, respectively A judicious combination of polymer- or semiconductor-supported Pt and RuO_2 particles has demonstrated cyclic water-cleavage[3] in homogeneous solutions.

An analogous, but more practical approach, involves a photoelectrochemical cell (PEC) in which the gases H_2 and O_2 are evolved in two separate compartments.[4,5] Instead of O_2, useful oxidants like Br_2 or Cl_2 can also be produced in the anode compartment. Oxidation of water at low pH or of chloride ion requires, however, the generation of rather high photopotentials [>1·30 V *vs.* normal hydrogen electrode (N.H.E.)] by visible-light irradiation. Herein we report the operation of a PEC where the irreversible photoredox reaction between the complex RuL_3^{2+} (**2**) (L = di-isopropyl 2,2′-bipyridine-4,4′-dicarboxylate) and



L

an electron acceptor $S_2O_8^{2-}$ is used to generate the required photopotentials to drive these oxidations on a RuO_2-coated electrode in the anode compartment. The isopropyl ester of the trisbipyridylruthenium(II) complex (**2**) is an attractive candidate[6] because of its high oxidation potential [$E_0(3^+/2^+)$ 1·59 V *vs.* standard calomel electrode (S.C.E.) in MeCN], good absorption and redox properties [ϵ_{max} (466 nm) $1·96 \times 10^4$ $M^{-1} cm^{-1}$], and excited-state lifetime [τ(MeCN) 2·39 μsec].

Type I

Carbon cloth	RuL_3^{2+}($1·5 \times 10^{-4}$ M) $S_2O_8^{2-}$(10^{-3} M) H_2SO_4(0·5 M)	H_2SO_4(10^{-2} M) Na_2SO_4(1 M)	RuO_2

Type II

Carbon cloth	RuL_3^{2+}($1·5 \times 10^{-4}$ M) $S_2O_8^{2-}$(10^{-3} M) H_2SO_4(0·5 M)	HCl(1 M) or NaCl(1 M) in H_2SO_4(0·5 M)	RuO_2

FIGURE 1. Type I and Type II PECs.

Visible-light-irradiation ($\lambda \geqslant 450$ nm) of the cathode compartment† in the PECs‡ (Type I for the oxidation of water and Type II for the oxidation of chloride ions) (Figure 1) leads to the generation of RuL_3^{3+} *via* the photoredox reaction given in equation (4).§ The RuL_3^{3+} ion is

$$2RuL_3^{2+} + S_2O_8^{2-} \xrightarrow{h\nu} 2RuL_3^{3+} + 2SO_4^{2-} \quad (4)$$

subsequently reduced at the carbon-cloth electrode with concomitant oxidation of either H_2O to O_2 or chloride ions to Cl_2 at the RuO_2 anode. Reaction (4) is irreversible and occurs with a quantum yield of 2·0.[5a,7] Visible-light photolysis in the PECs gives significant photocurrents (> 100 μA) in both Type I and Type II cells.¶ Interestingly enough, addition of a relay species, for example Ce^{3+} (at low concentrations to avoid a direct quenching of the RuL_3^{2+} excited state by Ce^{3+}), leads to a drastic augmentation of the photocurrent. In typical photolysis experiments with Ce^{3+} and a 250 W tungsten–halogen lamp (IR water filter and a 455 nm cut-off glass filter) we have observed maximum photocurrents of the order of 0·39 and 0·70 mA (potential 1·350 and 1·305 V *vs.* N.H.E., respectively) in Type I (water oxidation at pH 1·83) and Type II (chloride oxidation to Cl_2) cells, respectively. Interestingly, carbon-cloth anodes give approximately the same currents for Cl_2 evolution. After prolonged irradiation (1—2 h) the gaseous products (O_2 or Cl_2) were analysed** and were found to be stoicheiometric with respect to the charge carried. In Type II cells, increase in the Cl^- concentration to 5 M gives a further increase in photocurrents (0·800 mA at 1·250 V *vs.* N.H.E.).

The observed photopotentials and photocurrents can be correlated with Evans-type diagrams, as in Figure 2, by the intersection of the *i–E* curves for the respective redox processes involved, namely $H_2O \rightarrow O_2$ and $Cl^- \rightarrow Cl_2$ oxidations on the RuO_2 anode [curves (*a*)—(*c*)] and $RuL_3^{3+/2+}$ on the carbon electrode. For the RuL_3^{2+}–$S_2O_8^{2-}$ system, under illumination, the steady-state current *vs.* potential curve can be shown[5] to be of the form given in equation (5), where

$$i_{ss} = -I_0\phi_{eff} F(1 - 10 \exp \{\epsilon C_0 d [f(e) - (i_{ss}/i_d)]\}) \quad (5)$$

I_0 is the incident photon-flux, ϕ_{eff} the effective quantum yield for the formation of the electroactive oxidant, C_0 is the initial concentration of the Ru complex, ϵ the absorption coefficient for the Ru-complex, F the Faraday constant,

† In PEC experiments involving the hydrophobic RuL_3^{2+} complex, $S_2O_8^{2-}$ has to be used at concentrations $< 2 \times 10^{-3}$M. Higher $S_2O_8^{2-}$ concentrations cause slow precipitation of the Ru-complex. In our prolonged irradiation experiments, $S_2O_8^{2-}$ was added in small aliquots periodically.

‡ The experimental method for PECs is described in detail elsewhere (ref. 5a). The surface area of the carbon cloth electrode was about 40 cm^2.

§ In water, the Ru-complex (**2**) (chloride salt) has an emission lifetime of 940 nsec and the excited state is quenched by $S_2O_8^{2-}$ with a rate constant of $1·15 \times 10^8$ $M^{-1} s^{-1}$.

¶ It should be pointed out, however, that, in our experiments only the solution is photolysed, and hence the photocurrents are independent of the electrode surface area.

** O_2 was measured as described in ref. 5a. Cl_2 gas was bubbled through a KI solution and the I_2 generated was determined with the aid of an Oriel halogen-selective electrode.

f(e) a function which indicates the form of the oxidation wave of the electroactive oxidant, and i_d the mass-transfer-limited current of the oxidant. The steady state current, i_{SS}, cannot be expressed explicitly, but the curves can be measured experimentally for the RuL_3^{2+}–$S_2O_8^{2-}$ system and are shown in Figure 2 for irradiation with 78 and 250 W lamps. The intersection of these curves with the *i–E* curves for the respective anodes [curves (*a*) and (*b*)] determine the cell current and potential. The observed photocurrents and photopotentials (Figure 2) are in good agreement with these predictions.

TABLE 1. $Ru(bpy)_3^{2+}$-sensitized anodic oxidations in PECs.[a]

Expt.	Ru-complex	Illumination source/(W)	Oxidation	Anode	Photocathode potentials (V *vs.* N.H.E.)	Photo-currents (mA)
1	(1)	60	$H_2O \rightarrow O_2$ (pH 4·7)	RuO_2	1·245	0·12
2	(2)	250	$H_2O \rightarrow O_2$ (pH 1·83)	"	1·350	0·39
3	(1)	60	$Br^- \rightarrow Br_2$ (1 M)	Carbon cloth	0·95	1·40
4	(1)	250	"	"	0·96	4·70
5	(2)	250	$Cl^- \rightarrow Cl_2$ (1 M)	RuO_2	1·305	0·70
6	(2)	"	$Cl^- \rightarrow Cl_2$ (5 M)	"	1·275	0·80

[a] For the Ru-complex (1) 10^{-2} M $S_2O_8^{2-}$, and for the complex (2) 10^{-3} M $S_2O_8^{2-}$ and 5×10^{-4} M Ce^{3+} were used in the cathode compartment (all in 1 M H_2SO_4).

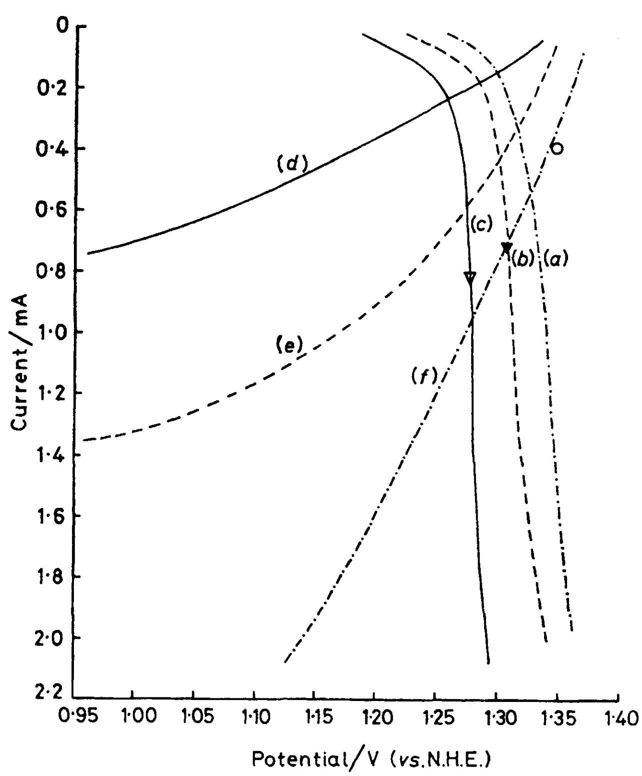


FIGURE 2. Current–potential curves for the various cathodic and anodic processes in the PEC. Curves (*a*)—(*c*) show the anodic oxidation of H_2O and of Cl^- (1 M and 5 M) on RuO_2-coated Ti electrodes. Curves (*d*)—(*f*) show the cathodic reduction of the photogenerated, electroactive oxidant on a carbon-cloth electrode. (*a*) $H_2O \rightarrow O_2$ (pH 1·83); (*b*) $Cl^- \rightarrow Cl_2$ (1 M NaCl); (*c*) $Cl^- \rightarrow Cl_2$ (5 M NaCl); (*d*) 78 W, *no* Ce^{3+}, $RuL_3^{3+/2+}$–$S_2O_8^{2-}$; (*e*) 78 W, with Ce^{3+}, $RuL_3^{3+/2+}$–$S_2O_8^{2-}$; (*f*) 250 W with Ce^{3+}, $RuL_3^{3+/2+}$–$S_2O_8^{2-}$. ○, Expt 2; ▼, Expt. 5; ▽, Expt. 6.

The useful role of Ce^{3+} ions in augmenting the photocurrent (and also providing a more stable system for extended photolysis) can be explained in terms of the short lifetime of the RuL_3^{3+} species. Continuous photolysis as well as rapid-scan cyclic-voltammetry experiments in aqueous media indicate that RuL_3^{3+} reacts quite rapidly with water (*no* oxygen was evolved in non-redox catalyst-assisted reductions); the lifetime is less than a few milliseconds even in 1 M acid solutions. Such short lifetimes significantly reduce the number of photogenerated oxidant molecules (RuL_3^{3+}) that reach the electrode. Rapid transfer of the charge to Ce^{3+}, *via* reaction (6), enables one to utilise all the

$$Ce^{3+} + RuL_3^{3+} \rightarrow RuL_3^{2+} + Ce^{4+} \quad (6)$$

electron equivalents which are produced from reaction (4), even though one loses *ca.* 200 mV of the oxidizing power of the photogenerated oxidant. *i–E* curves for the photosystem recorded under potentiostated conditions, with and without Ce^{3+} (shown in Figure 2), are in accord with this hypothesis. There is a significant increase in the photocurrent over the entire potential range. The *i–E* curves for the anodic reactions [curves (*a*) and (*b*)] clearly demonstrate the usefulness of RuO_2-coated Ti electrodes as anodes because of their low over-voltages for the oxidations under investigation. Also, the cathodic shift of the *i–E* curves for higher Cl^- concentrations (5 M) suggest that there are distinct advantages in employing high concentrations of Cl^- in the anode compartment.

For comparison, Table 1 summarizes the maximum photopotentials and currents measured in this work with those of our earlier study of water and bromide oxidations with the normal $Ru(bipy)_3^{2+}$ (1) complex.[5e] The redox potential of compound (1), E_0 1·26 V (*vs.* N.H.E.), renders it impossible to carry out the oxidations described in this work with compound (1) (water oxidation at low pH and oxidation of chloride).

In conclusion, the present study demonstrates several useful features in PEC development. (i) The use of sensitizers with higher oxidation potentials to achieve high photopotentials. (ii) The use of relay species to compensate for the loss of reactive intermediates. (iii) The use of RuO_2-based electrodes for O_2 and Cl_2 evolution.

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