Quantitative Light-assisted Oxidation of Tris(bipyridyl)ruthenium(II) with Molecular Oxygen and Application of the Reaction in a Photocatalysed Galvanic Cell

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$Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) is quantitatively photo-oxidized to $Ru(bpy)_3^{3+}$ in strongly acidic solutions containing dissolved oxygen, and application of the above chemistry has led to the design of an efficient photocatalysed galvanic cell.

Several studies have described the ground and excited state chemistry of $Ru(bpy)_3^{2+/3+}$ (bpy = 2,2′-bipyridine).[1,2] In particular equation (1) has taken on special importance, owing to its possible application in solution-based schemes for the light-assisted decomposition of water.[3] Equation (1) is predicted to exhibit a marked pH dependence, the forward reaction being thermodynamically spontaneous at pH >1 [$E°$ for $Ru(bpy)_3^{3+/2+}$ 1.23 V *vs.* normal hydrogen electrode (N.H.E.); $E°$ for O_2/OH^- (pH 1) 1.2 V *vs.* N.H.E.], while the reverse process becomes increasingly more favourable as the acidity of the solution increases.[4] The forward reaction has, in fact, been shown to produce O_2, albeit in the presence of a catalyst.[5,6] On the other hand, very little is known about the chemistry of $Ru(bpy)_3^{2+/3+}$ in strongly acidic media.[7] We therefore undertook such a study, and we report here the facile photocatalysed oxidation of $Ru(bpy)_3^{2+}$ in strongly acidic oxygenated solutions of aqueous sulphuric acid and describe an efficient light-activated cell based on the above reaction.

$$4Ru(bpy)_3^{3+} + 2OH^- \rightleftharpoons 4Ru(bpy)_3^{2+} + O_2 + 2H^+ \quad (1)$$

We have found that solutions of $Ru(bpy)_3^{2+}$ (0.1—2.0 mM), in 9 M H_2SO_4, rapidly change colour from orange to green upon exposure to bright sunlight and oxygen. No colour change was observed when either light or oxygen was excluded from the system. For an O_2-saturated solution containing 0.1 mM $Ru(bpy)_3^{2+}$, the quantum efficiency of $Ru(bpy)_3^{2+}$ disappearance was estimated to be *ca.* 0.25. Figure 1 shows the visible absorption spectra of the reactant (trace A) and product (trace B) solutions. The quantitative conversion of the reactant is evident from the disappearance of the 452 nm peak due to $Ru(bpy)_3^{2+}$. Spectrum (B) is the same as that of $Ru(bpy)^{3+}$, prepared from $Ru(bpy)_3^{2+}$ *via* chemical oxidation with PbO_2. Addition of Fe^{2+} to the product solution yielded trace (C), indicative of $Ru(bpy)_3^{2+}$. The photoproduced complex could also be reduced electrochemically. Spectroscopic (u.v.–vis., n.m.r.), chromatographic (h.p.l.c.), and cyclic voltammetric (c.v.) analyses of the regenerated Ru^{II} complex, after five turnovers in a photocatalysed galvanic cell (*vide infra*), indicated that this material was indeed the same as $Ru(bpy)_3^{2+}$. For experiments with (+)-$Ru(bpy)_3^{2+}$, the optical activities of the 'initial' and 'final' solutions were also the same.[8] Thus, the light-induced reaction led to clean formation of $Ru(bpy)_3^{3+}$, perhaps by a sequence such as that shown in equations (2) and (3).[9]

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (2)$$

$$Ru(bpy)_3^{2+*} + O_2 \longrightarrow Ru(bpy)_3^{3+} + O_2^- \quad (3)$$

However, what is the eventual fate of O_2^-? Previous studies in neutral media have shown that equation (3) is rapidly followed by equation (4), so that $Ru(bpy)_3^{3+}$ only has a transient existence in such solutions.[9,10] On the other hand, some irreversibility in the reaction has been noted in mildly acidic solutions, and attributed to the trapping of O_2^- as HO_2 followed by formation of H_2O_2.[11,12] Such an observation is important in as much as it suggests net storage of energy in the

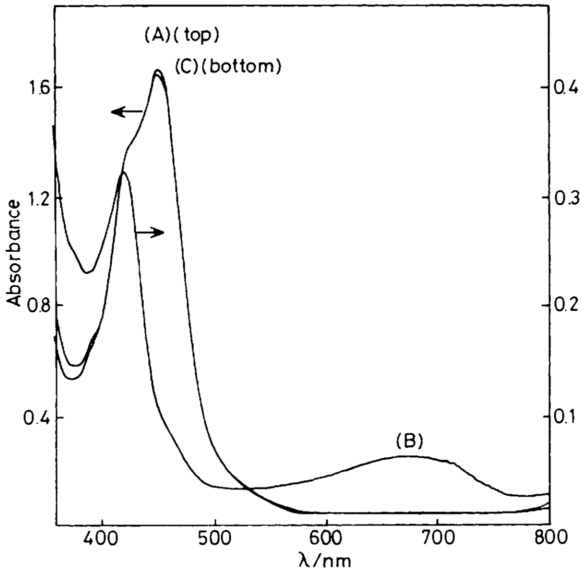

Figure 1. Visible absorption spectra of a ca. 0.1 mM solution of $Ru(bpy)_3^{2+}$, in 9 M H_2SO_4, which was initially stored in the dark under oxygen (trace A), subsequently exposed to bright sunlight for 2 min (trace B), and finally treated with crystals of iron(II) ammonium sulphate (trace C).

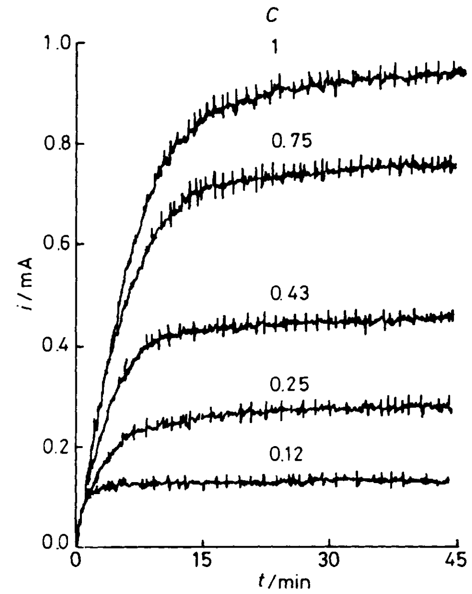

Figure 2. Chronoamperometric plots as a function of $Ru(bpy)_3^{2+}$ concentration (C/mM) in the cathodic chamber. The Ru complex was dissolved in 9 M H_2SO_4 and the cell was illuminated with a 200 W tungsten lamp. The anodic chamber contained *ca.* 1 M Fe^{2+} in 1 M H_2SO_4. Two platinum gauze electrodes (A ~3 cm²) served as anode and cathode. The open circuit voltage ($V_{o.c.}$) was 0.42 V.

form of a fuel. As described above, the reaction is completely irreversible in the present system. Yet no H_2O_2 could be detected in the product mixture.† Further, the formation of reduced bipyridine, either complexed or uncomplexed, was also ruled out based on our spectral and chromatographic evidence. The above results suggest that the reduced product in the present system is most likely H_2O and that the overall reaction is essentially the same as the reverse reaction in equation (1). This reaction, however, is thermodynamically spontaneous under the conditions employed, but kinetically slow in the dark as evident from our control experiments. Presumably, light catalyses this 4-electron transfer process by driving one or more of the endergonic intermediate steps [*e.g.* equation (3)] *via* the excited state of $Ru(bpy)_3^{2+}$. We note, however, that direct evidence in favour of H_2O as the reduced product has so far not been obtained.

$$Ru(bpy)_3^{3+} + O_2^- \longrightarrow Ru(bpy)_3^{2+} + O_2 \qquad (4)$$

A photocatalysed galvanic cell has been designed based on the above chemistry. $Ru(bpy)_3^{2+}$ (0.1—2.0 mM), in 7—9 M H_2SO_4, was placed in the cathodic chamber of a compartmentalised cell, and O_2 was bubbled through this solution. The anodic chamber contained an acidic solution of Fe^{2+}, or other reduced forms of compounds such as hydroquinone or iodide. Figure 2 shows the current–time profiles for an illuminated cell in which the Ru^{II} concentration was systematically varied while all other parameters were kept constant. While the dark current was negligibly small in all experiments, the current increased rapidly with the onset of illumination and finally levelled off at a steady-state value. This value of the current varied linearly with the initial concentration of the catalyst ($[Ru^{II}]$ 0.1—1.0 mM), and was as high as 1.2 mA ($V_{o.c.}$ 0.42 V) when the cell was illuminated with bright sunlight and the Ru^{II} concentration was *ca.* 1 mM. The chemistry of the cell may be described by equations (5)—(8), when Fe^{2+} is used as the reduced form.

$$4Ru(bpy)_3^{2+} + O_2 + 4H^+ \xrightarrow{h\nu} 4Ru(bpy)_3^{3+} + 2H_2O \qquad (5)$$

$$4Ru(bpy)_3^{3+} + 4e \longrightarrow 4Ru(bpy)_3^{2+} \qquad (6)$$

$$4Fe^{2+} \longrightarrow 4Fe^{3+} + 4e \qquad (7)$$

$$\text{Net: } 4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O + \text{electrical power} \qquad (8)$$

Prolonged illumination of a cell containing 1 mM Ru^{II}, in 7 M H_2SO_4, indicated that a stable photocurrent of *ca.* 1 mA could be sustained for periods exceeding 10 h.‡ Based on the number of coulombs of charge passed and absorption spectral analysis of the Ru complex, it was estimated that the catalyst was turned over 33 times with >95% retention of activity at the end of the experiment. The quantum electroconversion efficiency was *ca.* 0.1.

In conclusion, we have demonstrated the quantitative photoconversion of $Ru(bpy)_3^{2+}$ into $Ru(bpy)_3^{3+}$ in strongly acidic solutions containing O_2 and have devised an efficient photocatalysed galvanic cell based on this facile reaction. Such

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† H_2O_2 analysis was carried out as follows: 2—4 mM $Ru(bpy)_3^{2+}$, in 9 M H_2SO_4, was placed in one arm of an H-cell, and the solution photolysed until the colour changed to green. Next, a small amount of MnO_2 was placed in the other arm and the cell purged thoroughly with helium gas. The contents of the cell were then mixed so as to liberate O_2 from the reaction of MnO_2 and H_2O_2. Control experiments were carried out in an identical cell containing 1—2 mM H_2O_2, in 9 M H_2SO_4. Gas chromatographic detection of O_2 was carried out using a 5 Å molecular sieve column, using helium as carrier gas.

‡ To minimise problems due to thermal effects, the cell was immersed in a constant temperature (15—20 °C) bath.

a cell may be used for the oxidation of a variety of substrates, using O_2 as net oxidant.

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