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Photo-oxidation of Water Sensitised by Ruthenium(II) Tris(bipyrazine)

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Abstract

The excited state of ruthenium(II) tris(bipyrazine) ($Ru(bipyz)_3^{2+*}$) is quenched by the sacrificial electron acceptors, $S_2O_8^{2-}$ and $Co(NH_3)_5Cl^{2+}$. Under acidic conditions (pH 0), $Ru(bipyz)_3^{2+*}$ is quenched by protons and therefore quite short-lived ($\tau = 50$ ns). At pH 0, steady-state irradiation of the $Ru(bipyz)_3^{2+}$ in the presence or absence of either $S_2O_8^{2-}$ or $Co(NH_3)_5Cl^{2+}$ did not produce any permanent products. In addition, no O_2 evolution was observed when an O_2 catalyst was added. At pH 6, $Ru(bipyz)_3^{2+*}$ is much longer-lived ($\tau = 1.04$ μs) and steady-state irradiation of a $Ru(bipyz)_3^{2+}$ solution containing $S_2O_8^{2-}$, rather than $Co(NH_3)_5Cl^{2+}$, did produce changes in absorbance, emission and pH, due to the oxidative degradation of the sensitiser. Microsecond flash photolysis work indicated that $Ru(bipyz)_3^{2+*}$ is oxidatively quenched by the $S_2O_8^{2-}$ ions leading to the generation of $Ru(bipyz)_3^{3+}$, a very strong and unstable oxidant. Steady-state irradiations carried out on the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ photochemical system at pH 6, in the presence of an O_2 catalyst, resulted in O_2 generation ($\phi(O_2) = 0.0025$), however photodegradation of the $Ru(bipyz)_3^{2+}$ sensitiser still took place, albeit at a reduced rate.

Introduction

The development of a photochemical system capable of the efficient photodissociation of water into hydrogen and oxygen is a common objective of many of the research groups working in the area of solar energy conversion [1]. However, one of the major problems encountered by such workers is the lack of materials capable of sensitising the photo-oxidation of water, *i.e.*

$$2H_2O - 4e^- \longrightarrow 4H^+ + O_2\uparrow \qquad (1)$$

Ideally, a photosensitiser for reaction (1) should use visible, rather than ultraviolet light and be stable towards photodegradation. Unfortunately, amongst the heterogeneous semiconductor photocatalysts tested, greatest success has been achieved using oxides, such as TiO_2 and $SrTiO_3$, which absorb largely UV, and not the visible, light [2, 3]. In addition, most semiconductors which absorb visible light and are thermodynamically capable of mediating reaction (1) are also prone to photo-anodic corrosion, e.g. cadmium sulphide [4].

One of the first of the homogeneous dye photocatalysts used successfully [5] to sensitise reaction (1) was ruthenium(II) tris(bipyridyl), $Ru(bipy)_3^{2+}$, and surprisingly, despite extensive research, no other compounds have been found to match its stability and efficiency. Indeed, very few dyes have been found which are able to photosensitise reaction (1) at all [1, 6], and most of those that do also undergo extensive oxidative photodegradation [7].

Recently, Lever and Crutchley [8] have identified ruthenium(II) tris(bipyrazine), $Ru(bipyz)_3^{2+}$, as a homogeneous photosensitiser with a greater potential for the reduction of water than $Ru(bipy)_3^{2+}$. Thus, using $Ru(bipyz)_3^{2+}$ in the presence of triethanolamine (0.6 mol dm^{-3}) and methyl viologen (0.02 mol dm^{-3}), they recorded a quantum yield for reduced methylviologen formation ($\phi(MV^+)$) of 0.77 [8]; whereas under the same conditions, using $Ru(bipy)_3^{2+}$ as the sensitiser, they found $\phi(MV^+)$ to be significantly less (0.19). Subsequent work by Dürr and his group [9] has demonstrated that $Ru(bipy)_3^{2+}$ is able to sensitise the reduction of water to H_2 with a quantum yield ($\phi(1/2H_2)) = 0.243$, compared with $\phi(1/2H_2) = 0.085$ for $Ru(bipy)_3^{2+}$ under similar conditions. It appears that, under neutral or alkaline conditions, the quantum yield for the photoreduction of methylviologen by sacrificial electron donors, such as EDTA or TEOA, is significantly larger if $Ru(bipyz)_3^{2+}$ is used as the sensitiser, rather than $Ru(bipy)_3^{2+}$. Indeed, the limiting quantum yield of 1.4, reported by Prasad and Hoffman [10] for the $Ru(bipyz)_3^{2+}/MV^{2+}/EDTA$ system, is the highest reported for such sacrificial photochemical systems.

In Table I we have gathered together from the literature [8, 11] some relevant photophysical and redox data for $Ru(bipyz)_3^{2+}$ and $Ru(bipy)_3^{2+}$ in aqueous solution. The redox data for $Ru(bipyz)_3^{2+}$ given in Table I was calculated from the known values

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TABLE I. Photophysical and Redox Properties of $Ru(bipyz)_3^{2+}$ and $Ru(bipy)_3^{2+}$ in Aqueous Solution

	$Ru(bipyz)_3^{2+}$	$Ru(bipy)_3^{2+}$
Photophysical properties [8]		
Absorption λ (max) (nm)	443	453
Emission λ (max) (nm)	603	610
Excited state lifetime (μs)	1.04	0.685
Redox properties [8, 11] (half-wave potentials *vs.* NHE)		
$E_{1/2}$ (3+/2+)	1.76	1.26
$E_{1/2}$ (2+/1+)	−0.78	−1.28
$E_{1/2}$ (3+/2+*)	−0.36	−0.86
$E_{1/2}$ (2+*/1+)	1.34	0.84

for $Ru(bipy)_3^{2+}$ in aqueous solution, coupled with the assumption that the 0.5 V difference between both reduction and oxidation potentials observed for the two different sensitisers in acetonitrile will remain unaltered in water. From the data given in Table I it would appear that, not only is the excited state of $Ru(bipyz)_3^{2+}$ longer lived than $Ru(bipy)_3^{2+}$ but also, $Ru(bipyz)_3^{3+}$ is a much stronger oxidant than $Ru(bipy)_3^{3+}$ and, therefore, easily capable of oxidising water [12]. Surprisingly, $Ru(bipyz)_3^{2+}$ has not been tested as photosensitiser for the oxidation of water and in this paper we report the preliminary findings of such a study.

Experimental

Materials

$Ru(bipyz)_3^{2+}$ was prepared as its chloride salt as described in the literature [8]. Ruthenium(II) tris(bipyridyl) chloride hexahydrate was purchased from Strem Chemicals and used as received. Cobalt(III) pentammine chloride was synthesised as described elsewhere [13]. The ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) was purchased from Johnson Matthey and, before use, was 'thermally activated' (*i.e.* heat treated in air for 5 h) to convert it into a stable, active O_2 catalyst [14]. The $RuO_2 \cdot xH_2O$ colloid was prepared via the reduction of 1.5 dm^3 of a ruthenium tetroxide solution (0.124 g dm^{-3}) using 30 cm^3 of a sodium nitrite solution (10^{-3} mol dm^{-3}). The final solution was subsequently stirred for 48 h to ensure complete reduction of the RuO_4 to $RuO_2 \cdot xH_2O$ (0.1 mg dm^{-3}) and carbowax (0.2 mg dm^{-3}) was then added to help stabilise the colloid against aggregation and precipitation. All other materials used were obtained from BDH Chemicals in the most pure form available (usually AnalaR). The water used throughout this work was deionised before being doubly distilled from quartz vessels.

Methods

Steady-state irradiations in which the change in absorbance of the sensitiser as a function of irradiation time was monitored were carried out using light from a 100 W quartz-iodine lamp, which had been filtered through a 10% copper sulphate solution to remove the infrared component. In such work, typically, 4 cm^3 of solution were placed in a 1 cm fluorescence cell fitted with taps to allow the solution to be N_2 purged prior to irradiation in the cell.

Irradiations in which the evolution of O_2 was monitored as a function of time were carried out using the light from a 250 W Xe lamp with the infrared output removed. The solution under test (typically 30 cm^3) was placed in a cylindrical, thermostated quartz cell with an O_2-Membrane Polarographic Detector (O_2-MPD) fitted into the cell base. The solution contained in the irradiation cell/O_2-MPD was thermostated at 25 ± 0.05 °C and N_2 purged prior to illumination. A full description of the irradiation cell/O_2-MPD can be found elsewhere [15].

Microsecond flash photolysis experiments were carried out using an Applied Photophysics 200 J system, the details of which are given in a previous paper [16], and fluorescence spectra were recorded using a Perkin-Elmer LS-5 Luminescence Spectrometer.

Results and Discussion

In order to sensitise efficiently the photo-oxidation of water it is first necessary to photogenerate a strong oxidant which does not then back react. One way this can be achieved is by using a sacrificial electron acceptor, such as $Co(NH_3)_5Cl^{2+}$ or $S_2O_8^{2-}$, to quench the excited state of the dye (D), *i.e.*

$$D^* + A \longrightarrow D^+ + A^- \qquad (2)$$

The sacrificial electron acceptor is chosen so that once reduced, e.g. via reaction (2), it undergoes irreversible decomposition

$$A^- \longrightarrow \text{decomposition products} \qquad (3)$$

and so prevents the efficiency-lowering back reaction

$$D^+ + A^- \longrightarrow D + A \qquad (4)$$

As a consequence, steady-state irradiation of the dye in the presence of an ideal sacrificial electron acceptor should lead to the accumulation of the oxidised dye (D^+), provided it is stable. Unfortunately, most sensitisers once oxidised are not stable and, instead, are often bleached via subsequent irreversible decomposition reaction, *i.e.*

$$D^+ \longrightarrow \text{products} \qquad (5)$$

TABLE II. Bimolecular Quenching Rate Constants for $Ru(bipyz)_3^{2+*}$ and $Ru(bipy)_3^{2+*}$

Quencher	k_q (10^8 mol dm^3 s^{-1}) Value for excited state:	
	$Ru(bipyz)_3^{2+*}$	$Ru(bipy)_3^{2+*}$
$Co(NH_3)_5Cl^{2+}$	2.8	9.3
$S_2O_8^{2-}$	8.9	5.33

In contrast, it is worth noting that $Ru(bipy)_3^{3+}$ in aqueous solution at pH < 5 is quite stable ($t_{1/2} >$ 6.9 min [17]). Indeed, workers using sacrificial electron acceptors, such as $S_2O_8^{2-}$ or $Co(NH_3)_5Cl^{2+}$, have easily been able to record its absorption spectrum after photogeneration via reactions (2) and (3), using $Ru(bipy)_3^{2+}$ as the sensitiser [18, 19]. Provided the redox potential for the couple D^+/D is greater than that for water ($E(O_2/H_2O) = 1.23 - 0.059 \times pH$ V *versus* NHE), as is the case for both $Ru(bipy)_3^{3+}$ and $Ru(bipyz)_3^{3+}$, then the addition of an O_2 catalyst, such as activated $RuO_2 \cdot xH_2O$, should lead to the generation of O_2 via the reaction

$$4D^+ + 2H_2O \longrightarrow 4D + 4H^+ + O_2\uparrow \qquad (6)$$

Working at pH 3.5, the variation of the intensity of emission due to the excited state of the ruthenium(II) tris(bipyrazine) complex ($Ru(bipyz)_3^{2+*}$) was determined as a function of concentration for the quenchers $Co(NH_3)_5Cl^{2+}$ and $S_2O_8^{2-}$. The bimolecular quenching rate constants (k_q) were determined from a Stern–Volmer plot of the data and are given in Table II, alongside those for $Ru(bipy)_3^{2+}$ for comparison [18, 20]. The excited state of $Ru(bipyz)_3^{2+}$ is a poorer reducing agent than that of $Ru(bipy)_3^{2+}$ and this may be responsible for its substantially lower value for k_q using the weak oxidant, $Co(NH_3)_5Cl^{2+}$ ($E(Co(NH_3)_5Cl^{2+/1+}) = 0.51$ V *versus* NHE). However, using the much stronger oxidant $S_2O_8^{2-}$ ($E(S_2O_8^{2-}/SO_4^{2-})$ = 2.1 V *versus* NHE) k_q for both $Ru(bipyz)_3^{2+}$ and $Ru(bipy)_3^{2+}$ were found to be higher, although, maybe surprisingly, not diffusion controlled.

Research carried out by Creutz and Sutin and their co-workers has demonstrated that the oxidised form of $Ru(bipy)_3^{2+}$ is most stable in acidic solution ($t_{1/2} > 19.3$ h; 1 mol dm^{-3} H_2SO_4) [21, 22]. Under such acidic conditions $Ru(bipy)_3^{3+}$ can be efficiently photogenerated, via reactions (2) and (3), using $Co(NH_3)_5Cl^{2+}$ or $S_2O_8^{2-}$ as the sacrificial electron acceptor [23]. In contrast, steady-state irradiation of a solution containing $Ru(bipyz)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}) and $Co(NH_3)_5Cl^{2+}$, or $S_2O_8^{2-}$, (10^{-3} mol dm^{-3}) in 1 mol dm^{-3} H_2SO_4 did not produce any permanent products. In addition, in the absence or presence of either sacrificial electron acceptor, no luminescence due to the excited state of $Ru(bipyz)_3^{2+}$ was observed, indicating that, at pH 0, $Ru(bipyz)_3^{2+*}$ is completely quenched by the protons present.

Work carried out by Lever and his co-workers [24], and others [25], has demonstrated that the remote nitrogen atoms of the bipyrazine ring become better bases upon optical excitation, e.g. $pK_a = -2.2$; $pK_a^* = 2.0$ for the first protonation step for the ground and excited states, respectively. Unlike $Ru(bipyz)_3^{2+*}$ the first protonated excited state of ruthenium(II) tris(bipyrazine) does not luminescence strongly and is substantially shorther lived ($t_{1/2} = 35$ ns) than $Ru(bipyz)_3^{2+*}$ ($t_{1/2} = 721$ ns) or $Ru(bipy)_3^{2+*}$ ($t_{1/2} = 475$ ns) [24]. Thus, the lack of permanent products observed even after prolonged (>1 h) steady-state irradiation of $Ru(bipyz)_3^{2+}$ in the presence of either $S_2O_8^{2-}$, or $Co(NH_3)_5Cl^{2+}$, in 1 mol dm^{-3} H_2SO_4 can largely be attributed to the short lifetime of its protonated excited state, coupled with the low quencher concentration (10^{-3} mol dm^{-3}) employed.

Under more alkaline conditions (pH > 3) the excited state of $Ru(bipyz)_3^{2+}$ is no longer protonated and is longer lived ($t_{1/2} = 721$ ns). However, steady-state irradiation of a solution at pH 6 containing: $Ru(bipyz)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}) and $Co(NH_3)_5Cl^{2+}$ (10^{-3} mol dm^{-3}) once again did not produce any permanent products, even after prolonged irradiation of this system; presumably this is due to a very low cage escape yield for reaction (2) and/or a rapid back reaction (4). In contrast, steady-state irradiation of a similar solution containing $Ru(bipy)_3^{2+}$ and $Co(NH_3)_5Cl^{2+}$, resulted in the complete conversion of the $Ru(bipy)_3^{2+}$ into $Ru(bipy)_3^{3+}$ within 2 min. However, it should be noted that at the pH of the experiment (pH 6) $Ru(bipy)_3^{3+}$ is not stable ($t_{1/2} =$ *ca.* 3 min [17]) and the majority (*ca.* 90%) of the $Ru(bipy)_3^{3+}$ ions are reduced back to $Ru(bipy)_3^{2+}$ via the hydroxide ion or water-initiated oxidative degradation of a small fraction of the $Ru(bipy)_3^{3+}$ ions with the concomitant release of a proton for each electron transferred [21–23].

Prolonged steady-state irradiation of the $Ru(bipyz)_3^{2+}$ in the presence of $S_2O_8^{2-}$ under the same conditions did not produce any O_2 but did produce some permanent products as evidenced by changes in the UV–Vis absorption and emission spectra of the reaction solution recorded (see Fig. 1) and a concomitant drop in pH (final pH typically 2.7). These products did not appear to be strong oxidants since addition of an O_2 catalyst after irradiation did not lead to any O_2 generation or recovery of the luminescence or absorption characteristics of the original sensitiser, $Ru(bipyz)_3^{2+}$. The addition of buffers, such as acetate or phosphate, prior to irradiation appeared to increase the rate of sensitiser photodegradation.

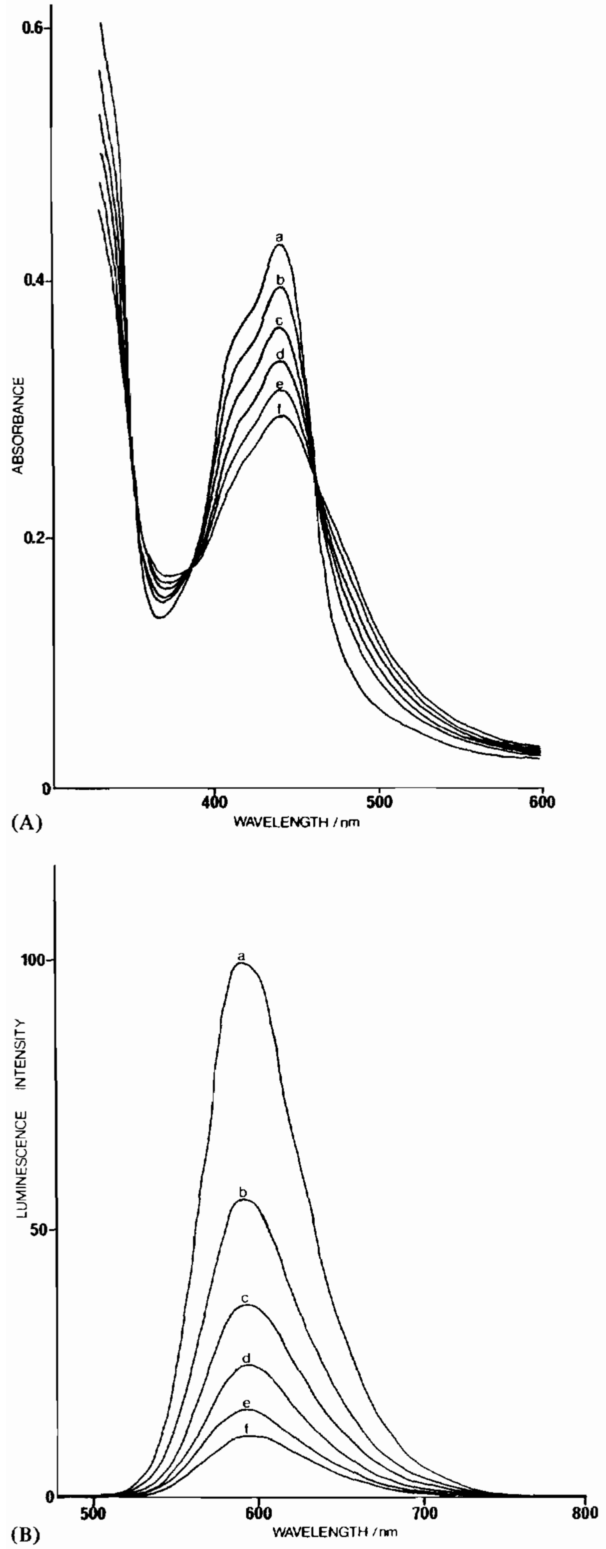

Fig. 1. UV–Vis absorption spectrum (A) and emission spectrum (B) of a N_2 purged solution containing $Ru(bipyz)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}) and $S_2O_8^{2-}$ (10^{-3} mol dm^{-3}) at pH 6 after irradiation for (a) 0, (b) 3, (c) 8, (d) 16, (e) 30 and (f) 50 min.

In order to rationalise these observations it is necessary to recognise that any $Ru(bipyz)_3^{3+}$, generated via reactions (2) and (3), is unlikely to be stable at this pH and, like $Ru(bipy)_3^{3+}$, will probably degrade oxidatively the bypz ligands of some of the $Ru(bipyz)_3^{3+}$ present. Indeed, work carried out by Shafirovich and Strelets [23] on the $Ru(bipy)_3^{2+}$/$Co(NH_3)_5Cl^{2+}$ system indicates that, even with the mild oxidant $Ru(bipy)_3^{3+}$, in the absence of an O_2 catalyst this process of oxidative degradation leads to the eventual loss/destruction of one, or more, of the bipy ligands, *i.e.* 'deep disintegration' of the complex [23]. In support of this we have found that irradiation of a solution containing $Ru(bipy)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}) and $S_2O_8^{2-}$ (10^{-3} mol dm^{-3}) at pH 9 for 1 h produced a shift in pH from pH 9 down to pH 3, with no concomitant O_2 evolution. Other workers have also found evidence for the 'deep disintegration' of the $Ru(bipy)_3^{2+}$ complex, *i.e.*

$$C_{10}H_8N_2 + 20H_2O - 48e^- \longrightarrow 10CO_2 + N_2 + 48H^+ \tag{7}$$

including N_2 and CO_2 evolution [17, 21, 22].

Since $Ru(bipyz)_3^{3+}$ is a much stronger oxidant than $Ru(bipy)_3^{2+}$ it seems likely that a similar 'deep disintegration' of the $Ru(bipyz)_3^{2+}$ will occur if its oxidised form is generated in aqueous solution. Although the destruction of a bipyz ligand would be a multi-step process, the overall reaction can be written as follows

$$C_8N_4H_6 + 16H_2O - 38e^- \longrightarrow 8CO_2 + 2N_2 + 38H^+ \tag{8}$$

The changes in pH (from pH 6 to 2.7) and absorption and emission spectra undergone by a solution containing $Ru(bipyz)_3^{2+}$ and $S_2O_8^{2-}$ during steady-sate irradiation (see Fig. 1) are consistent with the oxidation of the bipyz ligands of the sensitiser. Interestingly, the observed changes in absorption spectrum with irradiation time (see Fig. 1A) are consistent with, amongst many other possible oxidatively degraded forms of $Ru(bipyz)_3^{2+}$, the generation of a ruthenium(II) bis(bipyrazine) complex, such as $Ru(bipyz)_2(H_2O)_2^{2+}$, $\lambda(max) = 494$ and 360 nm, respectively [26, 27]. In addition, the shift in pH observed upon steady-state irradiation of the $Ru(bipyz)_3^{2+}$/$S_2O_8^{2-}$ system indicates that at the end of the irradiation each $Ru(bipyz)_3^{2+}$ molecule had lost, on average, 27 electrons.

A μs flash photolysis study was carried out on the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ system and the transient spectrum recorded shortly after the flash (0.2 ms) is illustrated in Fig. 2. It appears that the excited state of $Ru(bipyz)_3^{2+}$ reacts rapidly with $S_2O_8^{2-}$, thereby bleaching the dye and generating a species which absorbs weakly at $\lambda > 540$ nm and which is quite short lived (<10 ms). Even at longer times (*i.e.*

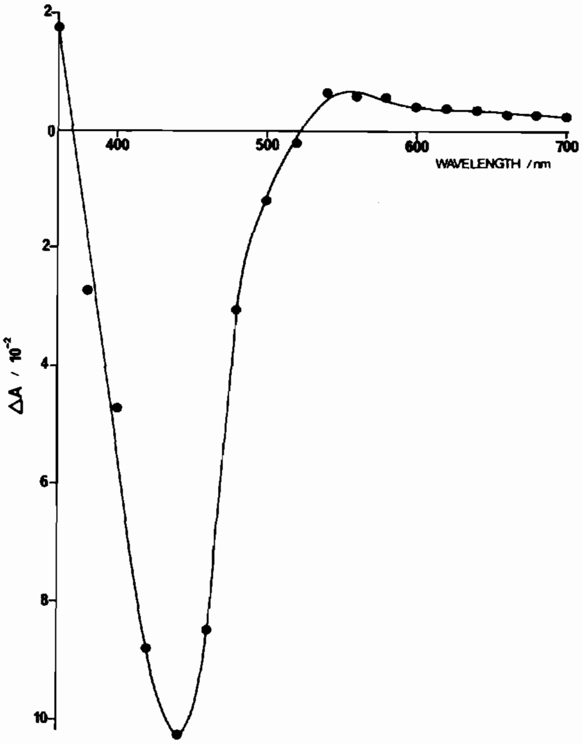

Fig. 2. Transient difference spectrum recorded 0.2 ms after the μs flash photolysis of a solution containing $Ru(bipyz)_3^{2+}$ (1.5×10^{-5} mol dm^{-3}) and $S_2O_8^{2-}$ (10^{-3} mol dm^{-3}) at pH 3.5.

> 0.1 s), over the wavelength range (540–700 nm), the transient absorbance did not return to zero. In the absence of $S_2O_8^{2-}$ no transients were observed.

Although $Ru(bipyz)_3^{2+*}$ is a weaker reducing agent than $Ru(bipy)_3^{2+*}$ (see Table I) it is quenched by $S_2O_8^{2-}$ at a similar rate (see Table II). It seems likely that the photo-induced electron transfer reactions which take place during the flash are similar to those found for $Ru(bipy)_3^{2+}$ [18], *i.e.*

$$Ru(bipyz)_3^{2+} \xrightarrow{h\nu} Ru(bipyz)_3^{2+*} \quad (9)$$

$$Ru(bipyz)_3^{2+*} + S_2O_8^{2-} \longrightarrow Ru(bipyz)_3^{3+} + SO_4^{-} + SO_4^{2-} \quad (10)$$

followed by the thermal reaction

$$Ru(bipyz)_3^{2+} + SO_4^{-} \longrightarrow Ru(bipyz)_3^{3+} + SO_4^{2-} \quad (11)$$

since the SO_4^- radical is such a very strong oxidant ($E(SO_4^-/SO_4^{2-}) > 3.4$ V *versus* NHE) [28]. In addition, as an alternative to reaction (11), the sulphate radical could participate directly in the oxidation of the ligands of $Ru(bipyz)_3^{2+}$, see eqn. (8).

According to the above reaction scheme one of the major products that should be generated by the flash is $Ru(bipyz)_3^{3+}$ and, by analogy with $Ru(bipy)_3^{3+}$ ($\lambda(max) = 420$; $\epsilon(420) = 2700$ mol^{-1} dm^3 cm^{-1} and 670 nm; $\epsilon(670) = 410$ mol^{-1} dm^3 cm^{-1}), such a species, if stable, would be expected to give rise to a weak but definite absorbance at wavelengths > 550 nm directly after the flash. It is likely, therefore, that at least part of the weak transient observed at $\lambda > 550$ nm (see Fig. 2) is due to $Ru(bipyz)_3^{3+}$. The appreciably shorter lifetime of this species, compared with $Ru(bipy)_3^{3+}$ generated under the same conditions, reflects a much lower stability, which is probably closely associated to its much more positive reduction potential (see Table I). The positive transient absorbance at these longer wavelengths, observed over a long timescale (0.1 s), is most likely due to the subsequent generation of oxidatively degraded forms of $Ru(bipyz)_3^{2+}$.

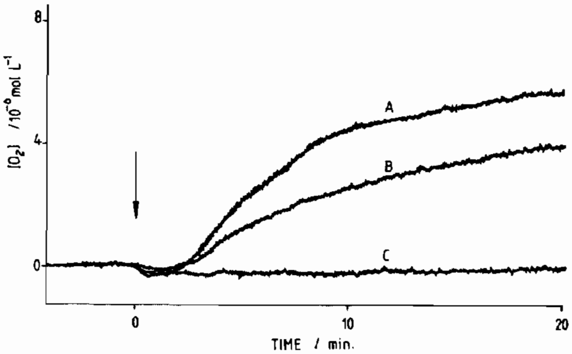

Fig. 3. Typical dissolved O_2 concentration, $[O_2]$, *vs.* time profiles recorded upon irradiation (at $t = 0$) of 30 cm^3 of a solution at pH 6 containing: $Ru(bipyz)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}) and $S_2O_8^{2-}$ (10^{-3} mol dm^{-3}) in the presence of: (A) an $RuO_2 \cdot xH_2O$ colloid (0.001% *w/v*), (B) thermally 'activated' $RuO_2 \cdot xH_2O$ powder (0.1 mg cm^{-3}), (C) no O_2 catalyst.

The addition of a $RuO_2 \cdot xH_2O$ colloid (5 mg dm^{-3}) to the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ flash photolysis solution reduced the lifetime of the weak transient at $\lambda > 550$ nm by a factor of *ca.* 5. In a separate set of experiments the same colloid was shown to be very stable against anodic corrosion and active as a mediator for the oxidation of water by a strong oxidant such as Ce^{4+}.

A set of steady-state irradiations were carried out at different starting pHs (covering the range pH 2 to pH 10) using a solution containing $Ru(bipyz)_3^{2+}$ (7.5×10^{-5} mol dm^{-3}), $S_2O_8^{2-}$ (10^{-3} mol dm^{-3}) and thermally 'activated' $RuO_2 \cdot xH_2O$ powder (0.1 mg cm^{-3}) and the dissolved O_2 concentration was monitored as a function of irradiation time using an O_2-MPD. Oxygen evolution was found to occur at all pHs and at an optimal rate at pH 6. Figure 3 illustrates some typical $[O_2]$ *versus* irradiation time profiles recorded during the steady-state irradiation of the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ photochemical system, in the presence of colloidal $RuO_2 \cdot xH_2O$ (curve A), thermally 'activated' $RuO_2 \cdot xH_2O$ powder (curve B), or no O_2 catalyst (curve C). Using the reaction conditions described above, and thermally 'activated' $RuO_2 \cdot xH_2O$ as an O_2 catalyst (0.1 mg cm^{-3}), the initial quantum yield for O_2 evolution ($\phi(O_2)_i$) was determined as 0.0025, whereas, using $Ru(bipy)_3^{2+}$ as the sensitiser under similar conditions, $\phi(O_2)_i$ was determined as 0.098, which is in good agreement with previous values determined for this system (0.06–0.03) [29].

From the results reported above it appears that O_2 catalysts, such as $RuO_2 \cdot xH_2O$ in powder or colloidal form, are able to mediate the oxidation of water by $Ru(bipyz)_3^{3+}$, *i.e.*

$$4Ru(bipyz)_3^{3+} + 2H_2O \longrightarrow 4Ru(bipyz)_3^{2+} + 4H^+ + O_2 \qquad (12)$$

In addition, it was observed for the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ system, that the rate of sensitiser photodegradation was lower if either of the O_2 catalysts were present, and this was taken as an indication that such catalysts are able, to some extent at least, to mediate reaction (11) over the oxidative degradation of the sensitiser, e.g. reaction (8). However, even in the presence of an O_2 catalyst, such as colloidal $RuO_2 \cdot xH_2O$ or thermally 'activated' $RuO_2 \cdot xH_2O$ powder, prolonged or repeated irradiation of the photosystem did lead eventually to a decrease in the rate of O_2 generation and concomitant spectral and pH changes associated with sensitiser degradation (see Fig. 1).

Conclusions

The excited state of ruthenium(II) tris(bypyrazine) is quenched by both $S_2O_8^{2-}$ and $Co(NH_3)_5Cl^{2+}$, both of which are capable of acting as sacrificial electron donors. Steady-state irradiation of $Ru(bipyz)_3^{2+}$ in the presence of either of these quenchers under acidic conditions (1 mol dm^{-3} H_2SO_4) does not lead to the photogeneration of any permanent products, probably due to the very short lifetime of the sensitiser's protonated excited state. However, permanent products, ascribed to the oxidative degradation of the sensitiser, are photogenerated, at pH 6, using $S_2O_8^{2-}$, rather than $Co(NH_3)_5Cl^{2+}$, as the quencher. Microsecond flash photolysis work indicates that, as with $Ru(bipy)_3^{2+}$, the excited state of $Ru(bipyz)_3^{2+}$ is quenched by $S_2O_8^{2-}$ via an oxidative electron transfer mechanism leading to the generation of $Ru(bipyz)_3^{3+}$. Steady-state irradiation of the $Ru(bipyz)_3^{2+}/S_2O_8^{2-}$ system in the presence of an O_2 catalyst $RuO_2 \cdot xH_2O$ (in powder or colloidal form) leads to the photogeneration of O_2 over a wide pH range *i.e.* 2–10, and is optimal at pH 6. At this pH the initial quantum yield for O_2 evolution was found to be 0.0025, however, photodegradation of $Ru(bipyz)_3^{2+}$ still occurs, albeit at a lower rate. Thus, although $Ru(bipyz)_3^{2+}$ can be described as a new sensitiser for the photo-oxidation of water, it is also prone to photo-oxidative degradation, even in the presence of an O_2 catalyst, and this represents a serious drawback in any future use as a photosensitiser for the oxidation of water.

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