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Tris(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium(II), a Redox Sensitizer Affording Water Oxidation to Oxygen in the Absence of Heterogeneous Catalyst***

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Abstract: Oxygen is generated under visible light illumination of highly acidic (0.5 M H_2SO_4) aqueous solutions of tris(2,2-bipyridine-4,4′-dicarboxylic acid)ruthenium(II) containing $S_2O_8^{2\ominus}$ as electron acceptor in the absence of heterogeneous redox catalyst. An autocatalytic reaction mechanism is proposed.

The oxidation of water to oxygen constitutes a crucial reaction in photochemical water cleavage systems. Recently, very active redox catalysts have been developed which allow to minimize the energy expenditure for this difficult process[1]. So far, few investigations have dealt with the optimization of sensitizers employed in these devices. Our earlier water decomposition studies in microheterogeneous solution have employed the isopropyl ester of tris(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium as a chromophore[2,3]. In subsequent investigations, we have scrutinized the properties of the hydrolyzed complex, i.e. tris(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium(II) dichloride, $[RuL_3]^{2\oplus}$, which was shown to sensitize titanium oxide with a charge injection quantum efficiency of 60% at pH 2[4]. The present investigation focusses on oxygen generation from water which is accomplished by this sensitizer in acidic solutions, even in the absence of redox catalyst.

$[RuL_3]^{2\oplus}$ $2Cl^{\ominus}$ was synthesized and purified according to literature procedure[5]. Deionized water was distilled twice. All other chemicals were at least reagent grade and employed as received by the vendor. Titania-supported RuO_2 was prepared by impregnating 1 g of TiO_2 powder (Degussa P-25, mainly anatase, surface area 55 m^2/g) with 10 mL H_2O containing 35 µmol $RuCl_3 \cdot aq$. The slurry was dried at 100 °C and subsequently calcined for 1 h in air at 300 °C. Calculated loading of TiO_2 with RuO_2 is 0.5% (w/w).

Illuminations were performed with a 450 Watt Xe lamp equipped with a water jacket and a 435 nm cut-off filter to remove infrared and ultraviolet radiations, respectively. Solution (20 mL) was contained in the inner part of a double-walled cylindrical pyrex glass vessel (headspace in the cell 11 mL) whose outer compartment was continuously flushed with thermostated water. Oxygen concentration in solution was monitored by a Clark type membrane electrode (Yellow Springs Instruments, Y-SI model 53) connected to a potentiostat. In addition, the appearance of oxygen in the gas phase above the solution was ascertained by GC analysis. A poropack 5 Å molecular sieve column was used in conjunction with a Gow-Mac thermal conductivity detector. Argon served as a carrier gas. Air leakage was negligible on the time scale of the present experiments and made no significant contribution to the observed oxygen generation rates.

Cyclic voltammetry was performed with a Wenking POS-73 potentiostat using a conducting SnO_2 electrode (area 0.66 cm^2) cut from a glass received from Balzers AG.

Fig. 1 shows oxygen evolution curves obtained from visible light illumination of 10^{-4} M $[RuL_3]^{2\oplus}$ solution in 0.5 M H_2SO_4 containing 2×10^{-2} M $S_2O_8^{2\ominus}$ as electron acceptor. The ordinate represents the amount of oxygen measured by the Clark sensor in solution which was calibrated by injection of air saturated water. Prior to irradiation, the solution was flushed with Ar. The cell was then closed, the gas stream turned off, and the solution stirred in the dark until the detector gave a reliable and stable baseline. The three curves in Fig. 1 were taken under the same experimental conditions. Unambiguous evidence was obtained that $[RuL_3]^{2\oplus}$ sensitizes water oxidation in the absence of RuO_2 redox catalyst. There is an induction period of ca. 1 min after which the rate of oxygen generation ($r(O_2)$) attains 10 µL/min. A plateau is reached after 6 min of irradiation when 30 µL of O_2 are present in solution. At this time, the amount of O_2 that escaped into the gas phase is 20 µL. Hence, a total volume of 50 µL of oxygen was generated, corresponding to a turnover number of 4 for $[RuL_3]^{2\oplus}$. Addition of 2×10^{-3} M $Ce_2(SO_4)_3$ suppresses the oxygen evolution. Here, illumination with visible light resulted in the formation of Ce^{IV}.

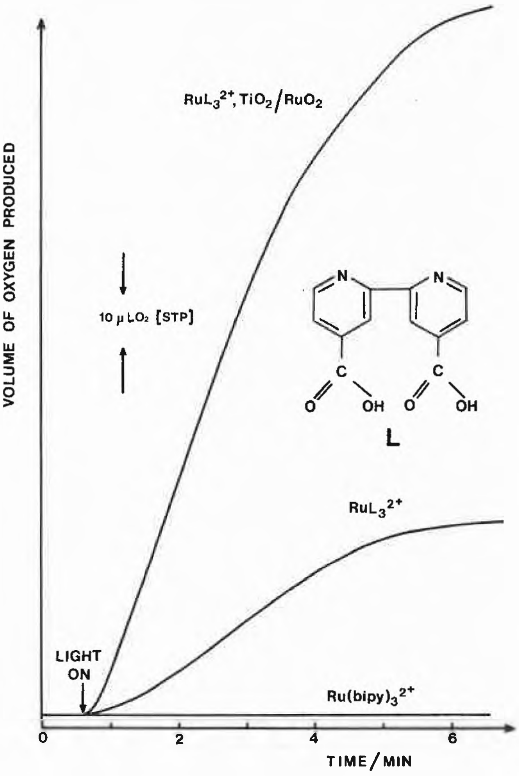

Fig. 1. Visible light induced oxygen evolution from aqueous solutions (0.5 M H_2SO_4) containing 10^{-4} M $[RuL_3]^{2\oplus}$ or $[Ru(bpy)_3]^{2\oplus}$ as a sensitizer and 2×10^{-2} M $S_2O_8^{2\ominus}$ as electron acceptor. The upper curve was obtained in the presence of 100 mg RuO_2/TiO_2 redox catalyst.

Addition of 100 mg RuO_2/TiO_2 increases the initial rate of O_2 generation to 35 µL/min. After 6 min the volume of oxygen present in solution is 130 µL and the total amount produced is 160 µL corresponding to a turnover number of 14 for $[RuL_3]^{2\oplus}$.

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Replacing $[RuL_3]^{2\oplus}$ by $[Ru(bpy)_3]^{2\oplus}$ resulted in the suppression of O_2 generation. Even in the presence of 100 mg TiO_2/RuO_2, we detected only traces of O_2 under illumination.

By analogy with $[Ru(bpy)_3]^{2\oplus}$ [6-8], the photoinduced reaction of $[RuL_3]^{2\oplus}$ with peroxodisulfate may be formulated as

$$2[RuL_3]^{2\oplus} + S_2O_8^{2\ominus} \xrightarrow{h\nu} 2[RuL_3]^{3\oplus} + 2SO_4^{2\ominus} \tag{1}$$

Subsequently, $[RuL_3]^{3\oplus}$ oxidizes water to oxygen:

$$4[RuL_3]^{3\oplus} + 2H_2O \rightarrow O_2 + 4[RuL_3]^{2\oplus} + 4H^{\oplus} \tag{2}$$

In the case of $[Ru(bpy)_3]^{2\oplus}$ the standard redox potential (E = 1.26 V (NHE)) is not sufficient to afford water oxidation at pH 0. However, due to the electron withdrawing property of the carboxylic acid ligand, the redox potential of the $[RuL_3]^{3\oplus}/[RuL_3]^{2\oplus}$ couple is 0.3 V more positive than that of the $[Ru(bpy)_3]^{3\oplus}/[Ru(bpy)_3]^{2\oplus}$ couple. From the cyclic voltammogram of a fresh solution of $[RuL_3]^{2\oplus}$ in 0.85 M H_2SO_4 shown in Fig. 2a, one derives a standard redox potential of 1.56 V (NHE). Interestingly, if such a solution is anodized at 1.64 V for ca. 60 min, one obtains a catalytic wave (Fig. 2b). The current rises in a sigmaoidal fashion to a plateau value, and the potential at which half of the limiting current flows corresponds to the standard redox potential of the $[RuL_3]^{3\oplus}/[RuL_3]^{2\oplus}$ couple, i.e. 1.56 V. The plateau current was little affected by the scanning speed. It increased from 23 to 27 µA upon increasing the scanning speed from 5 to 50 mV/s. Such a behavior is characteristic for a process where the reversible charge transfer at the electrode is coupled to a catalytic reaction in solution. The latter replenishes the reduced form of the sensitizer leading to higher oxidation currents than in the absence of catalyst and to the lack of a reduction wave during the cathodic scan. In such as case[9,10], the limiting current density is related to the rate constant for the catalytic reaction k_{cat} via

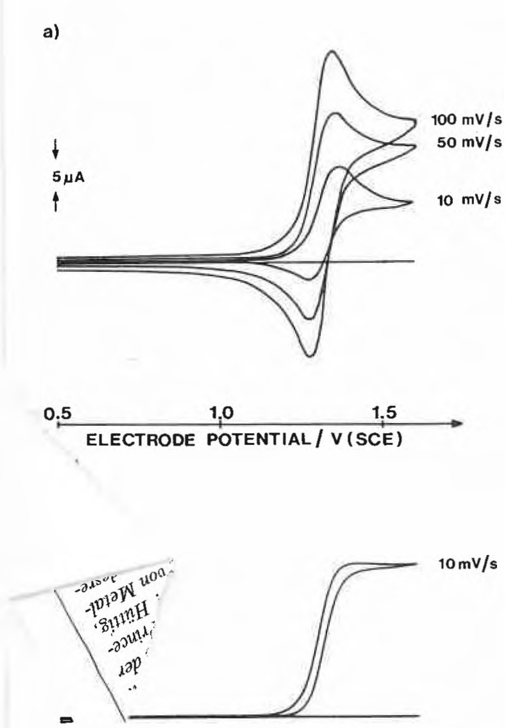

Fig. 2. Cyclic voltammetry of 4 × 10⁻⁴ M *$[RuL_3]^{2\oplus}$ solutions in 0.85* M *H_2SO_4: a) fresh solution; b) solution anodized at 1.4 V (SCE) for ca. 60 min. A conducting SnO_2 electrode (surface 0.66 cm²) was employed. The background current remained below 1 µA over the whole potential range investigated.*

$$i = n\,F\,c^0(D\,k_{cat})^{1/2} \tag{3}$$

where c^0 is the concentration of depolarizer in the bulk and D is its diffusion coefficient. Using $D = 3 \times 10^{-6}$ cm²/s, derived from Fig. 2a[11], one obtains $k_{cat} \simeq 0.3\ s^{-1}$.

The observation in Fig. 1 of visible light induced oxygen generation in $[RuL_3]^{2\oplus}$ solutions in the absence of RuO_2 can be rationalized in terms of an autocatalytic mechanism. It is suggested that a fraction of the $[RuL_3]^{3\oplus}$ produced via reaction (1) undergoes a chemical change giving rise to the formation of a molecular catalyst for water oxidation. Monomeric[12] and dimeric[13,14] ruthenium complexes derived from $[Ru(bpy)_3]^{2\oplus}$ have previously been shown to mediate oxygen evolution from water, and the catalyst operative in the present system could be structurally related to these species. Such a mechanism could explain the relatively low turnover number obtained in Fig. 1 since part of the sensitizer is used up for the generation of the catalyst[15]. Another possible reaction of $[RuL_3]^{2\oplus}$, which was found[7] to occur with $[Ru(bpy)_3]^{2\oplus}$, could be light-induced oxidation by peroxodisulfate. At present, it cannot be excluded that this reaction generates the water oxidation catalyst. A third possibility which may be envisaged is that the photoredox reaction of $[RuL_3]^{2\oplus}$ with $S_2O_8^{2\ominus}$ generates a catalyst for the thermal decomposition of peroxodisulfate into oxygen and sulfate. However, this pathway can be ruled out since oxygen generation stopped when the light was switched off, indicating that it is the redox reaction of the sensitizer which affords water oxidation.

The effect of Ce^III^, which suppresses photolytic oxygen generation in the absence of RuO_2/TiO_2, lends further support to this interpretation. Cerium(III) ions act as electron donors reducing $[RuL_3]^{3\oplus}$:

$$Ce^{3\oplus} + [RuL_3]^{3\oplus} \rightarrow Ce^{4\oplus} + [RuL_3]^{2\oplus} \tag{4}$$

In this way, Ce^{III} intercepts the formation of the water oxidation catalyst from $[RuL_3]^{3\oplus}$ preventing oxygen generation.

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[1] M. Grätzel: *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York 1983.
[2] D. Duonghong, E. Borgarello, M. Grätzel, *J. Am. Chem. Soc. 103* (1981) 4685.
[3] D. Duonghong, N. Serpone, M. Grätzel, *Helv. Chim. Acta 67* (1984) 1012.
[4] J. Desilvestro, M. Grätzel, L. Kavan, J. Moser, J. Augustynski, *J. Am. Chem. Soc.*, in press.
[5] $[RuL_3]^{2\oplus}$ $2Cl^{\ominus}$ was synthesized according to C. Foreman (Ph. D. Thesis, University of North Carolina, Chapel Hill NC, USA). We thank Prof. D. G. Whitten for providing us with a copy of this thesis.
[6] F. Boletta, A. Juris, M. Maestri, D. Sandini, *Inorg. Chim. Acta 44* (1980) L 175.
[7] M. Neumann-Spallart, K. Kalyanasundaram, C. K. Grätzel, M. Grätzel, *Helv. Chim. Acta 63* (1980) 1111.
[8] R. Humphry-Baker, J. Lilie, M. Grätzel, *J. Am. Chem. Soc. 104* (1982) 422.
[9] R. S. Nicholson, I. Shain, *Anal. Chem. 36* (1964) 707.
[10] J. M. Saveant, E. Vianello in I. S. Longmuir: *Advances in Polarography*, Vol. *I*, p. 367, Pergamon Press, New York 1960.
[11] A. J. Bard, L. Faulkner in: *Electrochemical Methods*, p. 218, Wiley, New York 1980.
[12] H. Nijs, M. Cruz, J. Fripiat, H. Van Damme, *Nouv. J. Chim. 6* (1982) 551.
[13] S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc. 104* (1982) 2049.
[14] K. Honda, A. J. Frank, *J. Chem. Soc. Chem. Commun.* (1984) 1635.
[15] The turnover number of $[RuL_3]^{2\oplus}$ is tripled by photolyzing solutions containing 5×10^{-5} M sensitizer and 8×10^{-3} M peroxodisulfate; J. Peterson, unpublished results.