The Photogeneration of Dihydrogen from Water Catalysed by Thin Films of Tris(bipyridine)ruthenium(II) Derivatives

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Irradiation with u.v.–visible light of a surface-active tris(bipyridine)ruthenium(II) derivative initially deposited as a supported monolayer on a glass slide and immersed in water produced dihydrogen; this process was accompanied by the migration of the ruthenium complex to another site within the experimental configuration; it redeposited onto the PTFE slide holder; this newly formed coating continued to act as an active catalyst; turnover numbers (H/Ru) of ca. 1400 were obtained after 260 h of irradiation.

Photochemical sensitizers based on the tris(bipyridine)-ruthenium(II) cation, $Ru(bpy)_3^{2+}$, have been extensively studied, especially in their application to the photolysis of water.[1,2] This sensitizer, in the form of the surface-active derivative bis(2,2'-bipyridine)(4,4'-dioctadecyloxycarbonyl-2,2'-bipyridine)ruthenium(II) perchlorate, (1), was reported to be able to photocleave water.[3] In that instance it appeared that the photolysis of water could proceed without the employment of either electron relays or other catalysts. Unfortunately those results could not be repeated by the original workers[4] or by several other groups.[5,6]

We have already investigated the photolysis of water using various monolayer assemblies of (1). Small amounts of dihydrogen were produced when some of these assemblies in water were illuminated by u.v.–visible light.[7] Subsequently we devised and studied a microheterogenous system comprising solid hydrocarbon particles, dispersed in water, which act as supports for the $Ru(bpy)_3^{2+}$ sensitizer. Again dihydrogen was generated on illumination of the suspension.[8] We found that dihydrogen formation is more efficient in deoxygenated photolytes because the dissolved dioxygen in normally aerated water inhibits the hydrogen-producing reaction. That led us to re-examine the irradiation of monolayer assemblies of (1) in deoxygenated photolytes.

Employing standard deposition techniques[7,9] a monolayer of (1) was deposited onto five layers of barium stearate–stearic acid, supported on a glass microscope slide which had

previously been rendered hydrophobic by polishing with iron(III) stearate powder. The surface pressure–area characteristics, together with the luminescence properties of our preparation of (1), have been reported previously.[7] 18 Slides were prepared in this fashion, and held parallel with 1 mm spacing in a polytetrafluoroethylene (PTFE) slide holder. This arrangement was immersed in the aqueous photolyte (AnalaR water) which had been nitrogen-purged. The results of the analysis of the gases collected, after various periods of illumination with a 500 W medium-pressure Hg lamp, are given in Table 1 and Figure 1. The turnover number (H/Ru), including dissolved gas, was ca. 1400 after 260 h.

(bpy)₂Ru CO_2R $]^{2+}(ClO_4^-)_2$ CO_2R
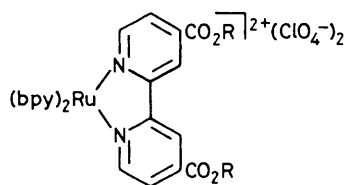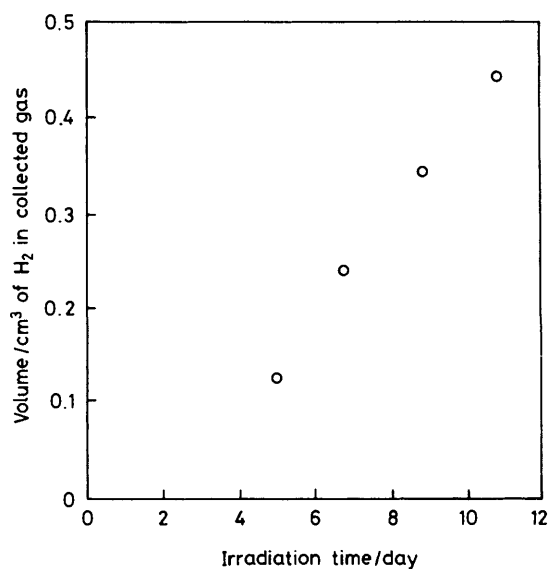
(1), R = $C_{18}H_{37}$

(2), R = H

Figure 1. Dihydrogen generation experiment with monolayers of (1) immersed in deoxygenated water and irradiated with a 500 W medium-pressure Hg lamp (18 microscope slides).
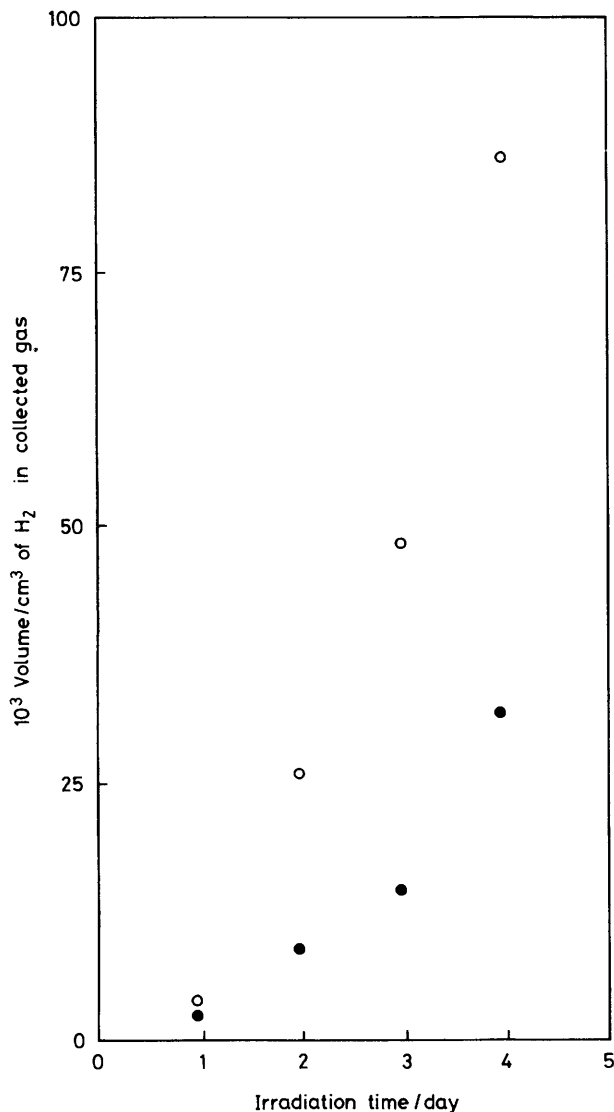
Figure 2. Dihydrogen generation experiment with PTFE sheet in aqueous deoxygenated solutions of (2); ○, initial irradiation with a 500 W medium-pressure Hg lamp; ●, re-irradiation in fresh deoxygenated photolyte.

Table 1. Gas chromatographic analysis of the gaseous products obtained from the u.v.–visible irradiation of glass-supported monolayers of complex (1) on barium stearate–stearic acid immersed in water.

Irradiation time/h	Volume/cm³ of gas collected	Detected gases as approximate percentage of the total volume[a]				
		H_2	O_2	N_2	CH_4	CO
120.0	3.00	4.3	0	101	0	1.2
162.5	1.00	11.2	0	81.9	0	1.4
212.0	0.75	13.9	0	90.7	0	1.1
260.0	0.50	19.9	0	68.3	0	1.5
120.0[b]	4.80	2.2	0	95.8	0.05	1.0
48.0[c]	1.05	0.17	13.9	80.1	0	0

[a] Differences from 100% are due to sampling technique or to the non-detection of other gas components. Gas component volumes determined by comparison with calibration samples and expressed as a percentage of the injected volume. [b] Re-irradiation of PTFE slide holder only; photolyte replaced by freshly deoxygenated AnalaR water. [c] Re-irradiation of PTFE slide holder only; photolyte replaced by normally aerated water.

At this stage the slides were removed from the reaction vessel and dried (vacuum desiccator). Spectroscopic examination of the slide surfaces showed no fluorescence activity, indicating the loss of sensitizer from the surface. Measurement of the photolyte pH after irradiation gave a value of 3.9 compared with an initial pH of 5.5. Visual inspection of the PTFE slide holder revealed a light brown colouration on surfaces that had been exposed to the most intense direct illumination: i.e. the surfaces directly opposite the glass envelope of the mercury lamp used for irradiation. The deposition of the sensitizer, or a derivative, appears to be the result of a photochemical reaction. If all the sensitizer initially deposited onto the barium stearate substrate had been uniformly transferred, then the visible film was ca. 55 monolayers thick.

Although the sensitizer had left the slide's surface, dihydrogen was still produced until the irradiation lamp was switched off. Therefore we placed the PTFE slide holder, without slides, in fresh deoxygenated photolyte and irradiated it for a further 120 h. Results of the analysis of the gas thus

collected are given Table 1; it can be seen that the irradiation of the coated slide holder produced an amount of dihydrogen comparable to that obtained previously.

This same coated component was further investigated as follows. The photolyte was again replaced, this time by aerated AnalaR-grade water. Upon irradiation the brown colour was rapidly lost from the holder's surfaces. Results of the analysis of the evolved gases after 48 h are shown in Table 1. Very little dihydrogen was detected, but the amount of dioxygen collected was less than that expected for outgassing from the given volume of aerated water. Therefore the loss of sensitizer from the PTFE surface was associated with the decrease in the amount of dissolved dioxygen in the photolyte. Calculation indicates an O_2/Ru turnover number of between 200 and 400 for the dioxygen depletion. From a comparison of this observation with those quoted above for H_2 evolution, we infer that dioxygen is not a product of the hydrogen-producing reaction.

The most likely first step in the transfer of ruthenium(II) from monolayer to PTFE is the ester hydrolysis of the surfactant to give the water-soluble diacid complex (2), bis(2,2′-bipyridine)(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) perchlorate.[10] To test this possibility we irradiated a flat rectangular sheet of PTFE (0.79 mm thickness; 250 × 45 mm²) in a deoxygenated aqueous solution of (2) $(1.56 \times 10^{-6}$ mol dm$^{-3})$. The plane of the sheet was placed normal to the principal axis of the Hg lamp. A plot of the volume of dihydrogen produced vs. time over a 4-day irradiation period is shown in Figure 2. The volume of dihydrogen after 4 days was comparable to that produced over a similar period in the previous experiment. The turnover number (H/Ru) was ca. 34. This is less than that in the monolayer experiment because more complex was present and it may not all have been photodeposited. However, dihydrogen was still produced with a turnover number in excess of unity and, as before, small amounts of carbon monoxide and methane were also detected.

Again the photolyte was replaced by fresh deoxygenated water and the experimental configuration was re-irradiated for 4 more days. The rate of dihydrogen formation is shown in Figure 2. It is approximately half that for the previous irradiation. We are not yet certain of the cause of this decline

in productivity. Figures 1 and 2 show induction periods before significant amounts of dihydrogen are produced, indicative of the time needed for the photochemical deposition of the sensitizer. As expected, the induction period was shorter when we began with a solution of the diacid complex (2). Visual inspection of the PTFE sheet after irradiation revealed a slight brown deposit on the side of the sheet facing the source of illumination, the colour being most intense opposite the middle of the lamp.

In the course of our continuing studies of the experimental conditions required to optimise the dihydrogen yield these observations have been reproduced many times. Additionally, an isotope experiment using D_2O as photolyte was carried out. High resolution mass spectral analysis of the gaseous products revealed D_2 with no increase in the H_2^+ ion peak relative to the background spectrum. This observation suggests that water is the source of the dihydrogen.

To summarise, dihydrogen was obtained from the u.v.–visible illumination of a $Ru(bpy)_3^{2+}$ sensitizer, constrained in a monolayer assembly, immersed in water. If the photodeposition of the sensitizer (or some compound derived from the latter) onto the PTFE slide holder had not occurred over a relatively small area, producing an intense colouration, then we might have assumed that the original monolayer had been solely responsible for the dihydrogen production. Our observations may explain the successful, but irreproducible, observations of other workers in this area of monolayer research. Admittedly a prerequisite for dihydrogen generation here is the use of deoxygenated photolyte, but during our investigation of $Ru(bpy)_3^{2+}$ octadecane dispersions we recorded two

high-hydrogen-yield experiments (turnover numbers for H/Ru >1000 after 40 h) in normally aerated water.[8] It is thus possible that a similar phenomenon could occur with single experiments involving the irradiation of such a monolayer assembly.

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