Attempts to Observe the Photocleavage of Water in the Presence of a Ruthenium Complex

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Abstract

Attempts to obtain the results claimed by Whitten *et al.*[1] for the photocleavage of water in the presence of a ruthenium complex have been unsuccessful. The reaction conditions are described in detail.

Recently Whitten *et al.*[1] reported the decomposition of water induced by the irradiation of monolayers of the ruthenium complex (4,4'-dioctadecyloxycarbonyl-2,2'-bipyridine)bis(2,2'-bipyridine)ruthenium(II) perchlorate (1) but the reaction was not reproducible.[2,3] We have done similar experiments and found no evidence of hydrogen produced in this way. Luminescence of monolayer films of (1) on glass substrates was partly quenched by water and could be partly restored on drying. Although a very small amount of hydrogen was evolved on illumination of the slides in water, 'blank' experiments showed that, under the experimental conditions used, most, if not all, of this hydrogen was derived from processes other than photocleavage of water by the ruthenium complex.

The ruthenium complex (1) was synthesized essentially by the method given by Whitten *et al.*[2] from *cis*-dichlorobis(bipyridine)ruthenium (recrystallized twice from acetone) and dioctadecyl 2,2'-bipyridine-4,4'-dicarboxylate (recrystallized from chloroform), sodium perchlorate being used to begin precipitation of (1). The complex (1) was purified by two recrystallizations from AR acetone. It had an absorption spectrum in chloroform similar to Whitten's[2] (λ_{max} 287, 314, 362, 432, 474 nm and an emission maximum at 654 nm in chloroform solution). Analysis of (1) by thin-layer chromatography (Merck SiO_2 and Al_2O_3, elution with methanol) and Sephadex LH-20 (elution with AR acetone, chloroform and ethanol) detected only one component. A minor impurity, however, was shown to be present from the p.m.r. spectra ($CDCl_3$/$SiMe_4$): small signals were observed at δ 5·12, 7·32, 8·76. These signals appeared to be related. Elementary analysis of (1) gave C, 58·9; H, 7·2; Cl, 4·9; N, 5·8; calc. for $C_{68}H_{96}Cl_2N_6O_{12}Ru$: C, 60·0; H, 7·1; Cl, 5·2; N, 6·2%.

[1] Sprintschnik, G., Sprintschnik, H. W., Kirsch, P. P., and Whitten, D. G., *J. Am. Chem. Soc.*, 1976, **98**, 2337.
[2] Sprintschnik, G., Sprintschnik, H. W., Kirsch, P. P., and Whitten, D. G., *J. Am. Chem. Soc.*, 1977, **99**, 4947.
[3] Valenty, S. J., and Gaines, G. L., Jr, *J. Am. Chem. Soc.*, 1977, **99**, 1285.

Monolayer assemblies of (1) were prepared on Corning 7059 glass slides. These slides were used as supplied, except that a high-pressure nitrogen jet was used to remove dust particles. The slides were withdrawn at a rate of $2 \cdot 4$ mm/min through a monolayer of (1). This was formed by spreading a $6 \cdot 6 \times 10^{-4}$ M solution of (1) in dichloromethane and n-hexane (1 : 1 by volume) on triply distilled water containing $CdCl_2$ ($2 \cdot 5 \times 10^{-4}$ M) and $NaHCO_3$ (2×10^{-5} M).* The dichloromethane/n-hexane mixture was substituted for chloroform[2] as the solvent as it readily dissolved (1) (the concentration used was indefinitely stable) and it spread well on water to give a monolayer. We had trouble spreading chloroform and dichloromethane solutions, these being denser than water. The surface pressure was kept constant at 40 mN m^{-1} throughout the process. The surface pressure–area isotherms were similar to those obtained by Whitten[2] although numerical values differed: (1) had an area per molecule of 70 Å^2 at a surface pressure of 30 mN m^{-1} whereas Whitten's original sample had an area per molecule of c. 40 Å^2 at the same pressure.

After each recrystallization of (1) monolayered slides were prepared. When these were used, the results of luminescence and gas evolution experiments were found to be independent of the purification process. Quantitative measurements of the luminescence of the monolayered slides were made by using the 476 nm line from an argon laser and a photoemissive tube (Mullard type 92AV) connected to a phase sensitive detector. The luminescence of monolayered slides was quenched, on average, by 68% on immersion in water and could be regenerated to 50% of its original value by heating at 58° for 7 h at 10 Torr. On further immersion in water the luminescence was quenched again to its previous value. Slides which had three monolayers deposited on them gave similar results to the monolayered slides although the luminescence was about three times as great. The quenching was not as high as that stated by Whitten[2] for his purified complex; in no case was quenching observed to be 100% nor was regeneration 100%. A further problem was revealed by the following observation: after prolonged irradiation the monolayered slides still exhibited some luminescence, although it was partial and non-uniform; this indicated that the monolayers had been destroyed or removed from the slides in the area on which the light beam had been incident.

In our first experiments, a glass reaction vessel joined by means of a neoprene O-ring to the evacuation system was used. This vessel proved unsatisfactory in that hydrogen was obtained even when no slides coated with (1) were present. The amount of hydrogen was similar to that shown in (ii) of Table 1; in addition the neoprene seemed to be responsible for the relatively large amounts of other gases detected.

A glass reaction vessel, with a greased glass joint, containing water and a glass slide holder with room for ten slides was used thereafter in all gas evolution experiments. The vessel was evacuated until the water was degassed. After irradiation by a 150-W xenon lamp, the vessel was re-evacuated by means of an automatic Toepler pump. The gas collected was analysed in a mass spectrometer (A.E.I. MS10) set up for analysing small quantities of gas. The maximum volume of gas collected in any experiment was about $0 \cdot 001$ cm^3 (s.t.p.). We also analysed the gases evolved from samples of the same grease which had been used in other experiments merely to seal

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the reaction vessel (Table 1). Such grease samples were contained in glass capillary tubes placed inside an evacuated glass tube.

Table 1. Results of mass spectrometer analysis of evolved gas

(i) Apiezon L grease, irradiated 50 h; (ii) silicone grease, irradiated 50 h; (iii) reaction vessel with silicone grease joint unshielded containing H_2O, irradiated 90 h; (iv) reaction vessel with silicone grease joint shielded containing D_2O, irradiated 90 h; (v) reaction vessel with silicone grease joint shielded containing 10 monolayers of (1) in D_2O, irradiated 200 h

m/e	Species	Net output (samples less background)/mV
		(i)	(ii)	(iii)	(iv)	(v)
2	$H_2{}^+$	413	130	2000	59	103
3	HD^+	—	—	—	2·3	8·3
4	$D_2{}^+$	—	—	—	2·5	10·6

In Table 1, 100 mV H_2 corresponds to approximately 10^{-9} mol H_2, so that 2×10^7 photons gave rise to one molecule of H_2. Species having $m/e > 12$ were also analysed to ensure that the system was reasonably well outgassed and vacuum tight. Small amounts of oxygen were detected by the mass spectrometer but this probably arose from residual air as the net output value was similar for all experiments.

Gas evolved from the prolonged irradiation of ten monolayered slides in water was attributed to the grease used in the glass joint. The amount of gas evolved from the grease was reduced by using silicone grease instead of Apiezon L grease (cf. (i) and (ii) in Table 1) and by shielding the greased joint from the light with aluminium foil (cf. (iii) and (iv)).

In order to determine whether any hydrogen detected came from the water, D_2O (99·75%) was used in place of H_2O in some experiments. No D_2 was evolved from the grease (cf. (i) and (ii)). In (iv) and (v), although hydrogen was still present, there was almost no D_2.

It has not been possible to reproduce the early results of Whitten[1] for gas evolution. Any gas evolution we observed and analysed in this series of experiments can be accounted for by the degassing and decomposition of the grease. Our employment of vacuum techniques would have given much greater sensitivity in the detection of evolved gases than the observation of gas bubbles.[1-3]

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