Short Communication

Photoproduction of hydrogen from reductive quenching of a water-soluble zinc porphyrin

ANTHONY HARRIMAN and MARIE-CLAUDE RICHOUX

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)

(Received November 17, 1980)

1. Introduction

Over the past few years there have been numerous reports describing photochemical systems capable of the production of hydrogen from water at the expense of consuming an organic substrate. The essential features of such systems [1 - 4] are contained in the following scheme:

$$S^* + A \rightarrow S^+ + A^-$$
$$S^+ + D \rightarrow S + D^+$$
$$2A^- + 2H^+ \rightarrow 2A + H_2$$
$$D^+ \rightarrow \text{products}$$
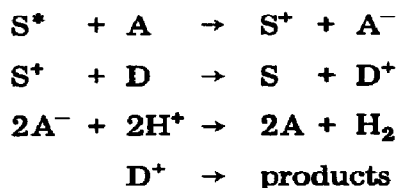
where S refers to the photosensitizer, A and D are electron acceptors and electron donors respectively and the electron exchange reaction between A^- and water usually requires a catalyst. In most systems tris(2,2'-bipyridyl)-ruthenium(II) ($(bipy)_3Ru^{2+}$) is used as the photosensitizer whilst methyl viologen (MV^{2+}) has enjoyed universal appeal as the electron acceptor and, under optimized conditions, the quantum yield $\phi_{1/2H_2}$ for the formation of hydrogen from this system approaches 0.3. A more promising system is that proposed recently by Kalyanasundaram and Gratzel [5] and subsequently developed in our laboratory [6], in which the $(bipy)_3Ru^{2+}$ photosensitizer was replaced with a water-soluble zinc porphyrin (zinc tetramethylpyridyl-porphyrin ($ZnTMPyP^{4+}$) (Fig. 1)) and used ethylenediaminetetraacetic acid (EDTA) as the irreversible donor D. This system gave $\phi_{1/2H_2} = 0.6$ whilst the porphyrin with its strong absorption throughout the visible region has genuine application to solar energy storage devices. Moreover, during the course of our investigations [6] it was observed that hydrogen formation occurred even in the absence of the electron acceptor and in this paper we describe our results concerning this effect.
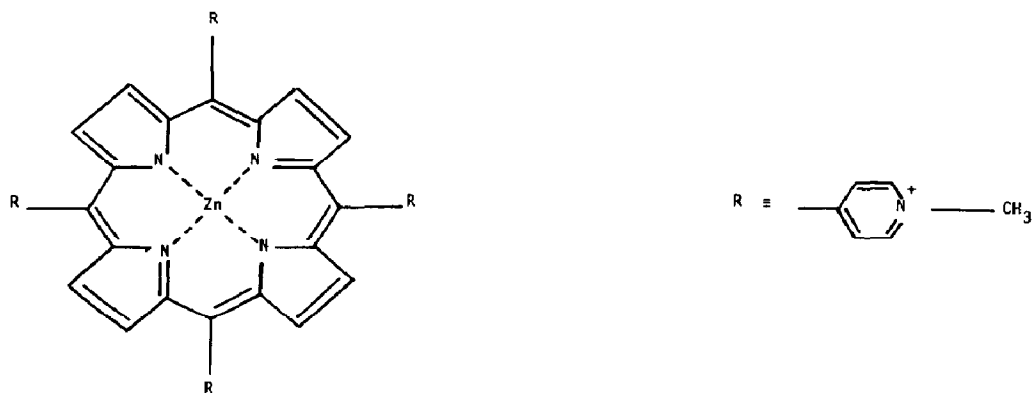
Fig. 1. The structure of ZnTMPyP^{4+}.

2. Experimental

ZnTMPyP^{4+} was prepared and purified as described in ref. 6 whilst EDTA (sodium salt) was obtained from BDH and used as received. Water was redistilled from an alkaline permanganate solution and all solutions were prepared to have a final pH of 5.5 using a phosphate buffer. Flash photolysis experiments were performed with a conventional instrument (Applied Photophysics model K2) using an aqueous chromate solution to remove excitation light of $\lambda < 440$ nm. In all cases the solutions contained ZnTMPyP^{4+} (4 $\times$ 10^{-6} M) and were outgassed using the freeze–pump–thaw method. Steady state irradiations were carried out using a Bausch and Lomb monochromator to isolate a spectral region of 550 $\pm$ 30 nm. The concentration of hydrogen was determined by gas chromatography using the conditions recommended by Valenty [7].

The platinum catalyst, which was supported on polyvinyl alcohol (PVA) (molecular weight, 16 000), was prepared from H$_2$PtCl$_6$ using the methods suggested by Rampino and Nord [8]. The effective particle size was measured by Dr. J. Kiwi (Ecole Polytechnique Fédérale de Lausanne) using the light-scattering technique.

3. Results and discussion

In ref. 6 we described the photophysical properties of ZnTMPyP^{4+} in dilute aqueous solution and we noted that the short singlet lifetime ($\tau_S = $ 1.4 ns) precluded singlet state photochemistry except at extremely high quencher concentrations. However, the triplet state was found to possess a relatively long lifetime ($\tau_T = 655$ μs) so that bimolecular reactions could compete with non-radiative decay. In fact the triplet state quenching rate constant for reaction with EDTA was found to be 1.1×10^5 M^{-1} s^{-1} at a fixed ionic strength of 0.05. Flash photolysis experiments have demonstrated that this triplet quenching reaction leads to the formation of the one-electron reduction product of the zinc porphyrin so that the reaction may be written as

$$*ZnTMPyP^{4+} + EDTA \rightarrow ZnTMPyP^{3+} + EDTA^{+}$$

$$EDTA^{+} \rightarrow products$$
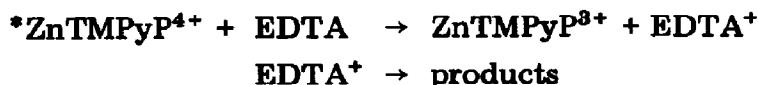
The decay of $ZnTMPyP^{3+}$ was found to follow second-order kinetics, presumably because of dismutation:

$$2ZnTMPyP^{3+} \rightleftharpoons ZnTMPyP^{4+} + ZnTMPyP^{2+}$$

In fact, steady state irradiation of $ZnTMPyP^{4+}$ in the presence of excess EDTA (0.1 M) resulted in the formation of the dihydroporphyrin ($ZnTMPyP^{2+}$), as monitored by absorption spectroscopy [9]. On prolonged irradiation the dihydroporphyrin product was reduced further to the tetrahydroporphyrin and the hexahydroporphyrin and the solution became bleached. Under these conditions the quantum yield ϕ_{BL} for the bleaching process was found to be 0.08.

In the presence of a Pt–PVA catalyst ϕ_{BL} was lowered as shown in Fig. 2. Although quite low concentrations of platinum restricted the amount of bleaching, it required very high platinum concentrations for complete inhibition of the photoreduction reaction. In the presence of Pt–PVA hydrogen was detected as a reaction product and the observed quantum yields $\phi_{1/2H_2}$ are also given in Fig. 2. At moderate concentrations of platinum there is a rough correlation between ϕ_{BL} and $\phi_{1/2H_2}$ in that more hydrogen is produced as the bleaching process is inhibited. At very high platinum concentrations the value of $\phi_{1/2H_2}$ observed falls but this may be because of adsorption of H_2 onto the catalyst surface. In the absence of platinum, EDTA or $ZnTMPyP^{4+}$ no hydrogen was produced and addition of Pt–PVA to a photolysed solution did not lead to the generation of hydrogen. Thus, platinum must intercept one of the intermediate species involved in the bleaching reaction and must mediate hydrogen production from water using this intermediate.
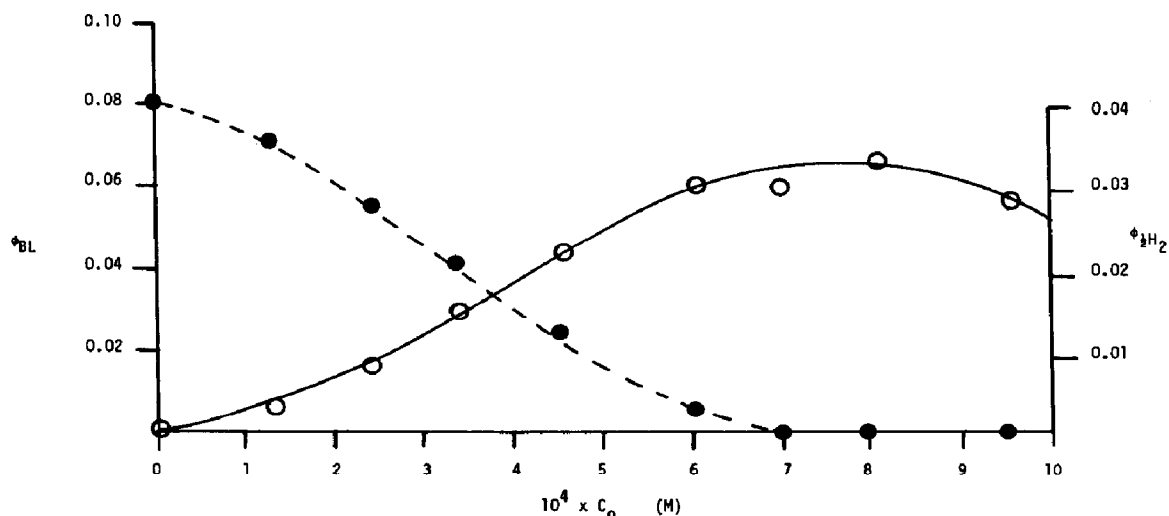

Fig. 2. The effect of Pt–PVA concentration on the quantum yields for the bleaching process (●) and for the formation of hydrogen (○).
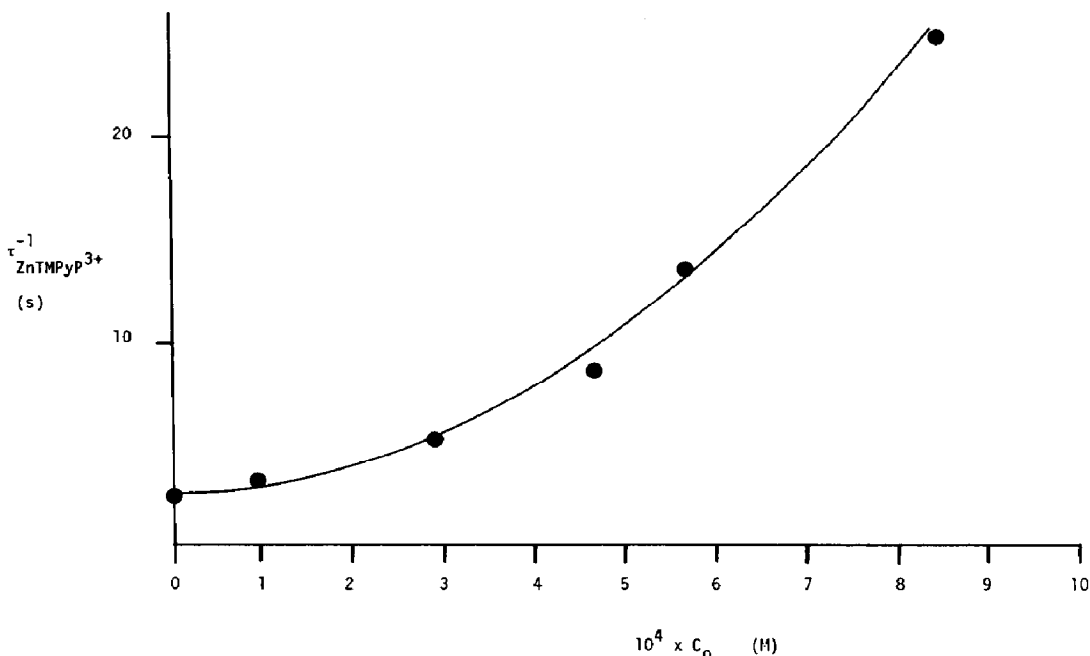
Fig. 3. The effect of Pt–PVA concentration on the half-life of ZnTMPyP^{3+}.

From flash photolysis studies it was found that the presence of Pt–PVA did not affect the yield of ZnTMPyP^{3+} but it did shorten its lifetime. This effect is shown in Fig. 3 and demonstrates clearly that the species responsible for the production of hydrogen is the one-electron reduction product of the zinc porphyrin. In the absence of platinum the half-life of ZnTMPyP^{3+} is quite short, because of the dismutation reaction, so that there is a limited time period available for the radical to reach a platinum particle. Therefore, to ensure that the majority of the ZnTMPyP^{3+} radicals produced in the photochemical reaction are used for hydrogen generation it is necessary to use a very high concentration of platinum. In this respect this system compares unfavourably with the corresponding system [6] containing MV^{2+} as the electron acceptor since in the MV^{2+} system the species responsible for hydrogen generation (MV^{+}) has a lifetime in excess of 1 h, and hence low concentrations of platinum can be used.

Of the total amount of platinum in the solution most is present in an inactive form since only the platinum that is freely exposed to the solution can form an active site. Thus an active site can be viewed as a small exposed region of a large particle. Unfortunately the particle size of our Pt–PVA was quite large; the effective radius was about 30 nm. For this radius the aggregation number [10] was calculated to be 7×10^6 so that the molar concentration of Pt–PVA particles can be expressed as

$$[\text{Pt–PVA}] = C_0/n$$

where C_0 is the total concentration of platinum in the solution (measured in moles per litre) and n is the aggregation number [10]. The rate of diffusional

encounter between an organic radical such as $ZnTMPyP^{3+}$ and a Pt—PVA particle of radius 30 nm was calculated [10] to be about 2.8×10^{11} (molar particles)$^{-1}$ s^{-1} so that for the Pt—PVA particle to compete favourably with the dismutation reaction by intercepting $ZnTMPyP^{3+}$ the total concentration of platinum in the solution must exceed 5×10^{-4} M. In fact, as shown in Figs. 2 and 3, we found that efficient production of hydrogen requires somewhat higher concentrations of platinum so that $ZnTMPyP^{3+}$ must, on average, encounter several Pt—PVA particles before it finds an active site.

In the presence of the optimum concentration of Pt—PVA ($C_0 = 8 \times 10^{-4}$ M) prolonged irradiation of an outgassed aqueous solution of $ZnTMPyP^{4+}$ (2×10^{-5} M) at pH 5.5 containing EDTA (0.1 M) gave a considerable quantity of hydrogen. In a separate experiment the hydrogen evolved was removed periodically by flushing with argon (to minimize hydrogenation of the porphyrin) and the solution was irradiated ($\lambda = 550$ nm) for 24 h. The total amount of hydrogen produced corresponded to a turn-over with respect to $ZnTMPyP^{4+}$ in excess of 10^3. The longevity of this system was slightly better than that of the $ZnTMPyP^{4+}$—EDTA—MV^{2+} system [6] so that, although $\phi_{1/2H_2}$ for the $ZnTMPyP^{4+}$—EDTA—MV^{2+} system was the higher of the two, the total amounts of hydrogen obtained from exhaustive photolyses were comparable for the two systems. However, the high concentration of platinum required for the $ZnTMPyP^{4+}$—EDTA system is a serious drawback to applying the system to a practical solar energy storing device. To overcome this problem we are extending our studies in three directions.

(1) We have synthesized platinum catalysts with much smaller effective radii (about 3 - 4 nm).

(2) We have synthesized zinc porphyrins which should show less inclination towards dismutation.

(3) We are in the process of designing porphyrin—Pt systems where encounter between a platinum particle and a reduced porphyrin is favoured by steric and electrostatic factors.

We shall report our results with these modified systems in a later paper.

1 B. V. Koryakin, T. S. Dzhabiev and A. E. Shilov, *Dokl. Akad. Nauk S.S.S.R., 238* (1977) 620.
2 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim., 1* (1977) 441.
3 K. Kalyanasundaram, J. Kiwi and M. Gratzel, *Helv. Chim. Acta, 61* (1978) 2720.
4 A. Moradpour, E. Amouyal, P. Keller and H. Kagan, *Nouv. J. Chim., 2* (1978) 547.
5 K. Kalyanasundaram and M. Gratzel, *Helv. Chim. Acta, 63* (1980) 478.
6 A. Harriman, G. Porter and M.-C. Richoux, *J. Chem. Soc., Faraday Trans. II*, in the press.
7 S. J. Valenty, *Anal. Chem., 50* (1978) 669.
8 L. D. Rampino and F. F. Nord, *J. Am. Chem. Soc., 63* (1941) 2745.
9 G. R. Seely and K. Talmadge, *Photochem. Photobiol., 3* (1964) 195.
10 A. Henglein, *J. Phys. Chem., 83* (1979) 2209.