

Short Communication

**Photochemistry of manganese porphyrins
V: The photoreduction of methyl viologen**

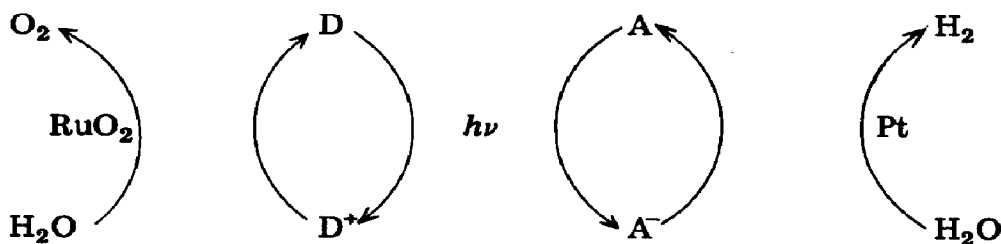
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In recent years many schemes have been proposed for the photochemical production of hydrogen or oxygen from water using two- and three-component systems [1]. One of the most important features of such systems has been the use of an irreversible redox couple (*e.g.* ethylenediaminetetraacetic acid, cysteine, persulphate, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$) to minimize reverse electron transfer so that hydrogen or oxygen is produced at the expense of consuming some sacrificial compound. These separate systems have been refined to a high degree but before they can be used in practical systems for the collection and storage of solar energy it is necessary that two such systems are coupled together so that the photodissociation of water into hydrogen and oxygen can be realized without the consumption of a sacrificial redox couple.

The simplest system for the photosensitized dissociation of water into hydrogen and oxygen is given in the following scheme:

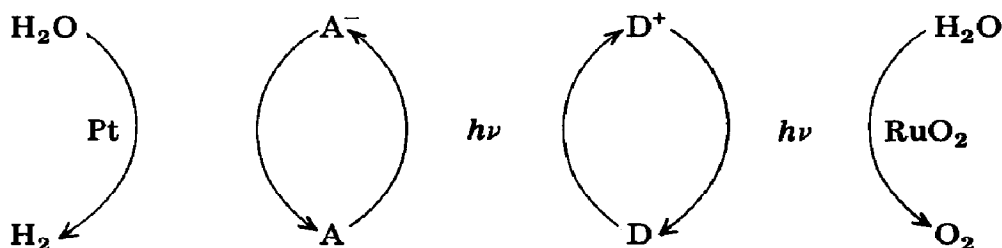


In this scheme light is used to drive an endergonic electron transfer reaction between a donor D and an acceptor A . The key feature of the scheme is that the products D^+ and A^- are capable of the oxidation and reduction of water respectively when suitable catalysts are incorporated into the system. For efficient photodissociation of water it is essential that the catalysts are specific and that they can compete with reverse electron transfer between D^+ and A^- . Despite the obvious problems it has been found that, under certain conditions, the photoredox reaction between tris(2,2'-bipyridyl)ruthenium(II)

($\text{bipy}_3\text{Ru}^{2+}$) and methyl viologen (MV^{2+}) can be used for the simultaneous production of hydrogen and oxygen from water [2] although the yield of gaseous products remains very low.

Even if the efficiency of this overall process can be improved by the development of more selective catalysts, the $\text{bipy}_3\text{Ru}^{2+}$ chromophore is not capable of collecting a high fraction of the solar spectrum. However, the replacement of $\text{bipy}_3\text{Ru}^{2+}$ with an electron donor having a better absorption profile is not a straightforward matter since there are very few compounds possessing the thermodynamic potential to oxidize water to oxygen that have favourable absorption spectra. Although the $\text{bipy}_3\text{Fe}^{2+/3+}$ redox couple has a suitable absorption profile and redox potential [3], the very short lifetime of $\text{bipy}_3\text{Fe}^{2+}$ is not conducive to photosensitization.

To improve the spectral properties of these systems it may be necessary to use a two-photon system. The following scheme shows one such system:



The difference between this scheme and the one-photon scheme is that here the oxidized electron donor D^+ is not capable of the thermal oxidation of water. Instead a second photon is required to provide the necessary oxidizing potential so that this step involves the photooxidation of water. Unfortunately there are very few compounds capable of the photooxidation of water using visible light excitation; however, in previous work [4] we have found that manganese porphyrins are photoreduced in outgassed aqueous solution. In other work [5] it has been shown that this photoreduction process is accompanied by the formation of H_2O_2 and this suggests that manganese porphyrins may be suitable chromophores for two-photon systems.

The stable oxidation state of a manganese ion contained within a porphyrin ring is +3 but this can be reduced to +2 by reaction with a suitable reducing agent [6]. A similar reduction was achieved by the irradiation of manganese(III) porphyrins in outgassed aqueous solution [4] and Fig. 1 shows the absorption spectral profile for the prolonged irradiation of manganese(III) tetra(4-pyridyl) porphine (Mn(III)TPyP) in water at pH 11. The reaction corresponds to



and in previous work Glikman and Zabroda [5] have found that some, if not most, of the hydroxyl radicals combine to form H_2O_2 . (We cannot confirm this finding because of the low concentrations of products involved in our

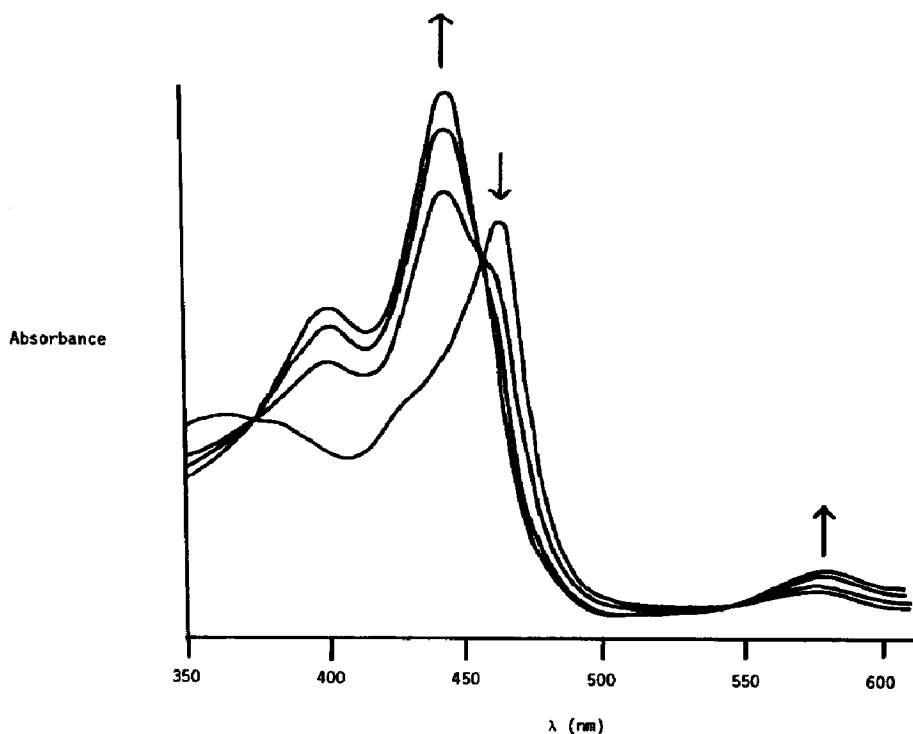


Fig. 1. Photoreduction spectra of Mn(III)TPyP in outgassed aqueous solution at pH 11 before irradiation and at irradiation times of 60, 90 and 120 min.

work.) The manganese(II) product was unstable with respect to atmospheric oxygen and on aeration of the solution manganese(III) was regenerated without loss.

The quantum yield ϕ_R was extremely low and was dependent on pH (Fig. 2). Even under optimum pH conditions the photoreduction was inefficient and long irradiation periods were required. Under these conditions the manganese(II) product was stable towards photoreduction and there was no loss of the porphyrin chromophore, as measured by absorption spectroscopy.

On prolonged irradiation of Mn(III)TPyP in aqueous solution at pH 6 in the absence or the presence of MV^{2+} (0.1 M) there was no observable change in the absorption spectrum. Under these conditions there was no formation of Mn(II)TPyP and no formation of reduced MV^{2+} . Furthermore, no transient formation of MV^+ was detected in flash photolysis experiments and we conclude that, under our experimental conditions, Mn(III)TPyP does not photoreduce MV^{2+} .

In contrast, the irradiation of Mn(III)TPyP in aqueous solution at pH 11 in the presence of MV^{2+} (0.1 M) resulted in the formation of MV^+ , as shown in Fig. 3. The yield of MV^+ was low and the form of Fig. 3 suggested that it was formed after the manganese(III) porphyrin had been photoreduced to the manganese(II) porphyrin. On prolonged irradiation a steady state yield of MV^+ was reached and, under such conditions, all the manganese porphyrin present in the system was in the form of Mn(II)TPyP.

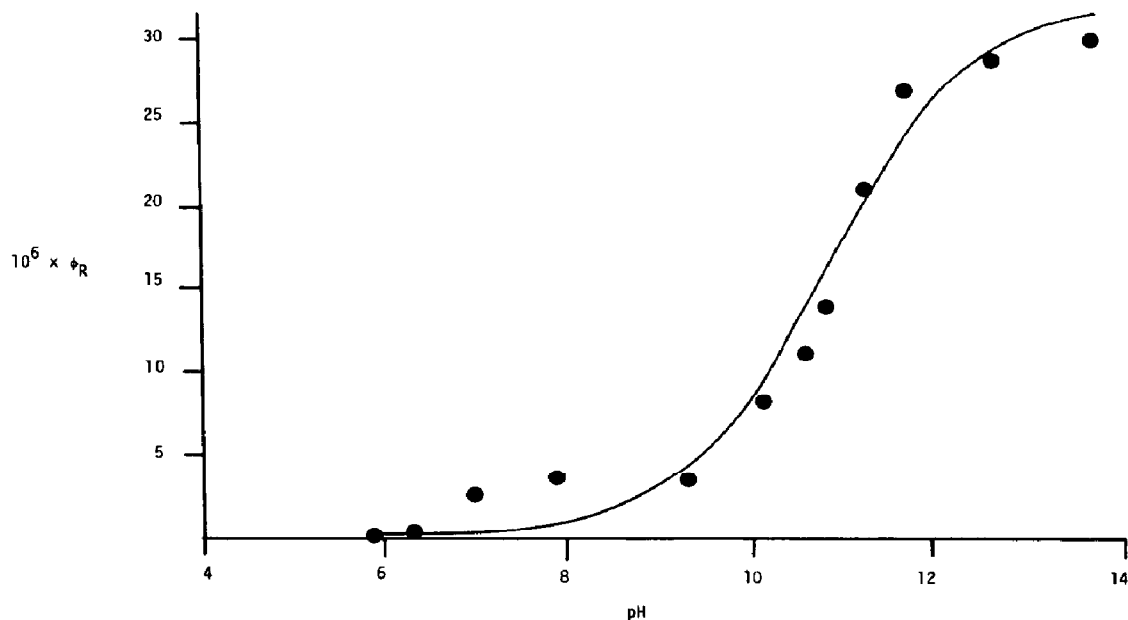


Fig. 2. The effect of pH on the quantum yield for photoreduction of Mn(III)TPyP in out-gassed aqueous solution.

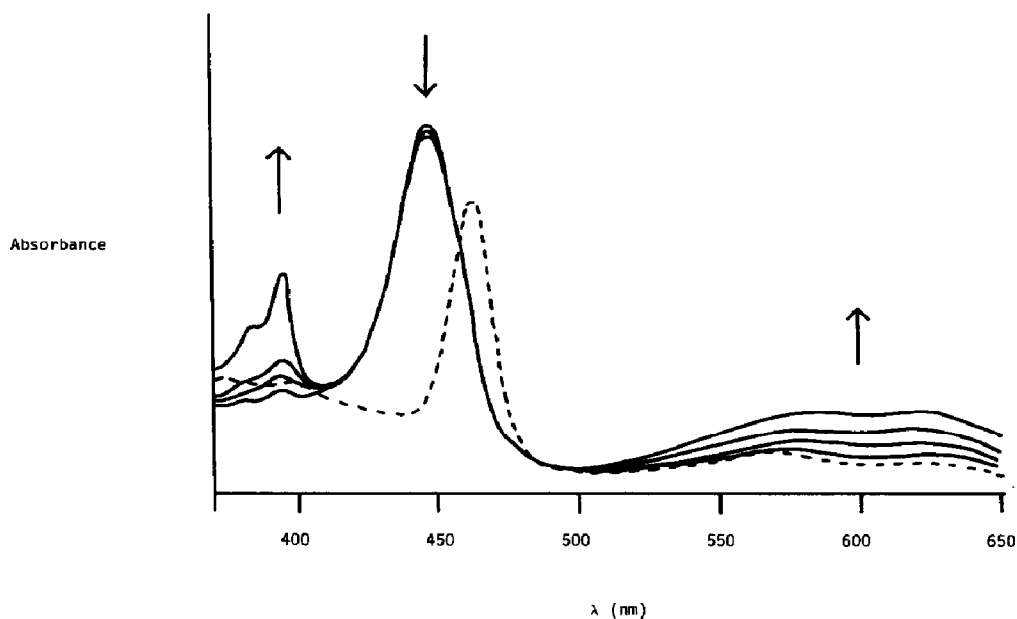


Fig. 3. Photoreduction spectra of Mn(III)TPyP in outgassed aqueous solution at pH 11 containing MV^{2+} (0.1 M) before irradiation (---) and at irradiation times of 60, 120, 240 and 600 min.

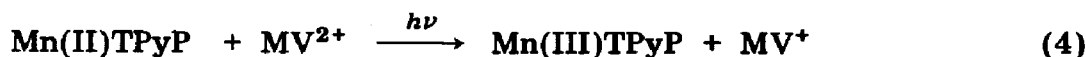
In separate experiments it was shown that there was no thermal reduction of MV^{2+} by Mn(II)TPyP in aqueous solution at pH values below 11. However, using the flash photolysis technique it was found that the excita-

tion of Mn(II)TPyP in aqueous solution (in the pH range 7 - 11) containing MV^{2+} (0.1 M) resulted in the transient formation of MV^+ and Mn(III)TPyP according to eqn. (2):

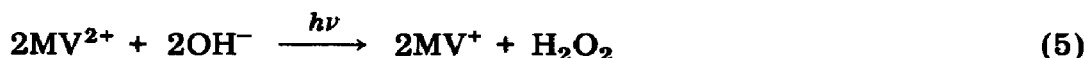


The reaction was completely reversible and the addition of MV^+ to an out-gassed solution of Mn(III)TPyP resulted in quantitative conversion to Mn(II)TPyP. The bimolecular rate constant for this reduction process, measured from the flash photolysis studies, was found to be about $10^4 \text{ M}^{-1} \text{ s}^{-1}$.

Based on these experimental findings the overall reaction scheme for the irradiation of Mn(III)TPyP in aqueous solution at pH 11 containing MV^{2+} can be written as follows:



If the findings of Glikman and Zabroda [5] are incorporated, there must be some combination of the hydroxyl radicals to give H_2O_2 so that the overall reaction can be expressed as



In principle, this manganese-porphyrin-photosensitized electron transfer from water to MV^{2+} fulfils the basic requirements for a two-photon dissociation of water into hydrogen and oxygen since it has been established [7] that, in the presence of a suitable catalyst, MV^+ will reduce water to hydrogen whilst the decomposition of H_2O_2 to oxygen has been known for a long time. However, there are many factors that count against the use of manganese porphyrins as photosensitizers for such processes. In particular the yield of products is extremely low and, in our experiments, the yield of H_2O_2 was too low to be detected. Furthermore, the reaction requires strongly alkaline conditions and, in such an environment, MV^+ does not possess sufficient reducing potential for the production of hydrogen, even in the presence of a catalyst. Thus, the MnTPyP- MV^{2+} system shows little promise for the photodissociation of water into hydrogen and oxygen.

Acknowledgment

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