

Short Communication

Attempted photo-oxidation of water to oxygen using zinc(II) porphyrins

ANTHONY HARRIMAN, GEORGE PORTER and PHILIP WALTERS

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

(Received November 11, 1981)

The photodissociation of water into H_2 and O_2 using visible light excitation presents severe experimental difficulties but, if these problems can be solved, a successful system may have genuine application as a solar energy storage device. At the present time, two major approaches towards the photodissociation of water in non-electrochemical systems are being advocated. One approach involves irradiation of a semiconductor powder, either with band gap excitation or with dye sensitization, but such systems generate a mixture of H_2 and O_2 that must be separated. The other approach, which has been less successful, involves coupling together two separate photoreactions in much the same way that photosynthesis has evolved. One of the two photoreactions must be capable of the reduction of water to H_2 , and in fact work from several laboratories [1 - 4] has demonstrated that this process can be realized with high efficiency. The second photoreaction must involve the oxidation of water to O_2 , which is a particularly difficult process, and this has not been realized with much success. The only well-developed system capable of the photo-oxidation of water to O_2 in homogeneous solution uses tris(2,2'-bipyridyl)ruthenium(II) as the photosensitizer, persulphate or $[Co(NH_3)_5Cl]^{2+}$ as the sacrificial electron acceptor and RuO_2 as the catalyst, but it suffers from several problems [5 - 7]. Notably, the photosensitizer is expensive and collects only a small fraction of the solar spectrum whilst the RuO_2 catalyst employed [7] is not sufficiently active to allow the sacrificial electron acceptor to be replaced with a reversible one. Thus there is an urgent need for us to identify some alternative O_2 -producing systems, and very recently Borgarello *et al.* [8] have reported that zinc(II) *meso*-tetra(*N*-methyl-4-pyridyl)porphine ($ZnTMPyP^{4+}$) in acidic solution is an efficient sensitizer of O_2 generation by visible light in the presence of electron acceptors, such as iron(III), and a colloidal RuO_2 - TiO_2 catalyst. We have been investigating the role of this sensitizer in oxidative cycles for some considerable time and we wish to report that O_2 generation from such systems is not a facile process. In fact, we have been unable to observe O_2 formation from the π radical cation of

the zinc porphyrin (ZnTMPyP^{5+}) in a homogeneous solution, even in the presence of an $\text{RuO}_2\text{-TiO}_2$ catalyst.

The triplet excited state of ZnTMPyP^{4+} is formed in high yield ($\Phi_T = 0.9$) and in the absence of O_2 it has a relatively long lifetime ($\tau_T = 655 \mu\text{s}$) [4]. The triplet state is quite a powerful reducing agent ($E_{\text{ZnTMPyP}^{5+}/^* \text{ZnTMPyP}^{4+}}^\circ = -0.39 \text{ V (NHE)}$) and it is oxidized by a variety of electron acceptors; some bimolecular quenching rate constants k_Q , measured by flash photolysis techniques, are collected in Table 1. Net electron transfer occurs for the systems described in Table 1, and Fig. 1 shows the transient difference spectrum observed following the flash excitation of ZnTMPyP^{4+} ($1.0 \times 10^{-5} \text{ M}$) in the presence of persulphate ($3.3 \times 10^{-5} \text{ M}$) at pH 5. Similar transient spectra are observed with the other electron acceptors and the spectra bear a strong resemblance to the absorption spectrum of the zinc(II) porphyrin π radical cation produced by controlled-potential electrolysis [9]. Consequently, the reaction can be written

TABLE 1

Bimolecular rate constants k_Q and k_R for quenching the triplet excited state of ZnTMPyP^{4+} and for the reverse electron transfer in an aqueous solution at pH 5

Quencher	k_Q ($\text{M}^{-1} \text{s}^{-1}$)	k_R ($\text{M}^{-1} \text{s}^{-1}$)
$\text{S}_2\text{O}_8^{2-}$	9×10^8	—
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	1.5×10^8	—
Fe^{3+}	2.2×10^8	2.6×10^9
Methyl viologen ^a	1.8×10^7	3.7×10^9

^aFrom ref. 4.

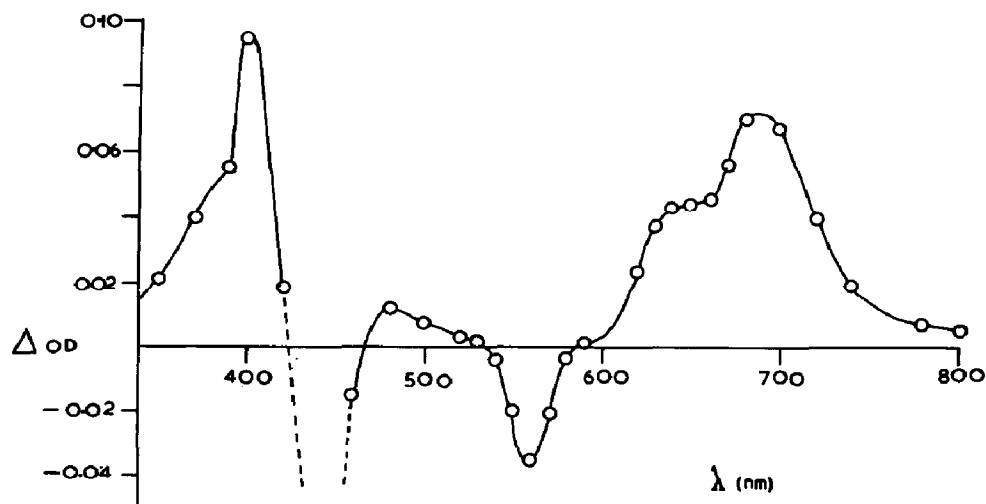
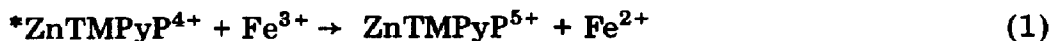


Fig. 1. Transient difference spectrum observed following the flash excitation of ZnTMPyP^{4+} ($1.0 \times 10^{-5} \text{ M}$) in aqueous solution containing persulphate ($3.3 \times 10^{-5} \text{ M}$) and Na_2SO_4 (0.1 M).



Even with the sacrificial systems where reverse electron transfer is inhibited, the lifetime of ZnTMPyP^{5+} is quite short and the species decays over a time scale of a few seconds. In fact, the rate of decay increases with decreasing pH throughout the range $2 < \text{pH} < 8$ although, as shown in Table 2, the kinetics are complex, being neither pure first order nor pure second order. At acidic pH (about pH 2) irradiation of ZnTMPyP^{4+} in the presence of persulphate results in the formation of the dication ZnTMPyP^{6+} , whilst at higher pH there is some isoporphyrin formation. In addition, since ZnTMPyP^{5+} is a powerful oxidant we must expect there to be some reaction with impurities in the aqueous solution, and in acidic solution demetallation of both ZnTMPyP^{4+} and ZnTMPyP^{5+} occurs. Also, it is known that the π radical cation can undergo photoredox processes under steady state conditions [10] and it may react in the dark with excess oxidant. Consequently, the overall decay of ZnTMPyP^{5+} in an aqueous solution involves a series of pathways but, in our hands at least, none of these pathways involves oxidation of water to O_2 .

Similar problems with the long-term stability of ZnTMPyP^{5+} have been reported from electrochemical and chemical oxidation studies [11]. It appears that the π radical cation undergoes facile oxidation to the dication which, in the presence of a nucleophile such as OH^- or Cl^- , will react to form an isoporphyrin derivative. These problems are not so marked when zinc(II) *meso*-tetra(4-sulphophenyl)porphine (ZnTSP^{4-}) is used, and here the π radical cation is relatively stable in aqueous solution ($t_{1/2} \approx 6$ min at pH 5). However, ZnTSP^{3-} is a poor oxidant by comparison with ZnTMPyP^{5+} and neither we nor Borgarello *et al.* [8] have observed O_2 formation with this species.

With iron(III) as the electron acceptor, the decay of ZnTMPyP^{5+} involves reverse electron transfer:

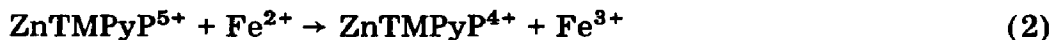


TABLE 2

First- and second-order rate constants k_1 and k_2 for the decay of ZnTMPyP^{5+} in an aqueous solution containing Na_2SO_4 (0.1 M)

pH	k_1 (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)
2.60	252.3 (0.9977)	3076 (0.9967)
3.55	43.5 (0.9931)	1469 (0.9972)
4.80	12.4 (0.9928)	844 (0.9972)
6.10	8.3 (0.9944)	731 (0.9856)
7.70	7.2 (0.9909)	700 (0.9979)

The numbers in parentheses refer to the correlation coefficient for the kinetic law fit.

The bimolecular rate constant k_R for this process increases with increasing pH; a similar situation was found for the $\text{bpy}_3\text{Ru}^{2+}\text{-Fe}^{3+}$ system [12]. At pH 5 the quantum yield for formation of ZnTMPyP^{5+} was approximately 0.55, as measured by nanosecond flash photolysis.

The redox potential for the one-electron oxidation of ZnTMPyP^{4+} in aqueous solution



has been measured [11] as 1.18 V(NHE) so that the π radical cation is a strong oxidant. On thermodynamic grounds it should be capable of O_2 evolution from water at $\text{pH} > 1$ since the redox potential for oxidation of water can be expressed as

$$E_{\text{H}_2\text{O}/\text{O}_2}^\circ = 1.23 - 0.059\text{pH V} \quad (4)$$

However, the liberation of O_2 from water requires a four-electron change:



If free-radical intermediates are to be avoided, it is necessary that the overall mechanism involves an intermediate species capable of charge accumulation. In other words, a catalyst capable of storing at least four oxidizing equivalents must be incorporated into the system if O_2 formation is to be observed, and prolonged irradiation of ZnTMPyP^{4+} in the presence of a sacrificial electron acceptor but in the absence of an added catalyst certainly does not lead to the formation of O_2 .

We have previously reported [7] that the quantum yield for the formation of O_2 from the $\text{bpy}_3\text{Ru}^{2+}$ photosensitized oxidation of water was markedly dependent upon the type of catalyst used. Both RuO_2 and CoSO_4 were found to be effective O_2 -producing catalysts, but the most efficient catalyst was RuO_2 supported on colloidal TiO_2 . Using both this $\text{RuO}_2\text{-TiO}_2$ catalyst and CoSO_4 , we were unable to observe O_2 formation from systems with ZnTMPyP^{4+} as the photosensitizer. Thus irradiation of ZnTMPyP^{4+} (1.0×10^{-5} M) in aqueous solution at pH 5 (acetate buffer) containing $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (1.0×10^{-3} M) and various amounts of the $\text{RuO}_2\text{-TiO}_2$ catalyst gave no observable yield of O_2 , as monitored with a membrane polarographic detector, and we estimate that the quantum yield for O_2 formation must be less than 10^{-3} . Similar negative results were observed for experiments performed at pH values between 2.0 and 6.7 and with CoSO_4 (5.0×10^{-3} M) as the catalyst. In no case was O_2 found as a reaction product.

Consequently, at this stage we are unable to confirm the findings of Borgarello *et al.* [8]. The most probable reason for this apparent discrepancy lies with the catalysts used by the two research groups. The $\text{RuO}_2\text{-TiO}_2$ catalyst used in our work was supported on Carbowax 20M (which is a mild reductant for ZnTMPyP^{5+}), although we have also used unsupported materials in a few experiments, and this has proved [7] to be a successful catalyst for the oxidation of water with Ce^{4+} and $\text{bpy}_3\text{Ru}^{3+}$. Borgarello

et al. suggest that a possible mechanism for O₂ evolution from the ZnTMPyP⁴⁺ system involves charge injection into the conduction band of TiO₂ from adsorbed porphyrin. With our catalyst adsorption onto the TiO₂ surface will be minimal because of the Carbowax 20M support, so that direct charge injection seems unlikely in our case. This appears to be the principal difference between the two systems, since our work suggests that ZnTMPyP⁵⁺ does not oxidize water to O₂ in homogeneous solutions. Further work is in progress to evaluate this hypothesis and, in particular, a great deal of emphasis will be placed on the role of the catalyst in these systems.

We thank the Science Research Council, the European Economic Community and General Electric (Schenectady) for financial support of this work.

- 1 B. V. Koryakin, T. S. Dzhabiev and A. E. Shilov, *Dokl. Akad. Nauk S.S.S.R.*, 233 (1977) 620.
- 2 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, 1 (1977) 449.
- 3 K. Kalyanasundaram and M. Gratzel, *Helv. Chim. Acta*, 63 (1980) 478.
- 4 A. Harriman, G. Porter and M. C. Richoux, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 833.
- 5 J. Kiwi and M. Gratzel, *Angew. Chem. Int. Edn. Engl.*, 17 (1978) 860; 18 (1979) 624.
- 6 J. M. Lehn, J. P. Sauvage and R. Ziessel, *Nouv. J. Chim.*, 4 (1980) 81.
- 7 A. Harriman, G. Porter and P. Walters, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 2373.
- 8 E. Borgarello, K. Kalyanasundaram, Y. Okuno and M. Gratzel, *Helv. Chim. Acta*, 64 (1981) 1937.
- 9 A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, 92 (1970) 2982.
- 10 W. Potter, R. N. Young and G. Levin, *J. Am. Chem. Soc.*, 102 (1980) 2471.
- 11 M. Neumann-Spallart and K. Kalyanasundaram, *Z. Naturforsch.*, 36b (1981) 596.
- 12 M. I. C. Ferreira and A. Harriman, *J. Chem. Soc., Faraday Trans. II*, 75 (1979) 874.