Photo-oxidation of Metalloporphyrins in Aqueous Solution

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Water-soluble, diamagnetic metalloporphyrins have been prepared which contain either zinc(II), palladium(II) or tin(IV) ions as the central metals and their photophysical properties have been measured in dilute aqueous solution. All the compounds undergo efficient intersystem crossing to form long-lived excited triplet states that can participate in electron-transfer reactions. Thus excitation of the metalloporphyrin in dilute aqueous solution containing an appropriate electron acceptor, such as iron(III), may result in formation of the metalloporphyrin π -radical cation in quite high yield. These π -radical cations are powerful oxidants, in some cases $E^{\circ} > 1$ *Y vs* NHE, but they undergo secondary reactions that lead to formation of π -dications and isoporphyrins. Despite the high redox potentials, it has not been possible to couple the one-electron reduction of the π -radical cations to the four-electron oxidation of water to molecular oxygen, even in the presence of a redox catalyst such as RuO₂. Therefore these compounds appear to possess little promise as water oxidants in homogeneous photosystems.

One of the outstanding mysteries concerning green-plant photosynthesis involves the ability of chlorophyll-a to photo-oxidise water to O, with high quantum efficiency. This is an intriguing reaction since it is essential to life, but we have no real understanding of the mechanism nor the intermediate species and catalysts that facilitate O2 formation. From O2- and proton-yield measurements and from lightintensity studies¹ it seems apparent that a single reaction centre is responsible for the four-photon/four-electron sequence required for oxidation of water to O_2 . Therefore the catalyst and/or an intermediate must be capable of charge accumulation. How the single-electron photochemistry of the reaction centre complex and the four-electron O₂-evolution step are coupled together has not yet been elucidated, and the intermediate electron carriers remain unidentified, although a manganese complex is believed to be involved.^{1, 2} However, if we are to understand how green plants function and if we are to construct a totally artificial solar-energy storage device based upon the photodissociation of water, then we need to obtain a clearer picture of this part of the photosynthetic process and be able to mimic it in the laboratory. The present paper is concerned with coupling the redox chemistry of metalloporphyrins with artificial O2-evolving catalysts (notably RuO2). Despite the importance of this reaction, there have been very few previous attempts to realise it in model systems, although there has been some work carried out using metalloporphyrin-coated electrodes for the photoelectrolysis of water.3-5

In a preliminary paper⁶ we reported that water-soluble zinc(II) porphyrins were photo-oxidised readily upon excitation to the triplet state in the presence of sacrificial or reversible redox couples. Although the redox potentials⁷ of the oxidised forms of these zinc porphyrins were in excess of the minimum required thermodynamically to oxidise water to O₂, we were unable to observe O₂ formation even in the presence of an efficient redox catalyst (RuO₂/TiO₂).⁶ Now, we present more details regarding this

work and extend it to include other metalloporphyrins, where the oxidised form of the porphyrin is an even more powerful oxidant. In no case could we observe molecular O₂ as a reaction product.



EXPERIMENTAL

MATERIALS

Water was double-distilled from a quartz still and all other reagents were of the best available grade. Where a RuO_2/TiO_2 catalyst was used, most work was carried out with the material described previously^{6,8} (we are greatly indebted to Dr A. Mackor, T.N.O., Utrecht for this material) although other batches of catalyst were tried. The preparation and characterisation of these materials will be described in a separate publication.⁹ A few experiments were performed with a sample of RuO_2/TiO_2 supplied by Dr. K. Kalyanasundaram (E.P.F.L., Lausanne).

Samples of ZnTSPP⁴⁻ and SnTSPP⁴⁻ were prepared by the method of Herrmann et al.¹⁰ using ZnO and SnO as the metal carriers and reaction times of 16 and 72 h, respectively. This method gave quantitative conversion, free from an excess of metal salt, and the samples required no further purification after dialysis against water. However, PdO was not a good metal carrier and samples of PdTSPP⁴⁻ had to be prepared by the method of Schmehl *et al.*¹¹ using methanol as principle solvent. The isolated samples were very impure and could be purified only by h.p.l.c. using THF + water as eluent.

Samples of ZnTPyP, SnTPyP and PdTPyP were prepared by refluxing H₂TPyP with a slight excess of the metal acetate in propionic acid for 2, 2 and 6 h, respectively. After cooling, filtering and evaporating to dryness, the isolated solids were chromatographed on neutral grade alumina using CHCl₃+pyridine as eluent. The final materials were dried under high vacuum at 60 °C and then treated with an excess of iodomethane at room temperature to obtain the Nmethylpyridinium iodides. The iodine counter-ion was replaced with chloride by careful treatment with Ag₂SO₄ followed by BaCl₂. The final materials were subjected to ion-exchange chromatography to remove any residual ionic impurities (this treatment is especially important

for SnTMPyP⁴⁺, which possesses two axial halide ligands). Full details of these preparations are available upon request. (Note that throughout this work the formal oxidation states of the central metal ions are: Zn = +2; Pd = +2; Sn = +4.)

METHODS

Absorption spectra were recorded with a Perkin-Elmer 554 spectrophotometer and luminescence spectra were recorded with a Perkin-Elmer MPF 4 spectrofluorimeter. All other experimental details regarding the flash-photolysis and steady-state irradiation studies have been given in earlier papers.^{6, 8, 12} Experiments to determine the quantity of O₂ evolved during an irradiation were performed with a membrane polarographic detector.¹³ In a typical experiment, an aqueous solution (37 cm³) containing metalloporphyrin (*ca.* 10⁻⁵ mol dm⁻³), buffer (acetate, borate, phosphate or HCl), electron acceptor (various concentrations) and, where necessary, a catalyst was placed in the MPD, thermostatted at 25 °C and purged thoroughly with N₂ for *ca.* 45 min. Then light of wavelength $\lambda > 400$ nm was focussed through a cold-water finger and onto a Pyrex window in the cell and the concentration of O₂ present in solution was monitored continuously *via* an x/t chart recorder. For quantum-yield measurements the intensity of the lamp was calibrated by ferrioxalate actinometry and with a Schwartz thermopile. Full details regarding the sensitivity, time response and reliability of the MPD have been given previously¹³ and its use for H₂ evolving photosystems has been described.¹⁴

Estimates of the quantum yield for formation of the triplet excited state were made by ns flash photolysis using a frequency-doubled Nd/glass laser (pulse duration 15 ns, maximum energy 100 mJ) and with tris(2,2'-bipyridyl)ruthenium(II) as the standard. First the molar extinction coefficients of the triplet state were determined by the complete bleaching method. Once the extinction coefficient of the excited state is known it is possible to determine the quantum yield for formation of the triplet excited state (ϕ_T) by calibration of the laser pulse or by reference to a well documented standard. Unfortunately there are few good standard materials for this type of work, but tris(2,2'-bipyridyl)ruthenium(II) ($\phi_T = 1.00$) allows a reasonable estimate of ϕ_T to be obtained. From calibration experiments we have determined that the difference in extinction coefficient between ground state and triplet excited state at 453 nm is 7000 ± 1000 mol⁻¹ dm³ cm⁻¹, which is in good agreement with values reported by Bensasson¹⁵ and Sutin¹⁶ and their coworkers but different from that obtained by Lachish *et al.*¹⁷ By direct comparison between the metalloporphyrin and the standard at a series of laser intensities it is possible to determine ϕ_T for the metalloporphyrin. At best such measurements give ϕ_T values with an accuracy of $\pm 10\%$.

Quantum yields for formation of redox-ion products (ϕ_{IONS}) were determined in a similar manner to the $\phi_{\rm T}$ values. Extinction coefficients for the metalloporphyrin π -radical cations were determined by pulse-radiolysis techniques; values for ZnTMPyP4+ and ZnTSPP4- have been published already,¹⁸ whilst the others (together with many more) will be published shortly.¹⁹ In all cases sufficient quencher was present to reduce the triplet-excited-state lifetime to ca. 200 ns, and the yield of metalloporphyrin π -radical cation was determined by measurement of the optical density change at an appropriate wavelength on a time scale of many μ s. Again, the laser intensity was calibrated by reference to the standard solutions, and the reported ϕ_{10NS} values had a reproducibility of $\pm 10\%$. This is the minimum error that can be associated with such measurements, especially when ϕ_{T} is less than unity, because here the excited-state population can be recycled so that the observed ϕ_{IONS} is higher than the true value. However, in the absence of a picosecond laser excitation source we are restricted to these measurements (even with a better excitation source the extinction coefficients of the metalloporphyrin π -radical cations have an accuracy no better than $\pm 10\%$). In the case of SnTMPyP⁴⁺ it was not possible to determine an extinction coefficient for the π -radical cation by pulse radiolysis owing to inefficient oxidation,¹⁹ and therefore for this compound we used the extinction coefficients derived for ZnTMPyP⁴⁺ at the relevant peaks. For this compound the ϕ_{IONS} value is an order-of-magnitude estimate only.

Redox potentials were determined using a Roth Scientific Co. potentiostat (model E611) coupled to a home-built triangle-wave generator. A three-electrode system was employed with a shielded glassy-carbon working electrode, a platinum-foil counter-electrode and a saturated

calomel reference electrode (SCE). Each electrode was housed in a separate compartment, electrical contact being maintained via glass frits, and the Luggin capillary of the SCE was positioned ca. 2 mm from the centre of the working electrode. In all cases an aqueous solution of the metalloporphyrin $[(2-11) \times 10^{-4} \text{ mol dm}^{-3}]$ containing Na₂SO₄ (0.5 mol dm⁻³) was placed in the working electrode compartment and purged thoroughly with N₂ for 10 min. A series of current-voltage profiles was recorded, on an X-Y recorder, for each system at a variety of porphyrin concentrations and voltage scan rates. A clean electrode was used for each experiment; the reported half-wave potentials, which were determined from the cyclic voltammograms by conventional methods, had a reproducibility of ± 15 mV.

RESULTS AND DISCUSSION

SPECTROSCOPIC STUDIES

Metalloporphyrin tetrasulphonates tend to dimerise in aqueous solution, even at modest concentrations of electrolyte, and the dimerisation constants follow the order $PdTSPP^{4-} > ZnTSPP^{4-} > SnTSPP^{4-}$. Dimerisation is most apparent by a broadening and decrease in extinction coefficient of the B band and by a non-linear Beer's-law plot. The N-methylpyridinium salts are much less prone to dimerise in aqueous solution. Using n.m.r. techniques we found previously²⁰ that the dimerisation constant for ZnTMPyP4+ was only ca. 8 mol⁻¹ dm³ compared with that of ZnTSPP4-, which is ca. 104 mol⁻¹ dm³. Absorption spectra for the monomeric species, recorded in dilute aqueous solution, are presented in fig. 1, where it can be seen that whilst zinc(II) and tin(IV) ions interact only fairly weakly with the porphyrin π -system palladium(II) ions interact very strongly with the ring. Strong interaction is exemplified²¹ by a high-energy Q(0,0) transition and a weak oscillator strength for the Q(0,0) band. As regards solar-energy collection, the zinc(II) porphyrin is the most interesting since it can collect some 40% of the energy available in sunlight.

All of the metalloporphyrins exhibit room-temperature fluorescence in dilute aqueous solution. The fluorescence quantum yields ($\phi_{\rm F}$), excited-singlet-state lifetimes $(\tau_{\rm S})$ and rate constants for fluorescence $(k_{\rm F})$, as calculated from the Strickler-Berg equation, are collected in table 1. In all cases fluorescence is fairly weak, and the lifetimes are too short for the excited singlet state to be useful in intermolecular photoredox processes. However, the triplet excited states are populated in very high quantum yield ($\phi_{\rm T}$). Furthermore, room-temperature triplet-state lifetimes ($\tau_{\rm T}$) are quite long (table 1), so that there is much more chance for intermolecular photoredox processes to occur via the triplet manifold although the triplet energies $(E_{\rm T})$ are quite low and there is a considerable loss in energy upon intersystem crossing to the triplet state (ca. 3900 cm^{-1}). This energy loss results in the triplet state being a much poorer electron donor than the corresponding singlet excited state but, unlike the singlet state, the long lifetime of the excited triplet state ensures many bimolecular diffusional encounters before non-radiative deactivation.21

Previous work by Bonnett et al.²² has shown that $ZnTSPP^{4-}$ undergoes some type of photoionisation during flash-photolysis experiments, and we have confirmed this finding. The quantum yield for product formation is ca. 0.01-0.05, depending upon light intensity, concentration and excitation wavelength, but we have made no real attempt to elaborate upon the reaction mechanism. This reaction is not so serious for the other metalloporphyrins, although we did notice that PdTMPyP⁵⁺ was formed in low yield ($\phi \approx 0.01$) when PdTMPyP⁴⁺ was flash-photolysed in O₂-saturated aqueous solution. This latter process is common to most metalloporphyrin triplet states, but the quantum yields appear to be very low.



FIG. 1.—Absorption spectra of dilute aqueous solutions of the metalloporphyrins: (a) $ZnTMPyP^{4+}$ (----), PdTMPyP⁴⁺ (----) and $SnTMPyP^{4+}$ (····); (b) $ZnTSPP^{4-}$ (----), PdTSPP⁴⁻ (----) and $SnTSPP^{4-}$ (····).

compound	$\phi_{ m F}$	$\tau_{\rm S}/{ m ns}$	$k_{\rm F}/10^7{ m s}^{-1}$	ϕ_{T}	$\tau_{\rm T}/{ m ms}$	$E_{\rm T}/{ m kJ\ mol^{-1}}$
ZnTSPP ⁴⁻	0.042	1.7	2.1	0.85	1.40	156
PdTSPP4-	ca. 10 ⁻⁴	< 0.5	1.8	1.00	0.38	172
SnTSPP ⁴⁻	0.036		2.0	0.95	1.0	158
ZnTMPyP ⁴⁺	0.035	1.5	2.2	0.90	1.22	157
PdTMPyP4+	ca. 10 ⁻⁴	< 0.5	2.0	1.00	0.17	174
SnTMPyP ⁴⁺	0.027		2.4	0.95	0.9	164

Table 1.—Photophysical properties of some metalloporphyrins in outgassed aqueous solution at pH 7 $\,$

REDOX STUDIES

Normally, the redox potential for an excited state is estimated by subtracting the energy of that state from the ground-state redox potential and, if the redox change does not involve a large conformational difference between initial and final forms, the calculated values agree within *ca*. 50 mV of the measured values.²³ Thus for oxidation of the triplet excited state of a metalloporphyrin the triplet redox potential (E_{P^+/P^+}) can be estimated from

$$E_{\mathbf{P}^{+}/\mathbf{P}^{*}}^{\Theta} = E^{\Theta} - E_{\mathbf{T}} \tag{I}$$

where E^{\ominus} refers to the redox couple

$$\mathbf{P}^+ + \mathbf{e} \to \mathbf{P} \tag{1}$$

and the triplet energy (table 1) is obtained from low-temperature phosphorescence spectra. Ground-state redox potentials have been measured for most of the watersoluble metalloporphyrins used here, but the tin(IV) porphyrins have not been studied by electrochemical techniques. Thus Neumann-Spallart and Kalyanasundaram^{7, 24} have reported E^{\ominus} values for ZnTSPP⁴⁻, PdTSPP⁴⁻, ZnTMPyP⁴⁺ and PdTMPyP⁴⁺ and their values are collected in table 2. We attempted to repeat their measurements using cyclic voltammetry, but we found that the oxidation waves were irreversible and the estimated redox potentials had limited significance. Certainly, for ZnTMPyP⁴⁺ a clear oxidation process can be seen at applied potentials > ca. 0.90 V vs SCE, whilst a second, poorly defined, oxidation wave appears at applied potentials > 1.05 V vs

TABLE 2.—Half-wave potentials (V vs NHE) for oxidation of the metalloporphyrins in aqueous solution

	$E_{\mathbf{P}}^{\mathbf{O}}$		
compound	this work ^a	ref. (24)	$E_{\mathbf{P}^{+}/\mathbf{P}^{*}}^{\ominus}$
 ZnTSPP ⁴⁻	0.90	0.87	-0.74
PdTSPP4-	1.16	1.09	-0.66
SnTSPP ⁴⁻	1.40	_	-0.24
ZnTMPyP ⁴⁺	1.18	1.18	-0.45
PdTMPyP ⁴⁺	1.41	1.40	-0.40
SnTMPyP ⁴⁺	> 1.50		>-0.20

SCE. However, the corresponding reduction scan shows only poorly resolved waves, indicating that a fast chemical process removes the oxidation products. In order to obtain even a moderate degree of reversibility it was necessary to restrict the applied potential to < 1.00 V vs SCE and to use high scan rates. Under such conditions there was a linear relationship between the peak current for the anodic step (i_n) and the square root of the scan rate $(v^{\frac{1}{2}})$. The value of E^{\ominus} , estimated from the forward and reverse scans, was 1.18 ± 0.01 V vs NHE, in excellent agreement with that reported previously.^{7, 24} Similar results were found with PdTMPyP⁴⁺ ($E^{\ominus} = 1.41 \pm 0.01$ V vs NHE), but no real oxidation wave could be resolved for SnTMPyP4+ and it is probable that for this compound $E^{\ominus} > 1.5 \text{ V}$ vs NHE. Redox potentials for the sulphonates were complicated by dimerisation (PdTSPP4- and ZnTSPP4-) and adsorption. Only for SnTSPP⁴⁻ was a clear, reversible cyclic voltammogram obtained; for the other sulphonates the E^{Θ} values given in table 2 should be regarded with some suspicion. Using these E^{\ominus} values in conjunction with the triplet energies, determined from well resolved phosphorescence spectra, the redox potentials for the triplet excited states $(E_{\mathbf{P}^+/\mathbf{P}^*})$ were calculated (table 2).

The values compiled in table 2 show that the triplet excited states of the metalloporphyrins are mild reductants; the average $E_{\rm P^+/P^*}^{\oplus}$ values are *ca.* -0.55 and *ca.* -0.35 V vs NHE for the tetrasulphonates and the N-methylpyridinium compounds, respectively. Consequently the triplet excited states are oxidised by a wide range of electron acceptors; a few bimolecular triplet quenching rate constants (k_Q) are collected in table 3. In all cases listed in table 3, net electron transfer occurs to form the metalloporphyrin π -radical cation

$$\mathbf{P}^* + \mathbf{Q} \to \mathbf{P}^{\cdot +} + \mathbf{Q}^{\cdot -} \tag{2}$$

as monitored by flash-photolysis techniques. As a typical example we show the transient difference spectrum observed after flash excitation of PdTMPyP⁴⁺ in the presence of sodium persulphate (10^{-4} mol dm⁻³) in aqueous solution at pH 4.7 and compare it with the difference spectrum observed following pulse radiolysis of PdTMPyP⁴⁺ in the presence of NaCl (10^{-2} mol dm⁻³) at pH 3 (fig. 2). In a preliminary report⁶ we showed a similar difference spectrum for ZnTMPyP⁴⁺.

Although reluctant to attach much significance to the apparent trends in rate constants given in table 3, since the values are not corrected for electrostatic terms or ionic-strength variations and the ΔG^{\ominus} values are subject to considerable doubt, we draw attention to the k_{Q} values found for quenching the N-methylpyridinium porphyrins with methyl viologen (MV^{2+}) and sodium persulphate. With MV^{2+} as quencher the thermodynamic driving forces are minimal, even for ZnTMPyP4+, and the triplet excited states of these metalloporphyrins are poor reductants for MV^{2+} . This is unfortunate, because the $MV^{2+/+}$ redox couple is a very good H₂-producing relay¹² but our work shows that only ZnTMPyP⁴⁺ is a suitable photosensitiser for reduction of MV^{2+} . With persulphate as electron acceptor, the thermodynamic driving forces are all extremely exergonic but the observed k_Q values are quite modest, especially considering the strong electrostatic attraction between the reagents. The observed k_{Ω} values do follow the expected order of ΔG^{\ominus} values but the relationship is not very marked. For ZnTMPyP4+ (and ZnTSPP4-) there is ground-state oxidation of the metalloporphyrin when high concentrations of persulphate are employed, but the other metalloporphyrins do not react in the dark. Furthermore, whereas $ZnTMPyP^{4+}$ (and $ZnTSPP^{4-}$) is oxidised by the sulphoxylate radical anion, we have found no evidence to suggest that PdTMPyP4+ or SnTMPyP4+ (or their tetrasulphonates) are oxidised by this radical, confirming their very high E^{\ominus} values. Thus the

porphyrin	quencher	$k_{\rm Q}/{ m mol^{-1}}~{ m dm^3}~{ m s^{-1}}$	$\Delta G^{\ominus}/\mathrm{eV}$	
ZnTSPP ⁴⁻	MV ²⁺	1.4 × 10 ¹⁰	-0.29	
	$S_2O_8^{2-}$	$6.9 imes 10^{6}$	-1.34	
PdTSPP ⁴⁻	MV^{2+}	ca. 1010	-0.21	
	$S_2O_8^{2-}$		-1.26	
SnTSPP ⁴⁻	MV ²⁺	< 104	0.21	
	$S_2O_8^{2-}$	ca. 10 ⁵	-0.84	
ZnTMPyP ⁴⁺	MV ²⁺	1.8×10^{7}	0	
-	$S_2O_8^{2-}$	9.0×10^{8}	-1.05	
	$Co(NH_3)_5Cl^{2+}$	1.5×10^{8}	-0.97	
	Fe ³⁺	1.9×10^{8}	-1.19	
PdTMPyP ⁴⁺	MV^{2+}	3.5×10^{4}	0.05	
-	$S_2O_8^{2-}$	1.9×10^{8}	-1.00	
	$Co(NH_3)_5Cl^{2+}$	1.4×10^{8}	-0.92	
	Fe ³⁺	6.9×10^{7}	-1.14	
SnTMPyP ⁴⁺	MV^{2+}	< 104	> 0.25	
-	$S_2O_8^{2-}$	1.0×10^{7}	<-0.80	
	Fe ³⁺	$ca. 10^{6}$	<-0.94	

TABLE 3.—RATE CONSTANTS AND STANDARD FREE-ENERGY CHANGES FOR QUENCHING THE METALLOPORPHYRIN TRIPLET EXCITED STATE

quantum yield for photo-oxidation of $ZnTMPyP^{4+}$ by persulphate should be much higher than found for the other metalloporphyrins used here:

$$*ZnTMPyP^{4+} + S_2O_8^{2-} \rightarrow ZnTMPyP^{\cdot 5+} + SO_4^{2-} + SO_4^{\cdot -}$$
 (3)

$$ZnTMPyP^{4+} + SO_4^{*-} \rightarrow ZnTMPyP^{*5+} + SO_4^{2-}.$$
 (4)

This hypothesis was confirmed by steady-state and flash-photolysis experiments which have shown the reluctance of both PdTMPyP⁴⁺ and SnTMPyP⁴⁺ to be photo-oxidised even by such strong oxidants as persulphate.

Where net electron transfer does take place, the initial product is the metalloporphyrin π -radical cation, as identified by absorption spectroscopy. In all cases the absorption spectra in the flash-photolysis studies were in good agreement with spectra of the π -radical cations produced by pulse-radiolysis techniques.¹⁹ The spectral details of these and many more water-soluble metalloporphyrin π -radical cations will be described in a later paper.¹⁹ Here we concentrate upon the stability of π -radical cations.

STABILITY OF THE π -RADICAL CATIONS IN SACRIFICIAL SYSTEMS

First let us consider the lifetimes and stabilities of the metalloporphyrin π -radical cations as observed in the absence of a reversible redox couple, *i.e.* as formed by flash excitation with a sacrificial electron acceptor such as persulphate or $[Co(NH_3)_5Cl]^{2+}$. Both of these sacrificial electron acceptors undergo secondary thermal reactions following reduction, and both give rise to some experimental uncertainties in that the SO_4^- radical produced by the one-electron reduction of persulphate is itself a powerful oxidant and may result in further oxidation

$$S_2O_8^{2-} + e \to SO_4^{2-} + SO_4^{2-}$$
 (5)

 $E^{\ominus} \approx 0.6 \text{ V} vs \text{ NHE}$



FIG. 2.—(a) Transient difference spectrum observed 10 μ s after flash excitation of PdTMPyP⁴⁺ in the presence of persulphate (10⁻⁴ mol dm⁻³) at pH 4.7. (b) Transient difference spectrum observed after pulse radiolytic oxidation of PdTMPyP⁴⁺ in the presence of NaCl (0.1 mol dm⁻³) at pH 3 [ref. (19)].

whilst $[Co(NH_3)_5Cl]^+$ undergoes rapid hydrolysis to give the simple aquated cobalt(II) species which is known to function as a redox catalyst²⁵

$$[\operatorname{Co}(\operatorname{NH}_3)_5\operatorname{Cl}]^{2+} + e + 5\operatorname{H}^+ \to \operatorname{Co}^{2+} + 5\operatorname{NH}_4^+ + \operatorname{Cl}^-$$
(6)
$$E^{\ominus} \approx 0.52 \text{ V } vs \text{ NHE}.$$

First consider the photo-oxidation of $ZnTMPyP^{4+}$ in aqueous solution. In all of our flash-photolysis experiments, ZnTMPyP⁵⁺ could be observed immediately after the flash but it decayed quite rapidly. The decay pathway was complex and the kinetics could not be fit to either first- or second-order processes as shown in table 4, where the decay rates and correlation coefficients are given for ZnTMPyP⁵⁺ at different pH values. The lifetime of $ZnTMPyP^{5+}$ decreases with decreasing pH throughout the

TABLE 4.—FIRST- AND SECOND-ORDER RATE CONSTANTS k_1 and k_2 for the decay of ZnTMPyP⁵⁺ in an aqueous solution containing Na₂SO₄ (0.1 mol dm⁻³)

pH	k_1/s^{-1}	$k_2/{ m mol}^{-1}{ m dm}^3{ m s}^{-1}$	
 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.

range 1.5 < pH < 8.0, and at the two extreme pH values the final products are different. Thus, as shown in fig. 3, monitoring the flash-photolysis records at long times (0.4 s after the flash) showed that at pH 1.6 there was a long-lived transient with absorption maximum around 340 nm whilst at pH 8.0 a long-lived product with absorption maxima at 760 and 840 nm was found. By comparison with water-insoluble zinc porphyrins,²⁶ the low pH species, with an absorption maximum at 340 nm, can be assigned to the porphyrin dication ZnTMPyP⁶⁺ and the higher pH species, with absorption maxima at 760 and 840 nm, appears to be the isoporphyrin. The isoporphyrin is formed by hydroxide ion attack upon the dication and it is the preferred product in alkaline solution. Both products can be obtained in high yield by steady-state irradiation of ZnTMPyP4+ in the presence of persulphate $(10^{-4} \text{ mol dm}^{-3})$ and, as shown in fig. 3(b), irradiation in 0.1 mol dm⁻³ HCl gives rise to the dication as a fairly stable species which can be converted into the isoporphyrin upon addition of NaOH. Identical irradiations carried out at pH 8.0 give only the isoporphyrin [fig. 3(b)].

Similar experiments performed with ZnTSPP⁴⁻ showed that the π -radical cation ZnTSPP'3-, which was formed in high yield, had a very much longer lifetime and decayed by a predominantly first-order process ($k \approx 3 \times 10^{-3} \text{ s}^{-1}$ at pH 5.0). In this case the rate of decay of ZnTSPP'³⁻ increased with increasing pH, unlike the behaviour observed with ZnTMPyP'5+, although isoporphyrin formation was observed.

Formation of the dication and isoporphyrin products from the zinc porphyrins means that a second electron is removed from the porphyrin ring, and this is most probably a thermal step: _ _ (**m**)

$$2 \operatorname{ZnP}^{+} \rightleftharpoons \operatorname{ZnP} + \operatorname{ZnP}^{2+} \tag{7}$$

$$ZnP^{+} + SO_4^{-} \to ZnP^{2+} + SO_4^{2-}$$
 (8)

$$ZnP^{+} + S_2O_8^{2-} \frac{\hbar\nu}{\sigma \Delta} ZnP^{2+} + SO_4^{2-} + SO_4^{--}.$$
 (9)



FIG. 3.—(a) Transient difference spectrum observed 0.4 s after flash excitation of ZnTMPyP⁴⁺ in the presence of persulphate (10⁻⁴ mol dm⁻³) at pH 1.6 (—) and 8.0 (---). (b) Absorption spectra of the porphyrin dication (—) and isoporphyrin (----) obtained by steady-state irradiation of ZnTMPyP⁴⁺ in the presence of persulphate (10⁻⁴ mol dm⁻³) at pH 1.6 and 8.0, respectively.

At the moment we cannot distinguish between the above processes, although disproportionation seems unlikely for ZnTSPP³⁻ because of its first-order decay. For ZnTMPyP⁵⁺, disproportionation may be an important decay route since we have had considerable difficulty in producing the one-electron oxidation product by controlled potential electrolysis. In fact, unless disproportionation is important for ZnTMPyP⁵⁺ it is difficult to explain the observation that ZnTSPP³⁻ has the much longer lifetime since this species is quite easy to oxidise. Furthermore, when $[Co(NH_3)_5Cl]^{2+}$ is used as electron acceptor, the observed lifetime of ZnTMPyP⁵⁺ remains almost identical to that found with persulphate as oxidant, so that further oxidation with persulphate is not the only product-forming route. Finally, the influence of pH upon the lifetime

of ZnTSPP³⁻ suggests oxidation of hydroxide ions by the π -radical cation, but we cannot understand why the lifetime of ZnTMPyP⁵⁺ decreases with decreased pH.

Neither PdTMPyP⁴⁺ nor PdTSPP⁴⁻ react with persulphate in the dark (it was noted, however, that high concentrations of persulphate tended to precipitate $PdTMPvP^{4+}$). but they were oxidised to the π -radical cations upon irradiation with visible light. Again, immediately after the flash the products were the π -radical cations but these species decayed quite rapidly to give secondary products. The secondary, thermal step is exemplified by fig. 4, which shows an oscilloscope trace recorded at 635 nm following ns flash excitation of PdTMPyP⁴⁺ (ca. 4×10^{-5} mol dm⁻³) in aqueous solution at pH 5.0 containing persulphate (10⁻⁴ mol dm⁻³). The initial 'spike' corresponds to formation of PdTMPyP'5+, as evidenced by its absorption spectrum, which decays rapidly to form the permanent product. As shown in fig. 4(b), this second product has its major absorption band centred at 655 nm for pH 5.0 ($t_{\rm k} \approx 3$ min) and at ca. 635 nm for higher pH ($t_{i} > 30$ min at pH 7.4). Identification of these long-lived products has been difficult because the absorption spectra are not really characteristic



FIG. 4.—(a) Oscilloscope trace recorded at 635 nm after ns flash excitation of PdTMPyP⁴⁺ $(4 \times 10^{-5} \text{ mol dm}^{-3})$ in aqueous solution containing persulphate ($10^{-4} \text{ mol dm}^{-3}$) at pH 5. (b) Absorption spectra of the longer-lived transients observed after flash excitation of PdTMPyP4+ in the presence of persulphate (10⁻⁴ mol dm⁻³) at pH 5.0 (----) and 7.4 (----).

of any known palladium porphyrin species. The two products appear to be e.p.r.inactive and they cannot be observed by absorption spectroscopy in acidic solution (pH < 2). As a tentative assignment, we note that Dolphin *et al.*²⁷ have invoked the hypothesis that palladium porphyrin π -radical cations can be oxidised further to palladium(iv) porphyrins and it is possible that the 655 nm absorbing product is a Pd^{IV} species:

$$*Pd^{u}P + S_{2}O_{8}^{2-} \rightarrow Pd^{u}P^{+} + SO_{4}^{2-} + SO_{4}^{*-}$$
(10)

$$Pd^{n}P^{+} + SO_{4}^{-} \rightarrow Pd^{n}P^{2+} + SO_{4}^{2-}$$

$$\tag{11}$$

$$Pd^{n}P^{+} + S_{2}O_{8}^{2-} \rightarrow Pd^{n}P^{2+} + SO_{4}^{2-} + SO_{4}^{2-}$$
 (12)

$$2 \operatorname{Pd^{u}P^{*+}} \rightleftharpoons \operatorname{Pd^{u}P} + \operatorname{Pd^{u}P^{2+}}$$
(13)

$$Pd^{II}P^{2+} \underset{H^{+}}{\overset{OH^{-}}{\Rightarrow}} Pd^{IV}P.$$
(14)

Tin(IV) porphyrins are extremely resistant to oxidation and we have had little success in our attempts to produce the π -radical cations by either electrolytic or pulse radiolytic techniques. There is no ground-state reaction between SnTMPyP⁴⁺ or SnTSPP⁴⁻ and persulphate but upon flash photolysis at pH 5.0 in the presence of persulphate (10⁻³ mol dm⁻³) there is inefficient formation of the metalloporphyrin π -radical cations.

STABILITY OF THE π -RADICAL CATIONS IN REVERSIBLE SYSTEMS

Flash photolysis in the presence of a reversible redox agent, such as $Ru(NH_3)_{6}^{3+}$, can produce the metalloporphyrin π -radical cations in quite high yield, but now decay involves recombination of the separated ion products and is a second-order process:

$$\mathbf{P}^* + \mathbf{Q} \xrightarrow{k_{\mathbf{Q}}} \mathbf{P}^{*+} + \mathbf{Q}^{*-}$$
(15)

$$\mathbf{P}^{\star} + \mathbf{Q}^{\star} \xrightarrow{\kappa_{\mathbf{R}}} \mathbf{P} + \mathbf{Q}. \tag{16}$$

The yields of ion products depend markedly upon the nature of the reactants and on the environment, as has been well documented for the ZnP/MV²⁺ system,²⁸⁻³⁰ and with iron(III) as reversible electron acceptor we have observed some quite remarkable pH effects upon the rate constant for reverse electron transfer ($k_{\rm R}$) and upon the quantum yield for formation of redox ion products. Such pH effects upon $k_{\rm R}$ have been noted previously³¹ with bipy₃Ru²⁺ as the photosensitiser and ascribed to changes in the self-exchange rate constant for the ion(III)/(II) couple, but the variation of the yield of products with pH has not been reported before.

With ZnTMPyP⁴⁺ the quantum yield for formation of ion products (ϕ_{IONS}) was close to unity at pH 1.5 but it decreased at higher pH. Similar effects were found with PdTMPyP⁴⁺ except that the maximum ϕ_{IONS} was only *ca.* 0.2,³² whilst with SnTMPyP⁴⁺ the ϕ_{IONS} value at pH 1.5 was estimated to be < 0.006. At pH > 5, no ion products were detected from any system. These effects may be associated with the pH-dependent terms in the self-exchange rate for the iron(II)/(III) couple^{31, 33, 34} but it must be noted that iron(III) begins to form clusters in aqueous solution at pH > 3.

PHOTOCHEMICAL OXYGEN-EVOLUTION EXPERIMENTS

Although the work reported in this paper has led to a better understanding of the characteristics of metalloporphryin π -radical cations in aqueous solution, the main purpose of the work was to attempt to use the π -radical cations to oxidise water to molecular O₂ catalyst

$$4 P^{+} + 2 H_2 O \xrightarrow{\text{catalyst}} 4P + 4H^+ + O_2.$$
(17)

The formal redox potential required to liberate O_2 from water is pH dependent

$$E_{O_{2}/H_{2}O}^{O} = (1.23 - 0.059 \text{ pH}) \text{ V}$$
 (II)

but all of the N-methylpyridinium metalloporphyrins used in this work should be thermodynamically capable of O_2 formation at pH > 1. Obviously a catalyst is required to couple the one-electron redox chemistry of the metalloporphyrin with the four-electron chemistry of water oxidation. From previous work it appears that the most suitable catalyst for this type of work is RuO₂ deposited upon colloidal TiO₂

and we have devoted considerable effort into developing active RuO_2/TiO_2 catalysts. As an alternative to heterogeneous RuO_2 catalysts, cobalt(II) ions appear to function as homogeneous catalysts for O_2 formation and such materials might have some application where kinetic difficulties are involved. However, in a preliminary report⁶ we showed that neither RuO_2/TiO_2 nor cobalt(II) ions were able to catalyse oxidation of water to O₂ using ZnTMPyP⁵⁺ or ZnTSPP³⁻ as oxidant although successful results had been reported by Borgarrello et al. It was our contention⁶ that the catalyst used in Borgarrello's experiments might differ from the one used in our experiments and somehow the discrepant results can be connected with this difference. Subsequent to this preliminary report we have prepared a wide range of RuO₂/TiO₂ catalysts, without any additional supporting material, and tested them as photochemical O_2 -evolving systems using ZnTMPyP⁴⁺ and PdTMPyP⁴⁺ as the photosensitisers.

In a typical experiment a solution of the metalloporphyrin (ca. 10^{-5} mol dm⁻³ so that the absorbance at the main Q band was ca. 2 in the photolysis cell) in aqueous buffer containing an electron acceptor was irradiated in the MPD cell after thorough purging with N₂. Various concentrations of RuO_2/TiO_2 catalysts were used (0-500 mg dm⁻³) and the catalysts contained various loadings of RuO₂ (0-10%). For all experiments the photolysate was thermostatted at 25 °C and the irradiation source was a 250 W Xe arc filtered through an i.r. filter and a glass filter to remove light of $\lambda < 400$ nm. Typical intensities were of the order of 10^{18} ein min⁻¹ cm⁻² and most irradiations were continued for *ca*. 60 min. The sensitivity of the MPD has been described previously¹³ and, in our experience, it is the most sensitive and reliable technique for the routine monitoring of photochemically produced O2. Under the above experimental conditions and using a reaction solution of 37 cm³ the drift in the baseline is $< 2 \text{ mm h}^{-1}$ and the instrument will detect, without difficulty, a change in O_2 concentration of 10^{-8} mol.

In a series of experiments using ZnTMPyP4+, ZnTSPP4- or PdTMPyP4+ as photosensitiser and with persulphate, $[Co(NH_3)_5Cl]^{2+}$, silver(I) or iron(III) as electron acceptor and with a wide range of different RuO₂/TiO₂ catalysts and throughout the pH range 1.6 to 7.0, we were unable to observe O, formation under the above experimental conditions. From such experiments we estimate that the quantum yield for O_2 formation must be $< 10^{-3}$. Similar negative results were obtained with a RuO₂/TiO₂ catalyst supplied by Dr K. Kalyanasundaram (E.P.F.L., Lausanne) and when cobalt(II) ions were used as homogeneous catalyst ($[Co^{2+}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$). Thus the metalloporphyrins compare very badly with $bipy_3Ru^{2+}$, which gives copious yields of O₂ under similar conditions. With a good RuO₂/TiO₂ catalyst, irradiation of bipy₃Ru²⁺ (5×10^{-5} mol dm⁻³) at pH 4.7 in the presence of $[Co(NH_3)_5Cl]^{2+}$ gave a signal on the chart recorder of 94 cm after 15 min irradiation. Under identical experimental conditions, $ZnTMPyP^{4+}$ gave no detectable change in the baseline even after 30 min irradiation. A few measurements were made with $PdTSPP^{4-}$ and with SnTMPyP⁴⁺, the π -radical cation of the latter compound should be amongst the most oxidising of all metalloporphyrin species, but no O, could be detected upon prolonged irradiation in the presence of either sacrificial or reversible electron acceptors and a RuO_2/TiO_2 catalyst. Therefore we are of the opinion that these water-soluble metalloporphyrins are not suitable for O_2 -evolving photosystems even when quite active catalysts are employed.

This opinion was augmented by a few stopped-flow measurements which confirmed that the lifetimes of ZnTMPyP⁵⁺ and ZnTSPP³⁻ were unaffected by the addition of RuO₂/TiO₂ catalyst. Although light scattering restricted the concentration of catalyst to fairly low levels (20 mg dm⁻³) these results exemplify the difficulty of transferring a 'hole' from a metalloporphyrin π -radical cation to an O₂-evolving catalyst.

CONCLUSIONS

We have shown that it is relatively easy to photo-oxidise a metalloporphyrin in aqueous solution using both sacrificial and reversible electron acceptors. For zinc(II), palladium(II) and tin(IV) porphyrins, the removal of one electron results in the formation of the π -radical cation which is unstable and readily undergoes further oxidation to form the porphyrin dication or isoporphyrin, depending upon the solution pH. With reversible electron acceptors, the yield of redox-ion products depends upon spin-orbit coupling properties of the central metal ion, whilst with iron(III) as guencher the yield of products increases markedly with decreased pH, probably due to the self-exchange reaction of the iron(III)/(II) couple. However, although the metalloporphyrin π -radical cations are powerful oxidants we have not been able to couple the one-electron redox chemistry of the metalloporphyrin with the four-electron oxidation of water to O₂. Indeed, prolonged steady-state irradiation of the metalloporphyrin in the presence of sacrificial or reversible electron acceptors and an O_2 -evolving catalyst based upon RuO_2/TiO_2 did not result in detectable yields of O_2 . Thus π -radical cations derived from diamagnetic metalloporphyrins do not appear to be good oxidants for water in homogeneous systems, despite the fact that green plants successfully photo-oxidise water to O_2 via the chlorophyll-a π -radical cation (albeit in a heterogeneous system). Unlike our in vitro models, nature uses a series of electron relays as intermediates between $chl-a^+$ and water, and our work suggests that these relays are not diamagnetic metalloporphyrins. More likely, they are paramagnetic species where the oxidising equivalents are stored at a metal centre, not on an organic species. Thus the logical extension of this work is to use a diamagnetic metalloporphyrin, such as ZnTMPyP4+, to photo-oxidise a paramagnetic metalloporphyrin, such as MnTMPyP⁴⁺, and subsequently to use the oxidised form of the latter compound to liberate O₂ from water. Such experiments are now in progress and the outcome will be reported shortly.

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