Redox Chemistry of Metalloporphyrins in Aqueous Solution¹

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A series of water-soluble metalloporphyrins has been prepared and the redox chemistry investigated by electrochemical and pulse radiolytic techniques. All of the metalloporphyrins exhibit reasonably intense absorption transitions ($\epsilon = ca. 2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the visible region and a strong absorption ($\epsilon = (2-7)$) $\times 10^5$ dm³ mol⁻¹ cm⁻¹) around 430 nm. Cyclic voltammetry showed that the compounds undergo well-defined reduction and oxidation steps, although the oxidation processes were not really reversible. For diamagnetic metalloporphyrins, the difference in $E_{1/2}$ between addition and removal of an electron for a particular compound was 2.05 \pm 0.20 V while the difference in $E_{1/2}$ between addition of one and two electrons was 0.28 \pm 0.12 V. Similarly, $E_{1/2}$ for the removal of a second electron from the porphyrin π system was some 0.25 ± 0.10 V higher than that for removal of the first electron. These findings are consistent with the central metal ion exerting only an inductive effect upon the porphyrin π levels. The absorption spectra of the one-electron reduction and oxidation products were recorded by pulse radiolysis methods. Both products exhibit broad absorption transitions stretching across the entire visible and near-IR regions. The reduction products were identified as π -radical anions and, in many cases, these were unstable with respect to disproportionation. The oxidation products were identified as π -radical cations and these were also unstable in aqueous solution but the decay route remains obscure.

Introduction

Nature makes extensive use of metalloporphyrins as agents for electron transfers and, in recent years, such materials have found prominent use in in vitro model systems, especially those aimed at the storage of solar In general, the redox chemistry of metalloenergy.² porphyrins can be divided into two major classifications: (i) systems where the redox process involves a change in formal oxidation state of the central metal ion and (ii) systems where addition or removal of an electron involves only the porphyrin π system. The former systems are exemplified by many transition-metal porphyrins, such as iron, cobalt, and manganese, and the redox chemistry of such compounds has been well documented over the past few years. Both oxidation and reduction processes can be brought about and the redox products have been characterized by spectroscopic, $^{3-5}$ electrochemical, $^{6-9}$ chemical, 10,11 and pulse radiolytic 12,13 techniques. The latter class of

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compounds, of which chlorophyll a is a member, has been well studied by chemical^{14,15} and electrochemical^{16,17} techniques and the one-electron oxidation and reduction products are the metalloporphyrin π -radical cations and anions, respectively. Although EPR spectral data are readily available for the π -radical ions,¹⁸ absorption spectra are not so well documented¹⁹—especially as regards the molar extinction coefficients.

Where metalloporphyrin π -radical ions have been well characterized, it has almost invariably been in a solvent such as CH_2Cl_2 , but the real attraction of these materials lies in their potential use in solar energy storage devices based upon the photodissociation of water.² As such, it is essential that preliminary experiments at least be conducted with water-soluble compounds. Rather surprisingly, only metal-free and zinc(II) porphyrins have been well described in aqueous solution and it is only very recently that absorption spectra of the π -radical cations and anions in water were reported.²⁰⁻²² In this paper, we describe the redox chemistry of a series of water-soluble metalloporphyrins using electrolytic and pulse radiolytic techniques. The main aim of the work was to characterize absorption spectral features of the metalloporphyrin π -

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radical cations and anions in aqueous solution and, to a large extent, this aim has been realized.

Experimental Section

Materials. All inorganic reagents were obtained from commercial sources and were of the highest available purity. The metal-free porphyrins, tetrakis(4-sulfophenyl)porphine and tetra(4-pyridyl)porphine, were obtained from



$$M = Zn.Pd.Aa.Cd,Cu,Sn,Pb$$

Strem Chemicals Ltd. The metalloporphyrin tetrakis (Nmethylpyridinium) salts were prepared as described previously,²³ with the intermediate metal tetra(4-pyridyl)porphyrins being purified by column chromatography on alumina using chloroform/pyridine as eluant. Methylation was achieved by stirring for several days at room temperature with an excess of iodomethane and the iodide counterions were exchanged for chloride ions either by ion-exchange chromatography or by treatment with $Ag_2SO_4/BaCl_2$ as described before.²³ Except for PdTSPP⁴⁻, the metalloporphyrin tetrakis(4-sulfophenyl)porphyrins were prepared by the heterogeneous template method of Herrman et al.²⁴ and were purified by dialysis and ion-exchange chromatography. Samples of PdTSPP⁴⁻ were prepared by the method of Schmehl and Whitten²⁵ and were purified by HPLC. In all cases, the purity of the final material was checked by HPLC; usually the purity was greater than 98% as monitored by visible absorption spectroscopy but samples of SnTMPyP4+ always contained small amounts (<2%) of the chlorin (λ_{max} 622 nm) and PbTMPyP4+ contained substantial amounts (5-10%) of an impurity that could not be removed by repeated column chromatography.

Methods. Absorption spectra were recorded with a Perkin-Elmer 554 spectrophotometer and extinction coefficients were determined by weighing out several aliquots of solid metalloporphyrin and diluting to various volumes with water containing phosphate buffer (1×10^{-3} mol dm⁻³). Extinction coefficients for CdTSPP⁴⁻ were obtained by direct comparison to the metal-free porphyrin at pH 9 following addition of a slight excess of $Cd(ClO_4)_2$ since metallation is quantitative after a few minutes of stirring at room temperature.

Half-wave potentials for the one-electron oxidation or reduction of the metalloporphyrins were determined by cyclic voltammetry using a Metrohm E611 potentiostat driven by a purpose-built triangle wave generator. Aqueous solutions at pH 5 (except for CdTSPP⁴⁻ and CdTMPyP⁴⁺ which were studied in borate buffer at pH 9) containing metalloporphyrin ((2-20) \times 10⁻⁴ mol dm⁻³) and either KCl (0.5 mol dm⁻³) or Na_2SO_4 (0.3 mol dm⁻³) were purged thoroughly with N_2 and kept in the dark throughout the electrolysis. For oxidations, a glassy C working electrode was used while reductions were made with a HMDE. In all cases, a saturated calomel electrode was used as the reference and a Pt foil was employed as counterelectrode. The general procedures used were those outlined by Felton²⁶ and the reproducibility of the derived half-wave potentials was ± 20 mV. In general, the TMPyP⁴⁺ complexes gave few problems but the TSPP⁴⁻ compounds adsorbed onto the electrode surface and for PdTSPP⁴⁻, CdTSPP⁴⁻, ZnTZP, and SnTPyP (Sn refers to Sn^{IV} throughout this paper) it was necessary to use dilute solutions (<10⁻⁴ mol dm⁻³) to overcome problems of dimerization or poor solubility. For the latter compound, adsorption was a particular problem.

The reversibility of reduction scans was quite good, as evidenced by the separation of anodic and cathodic peaks and the approximately equal peak heights for anodic and cathodic processes. However, the reversibility of the oxidation scans was poor, especially if the potential was swept past the anodic peak by more than 200 mV or if the potential was held close to the anodic peak for about 10 s. In all cases, there was a good correlation between the anodic peak current and the square of the potential scan rate but only with AgTMPyP⁴⁺ and PbTMPyP⁴⁺ were equal peak currents found for anodic and cathodic scans. For SnTMPyP⁴⁺, the oxidation process could not be resolved from oxidation of the aqueous solvent.

The computer-controlled pulse radiolytic apparatus has been described previously²⁷ and consists of an ARCO LP 7 linear accelerator, supplying 10-ns pulses of 8-MeV electrons, each pulse producing $(2-4) \times 10^{-6}$ mol dm⁻³ of solvent radicals, and a Xe lamp as monitoring source. Only on rare occasions was the Xe lamp used in a pulsed mode and, in all cases, band-pass filters were used to avoid undue photolysis of the metalloporphyrin.²⁸ The general handling conditions have been given in an earlier paper²⁰ and the aqueous solutions were purged thoroughly with N_2 or N₂O before radiolysis. Water was purified by a Millipore Milli Q system and the pH was adjusted by addition of phosphate (pH 7), HCl (pH 2-3), or phosphate/KOH (pH 12). Solutions of the metalloporphyrins were prepared within a few hours of beginning the experiment and, whenever possible, were protected from light until they entered the radiation cell.

Absorption spectra of the transient radical cations and anions were recorded after completion of the formation reaction (20–100 μ s after the pulse) and before any sufficient decay took place. They were measured point-bypoint with each wavelength point consisting of signal averaging up to 20 separate pulses. The data were stored on tape and analyzed sometime later. For experimental

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TABLE I: Absorption Spectral Details and Half-WavePotentials for One-Electron Reduction and Oxidationof the Metalloporphyrins in Aqueous Solution

			and the second sec
		$\epsilon/10^3$, dm ³	$E_{1/2},$
compd	λ, nm	mol ⁻¹ cm ⁻¹	V vs. NHE
7.nT7P	438	210	-0.81
20121	560	15	±1.91
	605	5	7 1,21
PdTMPvP4+	414	171	-0.68
i a i wii yi	500	1/3	±1 /1
	555	5.9	T 1.41
PATSPP4-	410	156	-1.00
141011	519	120	+1.00
	550	16	11.00
A oTMPvP4+	430	233	
iigi mi yi	546	16.0	+0.84
	590	57	10.01
	000	0.1	
CdTMPvP4+	443	228	-0.75
041001 91	578	17.7	+1.09
	620	9.1	
CdTSPP ⁴ ⁻	428	691	-1.05
	567	19.7	+0.77
	607	8.2	
CuTMPyP ⁴⁺	426	228	-0.70
-	546	21.0	+1.36
	585	6.1	
	b		
CuTSPP ⁴⁻	418	535	-1.05
	538	24.2	+0.77
	582	4.1	
SnTMPyP ⁴⁺	415	382	-0.30
	550	18.2	> 1.5
	590	4.6	
SnTPyP	414	510	-0.40
	548	25.0	>1.5
-	586	7.5	
SnTSPP ⁴	413	620	-0.56
	549	22.6	+1.38
	588	9.0	
PbTMPyP ⁴⁺	469	205	
	606	7.1	+0.86
	658	12.1	

^{*a*} Plus long tail with shoulders at 645, 740, and 860 nm with ϵ 1000, 145, and 110 dm³ mol⁻¹ cm⁻¹. ^{*b*} Plus long tail with shoulders at 690 and 725 nm with ϵ 190 and 120 dm³ mol⁻¹ cm⁻¹.

convenience, the absorption spectra were restricted to λ < 750 nm. Kinetic studies were made at selected wavelengths, again with averaging up to 20 separate pulses, and the quoted rate constants (±25%) were obtained by computer fitting. Further details of the pulse radiolysis experiments and the radiolytic production of reducing or oxidizing radicals have been discussed elsewhere.²⁹

Results and Discussion

Absorption Spectroscopy. Ground-state absorption spectroscopy of metalloporphyrins has been discussed in great detail by several authors.³⁻⁵ Following the treatment of Gouterman,³ most metalloporphyrins possess an intense B band at about 420 nm, which corresponds to the origin of the second excited $\pi\pi^*$ singlet state, and two moderately intense Q bands situated between 500 and 650 nm which correspond to transitions to the first excited $\pi\pi^*$ singlet state. Paramagnetic metalloporphyrins frequently possess charge-transfer and tripmultiplet absorption bands which can be resolved from the $\pi\pi^*$ bands, especially in the near-IR region. Absorption spectra for many of the water-soluble metalloporphyrins used in this study have not been reported previously but details for the corresponding water-insoluble derivatives are readily available. The positions of the B and Q bands are reported in Table I together with the molar extinction coefficients (ϵ) measured in dilute aqueous solution. Except for AgTMPyP⁴⁺, PbTMPyP⁴⁺, and the copper(II) porphyrins, the absorption spectra were quite normal and compared reasonably well with those of the water-insoluble compounds.³ For the two paramagnetic metalloporphyrins, weak tripmultiplet bands were observed in the near-IR while lead(II) porphyrins are known to possess unusual spectra.

Comparison of the TMPyP⁴⁺ and TSPP⁴⁻ complexes showed that the latter compounds possessed much sharper Q and B bands which were blue shifted while the ratio of the higher and lower energy Q bands was much greater. 30 For example, the lowest energy Q transition observed for CdTSPP⁴⁻ is blue shifted some 345 cm⁻¹ relative to $CdTMPyP^{4+}$ while the Q(0,0) half-widths and Q(1,0)/Q-(0,0) ratios are 905 and 1735 cm⁻¹ and 2.40 and 1.94 for CdTSPP⁴⁻ and CdTMPyP⁴⁺, respectively. Similar differences exist for the other divalent metal TSPP⁴⁻ and TMPyP⁴⁺ compounds while the TZP compounds show absorption spectra very similar to the $TMPyP^{4+}$ derivatives. However, these variations should not be taken too seriously because the absorption spectra of the different tin(IV) porphyrins are almost identical and, here, the effects of the water-solubilizing groups are masked. Presumably, this effect is associated with the two tightly bound axial ligands on the tin(IV) ion and, indeed, the absorption spectra of the tin porphyrins were markedly dependent upon pH as has been found for several other high-valent metalloporphyrins. Of all the compounds studied here, the absorption spectra of the TSPP⁴⁻ compounds most closely resemble those of the water-insoluble derivatives.

The positively charged compounds were readily soluble in water, giving concentrations in excess of 10^{-3} mol dm⁻³, although in some cases prolonged stirring was needed to break down crystal structures. These solutions were quite stable upon storage, even in the presence of room light, and aggregation was unimportant. Similarly, the TSPP⁴⁻ complexes dissolved readily in water but dimerization was a serious problem for both PdTSPP⁴⁻ and CdTSPP⁴⁻ (not for SnTSPP⁴⁻) and the solutions decomposed upon standing for several days in the light. The TZP compounds and SnTPyP were poorly soluble in water, having maximum solubilities around 10^{-4} mol dm⁻³, with the latter compound aggregating upon storage. For the cadmium and lead porphyrins, it was necessary to work at pH >7 to avoid demetallation.

Electrochemistry. With the exception of AgTMPyP⁴⁺, addition or removal of an electron from the metalloporphyrins results in formation of the metalloporphyrin π -radical anions and cations, respectively. For the water-insoluble compounds, the π -radical ions have been fully characterized, by using absorption spectroscopy,¹⁹ EPR,¹⁸ X-ray,³¹ and conductimetric³² techniques, and the half-wave potentials for the redox processes have been well documented.²⁶ This is not so for the water-soluble derivatives and there have been few studies aimed at determining the redox potentials of such metalloporphyrins.^{33,34} For silver(II) porphyrins, removal of an electron results

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in formation of the corresponding silver(III) porphyrin.

In aqueous solution containing KCl (0.5 mol dm⁻³), reduction of the diamagnetic metalloporphyrins at a HMDE was a fairly clean process although except for the TMPyP⁴⁺ complexes there were some problems with solubility, aggregation, and adsorption. For many metalloporphyrins, reduction was not restricted to a singleelectron process and formation of π -dianions, -trianions, etc., could be resolved from the cyclic voltammograms. For example, SnTMPyP⁴⁺ (which was the easiest compound to reduce) gave reversible reduction waves at -0.30, -0.47, and -0.67 V vs. NHE. Such multireduction steps are well-known in organic solvents¹⁷ and, in most examples, we observed that the differences in reduction peaks for the first and second electron additions was about 0.28 ± 0.12 V. The dianions were susceptible to protonation, with subsequent formation of phlorins and chlorins, even at quite alkaline pH (pH <10) and did not show such reversible electrochemistry as the π -radical anions. Therefore, we have restricted our attention to the single-electron-transfer step and the half-wave potentials, determined from cyclic voltammetry, are given in Table I. At pH > 10, reduction of the tin(IV) porphyrins resulted in formation of stable π -radical anions for which it was possible to confirm that reduction involved a single-electron transfer using coulometry. Such measurements were not possible with the other metalloporphyrins because the π -radical anions seemed to disproportionate.

Similar cyclic voltammetry studies were carried out for oxidation of the metalloporphyrins in aqueous solution containing Na₂SO₄ (0.3 mol dm⁻³) using a glassy C working electrode. The electrochemical behavior of all the metalloporphyrins, except AgTMPyP4+, was not fully reversible and the π -radical cations were easily oxidized further to the π -dications and isoporphyrins. In addition, chemical reactions occurred so that reversible behavior was observed only for fairly fast scan rates where the potential was taken only slightly past the first anodic peak. For these studies, half-wave potentials for one-electron oxidation were estimated from the anodic and cathodic peaks but the cathodic peak current was always less than the anodic one. The observed values are collected in Table I and for metalloporphyrins that gave a clear second oxidation wave this occurred at 0.25 ± 0.10 V more positive than formation of the π -radical cation. In no case was it possible to confirm a single-electron transfer by coulometry.

Comparison of the various $E_{1/2}$ values for the different metalloporphyrins confirms the hypothesis that the TSPP⁴⁻ complexes are the easiest to oxidize while the $TMPyP^{4+}$ complexes are the easiest to reduce. In fact, from the data collected in Table I it is clear that SnTMPvP⁴⁺ is the most easily reduced metalloporphyrin while the most readily oxidized compound is CdTSPP⁴⁻. For a particular metalloporphyrin, the difference in $E_{1/2}$ for addition and removal of an electron lies within the range 2.05 \pm 0.20 V and for a given metal ion the $E_{1/2}$ value found for the TMPyP⁴⁺ is about 0.32 ± 0.05 V more positive than the value for the TSPP⁴⁻ complex. Within the limited data, the TZP compounds show $E_{1/2}$ values slightly more positive than the corresponding TMPyP⁴⁺ complexes. In principle, the water-soluble metalloporphyrins can be regarded as substituted tetraphenylporphyrins, for which the redox potentials are a function of the Hammett constant of the substituent.³⁵ However, it is difficult to estimate an $E_{1/2}$ value for a metal tetraphenylporphyrin in water and our attempts to determine $E_{1/2}$ values for the TPyP complexes were restricted by poor

solubility. Until other water-soluble metalloporphyrin derivatives are available, it is not possible to see if the redox potentials for such compounds follow similar linear-free-energy relationships as found in organic solvents although it is known that, for many metal-free porphyrins, there is a correlation between $E_{1/2}$ and acid/base character.^{36,37}

With the corresponding water-insoluble metalloporphyrins,²⁶ the difference in half-wave potentials for the addition and removal of an electron is 2.20 ± 0.15 V, compared to the theoretical value of 2.1 V. When account is taken of the different solvation energies between organic solvents and water, our observed value of 2.05 ± 0.20 V seems quite reasonable. Solvation terms are even more important for the dianions and dications and in aqueous solution it is much easier to add or remove the second electron relative to organic solutions. Thus, in N,N-dimethylformamide the difference in $E_{1/2}$ values between formation of the π -radical anion and the π -dianion is ca. 0.45 V compared to the 0.28 \pm 0.12 V found in water and the analogous difference for formation of the π -radical cation and the π -dication in CH₂Cl₂ solution is ca. 0.3 V compared to 0.25 ± 0.10 V in water.

No real attempt was made to study the $E_{1/2}$ values as a function of pH. Only tin(IV) porphyrins are expected to show any significant pH dependence and, for these compounds, the absorption spectra do vary with pH. Presumably, this pH effect is concerned with the acid/base character of axially coordinated hydroxide ions, as has been observed for several other water-soluble metalloporphyrins, and with both $SnTSPP^{4-}$ and $SnTMPyP^{4+}$ increasing the pH from 5 to 12 resulted in a 90 \pm 10 mV more negative $E_{1/2}$ for the one-electron reduction process.

Cyclic voltammetry for aqueous solutions of AgTM-PyP⁴⁺ containing Na₂SO₄ (0.3 mol dm⁻³) showed a reversible oxidation at 0.84 ± 0.02 V vs. NHE. Coulometric studies showed this to be a one-electron process and comparison with water-insoluble silver(II) porphyrins suggests that the oxidation process is a metal-centered reaction.³⁸ Certainly, the absorption spectrum of the oxidation product formed by controlled potential electrolysis at 0.90 V vs. NHE in a thin-layer cell bears much more resemblance to a silver(III) porphyrin³⁶ than to the spectrum expected for a silver(II) porphyrin π -radical cation. At pH 5, the oxidation product was stable, at least over several minutes standing, and could be reduced quantitatively to the starting material by addition of ferrocyanide. The absorption spectrum of the oxidation product was identical with that obtained by pulse radiolytic oxidation (see later) and that obtained by chemical oxidation with persulfate.

Pulse Radiolytic Reductions. The radiation chemistry of water is very well-known and can be manipulated by addition of various substrates to produce strongly reducing or oxidizing radicals.²⁹ Irradiation of aqueous solutions containing propan-2-ol yields hydrated electrons and 2hydroxy-2-propyl radicals, both of which are powerful reductants. Saturation of the solution with N₂O removes the solvated electron so that the redox reactions of the two reductants can be resolved. Similarly, irradiation of N_2O -saturated aqueous solutions containing bromide or chloride ions yields Br_2^{-} or Cl_2^{-} radicals, which are strong oxidants. These different processes have been utilized to study the redox chemistry of several water-soluble me-

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talloporphyrins²⁰ and we have extended the earlier investigations by studying the radiation-induced oxidation and reduction chemistry of several diamagnetic metalloporphyrins. The aim of the study was to measure absorption spectra of the metalloporphyrin π -radical ions and monitor the stability of these π -radicals in aqueous solution.

Reduction of the various metalloporphyrins in aqueous solution, at pH 7 or 12, was studied in the presence of propan-2-ol (0.1 mol dm⁻³). Under such conditions, the important radiation chemistry may be written

$$H_2O \longrightarrow \dot{H} + \dot{O}H + e_{aq} + H_2 + H_2O_2 \qquad (1)$$

$$\dot{O}H + (CH_3)_2 CHOH \rightarrow H_2 O + (CH_3)_2 \dot{C}OH$$
 (2)

$$\dot{H} + (CH_3)_2 CHOH \rightarrow H_2 + (CH_3)_2 \dot{C}OH$$
 (3)

$$(CH_3)_2 \dot{C}OH \rightleftharpoons (CH_3)_2 CO^{-} + H^+ \qquad (4)$$

with both the hydrated electron and the 2-hydroxy-2propyl radical being able to reduce a metalloporphyrin (MP).

> $e_{ac}^{-} + MP \rightarrow MP^{-}$ (5)

$$(CH_3)_2\dot{C}OH + MP \rightarrow MP \rightarrow H^+ + (CH_3)_2CO \quad (6)$$

$$(CH_3)_2 CO^{-} + MP \rightarrow MP^{-} + (CH_3)_2 CO$$
(7)

In our experiments the total concentration of reducing radicals produced in the pulse was measured by thiocyanate dosimetry assuming a total radiation yield G =6.0. Provided sufficient metalloporphyrin is present in solution to ensure that the sole decay route for the reducing radicals involves electron transfer to the metalloporphyrin, the concentration of reduced porphyrin formed after the pulse can be determined. This permits facile calculation of the molar extinction coefficient of the porphyrin π radical anion at any particular wavelength. The absorption spectra so obtained are difference spectra; i.e., they are the difference in molar extinction coefficients between the metalloporphyrin π -radical anion and the ground-state metalloporphyrin.

The various reductants produced in reactions 1-4 reacted with a particular metalloporphyrin at quite different rates. When the solution is saturated with N_2O , there is only a fairly slow grow-in of the π -radical anion while in the absence of N_2O approximately one-half of the total π -radical anion is formed soon after the pulse and the remainder grows in at the same rate as found in the presence of N_2O . Since N_2O reacts rapidly with the hydrated electron

$$N_2O + e_{ag}^- + H_2O \rightarrow N_2 + OH^- + OH$$
 (8)

we can attribute the initial formation of the π -radical anion to reduction of the metalloporphyrin by the hydrated electron (reaction 5) and the slow grow-in to reduction via the 2-hydroxy-2-propyl radical (reaction 6 or 7). The two reductants gave products with identical absorption spectra and, by following the product buildup at varying concentrations of the metalloporphyrin, it was possible to determine the absolute rate constants for reactions 5 and 6. For ZnTZP at pH 7, k_5 and k_6 were 1×10^{10} and 8.6×10^8 mol⁻¹ dm³ s⁻¹, respectively, and, at pH 12, k_7 was 1.7×10^9 mol⁻¹ dm³ s⁻¹ (all rate constants accurate to ±25%). Similar values of k_5 were found for the other metalloporphyrins, although, depending upon the nature of the metalloporphyrin, k_7 fell within the range $(1-50) \times 10^8$ mol⁻¹ dm³ s⁻¹. The absorption spectra determined for the various metalloporphyrins upon one-electron reduction are collected in Figure 1.

Qualitatively, the absorption spectra collected in Figure 1 possess several common features and they bear strong resemblances to absorption spectra of ZnTSPP⁴⁻ and ZnTMPyP⁴⁺ π -radical anions obtained previously by pulse radiolysis²⁰ and to spectra of the π -radical anions of SnTSPP⁴⁻ and SnTMPyP⁴⁺ obtained by controlled potential electrolysis (Figure 2). All the spectra show a series of reasonably intense absorption transitions in the near-IR region, although our spectra are restricted to $\lambda < 750$ nm in most cases, and a very intense transition around 450 nm. There are no obvious differences caused by the type of water-solubilizing group used. Careful comparison of the absorption spectral details given in Table I with the spectra collected in Figures 1 and 2 shows that there is quite a good correlation between the energy of the first allowed transition for the ground-state metalloporphyrin (E_{Ω}) and the energy of the first observed transition of the corresponding π -radical anion (E_{p} -). This effect is shown in Figure 3 but it must be remembered that there could well be lower energy absorption maxima for the π -radical anions than the ones measured here.

Such a correlation can be explained in terms of simple MO theory assuming addition of an electron to a metalloporphyrin results in population of an e_{g} orbital on the porphyrin π system. In fact, the lowest lying vacant MO on the porphyrin ring is doubly degenerate, or nearly so, and the orbital can accommodate four electrons. This explains the observation of mono-, di-, tri-, and tetranegative ions for a number of metalloporphyrins.¹⁷ Provided the π -radical anion retains D_{4h} symmetry, which may well not be true, it will possess a ${}^{2}E_{g}$ ground state and excited states of ${}^{2}A_{1u}$, ${}^{2}A_{2u}$, ${}^{2}B_{1u}$, and ${}^{2}B_{2u}$ symmetry. According to theoretical calculations, 39 the π -radical anions should how an allowed a \rightarrow b. transition at large wavelengths show an allowed $e_g \rightarrow b_{1u}$ transition at long wavelengths (ca. 900 nm) which is outside the range covered in our work. Also, there should be a series of allowed transitions in the near-IR region (600-800 nm) which involve population of the ${}^{2}A_{1u}$, ${}^{2}A_{2u}$, and ${}^{2}B_{2u}$ excited states and a very intense transition at 430–450 nm. Implications⁴⁰ that the ground state has a distorted geometry have limited the scope of these calculations but they provide a good qualitative description of the absorption spectra. From the electrochemical studies, it is believed that there is only minimal mixing between metal-centered orbitals and the highest filled (a_{2u}, a_{1u}) or lowest empty $(e_g) \pi$ orbitals on the porphyrin ring so that the central metal ion exerts only an inductive effect on the porphyrin π levels. Since this inductive effect should be very similar for the π radical anion and the ground-state metalloporphyrin, it is expected that the correlation shown in Figure 3 should be observed.

In most cases, the π -radical anion had limited stability and decayed on a time scale of 0.01-1 s, in agreement with previous reports.^{20,41} In fact, the π -radical anion of $2nTMPyP^{4+}$ has been used to reduce water to H₂ in the presence of a colloidal Pt catalyst.⁴¹ In the absence of Pt, decay of the π -radical anions is by a bimolecular process. This effect is exemplified by Figure 4, which shows the decay of the ZnTZP π -radical anion at 620 nm and the bimolecular rate constants for decay of the various π radical anions $(k_{\rm D})$ are collected in Table II. It is seen that the central metal ion exerts a strong influence upon the relative stability of the π -radical anions and, in the case of tin(IV) porphyrins, the π -radical anions were stable over prolonged storage times (>10 min) in the absence of O_2 .

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 (41) Harriman, A.; Porter, G.; Richoux, M. C. J. Chem. Soc., Faraday Trans. 2 1981, 77, 1939.



Figure 1. Difference spectra observed following pulse radiolytic reduction of the metalloporphyrins in aqueous solution at pH 12.



Figure 2. Absorption spectra of the π -radical anions of SnTMPyP⁴⁺ (—) and SnTSPP⁴⁻ (···) obtained by spectroelectrochemical methods at pH 11.

TABLE II: Rate Constants and Standard Free Energy
Changes for Disproportionation of the Metalloporphyrin
 π -Radical Anions

radical	pH	$k_{\mathbf{D}}$, $a dm^{3}$ mol ⁻¹ s ⁻¹	∆G _D , ^b kJ mol⁻¹
ZnTZP-	6.8	4.1×10^{6}	31
CuTMPyP ³⁺ ·	6.8	$9.1 imes10^8$	27
PdTSPP ⁵	6.8	$2.4 imes10^7$	31
	12	1.3×10^{8}	31
CdTSPP ⁵⁻	12	$5.2 imes10^{8}$	29
SnTSPP ⁵	12	<103	25
SnTPyP-	12	<103	27
SnTMPyP ³⁺	12	<103	16

 $a \pm 25\%$. $b \pm 3 \text{ kJ mol}^{-1}$.

Presumably, this bimolecular decay route involves disproportionation of the π -radical anion to form the π -di-



Figure 3. Relationship between the energies of the first allowed absorption band in the ground state ($E_{\rm Q}$) and the first observed absorption band in the π -radical anion ($E_{\rm p}$ -.)

anion which can protonate, forming the phlorin, or rearrange to the chlorin.

$$2\mathbf{MP}^{-} \rightleftharpoons \mathbf{MP} + \mathbf{MP}^{2-} \tag{9}$$

Also given in Table II are the standard free energies of disproportionation calculated from

$$\Delta G_{\rm D} = -nF \left(E_{1/2}^2 - E_{1/2}^1 \right) \tag{10}$$

where $E_{1/2}^2$ and $E_{1/2}^1$ refer to the half-wave potentials for



Figure 4. Decay of the ZnTZP π -radical anion at 620 nm. The drawn line represents a fit to second-order kinetics.

the second and first reduction steps, respectively.

From the data in Table II it is quite clear that the metalloporphyrin π -radical anions should be reasonably stable toward disproportionation and that the tin(IV) porphyrin π -radical anions should be the most susceptible toward disproportionation. However, the experimental findings contrast sharply with such hypotheses and, in several cases, the rate constant for decay of the π -radical anions approaches the diffusion-controlled rate limit. The first step in the disproportionation process must involve formation of a π -radical dimer and for water-insoluble anions and dianions there is evidence for strong ion association.⁴² Formation of metalloporphyrin π -radical anion dimers has been suggested from pulse radiolysis studies.²¹ However, the geometry of such radical dimers remains unknown, at present, but, if electron transfer to form the π -dianion occurs, then it is possible that a specific symmetry is required. Formation of the π -dianion involves transfer of an electron from an e_g orbital on one π -radical anion to an eg orbital on the second anion and, since the resultant π -dianions are diamagnetic, either the initially formed π -dianion has singlet (${}^{1}B_{1g}$) character or else rapid spin reorientation within a triplet (${}^{3}A_{2g}$) dianion must occur. Usually, the dianions are unstable with respect to formation of phlorins and chlorins. Possibly a face-to-face dimer configuration would assist electron transfer and, if so, it seems probable that the trend in $k_{\rm D}$ values found in Table II reflects the ease of formation of such a specific complex. The π -radical anions that possess some degree of steric hindrance toward formation of a face-to-face dimer (e.g., the tin(IV) porphyrins with their axial ligands and ZnTZP with its bulky side chains) show the lowest $k_{\rm D}$ values. Unfortunately, there are too few experimental results to take this argument too far.

Pulse Radiolytic Oxidations. The oxidants most commonly employed in pulse radiolytic experiments are the halide radicals Br_2 - and Cl_2 - produced by OH attack on the halide ions in N₂O-saturated aqueous solution

$$2Br^{-} + OH \rightarrow Br_{2}^{-} + OH^{-}$$
(11)

and both reagents are known to oxidize water-soluble zinc(II) porphyrins to the corresponding π -radical cations.²⁰ These halide radicals are quite powerful one-electron oxidants but, when a more powerful oxidant is required, it is feasible to use the sulfoxylate radicals.

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^- + SO_4^{2-}$$
 (12)

We have utilized these techniques to obtain absorption spectra for the oxidized water-soluble metalloporphyrins in much the same manner as was used to derive spectra



Figure 5. (a) Difference spectrum observed after pulse radiolytic oxidation of AgTMPyP⁴⁺ with $Br_2^{-\bullet}$ at pH 7. (b) Absorption spectra recorded before (---) and after (---) electrochemical oxidation of AgTMPyP⁴⁺ at pH 7.

for the π -radical anions. For these studies, the pH was either adjusted to 6.8 with phosphate buffer (10⁻³ mol dm⁻³) or made acidic by addition of HCl and the solution contained sodium halide (0.1 mol dm⁻³) or sodium persulfate (0.02 mol dm⁻³) and was saturated with N₂O or N₂, respectively.

Oxidation of AgTMPyP⁴⁺ by Br₂⁻ was a clean and facile process. The observed difference spectrum is given in Figure 5 and compared with that obtained by controlled potential electrolysis (similar absorption changes were caused by chemical oxidation with hypochlorite). In all cases, the oxidation product is the diamagnetic silver(III) porphyrin; similar processes occur with water-insoluble porphyrins.³⁸ From the pulse radiolysis studies, the rate constant for oxidation

 $Ag^{II}TMPyP^{4+} + Br_2^{-} \rightarrow Ag^{III}TMPyP^{4+} + 2Br^{-}$ (13)

was found to be $(3.5 \pm 1.0) \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

From the cyclic voltammetry studies and taking account of previous work with water-insoluble metalloporphyrins, we expect all the other compounds studied here to give the π -radical cation upon removal of one electron. Previously, this was shown to be the case for ZnTSPP⁴⁻ and ZnTMPyP⁴⁺ while photochemical studies have confirmed π -radical cation formation for palladium(II) and tin(IV) porphyrins in aqueous solution.²³ Using Br₂⁻ as oxidant at pH 6.8, it was possible to obtain quantitative conversion to the π -radical cation for zinc(II) and cadmium(II) porphyrins. From thiocyanate dosimetry and by variation of the concentration of the metalloporphyrin, it was possible to derive molar extinction coefficients for the product absorption spectra and also to estimate rate constants for the oxidation process ($k_{\alpha x}$).

$$MP + Br_2 \rightarrow MP + + 2Br \qquad (14)$$

The derived absorption spectra are collected in Figure 6 and the $k_{\rm ox}$ values are given in Table III. The rate constants lie within the range $(2-7) \times 10^9$ mol⁻¹ dm³ s⁻¹, which is close to the diffusion-controlled rate limit when allow-

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Figure 6. Difference spectra observed following pulse radiolytic oxidation of the metalloporphyrins in aqueous solution. Oxidants used: ZnTZP, PbTMPyP⁴⁺, and CdTMPyP⁴⁺ with Br_2^{-} at pH 6.8; CuTMPyP⁴⁺ and PdTMPyP⁴⁺ with Cl_2^{-} at pH 3; PdTSPP⁴⁻ and SnTSPP⁴⁻ with Cl_2^{-} at pH 2.

ance is made for the electrostatic factors.

For several metalloporphyrins in aqueous solution at pH 7, oxidation with Br_2^- was inefficient and an anomalously low yield of product was obtained. With $CuTMPyP^{4+}$ and the palladium(II) porphyrins, decay of Br_2^- as monitored at 350 nm, was almost unaffected by the presence of up to 4×10^{-4} mol dm³ metalloporphyrin and k_{ox} was <10⁸ mol⁻¹ dm³ s⁻¹. Thus, it was necessary to use a more powerful oxidant and, for this purpose, Cl_2^- was used. This

presents a problem because it is necessary to use Cl_2 - at quite low pH, which lowers the yield of oxidant (by converting e_{aq} - into H instead of OH).

 $k = 2.5 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow N_2 + OH + OH^{-}$$
 (15)
 $k = 8 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
 $e_{a0}^{-} + H^+ \rightarrow H.$ (16)

TABLE III: Rate Constants for Oxidation of the Metalloporphyrins by Halide Radicals

compd	oxidant	pН	k_{ox} , ^a dm ³ mol ⁻¹ s ⁻¹
ZnTZP CdTMPyP ⁴⁺ AgTMPyP ⁴⁺ CuTMPyP ⁴⁺ PdTMPyP ⁴⁺ PdTSPP ⁴⁻ SnTSPP ⁴⁻	$\begin{array}{c} \mathbf{Br}_{2}^{-} \\ \mathbf{Br}_{2}^{-} \\ \mathbf{Br}_{2}^{-} \\ \mathbf{Cl}_{2}^{-} \\ \mathbf{Cl}_{2}^{-} \\ \mathbf{Cl}_{2}^{-} \\ \mathbf{Cl}_{2}^{-} \\ \mathbf{Cl}_{2}^{-} \end{array}$	$\begin{array}{c} 6.8 \\ 6.8 \\ 6.8 \\ 3.0 \\ 3.0 \\ 2.0 \\ 2.0 \end{array}$	$\begin{array}{c} 3.1 \times 10^{9} \\ 6.8 \times 10^{9} \\ 3.5 \times 10^{8} \\ 6.0 \times 10^{9} \\ 3.2 \times 10^{9} \\ 5.0 \times 10^{8} \\ 4.4 \times 10^{8} \end{array}$

 $[^]a$ $\pm\,25\%.$

It is possible to correct for this effect by using the above rate constants in conjunction with the appropriate concentrations of N₂O and protons but the extinction coefficients derived for the metalloporphyrin π -radical cations are subject to more uncertainty than those obtained with Br_2 • at pH 7. Under these conditions, it was possible to achieve quantitative oxidation for CuTMPyP4+ and the palladium(II) porphyrins (Figure 6) and the observed rate constants for oxidation are collected in Table III. Oxidation was found also for SnTSPP⁴⁻ but not for SnTPvP or SnTMPyP⁴⁺, in accord with their half-wave potentials.

In an effort to oxidize the tin(IV) porphyrins and to confirm oxidation of PdTMPyP4+, irradiations were performed in the presence of sodium persulfate (0.02 mol dm^{-3}). With PdTMPyP⁴⁺, the persulfate complex precipitated upon standing and, again, oxidation was incomplete for SnTMPyP⁴⁺ and SnTPyP. In these experiments, the most significant absorbance changes occurred in the near-UV region ($\lambda < 500$ nm) and were attributed to radical adducts.

Problems also arose with the attempted oxidation of PbTMPyP⁴⁺ which, from its $E_{1/2}$ value, should be easily oxidized. Oxidation did occur with Br_2^- at pH 7 but the product appeared to have a much lower molar extinction coefficient than had been anticipated and precipitation occurred during the course of the experiment. The stability of this compound is poor and, although the absorption spectrum of the π -radical cation given in Figure 6 is probably correct qualitatively, the derived extinction coefficients should be regarded with suspicion.

The absorption spectra of the various π -radical cations, as shown in Figure 6, consist of a series of poorly resolved transitions spread out across the entire visible region and stretching into the near-IR and an intense transition at about 450 nm.¹⁹ Qualitatively, the spectra are similar to those characterized for the π -radical anions, and they agree quite well with absorption spectra of the water-insoluble derivatives.¹⁹

The π -radical cations possess a half-filled a_{2u} orbital so that transitions from lower energy, filled orbitals to this half-filled orbital can occur and the diffuse nature of the absorption spectra has been attributed to the large number of available excited states.⁴³ As found with the π -radical anions, the central metal ion shows only an inductive effect and there is virtually no interaction between the porphyrin half-filled π level and orbitals on the metal ion. Thus, the electronegativity of the central metal ion determines the energy of the absorption transitions but has no real effect upon the absorption profile.

The metalloporphyrin π -radical cations are powerful oxidants and, on thermodynamic grounds, they are capable of the oxidation of water to O_2 in neutral solution. For this to occur, a redox catalyst must be present and, even then, there is some controversy about the formation of O_2 .^{23,44} From the cyclic voltammetry, it is clear that oxidation of the metalloporphyrins is not a clean process but that side reactions limit the reversibility. Similarly, photochemical studies have shown that the metalloporphyrin π -radical cations possess limited stability in aqueous solution and π -dications and isoporphyrins are formed.²³ In most of the pulse radiolysis experiments, a large excess of halide ions is present but, unlike the π -dications, the π -radical cations are stable toward nucleophilic addition. With the analogous water-insoluble compounds there is no evidence for formation of radical dimers (the octaethylporphyrins do form well-defined radical dimers⁴³) but it is believed that zinc(II) and magnesium(II) porphyrin π -radical cations possess a very tightly bound counterion (e.g., perchlorate) in both solid and solution phases.³¹ Thus, the π -radical cations may exist in the form of ion pairs rather than as free cations.

During the course of the pulse radiolysis experiments, it soon became clear that most of the π -radical cations were unstable in aqueous solution, at least under the conditions of the experiment. The absorption spectra collected in Figure 6 were recorded some 10–100 μ s after the pulse but, on longer time scales, the absorbance decreased. The kinetics for this decay were complex and, typically, halflives were in the order of a few milliseconds. Where comparison was possible, the TSPP⁴⁻ complexes were much more stable than the $TMPyP^{4+}$ compounds. We did not attempt a systematic study of these decay processes but it seems likely that they include disproportionation, oxidation of halide ions and impurities, and reaction with any H_2O_2 formed during irradiation. It is hoped that further work will lead to a clarification of these decay processes.

Registry No. ZnTZP, 84431-54-9; PdTMPyP⁴⁺, 83364-16-3; PdTSPP⁴, 79745-32-7; AgTMPyP⁴⁺, 87261-79-8; CdTMPyP⁴⁺, 73231-15-9; CdTSPP⁴, 87261-80-1; CuTMPyP⁴⁺, 48242-70-2; CuTSPP⁴⁻, 87261-81-2; SnTMPyP⁴⁺, 87261-82-3; SnTPyP, 87261-83-4; SnTSPP⁴⁻, 80004-36-0; PbTMPyP⁴⁺, 82762-06-9; ZnTZP-, 87261-84-5; CuTMPyP³⁺, 87261-85-6; PdTSPP⁵⁻, 87261-86-7; CdTSPP⁵⁻, 87261-87-8; SnTSPP⁵⁻, 87261-88-9; SnTPyP-, 87261-89-0; SnTMPyP³⁺, 87261-90-3; Br₂-, 12595-70-9; Cl₂-, 12595-89-0.

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