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Photooxidation of Tin (IV) Porphyrins in Aqueous Solution

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In aqueous solution, tin(IV) tetrakis(N-methyl-4-pyridyl)porphine is readily oxidised to the π-radical cation upon irradiation in the presence of sodium persulphate. The π-radical cation is oxidised further to form the π-dication which, being a strong electrophile, adds a hydroxide ion to form the isoporphyrin. This species is unstable with respect to rearrangement and a dihydroxychlorin is formed which fluoresces at room temperature. Over a period of 30 mins or so, the dihydroxychlorin decays, probably forming a ketoporphyrin.

Introduction

Since the pioneering work of Krasnovskii [1] and Calvin [2] and their coworkers, the photoreduction of metalloporphyrins has been investigated in considerable detail. In protic solvents, reaction involves the successive hydrogenation of the pyrrole units giving rise to chlorins, (iso)bacteriochlorins, hexahydroporphyrins and octahydroporphyrins [3] with intermediate formation of their π-radical anions. In basic solvents, reduction leads to formation of phlorins and porphyrinogens [4], both of which are readily reoxidised back to the original porphyrin upon aeration of the solution. A great amount of fundamental research remains to be done, especially with regard to the interconversion of the various reduction products and the mechanism of disproportionation of the π-radical anions, although the essential framework has been established. In contrast, few studies have centred upon the photooxidation of metalloporphyrins. It is known that the one-electron oxidation of many diamagnetic metalloporphyrins results in formation of the unstable π-radical cations which can be oxidised further to the π-dication. Unlike the π-radical cation, the π-dication is a strong electrophile and it undergoes nucleophilic addition to give isoporphyrin derivatives [5]. The isoporphyrins are not particularly stable unless substituted in the meso position and they tend to undergo reductive elimination processes and ring opening reactions.

Very few oxidation studies have been carried out in aqueous solution and we could not find any reports describing the oxidation of tin(IV) porphyrins. The latter compounds are important because they possess extremely high redox potentials for the one electron oxidation step and, therefore, tin (IV) porphyrin π-radical cations (or π-dications) appear to be promising oxidants for the liberation of O_2 from water [6]. In a previous report [6] we commented upon the difficulty of photooxidising tin(IV) porphyrins in aqueous solution but showed that persulphate was a suitable oxidant. In this paper, we report in more detail on the photooxidation of tin(IV) porphyrins in aqueous solution.

Experimental

Tin(IV) meso-tetrakis(N-methyl-4-pyridyl)porphine chloride ($SnTMPyP^{4+}$) was prepared as before [6] and water was doubly distilled from a quartz still. Commercial samples of persulphate are usually obtained by anodic electrolysis of ammonium bisulphate and this is the most common impurity. We used two samples of sodium persulphate (BDH Chemicals) and one sample of ammonium persulphate (BDH Chemicals) although there were no noticeable differences in the experimental results observed with the various samples. Some experiments were performed with a sample of $Na_2S_2O_8$ that had been electrooxidised with a Pt electrode to

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ensure the absence of any reducing impurities. Also, $NaHSO_4$ was used in blank experiments. The concentration of persulphate was measured by titration [7].

Photochemical experiments were performed with aqueous solutions (pH 2.6) containing $SnTMPyP^{4+}$ (*ca.* 10^{-5} mol dm^{-3}) and $Na_2S_2O_8$ (1×10^{-2} mol dm^{-3}). The solutions were purged with N_2 prior to irradiation and the light source was a 250 W Xe arc lamp filtered to remove light of $\lambda < 400$ nm. The course of reaction was followed by absorption spectroscopy. Flash photolysis experiments were made with a frequency-doubled Nd laser (pulse duration 15 ns) as described previously [6] using outgassed solutions.

Tin(IV) meso-tetrakis(N-methyl-4-pyridyl)chlorin ($SnTMPyC^{4+}$) was prepared by irradiation of $SnTMPyP^{4+}$ in aqueous solution (borate buffer at pH 9.4) containing sodium sulphite (10^{-2} mol dm^{-3}). The solution was purged thoroughly with N_2 and irradiated with visible light for about 30 sec. The course of reaction was followed by absorption spectroscopy.

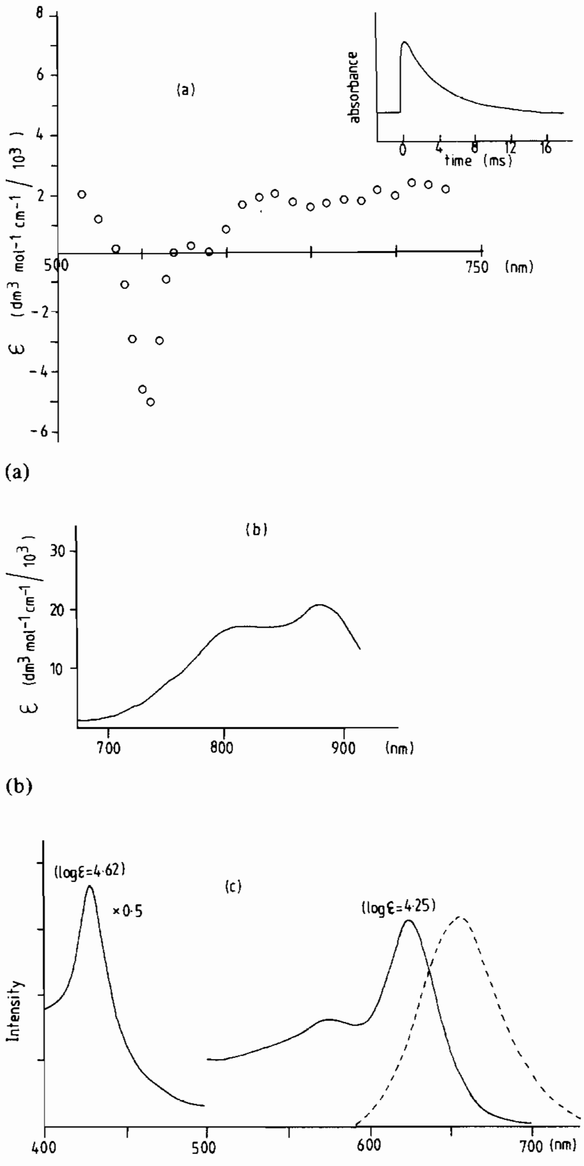
Results and Discussion

Upon excitation with visible light, $SnTMPyP^{4+}$ forms the triplet excited state with a quantum efficiency of 95% [6]. The triplet state possesses a reasonably long lifetime (τ_T = 0.9 ms) in outgassed aqueous solution which is quenched by $Na_2S_2O_8$ with a bimolecular rate constant of 1.0×10^7 mol^{-1} dm^3 s^{-1} at an ionic strength of 0.1 mol dm^{-3}. The product of this quenching act is the metalloporphyrin π-radical cation ($SnTMPyP^{5+\cdot}$)

$$SnTMPyP^{4+} + S_2O_8^{2-} \xrightarrow{h\nu} SnTMPyP^{5+\cdot} + SO_4^{-\cdot} + SO_4^{2-}$$

which has a characteristic absorption spectrum in the near IR region [8]. From flash photolysis studies, it was found that the π-radical cation had a fairly short half-life ($t_{1/2} \sim 3$ ms) and that it decayed by mixed kinetics. This thermal decay resulted in formation of two species; one with a sharp absorption maximum at 622 nm and the other with a broad absorption band centred around 880 nm. The latter species was unstable and it was converted into the 622 nm band upon standing in the dark for about 5 minutes. Thus, the final product was the species absorbing at 622 nm although this decayed to colourless products over a period of 30 minutes or so.

Absorption spectra of the various intermediate products are shown in Fig. 1. The π-radical cation ($SnTMPyP^{5+\cdot}$) can be identified by comparison to earlier pulse radiolysis work [8] whilst, from studies carried out with zinc porphyrins [5], the 880 nm band appears to be the tin(IV) isoporphyrin. However, the 622 nm band cannot be identified by comparison to earlier work (it does not possess the characteristic features of an oxoporphyrin or of a ring-opened product) – in fact, the absorption spectrum looks remarkably like that expected for a tin(IV) chlorin. The absorption spectrum shows that



(a)

(b)

(c)

Fig. 1. Absorption spectra of the intermediate species involved in the photooxidation of $SnTMPyP^{4+}$ with $Na_2S_2O_8$ in aqueous solution; (a) the π-radical cation $SnTMPyP^{5+\cdot}$. (the insert shows the rate of decay of $SnTMPyP^{5+\cdot}$ at 690 nm), (b) the isoporphyrin, (c) the dihydroxychlorin (the dashed curve shows the fluorescence spectrum).

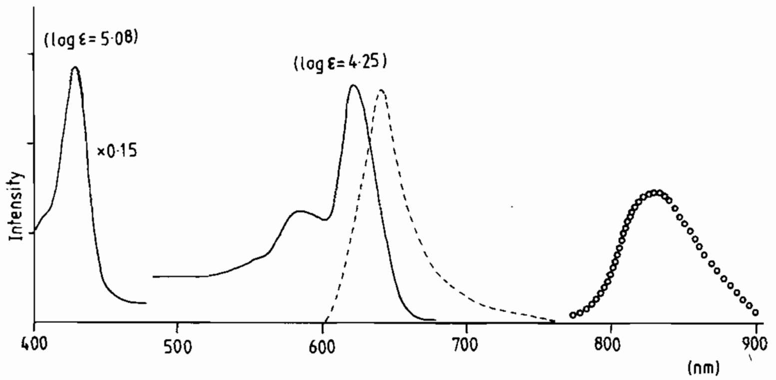
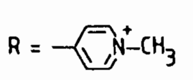


Fig. 2. Absorption (———), fluorescence (- - - - - -) and low temperature phosphorescence (ooooo) spectra of tin(IV) mesotetrakis-(N-methyl–4-pyridyl)chlorin in aqueous solution.

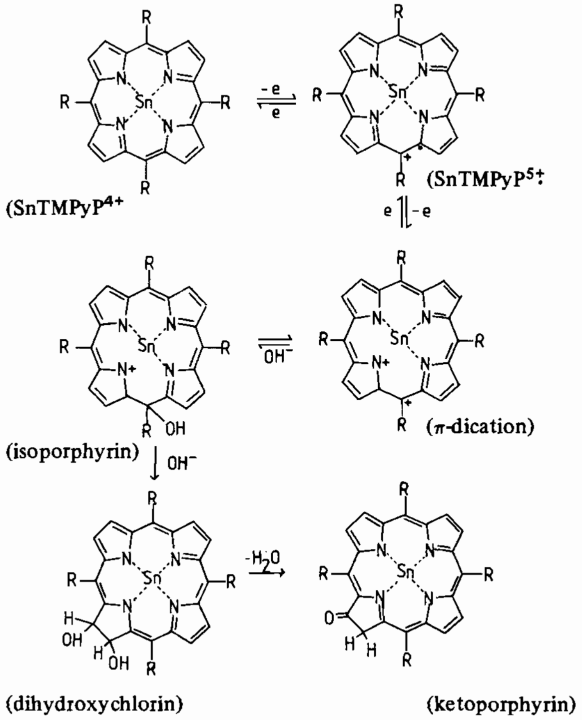
the principal conjugated sequence of the porphyrin is retained in the product which suggests that it arises from a thermal rearrangement of the isoporphyrin.

It was found that the 622 nm species fluoresced quite strongly in aqueous solution at room temperature (a quantum yield was not measured due to the presence of persulphate) but it showed no low temperature (77 K) phosphorescence. It is rare for porphyrin oxidation products to fluoresce and we became suspicious that the samples of persulphate contained a reducing impurity so that, upon excitation, we were forming the tin(IV) chlorin. However, several observations counted against this possibility. Firstly, several different samples of persulphate showed identical behaviour, as did a sample of persulphate that had been electrooxidised. Secondly, analysis of the persulphate samples showed that the only appreciable impurity was bisulphate and, in separate photochemical experiments, this was found to be unreactive with SnTMPyP^{4+}. Finally, the absorption spectrum of the appropriate tin(IV) chlorin, although very similar to the one shown in Fig. 1, differs significantly from that associated with the 622 nm absorbing species. The chlorin showed strong fluorescence at room temperature but it also exhibited low temperature (77 K) phosphorescence (Fig. 2). Thus, the chlorin and the 622 nm species appear to be structurally quite similar but they are not identical.

Based upon the above findings, we can propose the following reaction scheme.



(The two axial chloride ions have been omitted for simplicity of presentation)



Here, the first oxidation product is the π-radical cation, as identified by flash photolysis, which is oxidised further to form the π-dication. This second oxidation step probably involves contributions from several dark reactions, as suggested by the kinetics for decay of SnTMPyP$^{5+\cdot}$.

$$\mathrm{SnTMPyP}^{5+\cdot} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{SnTMPyP}^{6+} + \mathrm{SO_4^{-\cdot}} + \mathrm{SO_4}^{2-}$$

$$\mathrm{SnTMPyP}^{5+\cdot} + \mathrm{SO_4^{-\cdot}} \longrightarrow \mathrm{SnTMPyP}^{6+} + \mathrm{SO_4}^{2-}$$

$$2\mathrm{SnTMPyP}^{5+\cdot} \rightleftharpoons \mathrm{SnTMPyP}^{6+} + \mathrm{SnTMPyP}^{4+}$$

Unlike the π-radical cation, the π-dication is a powerful electrophile [5] and reacts with water to form the isoporphyrin. Often, isoporphyrins are unstable with respect to oxoporphyrin formation but, because N-methyl–4-pyridyl is a poor leaving group, this process is blocked in our case. Instead, rearrangement to a dihydroxychlorin seems to occur. The assignment of the 622 nm species as the dihydroxychlorin is based upon the close similarity between absorption and fluorescence spectra recorded for this species and the analogous chlorin. From its structure, we would expect the dihydroxychlorin to undergo elimination of a water molecule so that the ketoporphyrin is the final product.

At this point, it is interesting to consider the factors that influence the stability of the π-dication or isoporphyrin. The π-dication is a powerful oxidant which, if stable with respect to nucleophilic addition and rearrangement, might be suitable for oxidation of water to O_2 in the presence of a redox catalyst. To be stable it is necessary that the oxidising equivalents reside mainly on the meso positions of the porphyrin ring and whether or not this happens depends upon the nature of the central metal ion and upon the type of meso substituent. If the meso substitutent is a good leaving group (*e.g.* $H^{\bullet}$) then the isoporphyrin will be unstable with respect to reductive elimination [9] but this is easily prevented by using a porphyrin with phenyl groups positioned at the meso positions. The type of water-solubilising group attached to the phenyl group should have a pronounced effect upon the electron density at the meso position and, from a limited number of experiments, it appears that tetrakis(4-sulphophenyl)porphyrins give the most stable π-radical cations and π-dications. The electron density around the porphyrin ring is also affected by the central metal ion although few comparative experiments have been performed. In aqueous solution, the stability of isoporphyrins decreases in the order

$$Zn^{II} > Pd^{II} > Sn^{IV}$$

and it is interesting to note that Pd^{II} isoporphyrin seems to be unstable with respect to rearrangement to a Pd^{IV} porphyrin [6]. So far, the most stable π-radical cation and isoporphyrin have been found with zinc(II) tetrakis(4-sulphophenyl)porphine although we are continuing our studies in this field.

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