Photochemistry of Manganese Porphyrins. Part 7.† Characterisation of Manganese Porphyrins in Organic and Aqueous/Organic Microheterogeneous Systems

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Studies with aqueous and organic solvents and with micelles, membranes, and microemulsions showed that the environment had little effect upon the spectroscopic and chemical properties of Mn^{II} and Mn^{III} porphyrins. However, for oxidation of a Mn^{III} porphyrin, the environment makes important contributions towards the ease of oxidation and the nature of the oxidation process. In alkaline aqueous solution, oxidation was facile and resulted in formation of Mn^{IV} and Mn^{V} porphyrins. Identical, but less efficient, oxidation processes were observed in membranes and positively charged micelles but in both negatively charged micelles and microemulsions oxidation was extremely inefficient and the Mn^{V} porphyrin was not observed. In CH_2Cl_2 solution, reaction with phenoxathiinylium hexachloroantimonate gave the Mn^{III} porphyrin π-radical cation whilst reaction with iodosylbenzene resulted in formation of the Mn^{IV} porphyrin μ-oxo-dimer.

IT is commonly believed that a manganese complex functions as an important oxidant in the natural photosynthetic oxidation of water to molecular oxygen.[1] In order to form O_2 from water without the intermediate involvement of free radicals, the oxidant must possess a high redox potential ($E° > 0.82$ V at pH 7) and must also be able to supply the four oxidising equivalents inherent in the oxidation of water, equation (1). This latter

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e \qquad (1)$$

requirement necessitates concerted co-operation of four positive holes and, in recent years, it has been found that colloidal dispersions of noble metal oxides, such as RuO_2, can function in this manner and mediate the oxidation of water by strong, single-electron oxidants such as Ce^{4+} [2-5] In previous work, we have shown that manganese porphyrins are also capable of storing several oxidising equivalents on one molecule [6-9] and, in neutral or acidic solution, these compounds possess the necessary thermodynamic potential to liberate O_2 from water.[10] Thus, manganese porphyrins may be good model systems for the natural water-splitting enzyme although very little is known about the detailed mechanism of this natural process.

Recently, we described [10] the preparation and characterisation of Mn^{IV} and Mn^{V} porphyrins in alkaline aqueous solution and it was found that the nature of the environment had a strong influence upon the properties of these oxidised metalloporphyrins. In particular, the stability of Mn^{IV} porphyrins was markedly decreased as the solution pH was lowered and, in acidic solution, there appeared to be a strong possibility that the Mn^{IV} porphyrin could undergo an intramolecular electron transfer to form the isoelectronic Mn^{III} porphyrin π-radical cation, equation (2) (P = a porphyrin anion). In order to

$$Mn^{IV}P \longleftrightarrow Mn^{III}P^{\cdot +} \qquad (2)$$

investigate this possibility in more detail, we have studied the oxidation of Mn^{III} porphyrins in organic and aqueous micellar solutions where the environment is a better model for that found within the plant. As described below, the solvent plays an important role in determining the nature and properties of the oxidised manganese porphyrins and we have now a clear identification of the various manganese porphyrin oxidation states under a wide range of conditions. Armed with this knowledge, it is possible to attempt the construction of a homogeneous model system capable of mimicking the essential features of the photosynthetic process based upon manganese porphyrins and we will report on such studies in a subsequent paper.

EXPERIMENTAL

Materials.—5,10,15,20-Tetraphenylporphyrinatomanganese(III), $[Mn^{III}(tpp)]$, was prepared as described previously [11] and the water-soluble manganese porphyrins were prepared as for previous papers in this series [6] whilst the surfactant manganese porphyrin [Mn(tocp)] was prepared from [Mn(tcpp)] by esterification with n-octadecanol. Sodium lauryl sulphate, $NaO_3SC_{18}H_{37}$ (sls), was recrystallised twice from ethanol and cetyltrimethylammonium chloride, $[NMe_3(C_{16}H_{33})]Cl$ (ctac), was obtained from Eastman and used as received. The oxidants and reductants (B.D.H. Chemicals) were used as received and were standardised by titration. Iodosylbenzene (Sigma) was used as received and phenoxathiinylium hexachloroantimonate prepared according to a literature method.[12] Dichloromethane was spectroscopic grade and was dried with P_2O_5 whilst all other organic solvents were of the highest available grade. Aqueous solutions were prepared from deionised water redistilled from alkaline permanganate and the pH was adjusted by addition of NaOH solution.

Methods.—Absorption spectra were recorded with a Perkin-Elmer model 554 spectrophotometer and pH measurements were made with a Pye–Unicam 292 pH meter. Except where stated otherwise, the concentration of sls or ctac was 0.05 mol dm^{-3} and the pH of the bulk solution was adjusted immediately prior to use. Oil–water emulsions were prepared according to a literature method [13] and bilayer membranes were supported on millipore filters.[14] All oxidation and reduction studies were carried out under an

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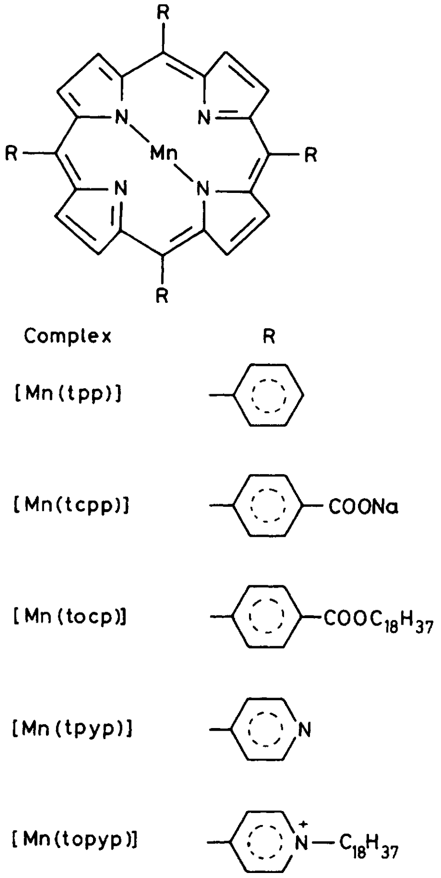
† Part 6 is ref. 10.

atmosphere of N_2 and solutions of the oxidant or reductant were injected into the manganese(III) porphyrin solution from a microsyringe. The course of reaction was followed by absorption spectroscopy.



[Mn^{III}(tpp)] was introduced into aqueous solutions of sls (0.05 mol dm^{-3}) as a concentrated solution in acetone and the residual acetone was removed by purging the warmed solution (*ca.* 50 °C) with a stream of N_2 for about one hour. Solutions of [Mn^{III}(tpp)] in aqueous sls were stable over a wide pH range for several weeks. At high pH ($>$13) some precipitation occurred after a few days standing in the dark but the solutions remained homogeneous for the time course of the experiments reported here ($<$3 h). A similar procedure was used to introduce [Mn^{III}(tpp)] into aqueous solutions of ctac (0.05 mol dm^{-3}) except that chloroform solutions were used in preference to acetone and similar stabilities were observed.

For studies with the oil–water microemulsions, the system described by Mackay *et al.*[13] was used. A co-surfactant, n-pentanol (10.8% w/w), and an oil, hexadecane (3.2% w/w), were mixed with sls (7.6% w/w) and the well dispersed mixture was diluted with water. The hydrodynamic radius of the droplet was about 18 nm and the aqueous solution was transparent and stable. The [Mn^{III}(tpp)] was dispersed in the microemulsion by stirring a solid sample in a N_2-purged solution for 24 h in the dark. This stock solution was stable over several months standing and the pH was adjusted by addition of NaOH solution. With the thin-layer membranes, the surfactant manganese porphyrins were supported on transparent millipore filters[14] held in a specially constructed frame. The whole assembly was placed in a glass vessel fitted with optical windows so that absorption spectra could be recorded *in situ*.

Oxidation of [Mn^{III}(tpp)] in CH_2Cl_2 solution with iodosylbenzene and phenoxathiinylium hexachloroantimonate was achieved by adding a slight excess of oxidant to a stirred solution of [Mn^{III}(tpp)] under an atmosphere of N_2. After a few minutes stirring, the mixture was filtered under vacuum and the filtrate collected in a receiver maintained at -70 °C. At this temperature, the product was stable over several hours and could be precipitated by addition of heptane.

Magnetic moments were measured by the Evans method[15] using concentric tubes and with Bu^{t}OH, benzene, or tetramethylammonium chloride as reference. Electrochemical studies were made in CH_2Cl_2 solution using conventional methods[16] and with a saturated calomel electrode (s.c.e.) as reference.

RESULTS AND DISCUSSION

Characterisation of [Mn^{III}(tpp)].—The stable oxidation state of a manganese ion contained within a porphyrin ligand is +3 and this state has been well characterised, in particular the absorption spectrum of a ' Mn^{III}P ' is highly characteristic due to its split *B* band.[17] Incorporation of Mn^{III}P into either an oil–water emulsion, a membrane, or an aqueous micellar system retains the +3 oxidation state, as evidenced by absorption spectroscopy.

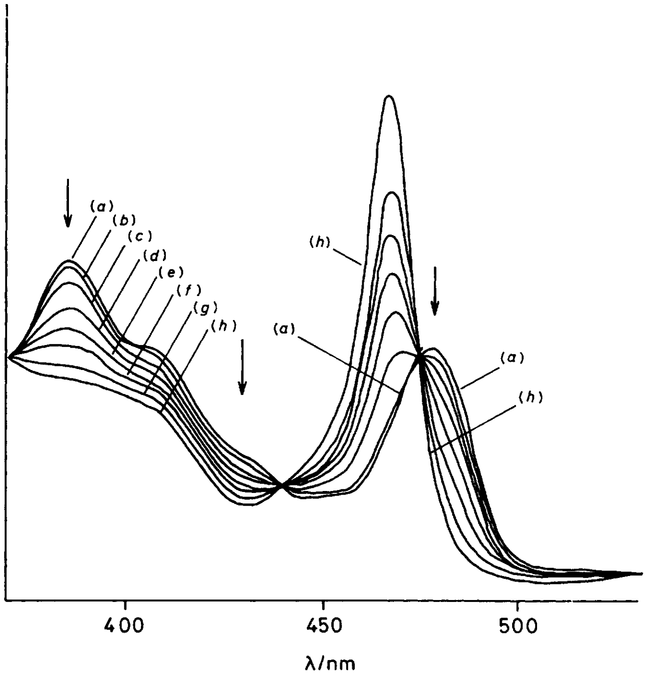


FIGURE 1 Absorption spectrum of [Mn^{III}(tpp)] in sls micelles as a function of pH: (*a*) 7.8, (*b*) 9.7, (*c*) 10.1, (*d*) 11.0, (*e*) 11.4, (*f*) 11.6, (*g*) 12.0, (*h*) 12.2

The absorption spectra of [Mn^{III}(tpp)] in an aqueous sls system and in an oil–water emulsion are given in Figures 1 and 2. In all systems and at bulk aqueous-phase pH values of 7 and 12, the absorption spectra of [Mn^{III}(tpp)] were independent of concentration of the manganese porphyrin within the range 10^{-7} to 10^{-3} mol dm^{-3}. Even where the concentration of [Mn^{III}(tpp)] exceeded the concentration of sls or ctac micelles in the solution, there was no evidence for dimerisation and the spectra followed Beer's law under all conditions studied.

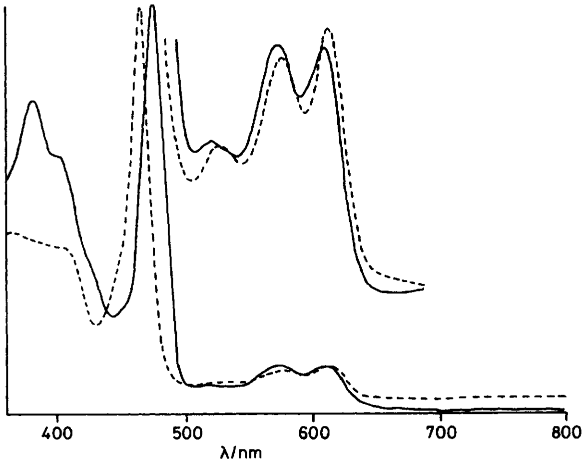
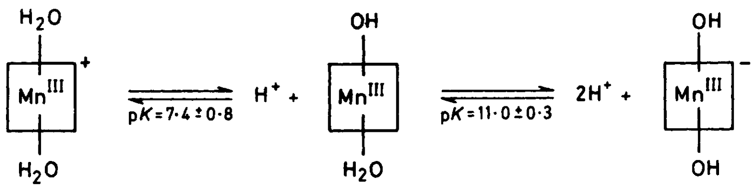


FIGURE 2 Absorption spectrum of [Mn^{III}(tpp)] in microemulsion at pH 7 (——) and pH 12 (– – –)

As shown in Figure 1, the absorption spectrum of [Mn^{III}(tpp)] was dependent upon pH in a similar manner to the corresponding water-soluble analogues.[6] Figure 1 shows the absorption spectra of [Mn^{III}(tpp)] in aqueous sls within the range $7.8 < \text{pH} < 12.2$ and it is seen that there is a clear pK transition (p$K = 11.0 \pm 0.3$). At pH > 11.5, the absorption maximum occurs at 468 nm whilst at pH < 10 the maximum is at 478 nm. At lower pH values, the absorption spectrum shows a slight pH dependence in that the absorption maximum shifts slightly to 480 nm and for this transition the pK is *ca.* 7.4 ± 0.8. Based upon our previous findings[6] with water-soluble manganese(III) porphyrins, the above pK transitions have been assigned as shown in equation (3) (the squares represent tpp^{2-}).



(3)

Characterisation of [Mn^{II}(tpp)].—Previous work has established that Mn^{III}P can be reduced to the corresponding Mn^{II}P by addition of a suitable reductant to an outgassed solution of Mn^{III}P.[6,8] A similar reduction was achieved by adding an alkaline solution of sodium dithionite to an outgassed aqueous sls or ctac solution of [Mn^{III}(tpp)]. The reaction was stoicheiometric for a one-electron reduction throughout the range $8 < \text{pH} < 12$ although the rate of reduction appeared to decrease with decreased pH. At pH < 8, [Mn^{II}(tpp)] was unstable towards demetallation; the rate of this process was increased substantially at lower pH levels. The absorption spectrum of the [Mn^{II}(tpp)] product is given in Figure 3 and compares well with that obtained by electrochemical reduction of [Mn^{III}(tpp)] in CH_2Cl_2 solution whilst, at all pH values and at different concentrations of [Mn^{II}(tpp)], aeration of the solution resulted in rapid conversion to [Mn^{III}(tpp)] without loss of the porphyrin. Identical results were obtained when [Mn^{II}(tpp)] was produced in a membrane or an oil–water emulsion.

No clear pK transition could be observed for [Mn^{II}(tpp)] in aqueous sls solution in the range $8 < \text{pH} < 12$. At pH > 12, addition of dithionite caused the micelle solution to become viscous and precipitation occurred upon standing whilst at pH < 8 demetallation was too rapid to allow the pH dependence to be investigated with any real significance.

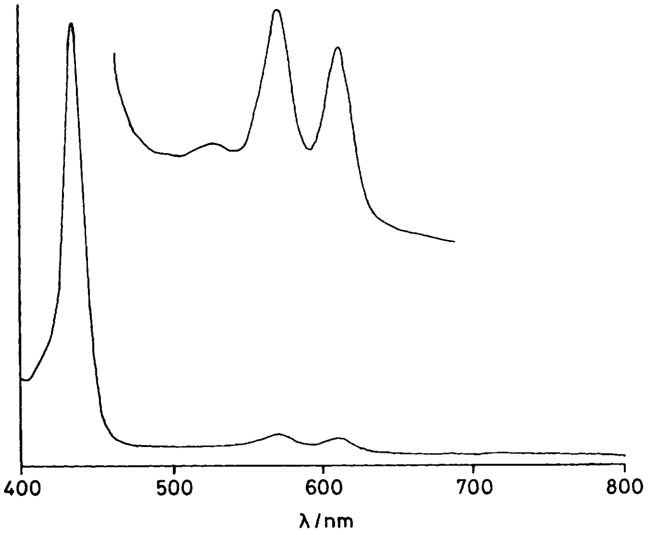


FIGURE 3 Absorption spectrum of [Mn^{II}(tpp)] in microemulsion at pH 10

A limited number of concentration dependence studies were carried out with [Mn^{II}(tpp)] dispersed in aqueous sls solution at pH 9.5. The absorption spectra followed Beer's law within the concentration range 10^{-7} to 10^{-5} mol dm^{-3} but at higher concentrations negative deviation from Beer's law was found. Thus, [Mn^{II}(tpp)] appears to undergo some kind of aggregation at high concentrations.

Oxidation of [Mn^{III}(tpp)].—Comparison of the experimental data reported here for [Mn^{II}(tpp)] and [Mn^{III}(tpp)] dispersed in the various microheterogeneous phases with that described previously[6-9] for water-soluble analogues shows that the environment has very little, if any effect upon the system. This is to be expected since both Mn^{II} and Mn^{III} porphyrins have similar properties when dissolved in organic or aqueous solvents. That is, the nature of the solvent has virtually no effect upon the spectroscopic properties of Mn^{II} and Mn^{III} porphyrins. However, from absorption spectroscopy it seems that the Mn(tpp) moiety resides well within the interior of the organic phase and since we have reported previously that oxidation of Mn^{III} porphyrins could be achieved only in neutral or alkaline aqueous solution, the use of mixed-phase systems may allow evaluation of the properties of the oxidised porphyrins in an organic environment.

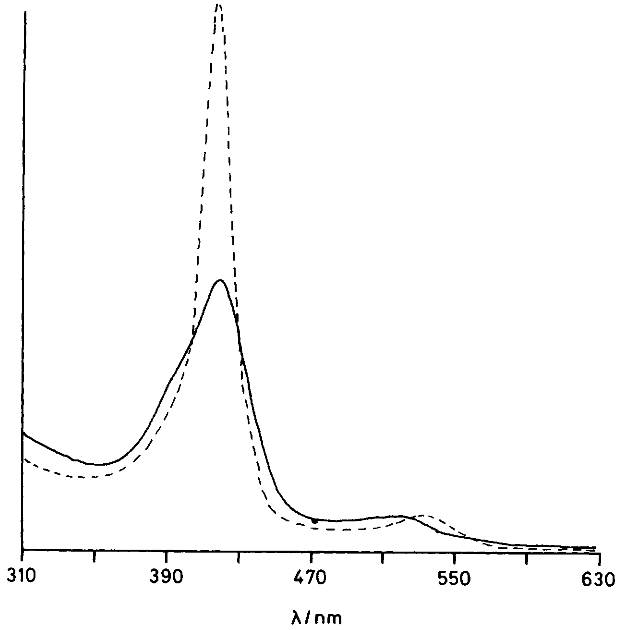


FIGURE 4 Absorption spectra of $[Mn^{IV}(tpp)]$ (——) and $[Mn^{V}(tpp)]$ (— — —) in ctac micelles at pH 12 formed by reaction with bromate and hypochlorite respectively

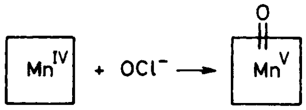
It has been recognised for a considerable time that addition of a powerful oxidant, such as hypochlorite, to an alkaline aqueous solution of $Mn^{III}P$ results in oxidation of the metalloporphyrin but the product of the reaction has only recently been identified with any real certainty.[10] We know now that oxidation of $Mn^{III}P$ with a fairly mild oxidant, such as ferricyanide, permanganate, or bromate, results in quantitative formation of the corresponding $Mn^{IV}P$ which exists in solution as a μ-oxo-dimer. With more powerful oxidants that can also transfer oxygen atoms during the electron-transfer step, such as hypochlorite, oxidation can lead to formation of a Mn^{V} oxoporphyrin. Also, it was considered[10] that, in acidic solution, the Mn^{IV} could undergo an intramolecular rearrangement to form a Mn^{III} porphyrin π-radical cation although this latter species was not characterised.

Because the stability of manganese(IV) porphyrins increases with increased pH,[10] it is desirable to carry out the oxidation studies in alkaline solution but aqueous dispersions of both ctac and sls micelles were precipitated at pH > 13 when high concentrations of electrolyte were added. Consequently, all oxidation studies were restricted to pH ⩽ 12 and it was found that addition of high concentrations (*ca.* 10^{-3} mol dm^{-3}) of ferricyanide, permanganate, PbO_2, molybdenum hexacyanide, or peroxodisulphate had no effect upon the absorption spectrum of $[Mn^{III}(tpp)]$ in either ctac or sls micelles at pH 12. Thus, in contrast to the studies carried out with water-soluble manganese porphyrins, these oxidants are unable to bring about the one-electron oxidation of $[Mn^{III}(tpp)]$ in a micellar environment.

Oxidation was achieved in ctac micelles at pH 12 by using bromate or hypochlorite as oxidant but, in both cases, a large excess (*ca.* 100 fold) of oxidant was required for complete oxidation of $[Mn^{III}(tpp)]$. Similar effects were observed with sls micelles except that an even larger excess of oxidant was required for complete conversion.

The absorption spectra of the products formed by oxidation of $[Mn^{III}(tpp)]$ in ctac micelles at pH 12 with bromate and hypochlorite are given in Figure 4. Careful comparison of these two spectra shows that the two products are different and, from our previous work[10] in alkaline aqueous solution, the bromate oxidation gives rise to $[Mn^{IV}(tpp)]$ whilst the hypochlorite oxidation results in formation of a Mn^{V} oxoporphyrin [equations (4) and (5)]. In ctac micelles at pH 12, both oxidation products were unstable and reverted back to $[Mn^{III}(tpp)]$ upon standing in the dark for a few hours. These reduction processes were catalysed by red light or by the addition of a reductant such as ferrocyanide or edta (ethylenediaminetetra-acetate) and, in all cases, $[Mn^{III}(tpp)]$ was regenerated with virtually no loss. A similar reduction occurred if the pH was lowered and at pH < 9 the half-life of the $[Mn^{IV}(tpp)]$ product was less than one minute.

$$\boxed{Mn^{III}} + Ox \longrightarrow \boxed{Mn^{IV}} + Red \qquad (4)$$



$$\boxed{Mn^{IV}} + OCl^{-} \longrightarrow \overset{\displaystyle O \atop \|}{\boxed{Mn^{V}}} + Cl^{-} \qquad (5)$$

Although there was good qualitative agreement between the absorption spectra of the $Mn^{IV}P$ formed by bromate oxidation in ctac at pH 12 and that formed by bromate oxidation of $[Mn^{III}(tcpp)]$ in water at pH 12, there were a few minor differences. In particular, in ctac micelles the absorption coefficient of the *B* band was somewhat higher than in water and the half-width of this band was considerably reduced in the micellar system. These findings suggest that the $[Mn^{IV}(tpp)]$ formed in ctac micelles may be a monomer rather than the μ-oxo-dimer found in aqueous solution. This is not too surprising in view of the micellar structure which should inhibit bimolecular processes[18] and, in fact, the absorption spectrum of the product remained unaffected by the concentration of the porphyrin provided that the molar concentration of micelles exceeded that of the porphyrin. Where the concentration of porphyrin approached the concentration of micelles in the solution, the absorption spectrum of the $Mn^{IV}P$ product was more characteristic of the μ-oxo-dimer than of the monomer. Since the dimerisation constants for manganese(IV) porphyrins in alkaline aqueous solution seem to be extremely high, the micelle environment is very effective at preventing association of two $Mn^{IV}P$ molecules and this is the first time that we have been able to characterise the absorption spectrum of a monomeric $Mn^{IV}P$ although we have no magnetic moment data to support this assignment.

Oxidation of the monomeric $[Mn^{IV}(tpp)]$ in ctac micelles with excess hypochlorite resulted in formation of the manganese(V) oxoporphyrin which was unstable with respect to its environment and reverted back to $[Mn^{III}(tpp)]$. Impurities in the surfactant enhanced this reduction step, as did addition of a reductant such as edta, dithionite, or tetrabutylammonium salts or lowering the pH of the aqueous phase. As found in aqueous solutions, of the oxidants used only hypochlorite was effective in producing the $Mn^{V}P$ and it is of interest to note that hypochlorite oxidises both monomeric and μ-oxo-dimeric manganese(IV) porphyrins.

Oxidation in sls micelles was extremely inefficient, even by comparison with ctac micelles, probably due to electrostatic repulsion between the micelle head groups and the negatively charged oxidants. With both bromate and hypochlorite, the oxidation product appeared to be monomeric $Mn^{IV}P$ but, with excess hypochlorite there was no further oxidation to $Mn^{V}P$. At fairly high concentrations of porphyrin (*ca.* 5×10^{-5} mol dm^{-3}), the absorption spectrum of the oxidation product showed a broad *B* band whilst at the maximum concentration that could be attained (*ca.* 2×10^{-4} mol dm^{-3}) the *B* band was centred at 405 nm rather than the 418 nm found in dilute solution. However, a large excess of oxidant was required to achieve complete oxidation and we are reluctant to attach much significance to the studies carried out with high concentrations of Mn porphyrins in sls micelles.

Even after correction for oxidation of any impurities present in the surfactant, oxidation of $[Mn^{III}(tpp)]$ in a micellar environment required excess oxidant and only strong oxidants were capable of bringing about the one-electron oxidation. These two findings can be explained in terms of the micelle structure since the polar head groups provide a strong electrostatic field. For sls micelles, there will be strong repulsion between the surface charge and the negatively charged oxidants so that the inefficient oxidation observed under such conditions can be ascribed to kinetic factors. With ctac micelles, there should be fairly strong association between the head groups and the negatively charged oxidants. This association disperses the oxidant around the exterior of the micelle and since, in most experiments, only a small fraction of the micelles contained a $Mn^{III}P$ molecule the effective concentration of available oxidant was low. The most probable substrate solubilisation sites in micelles are the interface and the Stern regions;[18,19] there is little evidence to suggest deep penetration into the micellar core. Even so, the midpoint potential for oxidation of $Mn^{III}P$ is known to increase sharply with decreased pH and it seems plausible to expect the midpoint potential for $Mn^{III}P$ dispersed in an aqueous micellar system to be somewhat greater than that of the compound dissolved in water at the same bulk-phase pH. If this is so, we might expect that only strong oxidants would be capable of oxidising manganese(III) porphyrins in ctac or sls micelles.

In order to investigate this latter effect in more detail, attempts were made to oxidise $Mn^{III}P$ in oil–water microemulsions and in membranes. For the studies with supported thin-layer membranes, surfactant derivatives of $Mn^{III}P$ were used so that the porphyrin could be positioned at the oil–water interface. Under such conditions, the surfactant manganese porphyrins exhibited behaviour similar to that described previously[10] for water-soluble $[Mn^{III}(tcpp)]$. That is, oxidation with mild oxidants (ferricyanide, bromate, or permanganate) resulted in formation of the $Mn^{IV}P$ μ-oxo-dimer whilst in the presence of excess hypochlorite the Mn^{V} oxoporphyrin was formed. Thus, such thin membranes do not appear to impose significant barriers to oxidation of $Mn^{III}P$.

With a microemulsion, we would expect to find the manganese porphyrin localised somewhere near the interface[10] which, in this case, will carry a negative charge due to the presence of sls. However, the surface potential should be considerably less than for sls micelles and, indeed, it was found that oxidation in the microemulsion was much more efficient than in sls micelles although excess oxidant was still required. No oxidation occurred with ferricyanide or permanganate whilst both bromate and hypochlorite oxidised $[Mn^{III}(tpp)]$ to the corresponding monomeric $[Mn^{IV}(tpp)]$. At fairly high concentrations of porphyrin ($>5 \times 10^{-5}$ mol dm^{-3}), oxidation resulted in formation of the μ-oxo-dimer of $[Mn^{IV}(tpp)]$ but, even with a large excess of hypochlorite, the Mn^{V} oxoporphyrin was not observed. Overall, the microemulsion behaved in a similar fashion to sls micelles although oxidation was much easier and the species at 405 nm was not seen in the microemulsion.

Our inability to produce the Mn^{V} oxoporphyrin in negatively charged micelles or microemulsions suggests that either it is not formed under such conditions (possibly due to kinetic factors) or else it is unstable in these environments. From our previous work, it seems probable that $Mn^{IV}P$ possesses an overall negative charge at pH > 11 which may help it associate with the surface groups in ctac micelles but force the molecule deeper into the hydrocarbon interior in sls micelles and microemulsions. If this is so, then there will be a considerable barrier to formation of the Mn^{V} porphyrin in negatively charged heterogeneous systems and this barrier will increase with increased potential around the interface.

The above argument infers that a Mn porphyrin contained within an organic environment will be more difficult to oxidise than one dissolved in water but this depends very much upon the pH of the aqueous solution. Previously,[10] it was found that the ease of formation of both $Mn^{IV}P$ and $Mn^{V}P$ increased with increased pH and whilst $Mn^{IV}P$ could be produced at pH > 7, $Mn^{V}P$ was observed only at pH > 10. Similar pH effects were found with the membrane systems but in both ctac micelles and the microemulsion [Mn^{IV}(tpp)] was formed only at pH > 9 and [Mn^{V}(tpp)] was produced only in ctac micelles at pH > 11. Thus, incorporating a manganese porphyrin into the hydrocarbon region of a microheterogeneous system does render the molecule more difficult to oxidise (presumably the midpoint potential for oxidation is increased) relative to aqueous solution at the same pH and we would expect that in hydrocarbon solvents it is difficult to produce $Mn^{IV}P$ and extremely difficult to form $Mn^{V}P$.

[Mn^{III}(tpp)] dissolved readily in dried CH_2Cl_2 and the resultant solution was stable over many months standing in the dark. Stirring the solution with excess PbO_2 or $Tl(OOCCF_3)_3$ had no effect upon the absorption spectrum and it appears that these oxidants are not able to oxidise [Mn^{III}(tpp)] in CH_2Cl_2 solution. In contrast, titration of the [Mn^{III}(tpp)] solution with a saturated solution of Cl_2 in CH_2Cl_2 resulted in inefficient oxidation of the metalloporphyrin, as evidenced by absorption spectroscopy. Similar, but even less efficient oxidation was achieved with Br_2 in CH_2Cl_2 and, in both cases, the oxidation product showed strong absorption bands at 383 and 479 nm. Addition of excess reductant, such as triethylamine, restored the original [Mn^{III}(tpp)] with very little overall loss, as did dilution of the CH_2Cl_2 solution with alcoholic solvents. The absorption spectrum of the product was unlike that found for any other Mn porphyrin but the poor oxidising efficiency of Cl_2 and Br_2, under these conditions, limited the characterisation of the product.

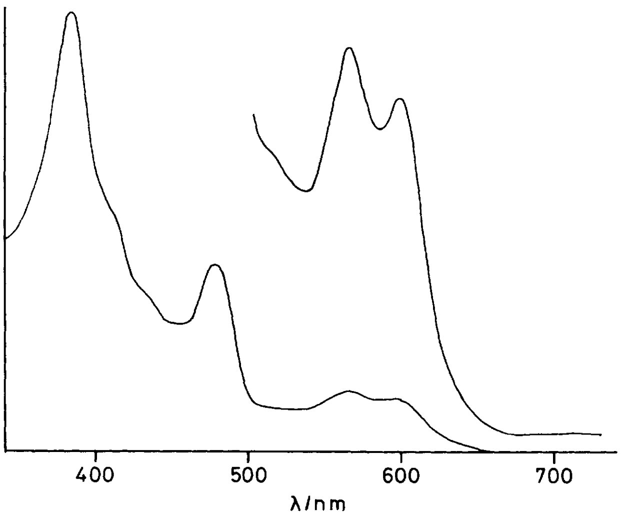


FIGURE 5 Absorption spectrum of the π-radical cation of [Mn^{III}(tpp)] formed by reaction of [Mn^{III}(tpp)] with phenoxathiinylium hexachloroantimonate in CH_2Cl_2 solution

However, a product possessing an identical absorption spectrum to that above was produced by addition of a slight excess of phenoxathiinylium hexachloroantimonate to a solution of [Mn^{III}(tpp)] in CH_2Cl_2 (Figure 5). Here, oxidation was much more efficient than found with Cl_2 or Br_2 and the product could be precipitated by addition of dry heptane. No e.s.r. signal could be detected for the product whilst the magnetic moment was found to be 3.9 B.M.* which is consistent with an $S = 3/2$ state. Controlled potential electrolysis of [Mn^{III}(tpp)] in CH_2Cl_2 at +1.2 V (*versus* s.c.e.) resulted in formation of a product having the same absorption spectrum as that shown in Figure 5 and, from coulometry measurements, it was shown that the product involved a one-electron oxidation of [Mn^{III}(tpp)].

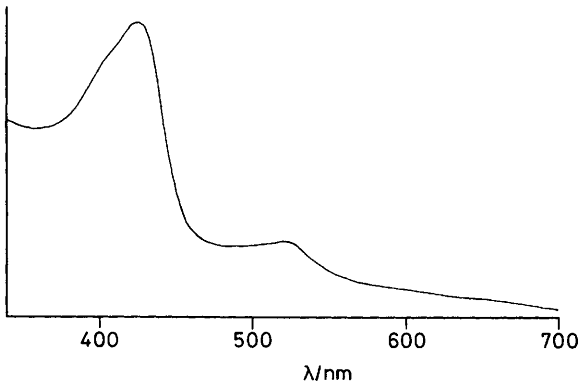


FIGURE 6 Absorption spectrum of the μ-oxo-dimer of [Mn^{IV}(tpp)] formed by reaction of [Mn^{III}(tpp)] with iodosylbenzene in CH_2Cl_2 solution

The absorption spectrum of the product (Figure 5) is not characteristic of a metalloporphyrin but it looks similar to the spectra of many metalloporphyrin π-radical cations.[20] In particular, there is a strong resemblance between reactions of phenoxathiinylium hexachloroantimonate with [Fe^{III}(tpp)] and [Mn^{III}(tpp)] and for the former reaction all available evidence favours formation of a π-radical cation of [Fe^{III}(tpp)].[12] These findings, together with the measured magnetic moment, point clearly towards our oxidation product being a π-radical cation of [Mn^{III}(tpp)], equation (6). From the electrochemical studies, only one oxidation wave could be observed at potentials less than +1.4 V (*versus* s.c.e.) and this occurred at 1.1 V which agrees well with the value of +1.06 V (*versus* s.c.e.) reported by Goff and coworkers.[21] Since this wave refers to removal of an electron from the porphyrin ring we conclude that, in

$$\boxed{\mathrm{Mn^{III}}} + \mathrm{Ox} \longrightarrow \boxed{\mathrm{Mn^{III}}}^{\cdot +} + \mathrm{Red} \qquad (6)$$

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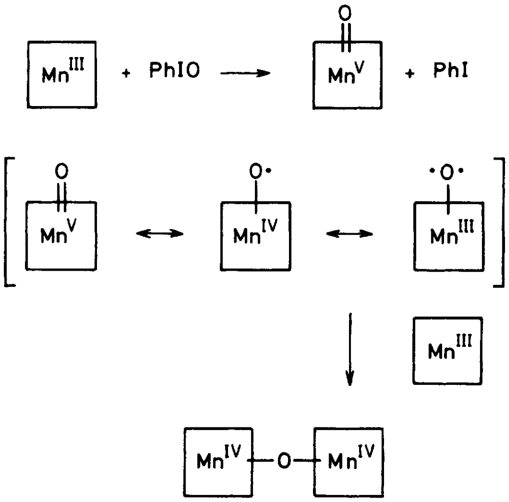
* Throughout this paper: 1 B.M. = 9.274×10^{-24} J T^{-1}.

CH_2Cl_2, oxidation of Mn^{III} to Mn^{IV} must be a very unfavourable process. Thus, there is a remarkable change in the redox properties of $[Mn^{III}(tpp)]$ when the solvent is changed from aqueous alkali to CH_2Cl_2 and, consequently, it is not too surprising that it is more difficult to oxidise $Mn^{III}P$ in a micelle than in aqueous alkaline solution.

The electrochemical studies gave no evidence for a second oxidation step and, instead, the solvent was oxidised before removal of a second electron from the metalloporphyrin. Similarly, reaction of $[Mn^{III}(tpp)]$ with excess phenoxathiinylium hexachloroantimonate or treatment of the π-radical cation of $[Mn^{III}(tpp)]$ with Cl_2 or Br_2 failed to give further oxidation and, by such techniques, we were unable to produce a Mn^{IV} or Mn^{V} porphyrin.

However, treatment of $[Mn^{III}(tpp)]$ in CH_2Cl_2 solution with iodosylbenzene resulted in formation of $Mn^{IV}P$. Very recently,[22] *X*-ray crystallography has established that this oxidation product is a μ-oxo-dimer of $[Mn^{IV}(tpp)]$ and our absorption spectrum (Figure 6) and magnetic moment (2.1 B.M.) support this assignment. It is only with iodosylbenzene that we have been able to produce Mn^{IV} in organic solvents, which suggests that the mechanism for oxidation with this oxidant may be complex. For other metalloporphyrins, it has been reported [23,24] that the reaction with iodosylbenzene produced high-valence oxoporphyrins due to O-atom transfer so that a plausible mechanism for the $[Mn^{III}(tpp)]$ reaction is shown by equations (7)—(9). In aqueous alkaline solution, the Mn^{V} oxoporphyrin did not react [10] with added Mn^{III} so that, if the above mechanism is correct, there must be some important differences in the properties of Mn^{V} porphyrins in aqueous and organic solvents. Such differences may help to explain our failure to observe $Mn^{V}P$ in sls micelles and microemulsions.



(7)

(8)

(9)

The above work has confirmed the formation of Mn^{IV} and Mn^{V} porphyrins in aqueous environments and has shown that, except under special circumstances, the first oxidation product for $Mn^{III}P$ in organic environments is the $Mn^{III}P$ π-radical cation. The π-radical cation is a powerful oxidant, it should be capable of oxidising water to O_2 at pH 7, but the redox potential of $Mn^{IV}P$ is strongly dependent upon pH and increases with decreased pH. In order to use a Mn porphyrin to oxidise water to O_2 (ultimately in a photochemical system aimed at mimicking photosynthesis) the value of the redox potential is of critical importance: it must be above the redox potential of the O_2/H_2O couple but, at the same time, it must be low enough for oxidation of the Mn porphyrin to be brought about readily. The latter requirement seems to rule out the $Mn^{III}P$ π-radical cation and, in fact, it has not yet been demonstrated that an organic radical cation can liberate O_2 from water whereas there are several metal-centred oxidants that are known to oxidise water to O_2. The redox potential for the O_2/H_2O couple depends upon pH [equation (10)] so, if

$$E^{\circ}_{O_2/H_2O} = (1.23 - 0.059\,\mathrm{pH})\ \mathrm{V} \qquad (10)$$

we are to use $Mn^{IV}P$ as oxidant, the choice of pH will be crucial for formation of O_2 and, from our previous work with water-soluble Mn porphyrins,[10] it appears that at pH 7 $Mn^{IV}P$ may just possess the necessary thermodynamic potential to oxidise water to O_2. The overpotential needed to drive this reaction may be attained by positioning the Mn porphyrin on the hydrocarbon side of an aqueous–organic interface since the redox potential for oxidation of a Mn porphyrin seems to increase markedly when the porphyrin is in an organic environment. By holding the Mn porphyrin at an optimum site near the interface it may be possible to ' tune ' the redox potential for the photo-oxidation of water to O_2.

This may help to explain how plants successfully photo-oxidise water to O_2 using chlorophyll as sensitiser and a manganese complex as oxidant although there is no available evidence to show that a Mn porphyrin is involved in the natural process. For our part, before a Mn porphyrin can be proposed as a possible oxidant in the photosynthetic process we must show that there exists a mechanism for water oxidation by Mn porphyrin in model systems and this will be described in the next paper in this series.

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