# Photochemistry of Manganese Porphyrins. Part 6.† Oxidation–Reduction Equilibria of Manganese(III) Porphyrins in Aqueous Solution

By **Nilton Carnieri, Anthony Harriman,*** and **George Porter,** Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS

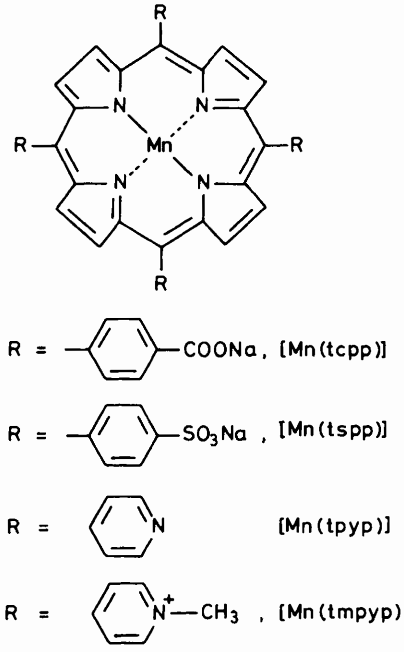
Water-soluble manganese(III) porphyrins are oxidised in alkaline aqueous solution to the corresponding manganese(IV) porphyrins which, from magnetic moment measurements, appear to exist in solution as μ-oxo-dimers. Midpoint potentials and rate constants for oxidation of the manganese(III) porphyrins have been measured for a series of oxidants and throughout the range $9 < pH < 14$, but the overall electronic charge on the metalloporphyrin had little effect upon either parameter. The midpoint potentials for the $Mn^{III/IV}$ couple are strongly dependent upon pH and increase with decreasing pH. Although manganese(IV) porphyrins are mild oxidants at pH 14, they should be capable of oxidising water to molecular oxygen in neutral solution. With hypochlorite as oxidant, a second oxidation step is possible and the final product is believed to be a manganese(V) oxo-porphyrin.

It is commonly believed that some, as yet unidentified, manganese compound functions as a catalyst to facilitate oxygen evolution in green plant photosynthesis.[1] The oxygen-evolving step in the natural process can be described as the chlorophyll-photosensitised oxidation of water to $O_2$ with the reduction equivalents being stored in the form of hydroquinone, equation (1) (Q = quinone).

$$2\,H_2O + 2\,Q \xrightarrow{h\nu} 2\,QH_2 + O_2 \qquad (1)$$

So far, this reaction has not been achieved in the laboratory[2] although recent years have witnessed great advances in the development of *in-vitro* systems for the photo-oxidation of water. One of the most severe problems associated with the formation of $O_2$ is that the reaction requires a four-electron change and, if free-radical intermediates are to be avoided, then one of the reactants must be able to store a minimum of four oxidising equivalents. Successful model systems have utilised dispersions of noble metal oxides such as $RuO_2$, $PtO_2$, or $IrO_2$ as the store for these oxidising equivalents[3-6] and, from available data, it appears quite probable that nature uses a manganese compound for this purpose.

For a simple manganese compound to undergo charge accumulation it must possess a series of available redox states and, in previous work, we have shown that this condition is fulfilled by manganese porphyrins.[7,8] Here, the most stable oxidation state of the central manganese ion is +3 but this can be reduced to the +2 state or oxidised to a +4 state.[7] The reduction step has been well characterised and we have a good understanding of the chemistry of both manganese(II) and manganese(III) porphyrins.[9,10] In contrast, the oxidation step, which in many respects is the most important one, remains a mystery. The oxidation product has been described as both a manganese(IV) porphyrin[11] and a manganese(III) porphyrin π-radical cation[7] whilst the involvement of a manganese(V) porphyrin has been inferred.[11,12] However, if this oxidation product is to play a key role in the oxidation of water to $O_2$ then we must obtain a better understanding of its nature and properties, and in this paper we attempt to characterise the oxidation of manganese(III) porphyrins in aqueous solution. In a subsequent paper we will describe the corresponding processes in organic solvents and in mixed aqueous–organic phases where the environment surrounding the porphyrin may be a better model for that found within the plant.



EXPERIMENTAL

*Materials.*—The preparation, purification, and characterisation of the water-soluble manganese(III) porphyrins have been described previously (their overall charges have been omitted since they are dependent on pH, see ref. 7). The oxidants were commercial samples of the highest available purity and were standardised by titration before use. Aqueous solutions were prepared from doubly distilled deionised water and the pH was adjusted by addition of carbonate-free NaOH. For studies at pH 7.0, a phosphate buffer was used and for all kinetic measurements $Na_2SO_4$ (0.5 mol $dm^{-3}$) was used as an ionic strength mediator.

*Methods.*—Absorption spectra were recorded with a

---

† For Part 5, see N. Carnieri and A. Harriman, *J. Photochem.*, 1981, **15**, 341.

Perkin-Elmer 554 spectrophotometer. Stock solutions of the manganese(III) porphyrins (*ca.* $5 \times 10^{-6}$ mol dm$^{-3}$) were used for all oxidation studies and, after adjustment of the pH, aliquots of the oxidant solution, maintained at the same pH, were added *via* a microsyringe. The course of reaction was followed by absorption spectroscopy.

Potentiometric titrations were made using the methods described by Loach and Calvin [11] and each measurement was repeated several times. Kinetic studies were made with an Applied Photophysics Ltd. stopped-flow instrument (dead time 2 ms) and all measurements were made under pseudo-first-order conditions.[9] Solutions of the manganese(III) porphyrin (*ca.* $2 \times 10^{-6}$ mol dm$^{-3}$) were mixed with solutions containing various amounts of the oxidant ($1 \times 10^{-5}$—$10 \times 10^{-5}$ mol dm$^{-3}$) and the derived bimolecular rate constants had a reproducibility of $\pm 5\%$.

Magnetic susceptibilities were measured in alkaline $D_2O$ solution by Evans method [13] using concentric tubes. Tetramethylammonium chloride and t-butyl alcohol were used as reference compounds and the n.m.r. spectra were recorded with a 100-MHz instrument at room temperature.

## RESULTS AND DISCUSSION

*Oxidation at* pH 14.—In the absence of an oxidising agent, manganese(III) porphyrins are stable in aqueous solution at pH 14 over several weeks standing in the dark. However, as shown in Figure 1, upon addition of an oxidising agent the absorption spectrum changes and a new species is formed. Identical absorption spectral changes were obtained for oxidation by a whole series of oxidants, including peroxodisulphate, hypochlorite, bromate, chlorite, hydrogen peroxide, permanganate, lead dioxide, and ferricyanide, and the nature of the porphyrin periphery groups had virtually no effect on the absorption spectrum of the product. With ferricyanide, $[Fe(CN)_6]^{3-}$, the process was quite reversible and addition of ferrocyanide, $[Fe(CN)_6]^{4-}$, to the product solution caused reversion to the original manganese(III) porphyrin without loss. With some of the more powerful oxidants (*e.g.* hypochlorite) there was some loss of the porphyrin chromophore following reduction of the product with ferrocyanide but, in all cases, this effect was very small. From titration studies with ferricyanide, chlorite, bromate, and hypochlorite it was found that the oxidation reaction corresponded to a one-electron change with respect to the manganese(III) porphyrin and there was a series of clear isosbestic points (Figure 2). Thus, the reaction appears to be a simple one-electron step leading to formation of either a manganese(IV) porphyrin or a manganese(III) porphyrin $\pi$-radical cation depending upon which part of the metalloporphyrin molecule donates the electron to the oxidant. In the absence of excess of oxidant, the product had limited stability and slowly reverted to the manganese(III) porphyrin upon standing in the dark ($t_{\frac{1}{2}}$ *ca.* 4 h) and, again, the series of isosbestic points were observed. This latter step was catalysed by irradiation with red light.

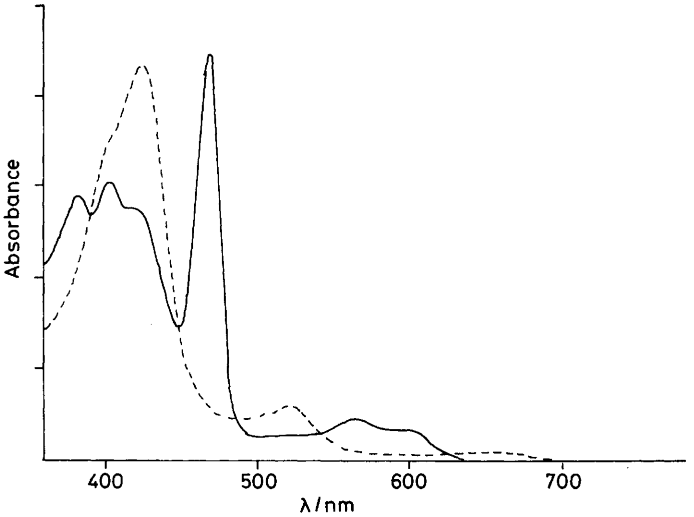


FIGURE 1 Absorption spectrum of [Mn$^{III}$(tcpp)] in aqueous solution at pH 14 in the absence (——) and presence (– – – –) of the stoicheiometric amount of bromate

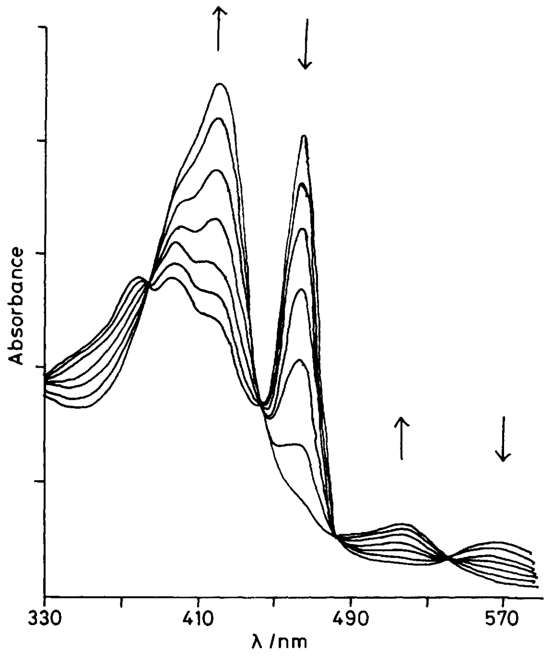


FIGURE 2 Absorption spectral profile for oxidation of [Mn$^{III}$(tcpp)] in aqueous solution at pH 14 with ferricyanide

The high degree of reversibility of the reaction between a manganese(III) porphyrin and the ferricyanide–ferrocyanide couple allowed potentiometric measurements to be used for calculation of midpoint potentials. Thus, for a reversible system involving oxidation of a manganese(III) porphyrin (MnP) with an oxidant (Ox), equation (2), the potentials of the MnP$^+$/MnP and the

$$\mathrm{MnP} + \mathrm{Ox} \rightleftharpoons \mathrm{MnP}^+ + \mathrm{Red} \qquad (2)$$

Ox/Red couples are equal to each other at the equilibrium position and, to a first approximation, an equilibrium constant ($K$) can be defined [11] [equations (3) and (4)].

$$K = [\mathrm{Red}][\mathrm{MnP}^+]/[\mathrm{Ox}][\mathrm{MnP}] \qquad (3)$$

$$\log K = 2.303\, nF\left(\frac{E^{\mathrm{Ox/Red}} - E^{\mathrm{MnP^+/MnP}}}{RT}\right) \qquad (4)$$

By using a combination of potentiometry and spectrophotometry, and with ferricyanide as oxidant at pH 14, the midpoint potentials ($E_m$) for oxidation of the various manganese(III) porphyrins were determined (Table 1). The observed values lie close to +0.39 V (*vs.* normal hydrogen electrode, n.h.e.) and there is only a slight dependence upon the type of group used to assist solubility of the metalloporphyrin in water. This is a somewhat surprising result since, based upon previous findings,[14,15] we might expect that $E_m$ for the negatively charged porphyrins would be considerably lower than those for the neutral or positively charged compounds, as found for oxidation of water-soluble zinc(II) porphyrins,[15] but our work shows that this effect is minor for oxidation of manganese(III) porphyrins at pH 14. Consequently, there may be fundamental differences in the mechanisms for oxidation of zinc(II) and manganese(III) porphyrins in aqueous solution.

TABLE 1

Midpoint potentials and rate constants for oxidation of manganese(III) porphyrins with ferricyanide in aqueous solution at pH 14 containing 0.05 mol dm$^{-3}$ $Na_2SO_4$

| Compound | $E_m$/ V *vs.* n.h.e. | $10^{-4}k_{Ox}$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| [$Mn^{III}$(tcpp)] | 0.388 | 2.0 |
| [$Mn^{III}$(tspp)] | 0.382 | 10.8 |
| [$Mn^{III}$(tpyp)] | 0.393 | 74.5 |
| [$Mn^{III}$(tmpyp)] | 0.406 | 1 010.0 |

However, the rate of oxidation ($k_{Ox}$) of a manganese(III) porphyrin with ferricyanide in aqueous solution at pH 14 was found to be markedly dependent upon the nature of the porphyrin periphery groups (Table 1). The negatively charged porphyrins were oxidised at a very slow rate relative to the neutral porphyrins whilst the positively charged porphyrins were oxidised at an even faster rate. Since the standard free-energy changes associated with these oxidation processes remain virtually identical for all four manganese(III) porphyrins used, the differences in $k_{Ox}$ are most probably due to electrostatic factors. Thus, the rate constant for a redox process between ions of charge $Z_A$ and $Z_B$ in electrolyte solutions of fairly high ionic strength ($I$) can be expressed in the form [16] of equation (5) where $k_{Ox}^0$ is

$$\log k_{Ox} = \log k_{Ox}^0 - \frac{NZ_AZ_Be^2}{2.3\,RTDr_{AB}} + \frac{NZ_AZ_Be^2\kappa}{2.3\,RTD(1+\kappa a)} \qquad (5)$$

the rate constant in the absence of electrostatic factors, $D$ is the dielectric constant of the medium, $r_{AB}$ is the radius of an activated complex formed between the two ions, $\kappa$ is the reciprocal Debye length, and $a$ is an adjustable constant. The form of equation (5) predicts a linear relationship between log $k_{Ox}$ and the electrostatic term $Z_AZ_B$ and the gradient of such a plot could be used to estimate the radius of the activated complex if it is assumed [16] that the constant $a$ (which, in simple terms, represents the closest approach of the two ions) has the same value as $r_{AB}$. At pH 14, ferricyanide possesses an overall electronic charge of −3 whilst [Mn(tcpp)], [Mn(tspp)], [Mn(tpyp)], and [Mn(tmpyp)] possess overall charges of −5, −5, −1, and +3 respectively and, using these values, there is a reasonably linear plot to equation (5) within the rather limited data (Figure 3). From the gradient of Figure 3 and evaluating $\kappa$ from equation (6),

$$\kappa = \left(\frac{8\,Ne}{10^3DkT}\right)^{\frac{1}{2}} I^{\frac{1}{2}} \qquad (6)$$

the radius of the activated complex was calculated to be *ca.* 9 Å. This is quite a reasonable value since, based upon the approximate molecular sizes of the two reactants, we would expect to find $r_{AB}$ within the range 5—12 Å. Figure 3 also allows the determination of the rate constant for oxidation of a manganese(III) porphyrin in the absence of any electrostatic factors ($k_{Ox}^0$) and the determined value ($k_{Ox}^0 = 2.0 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$) is surprisingly high in view of the poor thermodynamic driving force.

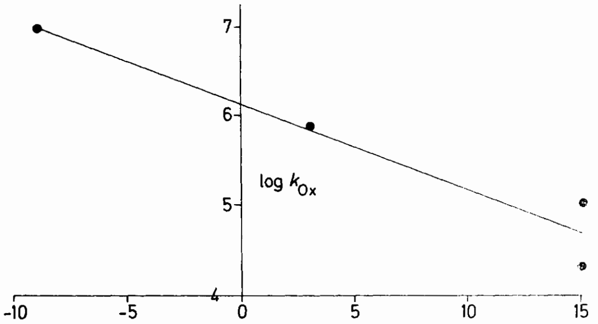


FIGURE 3 Relationship between log $k_{Ox}$ and the product of the electronic charges for oxidation of manganese(III) porphyrins in aqueous solution at pH 14 with ferricyanide

TABLE 2

Standard free-energy changes and rate constants for oxidation of [$Mn^{III}$(tcpp)] in aqueous solution at pH 14 containing 0.05 mol dm$^{-3}$ $Na_2SO_4$

| Oxidant | $\Delta G^\ominus$/ kJ mol$^{-1}$ | $10^{-4}k_{Ox}$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| $S_2O_8^{2-}$ | −313 | 0.08 |
| $BrO_3^-$ | −127 | *ca.* 25 |
| $ClO^-$ | −97 | 24.9 |
| $H_2O_2$ | −95 | 18.9 |
| $Fe(CN)_6^{3-}$ | +3 | 2.0 |

Oxidation of a manganese(III) porphyrin with ferricyanide, and the corresponding reduction of the oxidation product with ferrocyanide, are most probably outer-sphere processes since the ferricyanide–ferrocyanide redox couple is substitution inert. For oxidation of all four manganese(III) porphyrins with ferricyanide at pH 14, the

$$\Delta G^\ominus = -\,nF(E^{Ox/Red} - E^{MnP^+/MnP}) \qquad (7)$$

thermodynamic driving forces ($\Delta G^\ominus$) [equation (7)] are minimal (Table 2) although the observed $k_{Ox}$ values are modestly high. Oxidation of manganese(III) porphyrins with more powerful oxidants gave rise to the same oxidation product but, with several of the oxidants, the reaction may involve formation of an inner-sphere complex. In fact, with hypochlorite as oxidant at pH 14, stopped-flow studies showed a short-lived intermediate ($\lambda_{max.}$ *ca.* 430 nm) which may be an adduct. The observed $k_{Ox}$ and calculated $\Delta G^\ominus$ values for oxidation of [Mn$^{III}$(tcpp)] at pH 14 are collected in Table 2 and it can be seen that, with the exception of peroxodisulphate, there is a general increase in $k_{Ox}$ as $\Delta G^\ominus$ becomes more negative. Such a relationship is to be expected on thermodynamic grounds although, since the electrostatic charge varies for the different oxidants, it is not a simple reflection of the thermodynamic factors.

As shown in Table 2, peroxodisulphate is a poor oxidant for manganese(III) porphyrins and, in all cases, a large excess of oxidant was required for complete oxidation. This may seem surprising in view of the large thermodynamic driving force available for this reaction but previous work[17] has established that the rate-determining step in peroxodisulphate oxidations involves dissociation of the peroxodisulphate molecule and, in most cases, this is a very slow step [equation (8)].

$$\mathrm{MnP} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{MnP}^+ + \mathrm{SO_4}^{2-} + \mathrm{SO_4}^{\bullet -} \qquad (8)$$

$$\mathrm{MnP} + \mathrm{SO_4}^{\bullet -} \longrightarrow \mathrm{MnP}^+ + \mathrm{SO_4}^{2-} \qquad (9)$$

The resultant sulphate radical anion is a powerful oxidant[17] and is capable of oxidising a second molecule of the manganese(III) porphyrin and this step is probably rapid [equation (9)].

For an outer-sphere electron-transfer process in a dilute electrolyte medium the rate constant for the electron-transfer step can be related to the free energy of activation ($\Delta G^\ddagger$) by the Marcus relationship[18] where

$$k = \alpha\rho Z\ \mathrm{e}^{-\Delta G^*/RT} \qquad (10)$$

$$\Delta G^\ddagger = \Delta G^* + RT\ \ln(k_\mathrm{B}T/\rho Z h) \qquad (11)$$

$k_\mathrm{B}$ is the Boltzmann constant, $\alpha$ is a transmission coefficient, $\rho$ is a dimensionless statistical factor having a value close to unity, and $Z$ is the bimolecular collision frequency of the two reactants in solution at unit concentration. In turn, the free energy of activation can be divided into several terms which are concerned with electrostatic factors ($\Delta G^\ddagger_\mathrm{ES}$), internal reorganisation forces ($\Delta G^\ddagger_\mathrm{RI}$), and outer reorganisation forces ($\Delta G^\ddagger_\mathrm{RO}$) [equation (12)].

$$\Delta G^\ddagger = \Delta G^\ddagger_\mathrm{ES} + \Delta G^\ddagger_\mathrm{RI} + \Delta G^\ddagger_\mathrm{RO} \qquad (12)$$

The reorganisation terms arise from the Franck–Condon principle and are concerned with rearrangement of the co-ordinated ligands and solvent molecules following electron transfer. The form of equation (10) predicts a linear relationship between log $k_{Ox}$ and $1/T$ whilst equation (12) predicts that the observed $\Delta G^\ddagger$ term should depend upon the magnitude of electrostatic forces between the reactants. As shown in Figure 4, the rate constants for oxidation of [Mn$^{III}$(tcpp)] and [Mn$^{III}$(tpyp)] with ferricyanide at pH 14 did depend upon temperature but not in the expected manner. Thus, increasing the temperature resulted in a decrease in $k_{Ox}$ and the observed temperature dependence was similar for both manganese(III) porphyrins although there is a large difference in the overall electronic charge on the porphyrin rings of these two compounds. The absence of a strong electrostatic effect is not too surprising in view of the fairly high ionic strengths used in these studies. However, the apparent negative temperature effect is more puzzling and requires some comment.

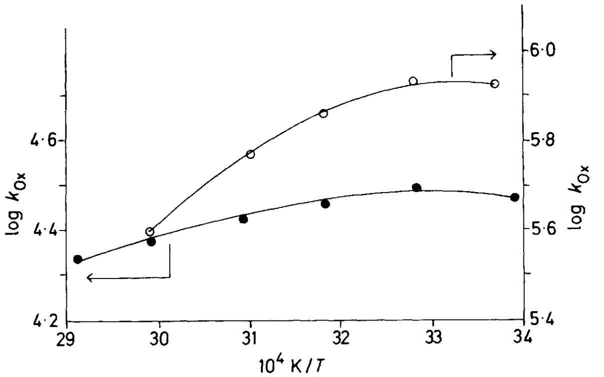


FIGURE 4 Relationship between log $k_{Ox}$ and reciprocal temperature for oxidation of [Mn$^{III}$(tcpp)] (○) and [Mn$^{III}$(tpyp)] (●) in aqueous solution at pH 14 with ferricyanide

The free energy of activation arising from electrostatic factors in equation (12) appears to be minimal since the form of Figure 4 shows virtually no dependence upon the electronic charge on the porphyrin and consequently equation (13) holds. This finding implies that

$$\Delta G^\ddagger_\mathrm{ES} < \Delta G^\ddagger_\mathrm{RI} + \Delta G^\ddagger_\mathrm{RO} \qquad (13)$$

the negative temperature dependence refers to reorganisation terms but it must also be remembered that the oxidised manganese porphyrin (MnP$^+$) is unstable in aqueous solution. The rate of the thermal reduction of MnP$^+$, back to MnP, increases with increased temperature and the observed temperature dependence found for $k_{Ox}$ may simply reflect the relative stability of the product as a function of temperature, especially if dimerisation processes are involved.

*Oxidation at Lower* pH.—The ferricyanide–ferrocyanide redox couple was used to oxidise [Mn$^{III}$(tcpp)] in aqueous solution at different pH values. Oxidation became progressively more difficult as the pH was decreased, as evidenced by the observed $k_{Ox}$ values (Table 3), and at pH <11 even a very large excess of ferricyanide had no effect upon the absorption spectrum of [Mn$^{III}$(tcpp)].

TABLE 3

Midpoint potentials and rate constants for oxidation of [Mn$^{III}$(tcpp)] with ferricyanide in aqueous solution containing 0.05 mol dm$^{-3}$ $\mathrm{Na_2SO_4}$

| pH | $E_\mathrm{m}$/ V *vs.* n.h.e. | $10^{-4}k_{Ox}$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 14 | 0.388 | 2.0 |
| 13 | 0.398 | 0.23 |
| 12 | 0.478 | 0.032 |
| 11 | 0.590 | |
| 10 | 0.68 | |
| 9 | *ca.* 0.75 | |

For the lower pH region, reversible oxidation was achieved with molybdenum hexacyanide and Table 3 contains the measured $E_m$ values as a function of pH. The $E_m$ determinations were restricted to pH $\geqslant 9$ due to the increasing instability of the oxidation product as the solution pH was lowered. However, with an excess of a strong oxidant ($H_2O_2$, peroxodisulphate, hypochlorite, $Cl_2$, or $Br_2$) it was possible to oxidise [Mn$^{III}$(tcpp)] even at pH as low as 7.0 and, in all cases, the absorption spectrum of the product was similar to that observed at pH 14. Less powerful oxidants, such as $PbO_2$ and $KMnO_4$, were ineffective oxidants at pH $\leqslant 10$ even at very high concentration.

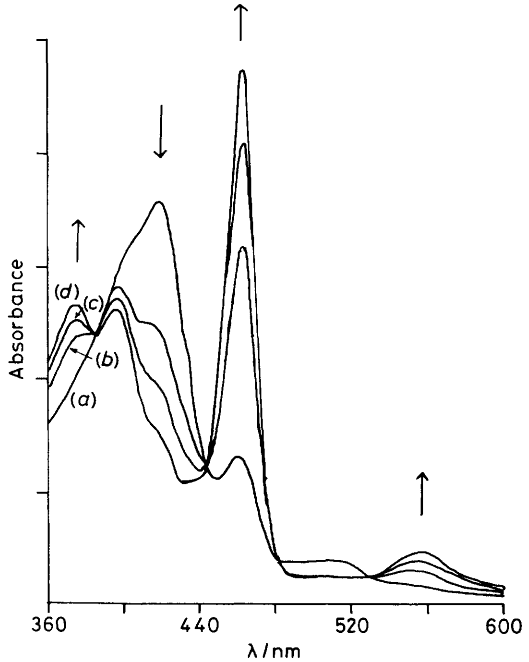


**FIGURE 5** Absorption spectral profile showing the decay of the product formed by oxidation of [Mn$^{III}$(tcpp)] with bromine in aqueous solution at pH 7 after 0 (*a*), 3 (*b*), 6 (*c*), and 9 min (*d*)

However, with some of the strong oxidants, formation of the oxidised manganese porphyrin at lower pH resulted in extensive loss of the porphyrin chromophore and the extent of decomposition increased with decreased pH. In neutral solution, oxidation of [Mn$^{III}$(tcpp)] with excess of $Cl_2$, hypochlorite, or $H_2O_2$ resulted in almost complete bleaching of the porphyrin chromophore over *ca.* 1 h standing in the dark. This bleaching effect was particularly strong for oxidation with $H_2O_2$ and, in this case, the reaction resulted in formation of oxygen from the catalysed breakdown of the oxidant. Interestingly, oxidation of [Mn$^{III}$(tcpp)] in aqueous solution at pH 7.0 with excess of peroxodisulphate or $Br_2$ did not involve destruction of the porphyrin and the oxidation product was formed in quantitative yield. As shown in Figure 5, the stability of the oxidation product was limited, even in the presence of excess of oxidant, and the original [Mn$^{III}$(tcpp)] was reformed without loss.

Similar results were obtained with the other water-soluble manganese(III) porphyrins and Figure 6 gives the pH profile for the determined $E_m$ values for [Mn(tcpp)] and [Mn(tpyp)]. For both compounds, $E_m$ increased as the pH was decreased and the form of Figure 6 suggests that this dependence arises from an acid–base equilibrium and, in fact, previous work[7] has established that the manganese(III) porphyrins have a p*K* transition in the pH range 10—12. In addition, the oxidation product may have a p*K* transition[7] around pH 10 so that Figure 6 probably reflects both acid–base equilibria. From the observed data, the acidic form of the oxidised manganese porphyrin is the stronger oxidant and for [Mn(tcpp)] the $E_m$ values for the acidic and basic forms of porphyrin are 0.75 and 0.39 V respectively. Thus, there is quite a marked increase in $E_m$ for the acidic form.

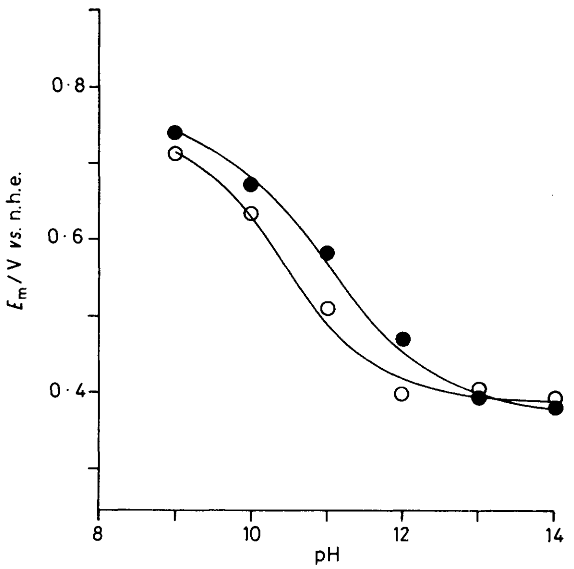


**FIGURE 6** The dependence of $E_m$ upon pH for [Mn$^{III}$(tcpp)] (○) and [Mn$^{III}$(tpyp)] (●)

*Reaction with Excess of Oxidant.*—At pH 14, the absorption spectrum of the product remained unaffected by the addition of excess of oxidant when the oxidant was $H_2O_2$, $PbO_2$, bromate, $KMnO_4$, peroxodisulphate, or ferricyanide and addition of excess of ferrocyanide restored the original manganese(III) porphyrin with virtually no loss. However, as shown in Figure 7, addition of more than stoicheiometric amounts of hypochlorite resulted in changes in the absorption spectrum of the oxidation product. The main band at 420 nm became sharper and increased in intensity whilst there were minor changes in the spectrum around 530 nm. Again, these spectral changes were quite reversible and addition of excess of ferrocyanide, dithionite, or ethylenediaminetetra-acetate (edta) restored the original manganese(III) porphyrin without loss. Thus, hypochlorite is able to bring about a second oxidation step with respect to the manganese porphyrin although none of the other oxidants was effective and since some of these oxidants possess an

$E^{Ox/Red}$ similar to that of hypochlorite the reaction may not be a simple one-electron oxidation.

The second oxidation product of [Mn(tcpp)] was prepared in aqueous solution at pH 14 by addition of three equivalents of hypochlorite and, in the absence of an added reductant, it was found to be quite stable. Thus, although the product decayed slowly to reform the original [$Mn^{III}$(tcpp)] the half-life for this process was in excess of 8 h at pH 14. In the presence of a reductant, such as edta or ferrocyanide, rapid reduction occurred to reform [$Mn^{III}$(tcpp)] without loss. Similarly, addition of hydrochloric or acetic acids resulted in quantitative formation of [$Mn^{III}$(tcpp)] and, like the first oxidation product, this species is stable only in strongly alkaline solution.

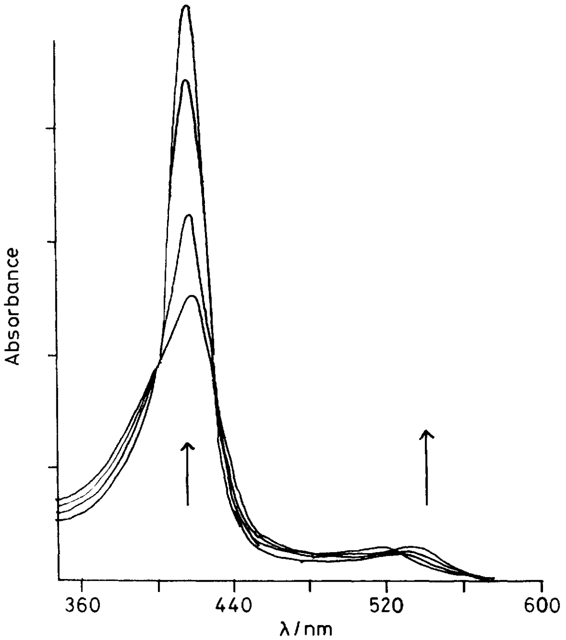


FIGURE 7 Absorption spectral profile for addition of excess of hypochlorite to [$Mn^{IV}$(tcpp)] in aqueous solution at pH 14

Rather surprisingly there was no apparent reaction between the second oxidation product and [$Mn^{III}$(tcpp)] in aqueous solution at pH 14. Addition of an equimolar amount of [$Mn^{III}$(tcpp)] to a solution of the oxidised manganese porphyrin resulted in no chemical reaction and the final absorption spectrum was identical to that obtained by adding together the two individual spectra.

*Identity of the Oxidation Products.*—The first oxidation step involves the reversible removal of an electron from a molecule of manganese(III) porphyrin, and at pH 14, it is a reasonably facile process. The $E_m$ is low and the product is a mild oxidant although its half-life in aqueous solution is quite short. Depending upon which part of the manganese(III) porphyrin molecule donates the electron, the product may be described as either a manganese(IV) porphyrin or a manganese(III) porphyrin $\pi$-radical cation and the available experimental data tend to support the former assignment. Thus, the absorption spectrum of the oxidation product shows an intense *B* band at 420 nm and two weak *Q* bands at 520 and 662 nm with no clear bands in the near-i.r. region. Such a spectrum is more characteristic of a metalloporphyrin than of a porphyrin $\pi$-radical cation.[19] However, the most convincing evidence for the assignment of the oxidation product as a manganese(IV) porphyrin is derived from the midpoint potential measurements where the observed $E_m$ values are *ca.* 0.39 V *vs.* n.h.e. and almost independent of the type of porphyrin ring used. For diamagnetic metalloporphyrins, removal of an electron from the porphyrin ring involves [15] a midpoint potential of *ca.* 1 V so that the observed measurements for manganese porphyrins seem to be somewhat too low for the oxidation product to be a $\pi$-radical cation. Furthermore, it seems most unlikely that the $E_m$ value could remain independent of the groups on the porphyrin-ring periphery if the electron was removed from this part of the molecule.[15] Consequently, we are of the opinion that, under such experimental conditions, oxidation of a manganese(III) porphyrin results in formation of a manganese(IV) porphyrin.

$$Mn^{III}P + Ox \rightleftharpoons Mn^{IV}P + Red \qquad (14)$$

No e.s.r. signal was detected at room temperature whilst the magnetic moment was found to be 1.9 B.M.* which is inconsistent with a formal $d^3$ configuration. This anomalously low magnetic moment infers that the manganese(IV) porphyrin may be present in the form of a $\mu$-oxo-dimer in which there is antiferromagnetic coupling interaction between the two manganese(IV) atoms. The occurrence of $\mu$-oxo-dimers is well known in the chemistry of iron porphyrins whilst it has been reported [20] that manganese(III) porphyrins form $\mu$-oxo-dimers in extremely alkaline solution. Since the absorption spectrum of the manganese(IV) porphyrins remained independent of concentration within the range $10^{-6}$—$10^{-4}$ mol dm$^{-3}$, either the dimerisation constant must be very high or the monomer and dimer must have similar absorption spectra. The somewhat low molar absorption coefficient and the large half-width found for the *B* band of the first oxidation product, together with recent work describing the oxidation of manganese(III) porphyrins with iodosylbenzene,[21] are in agreement with the product being a manganese(IV) porphyrin $\mu$-oxo-dimer.

$$2\,Mn^{IV}P \rightleftharpoons Mn^{IV}P\text{-}O\text{-}Mn^{IV}P \qquad (15)$$

The assignment of the final manganese(IV) porphyrin as a $\mu$-oxo-dimer must raise some doubts about the validity of the midpoint potentials since such measurements require there to be a high degree of reversibility within the system. However, the oxidation of a manganese(III) porphyrin was a stoicheiometric process, there was no loss of porphyrin from the system and, overall, the process was fully reversible so that the observed $E_m$ for oxidation of a particular manganese(III)

---

* Throughout this paper: 1 B.M. = $9.274 \times 10^{-24}$ A m$^2$.

porphyrin should give a reasonable estimate of the redox potential for the $Mn^{III/IV}$ couple. Even so, the actual redox potentials for the μ-oxo-dimer may be somewhat lower than the measured $E_m$ values which probably refer to the monomeric species.

From Figure 6, it is known that for a manganese(III) porphyrin the $E_m$ value increases as the solution pH is decreased. Measurements have been made down to pH 9 and, from kinetic studies, it seems that $E_m$ continues to increase at lower pH. If this is so, then there is a strong possibility that in acidic solution the $E_m$ value for formation of the manganese(IV) porphyrin must be similar to that expected for formation of a manganese(III) porphyrin π-radical cation (*ca.* 1 V). Thus, in acid solution the first oxidation product may be a manganese(III) porphyrin π-radical cation whilst acidification of an alkaline solution of a manganese(IV) porphyrin may result in an intramolecular rearrangement to form the π-radical cation.[22]

$$Mn^{IV}P \longleftrightarrow Mn^{III}P^{\cdot+} \qquad (16)$$

Formation of the second oxidation product seems to involve the reversible removal of two electrons from a molecule of manganese(III) porphyrin and, at pH 14, we would expect the product to be either a manganese(V) porphyrin or a manganese(IV) porphyrin π-radical cation (or their dimers). The absorption spectrum shows an intense *B* band at 418 nm and weak *Q* bands at 528 and 662 nm and appears quite characteristic of a metalloporphyrin,[19] suggesting that the product is a manganese(V) porphyrin. No e.s.r. signal could be detected at room temperature whilst the magnetic moment was found to be 2.7 B.M. which is consistent with a formal $d^2$ configuration. However, the fact that the second oxidation product can only be formed by reaction with hypochlorite, an oxidant known sometimes to transfer oxygen atoms during the electron-transfer step,[23] suggests that the structure of this oxidation product may be somewhat more complex than a simple manganese(V) porphyrin.

Previously, the involvement of a manganese(V) porphyrin has been tentatively inferred from redox studies in aqueous solution [11] whilst it has been reported that reaction of a manganese(III) porphyrin with iodosylbenzene in organic solvents forms a manganese(V) oxo-porphyrin [12] although very recent work [21] has shown that the purified product isolated from the iodosylbenzene reaction is, in fact, a manganese(IV) porphyrin μ-oxo-dimer. Other metalloporphyrins that exist in high oxidation states invariably do so in the form of oxo-compounds, as found with the porphyrins of Ti,[24] V,[25] Mo,[26] Cr,[27] and Fe,[28] so there is a good possibility that the second oxidation product reported here could be a manganese(V) oxo-porphyrin. Such a structure may help explain why hypochlorite is the only effective oxidant and, if this assignment is correct, oxidation of the manganese(IV) porphyrin with hypochlorite must involve dissociation of the μ-oxo-dimer, equation (17). The

$$Mn^{IV}P{-}O{-}Mn^{IV}P + OCl^- \longrightarrow 2\,Mn^{V}P{=}O + Cl^- \qquad (17)$$

absorption spectrum of the product is consistent with a monomeric structure and, overall, we are of the opinion that the second oxidation product is a manganese(V) oxo-porphyrin. Although all available spectroscopic evidence is in good agreement with this assignment (especially the magnetic moment), we are somewhat surprised that there is no apparent reaction between the manganese(V) oxo-porphyrin and $[Mn^{III}(tcpp)]$.

The experimental work described above has identified and characterised manganese(IV) and manganese(V) porphyrins in alkaline aqueous solution. These metalloporphyrins have limited stability in aqueous solution and revert to the stable manganese(III) porphyrin upon standing in the dark for a few hours. The rates of these reduction processes increase with decreasing pH and extrapolation of the measured midpoint potentials suggests that in neutral or acidic solution manganese(IV) porphyrins possess the necessary thermodynamic potential for oxidation of water to molecular $O_2$ ($E^\ominus = 0.82$ V at pH 7). This is a particularly interesting observation and it suggests that a manganese(IV) or manganese(V) porphyrin could be a key intermediate in a model system for the homogeneous oxidation of water. In fact, now that we have a better understanding of the nature, reactivity, and thermodynamic properties of the oxidised manganese porphyrins it should be possible to attempt to use these compounds as oxidants for water. The fact that both manganese(IV) and manganese(V) porphyrins are unstable in aqueous solution together with the expectation that, under certain conditions, these compounds should be capable of $O_2$ liberation from water encourage further work in this area and we will report on such studies in a later paper.

A second interesting point to emerge from this study is the consideration that the solution pH may affect the nature of the first oxidation product. Thus, in alkaline and neutral solution the first oxidation product is a manganese(IV) porphyrin but in acidic solution the relevant redox potentials may favour removal of the first electron from the porphyrin π system. This raises doubts about the identity of the first oxidation product of manganese(III) porphyrins in organic solvents or within a natural environment and we note with interest the controversy over the identity of the oxidised iron(III) porphyrins in organic solvents. In a subsequent paper, we will describe the characterisation of manganese(IV) and manganese(V) porphyrins in organic solvents, membranes, oil–water emulsions, and micelles and, indeed, it is seen that the nature of the environment has a strong influence on the type and properties of the first oxidation product.

We thank the S.R.C., the E.E.C., and G.E. (Schenectady) for financial support of this work, and one of us (N. C.) thanks the Conselho Nacionale de Pesquisas SDC, Brazil, for the award of a studentship. We are greatly indebted to P. Douglas for many helpful discussions.

[1/1613 *Received, 15th October*, 1981]

## REFERENCES

[1] A. Harriman and J. Barber, ' Topics in Photosynthesis,' ed. J. Barber, Elsevier, Amsterdam, 1979, vol. 3, ch. 8.

[2] G. Porter, *Proc. R. Soc. London, Ser. A*, 1978, **362**, 281.

[3] J. Kiwi and M. Gratzel, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 860; 1979, **18**, 624.

[4] J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, 1980, **4**, 81.

[5] A. Harriman, G. Porter, and P. Walters, *J. Chem. Soc., Faraday Trans. 2*, 1981, 2373.

[6] V. Ya. Shafirovich, N. K. Khannou, and V. V. Stelets, *Nouv. J. Chim.*, 1978, **2**, 199.

[7] A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1979, 1532.

[8] A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1979, 1543.

[9] I. A. Duncan, A. Harriman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1980, 1415.

[10] A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1980, 1429.

[11] P. A. Loach and M. Calvin, *Biochemistry*, 1963, **2**, 361.

[12] J. T. Groves, W. J. Kruper, and R. C. Haushalter, *J. Am. Chem. Soc.*, 1980, **102**, 6375.

[13] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[14] ' Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975.

[15] M. Neumann-Spallart and K. Kalyanasundaram, *Z. Naturforsch., Teil B*, 1981, **36**, 596.

[16] I. D. Clark and R. P. Wayne, ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1969, vol. 2, ch. 4.

[17] D. A. House, *Chem. Rev.*, 1962, **62**, 185.

[18] R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679.

[19] J-H. Fuhrhop, *Struct. Bonding (Berlin)*, 1974, **18**, 1.

[20] E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162.

[21] B. C. Schardt, F. J. Hollander, and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1981, 765.

[22] I. Tabushi and S. Kojo, *Tetrahedron Lett.*, 1974, 1577.

[23] J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' Longmans, Green and Co., London, 1956.

[24] J. W. Buchler, ' The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, vol. 1, ch. 10.

[25] T. S. Srivastava and E. B. Fleisher, *Inorg. Chim. Acta*, 1971, **5**, 151.

[26] T. S. Srivastava and E. B. Fleisher, *J. Am. Chem. Soc.*, 1970, **92**, 5518.

[27] J. T. Groves and W. J. Kruper, *J. Am. Chem. Soc.*, 1979, **101**, 7613.

[28] D. H. Chin, A. L. Balch, and G. N. La Mar, *J. Am. Chem. Soc.*, 1980, **102**, 1446.