Photochemistry of Manganese Porphyrins. Part 8.* Electrochemistry

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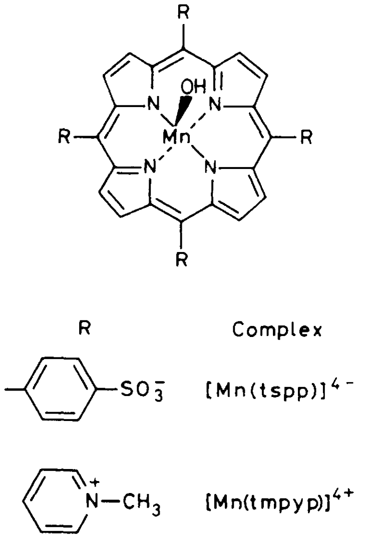
Water-soluble manganese(III) porphyrins undergo a well defined, one-electron reduction to the corresponding manganese(II) derivative for which the overall reversibility is very high. The intrinsic electrochemical rate constant (k^0) was $(1.2 \pm 0.4) \times 10^{-3}$ cm s^{-1} and it remained essentially independent of pH. The nature of the porphyrin ligand affected the magnitude of $E_{\frac{1}{2}}$ but caused no significant differences in electrode behaviour. One-electron oxidations were observed for which both $E_{\frac{1}{2}}$ and k^0 depended markedly upon pH. At pH > 13, oxidation approached the fully reversible case but as the pH was decreased oxidation became progressively more difficult and less reversible. These differences are associated with acid–base equilibria of axially co-ordinated water molecules.

In previous papers,[1] we have described the redox chemistry of water-soluble manganese porphyrins and characterised compounds in which the central manganese ion possesses a formal valence of +2, +3, +4, and +5. Similar species have been characterised for water-insoluble derivatives [2,3] and, in several instances, *X*-ray structural determinations have been made.[4,5] Thus, the manganese porphyrins exhibit a rich variety of oxidation states and this makes them promising homogeneous redox catalysts. Already, it has been reported that manganese porphyrins can catalyse the oxidation of hydrocarbons [6,7] and further developments in the field can be expected. We have long been interested in the possible use of the water-soluble porphyrins as homogeneous catalysts for the oxidation of water to O_2; a reaction that might have considerable importance in the natural photosynthetic process.[8] As such, it is crucial to obtain a good understanding of the interconversions between the various oxidation states and, in this paper, I describe the electrochemistry of manganese porphyrins in aqueous solution.

Little information exists on the electrochemical properties of water-soluble porphyrins [9–11] although several groups have reported [12–14] half-wave potentials for reduction of manganese(III) porphyrins. Only Davis and Montalvo [14] have carried out a thorough study and their report on the one-electron reduction of manganese(III) hematoporphyrin forms a cornerstone for the redox chemistry of manganese porphyrins. Reports on the oxidation of water-soluble metalloporphyrins are even more scarce and, in most cases, estimates of half-wave potentials have been made only by chemical titration.[1] From such studies,[1] it is known that the ease of formation and the stability of manganese(IV) porphyrins increase markedly with increased pH and herein I have tried to obtain a more quantitative understanding of these phenomena.



Experimental

The water-soluble manganese(III) porphyrins were prepared and purified as described previously.[1] Water was deionised, doubly distilled and all solutions for electrochemical experiments contained Na_2SO_4 (0.3 mol dm^{-3}). Appropriate pH values were obtained by addition of H_2SO_4 or NaOH to aqueous solutions containing either only Na_2SO_4 or mixtures of Na_2SO_4 with borate (0.1 mol dm^{-3}) or carbonate (0.1 mol dm^{-3}). All electrochemical studies were made with N_2-purged aqueous solutions containing $(5—80) \times 10^{-4}$ mol dm^{-3} of the manganese porphyrin. A conventional three-electrode arrangement was used with a glassy carbon working electrode, a Pt-foil counter electrode and a saturated calomel electrode (s.c.e.) reference. Cyclic voltammetry was performed with a Rank E611 potentiostat driven by a purpose built triangle-wave generator. For the chronocoulometric studies, the rise time of the potentiostat was less than 2 ms and the output was displayed on a storage oscilloscope. The electrochemical area of the glassy carbon working electrode used in these experiments was 0.105 ± 0.015 cm^2, as determined by oxidation of ferrocyanide, $[Fe(CN)_6]^{4-}$. For kinetic studies, a Rank 628-10 rotating disc electrode (r.d.e.) was employed ($A = 0.066 \pm 0.010$ cm^2).

Spectroelectrochemistry was conducted with an airtight optically transparent thin-layer electrode constructed from a highly conductive SnO_2/In_2O_3 plate and a matching quartz plate.[15] The distance between the two plates was controlled by various thicknesses of Teflon spacers and the pathlength of the cell was determined by monitoring the absorbance of known solutions of the manganese porphyrins. The volume of the cell was measured by coulometric studies with ferricyanide, $[Fe(CN)_6]^{3-}$, solutions.

All working electrode surfaces were highly polished with Al_2O_3 paste prior to each experiment. The reproducibility of individual $E_{\frac{1}{2}}$ values was ±8 mV.

Results and Discussion

Properties of Manganese(III) *Porphyrins*.—Under the conditions of the electrochemical experiments, both $[Mn^{III}(tspp)]^{4-}$ and $[Mn^{III}(tmpyp)]^{4+}$* exist in aqueous solution as

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* Part 7 is ref. 2.

Table 1. Electrochemical properties for the reduction of manganese(III) porphyrins in aqueous solution *

Compound	pH	$D/10^{-6}$ cm^2 s^{-1}		n (s.e.)	$k^0/10^{-3}$ cm s^{-1}		α (r.d.e.)
		(c.v.)	(c.c.)		(c.v.)	(r.d.e.)	
$[Mn^{III}(tmpyp)]^{4+}$	13.0	2.3	2.7	0.95	0.8	1.05	0.54
	12.3	—	2.6	0.97	—	0.85	0.58
	9.8	2.0	2.9	0.94	1.1	0.98	0.53
	9.4	—	2.6	1.06	—	1.50	0.59
	8.2	2.1	2.7	0.97	0.9	1.05	0.52
$[Mn^{III}(tspp)]^{4-}$	13.0	1.6	2.2	0.99	—	1.20	0.57
	11.8	—	2.2	1.01	—	1.42	0.51
	9.6	2.1	2.0	0.97	—	1.70	0.52
	8.4	—	2.0	0.96	—	1.38	0.52

* Abbreviations: c.v. = cyclic voltammetry, c.c. = chronocoulometry, s.e. = spectroelectrochemistry, and r.d.e. = rotating disc electrode

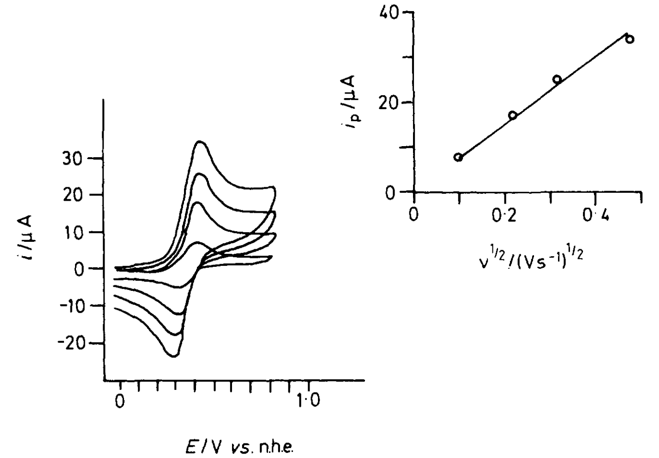

Figure 1. Typical cyclic voltammograms for oxidation of $[Mn^{III}(tmpyp)]^{4+}$ in aqueous solution at pH 13. The insert shows a plot of peak current *vs.* scan rate (v)

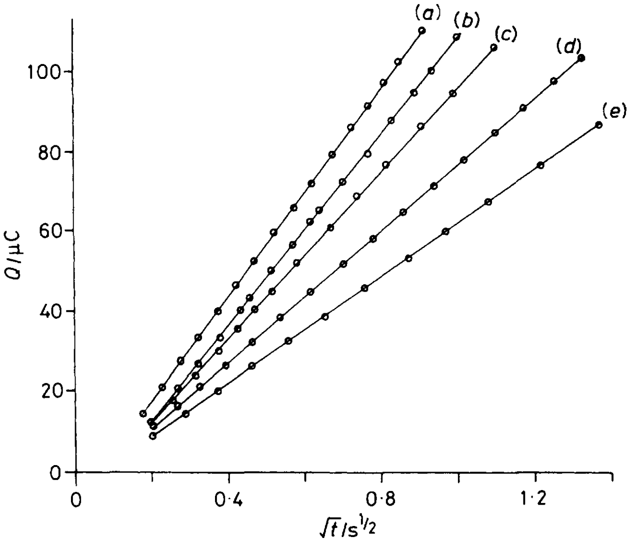

Figure 2. Plot of charge ($Q_{obs.} - Q_{DL}$) *vs.* $t^{\frac{1}{2}}$ as determined by chronocoulometry for various concentrations of $[Mn^{III}(tmpyp)]^{4+}$ in aqueous solution at pH 13: (*a*) 8.4×10^{-3}, (*b*) 7.3×10^{-3}, (*c*) 6.5×10^{-3}, (*d*) 4.9×10^{-3}, and (*e*) 3.9×10^{-3} mol dm^{-3}. The Q_{DL} term was assumed to be equal to the ' instantaneous ' charge passed in an identical experiment performed in the absence of $[Mn^{III}(tmpyp)]^{4+}$

monomers for which the state of protonation of axially co-ordinated water molecules is known. Before describing the electrochemical properties of these molecules it is necessary to ascertain that there is minimal adsorption of the porphyrins onto the glassy carbon working electrode and to determine the magnitude of the diffusion coefficients. Previous work [14] with manganese(III) hematoporphyrins encountered problems with adsorption onto the Hg working electrode surface and reported a low diffusion coefficient ($D = 0.93 \times 10^{-6}$ cm^2 s^{-1}).

Typical cyclic voltammogram current *versus* voltage (*i versus E*) curves for the oxidation of $[Mn^{III}(tmpyp)]^{4+}$ in aqueous solution at pH 13 at various scan rates are shown in Figure 1. The waves are well defined and, at the lower scan rates, the peak separation approaches 59 mV, as expected for a quasi-reversible reaction. The insert to Figure 1 shows that the peak current (i_p) is a linear function of the square root of the scan rate ($v^{\frac{1}{2}}$) and, assuming the validity of the Randles–Sevcik equation and that the reaction involves a single electron change (see below), the diffusion coefficient (*D*) for $[Mn^{III}(tmpyp)]^{4+}$ at pH 13 has a value of 2.3×10^{-6} cm^2 s^{-1}. Similar *i versus E* curves were found at lower pH values and also for reduction of $[Mn^{III}(tmpyp)]^{4+}$ to the corresponding Mn^{II} derivative. The observed *D* values, together with those determined for $[Mn^{III}(tspp)]^{4-}$, are compiled in Table 1.

A series of chronocoulometric experiments was made in which the potential was stepped some 250 mV more negative or more positive than the half-wave potentials for reduction or oxidation, respectively, of $[Mn^{III}(tmpyp)]^{4+}$. The charge (*Q*) was monitored as a function of time (*t*) for a series of solutions at fixed pH but varying concentration of $[Mn^{III}(tmpyp)]^{4+}$. For a diffusion-controlled electrode reaction,[16] there should be a linear correlation between *Q* and $t^{\frac{1}{2}}$ [equation (1)], where *A* is the electrochemical area of the electrode,

$$Q = 2(nFAC_0\sqrt{Dt/\pi}) + nFA\Gamma_0 + Q_{DL} \qquad (1)$$

C_0 is the bulk concentration of $[Mn^{III}(tmpyp)]^{4+}$, Γ_0 is the amount of reactant adsorbed onto the surface of the electrode, and Q_{DL} is the charge consumed by the electrode–electrolyte double-layer capacitance. Such a plot is shown in Figure 2 as a function of C_0. The average *D* values calculated from these plots are collected in Table 1 and they are believed to be somewhat more reliable than those determined by cyclic voltammetry. These *D* values, which were not corrected for any changes in solvent viscosity, are independent of pH, within the range studied, and they agree very well with those

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* The formulae of the manganese porphyrins follow those used in ref. 1 and ignore the axial ligands.

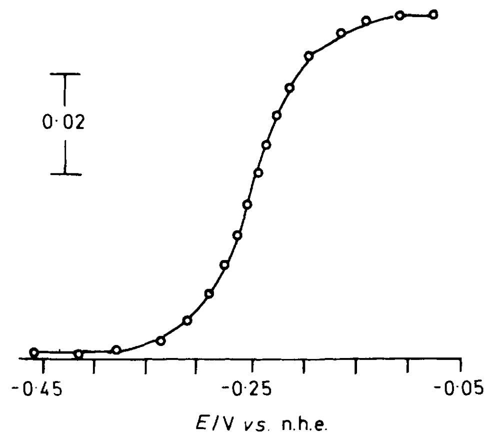


Figure 3. Absorbance change as a function of applied potential for $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$ in aqueous solution at pH 13

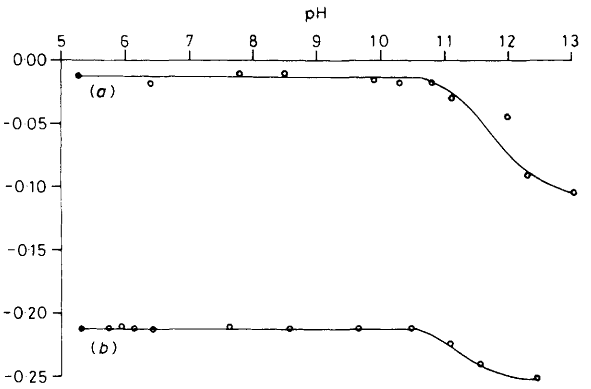


Figure 4. Effect of pH upon the half-wave potential for reduction of (*a*) $[\text{Mn}^{\text{III}}(\text{tmpyp})]^{4+}$ and (*b*) $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$ in aqueous solution

found [17] for $[\text{Fe}^{\text{III}}(\text{tmpyp})]^{4+}$. However, they are much higher than those measured by Davis and Montalvo [14] for manganese hematoporphyrin.

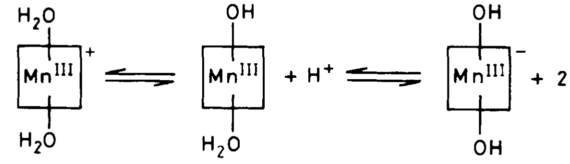
After correction for the Q_{DL} term,[16] extrapolation of the Q *versus* $t^{\frac{1}{2}}$ plots gave intercepts at or slightly below the origin. An adsorbed layer of $[\text{Mn}^{\text{III}}(\text{tmpyp})]^{4+}$ would have given a positive intercept ($nFA\Gamma_0$) so that there appears to be no significant adsorption onto glassy carbon within the pH range 8—13. A similar conclusion was obtained with $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$.

Electroreduction.—The absorption spectra of Mn^{II} and Mn^{III} porphyrins are quite distinct and the B bands are well resolved.[1] This allows spectroelectrochemical experiments to be performed and the results of such an experiment are shown in Figure 3. The plot concerns the reduction of $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$ in aqueous solution at pH 13 with the absorbance at the B band being monitored as a function of the applied potential. It allows evaluation of the number of electrons transferred during the redox process (n),[15] assuming the validity of a Nernst-type equation [equation (2); E_1^0 = standard potential; [Ox] and [Red] are the oxidant and reductant concentrations], where equation (3) applies, with A_2 being the absorbance reading at any particular applied potential and A_1 and A_3 the absorbances of the $[\text{Mn}^{\text{II}}(\text{tspp})]^{4-}$ and $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$ species respectively. For several concentrations of $[\text{Mn}^{\text{III}}(\text{tspp})]^{4-}$ and at a range of pH values, n had a value close to unity (Table 1) and, in the absence of O_2, the overall reversibility was high (as evaluated by the close coincidence of cathodic and anodic steps). From Figure 3, $E_{\frac{1}{2}}$ had a value of -0.25 ± 0.02 V *vs.* a normal hydrogen electrode (n.h.e.) at pH 13.

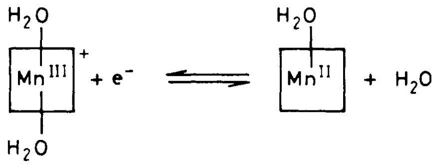
$$E_{\text{applied}} = E_1^0 + \frac{2.303\,RT}{nF}\log\frac{[\text{Ox}]}{[\text{Red}]} \qquad (2)$$

$$\frac{[\text{Ox}]}{[\text{Red}]} = \frac{A_3 - A_1}{A_2 - A_1} \qquad (3)$$

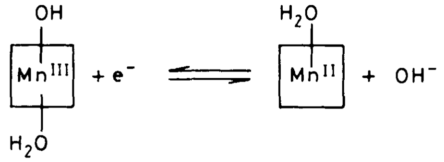
Cyclic voltammetry was used to measure $E_{\frac{1}{2}}$ as a function of pH [$E_{\frac{1}{2}}$ was defined as $E_{\frac{1}{2}} = E_{\text{p}/2} - 28/n$ (mV), where $E_{\text{p}/2}$ is the potential at half peak current and the quoted values are the average of anodic and cathodic scans] and the results are given in Figure 4. It is quite clear from these data that the electrode potential is essentially independent of pH throughout the range 5—11. In this pH range, $[\text{Mn}^{\text{III}}(\text{tmpyp})]^{4+}$ undergoes at least two pK transitions [1] [equation (4)] (where the squares represent the ' dianion ' of tmpyp^{4+}, *i.e.* tmpyp^{2+}) and the indifference of $E_{\frac{1}{2}}$ towards pH implies that reduction of Mn^{III} does not involve a protonation/deprotonation step. Measurement of pK transitions for Mn^{II} porphyrins is rendered difficult by their susceptibility to demetallation and aerial oxidation but there seems to be only one pK transition, which is located at *ca.* 12.3.[1] Since Mn^{II} porphyrins possess a single axial water molecule, we can describe the reduction processes in the pH range 3—11 by equations (5) and (6).


(4)

$$[\text{H}_2\text{O}\,\text{Mn}^{\text{III}}\,\text{H}_2\text{O}]^{+} \rightleftharpoons [\text{OH}\,\text{Mn}^{\text{III}}\,\text{H}_2\text{O}] + \text{H}^+ \rightleftharpoons [\text{OH}\,\text{Mn}^{\text{III}}\,\text{OH}]^{-} + 2\text{H}^+ \qquad (4)$$

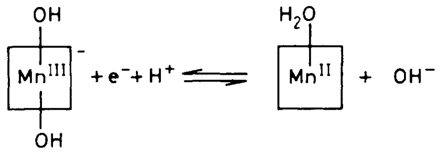

(5)

$$[\text{H}_2\text{O}\,\text{Mn}^{\text{III}}\,\text{H}_2\text{O}]^{+} + e^- \rightleftharpoons [\text{H}_2\text{O}\,\text{Mn}^{\text{II}}] + \text{H}_2\text{O} \qquad (5)$$

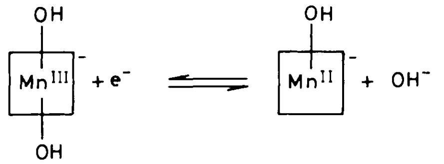

(6)

$$[\text{OH}\,\text{Mn}^{\text{III}}\,\text{H}_2\text{O}] + e^- \rightleftharpoons [\text{H}_2\text{O}\,\text{Mn}^{\text{II}}] + \text{OH}^- \qquad (6)$$

Above pH 11, there is a small dependence of $E_{\frac{1}{2}}$ upon pH. This can be expressed by equations (7) and (8).


(7)

$$[\text{OH}\,\text{Mn}^{\text{III}}\,\text{OH}]^{-} + e^- + \text{H}^+ \rightleftharpoons [\text{H}_2\text{O}\,\text{Mn}^{\text{II}}] + \text{OH}^- \qquad (7)$$


(8)

$$[\text{OH}\,\text{Mn}^{\text{III}}\,\text{OH}]^{-} + e^- \rightleftharpoons [\text{OH}\,\text{Mn}^{\text{II}}]^{-} + \text{OH}^- \qquad (8)$$

Both $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ and $[\mathrm{Mn^{III}(tspp)}]^{4-}$ exhibit similar qualitative pH dependences and it should be noted that the $\mathrm{Mn^{II}}$ porphyrins are unstable at pH < 8. Thus, at slow scan rates in acidic solution, the cyclic voltammograms resemble the electrode/chemical case.

The cyclic voltammograms were used to estimate the heterogeneous rate constant (k^0) for the reduction process according to equation (9), where the ratio of diffusion coefficients

$$k^0 = \psi\left(\frac{\pi n F v D_{\mathrm{Ox}}}{RT}\right)^{\frac{1}{2}}\left(\frac{D_{\mathrm{Red}}}{D_{\mathrm{Ox}}}\right)^{\alpha/2} \qquad (9)$$

($D_{\mathrm{Red}}/D_{\mathrm{Ox}}$) was taken as unity and ψ was evaluated from the table of Nicholson and Shain.[18] The heterogeneous rate constants so obtained are collected in Table 1 and they are independent of pH and concentration of porphyrin. The average k^0 was $(0.93 \pm 0.17) \times 10^{-3}$ cm $\mathrm{s^{-1}}$ which is quite high. It is possible that some uncompensated resistance distorts the cyclic voltammetry data, and therefore the k^0 values, even though the conductivity of the medium was high, the area of the working electrode was small and the reference electrode was kept as close as possible to the working electrode.

More reliable estimates of the heterogeneous rate constants were made by r.d.e. studies, again using a glassy carbon working electrode. For a quasi-reversible process at a r.d.e., the current (i) is related to the rotation speed (ω)[19] by equation (10), where ζ is the kinematic viscosity of the electrolyte

$$\frac{1}{i} = \frac{1}{i_{\mathrm{K}}} + \frac{1}{0.62\,nFA\,C_0 D^{2/3}\,\zeta^{-1/6}\,\omega^{\frac{1}{2}}} \qquad (10)$$

solution. The current in the absence of any mass-transfer effects (i_{K}) can be expressed in the form of equation (11),

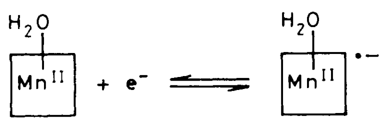
$$i_{\mathrm{K}} = nFAk_{\mathrm{f}}C_0 \qquad (11)$$

where k_{f} is the rate constant for the electrode process. In fact, k_{f} is a function of the applied potential [equation (12)], where

$$k_{\mathrm{f}} = k^0\exp[-\alpha nF(E - E_1^{\circ})/RT] \qquad (12)$$

k^0 is the standard heterogeneous rate constant (independent of potential) for the electrode process and α is a transmission coefficient. Plots of $1/i$ vs. $1/\omega^{\frac{1}{2}}$ were linear and by extrapolating to $\omega^{-\frac{1}{2}} = 0$ it was possible to obtain values for $1/i_{\mathrm{K}}$ as a function of applied potential (E) and C_0. From these values, both k^0 and α were obtained as a function of pH and the values are given in Table 1. In all cases, α was close to 0.5 (the average was 0.54 ± 0.03) and the average value of k_0 was $(1.2 \pm 0.4) \times 10^{-3}$ cm $\mathrm{s^{-1}}$. Thus, there is quite good agreement between the rate constants determined by cyclic voltammetry and r.d.e. studies.

In principle, it should be possible to add a second electron onto the reduced porphyrin to form the $\mathrm{Mn^{II}}$ porphyrin π-radical anion. Using a hanging mercury drop electrode rather than the glassy carbon working electrode, the half-wave potential for the second electron addition was determined. At pH 13, this second step had an $E_{\frac{1}{2}}$ of -0.78 ± 0.05 V *vs.* n.h.e. for $[\mathrm{Mn^{II}(tmpyp)}]^{4+}$ [equation (13)].



(13)

Electro-oxidation.—Again, the absorption spectrum of $[\mathrm{Mn^{IV}(tmpyp)}]^{4+}$ is sufficiently resolved from that of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ to enable a spectroelectrochemical determination of n. However, the difference in molar absorption coefficients for the reactants and products is large only at the B band of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ and analysis was restricted to this wavelength.[1] By a method similar to that described above, oxidation of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ at pH 13 gave an average n of 0.88 ± 0.06. Thus, the reaction involves a single electron transfer and, from these studies, the average $E_{\frac{1}{2}}$ was (0.37 ± 0.04) V *vs.* n.h.e.

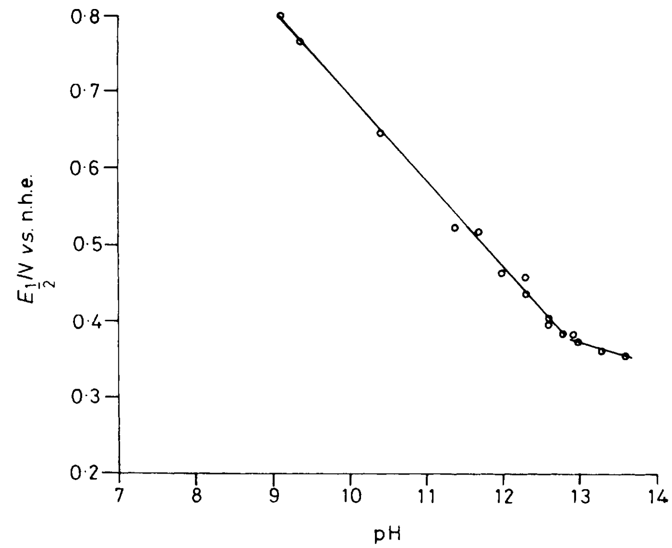
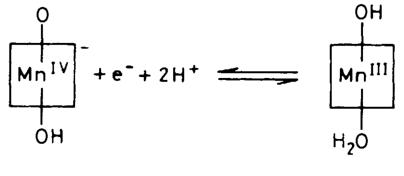


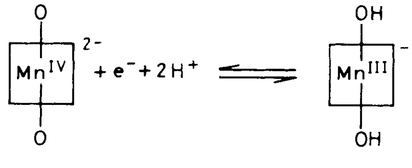
Figure 5. Effect of pH upon the half-wave potential for oxidation of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ in aqueous solution

Using cyclic voltammetry, $E_{\frac{1}{2}}$ was measured as a function of pH and the results are shown in Figure 5 (a typical voltammogram is given in Figure 1). At pH > 12.5 a well defined wave was found but as the pH was dropped below 12.5 the peak current was reduced and the wave became difficult to resolve from the background. In fact, it was not possible to resolve a wave for solutions of 7.0 < pH < 9.0. From such studies it is clear that the oxidation reaction becomes more difficult, both kinetically and thermodynamically, as the solution pH is decreased and this finding is in good agreement with the results of chemical oxidation studies.[1]

Within the pH range 9—14 the $E_{\frac{1}{2}}$ for the oxidation process shows a marked dependence upon pH. As shown in Figure 5, there is a linear relationship between $E_{\frac{1}{2}}$ and pH throughout the range 9.0 < pH < 12.5 where the slope (−108 mV per pH unit) implies that the electrode process involves transfer of two protons [equations (14) and (15)].



(14)



(15)

At pH > 12.5, the slope of Figure 5 approaches *ca.* −40 mV per pH unit so that a single proton change might accom-

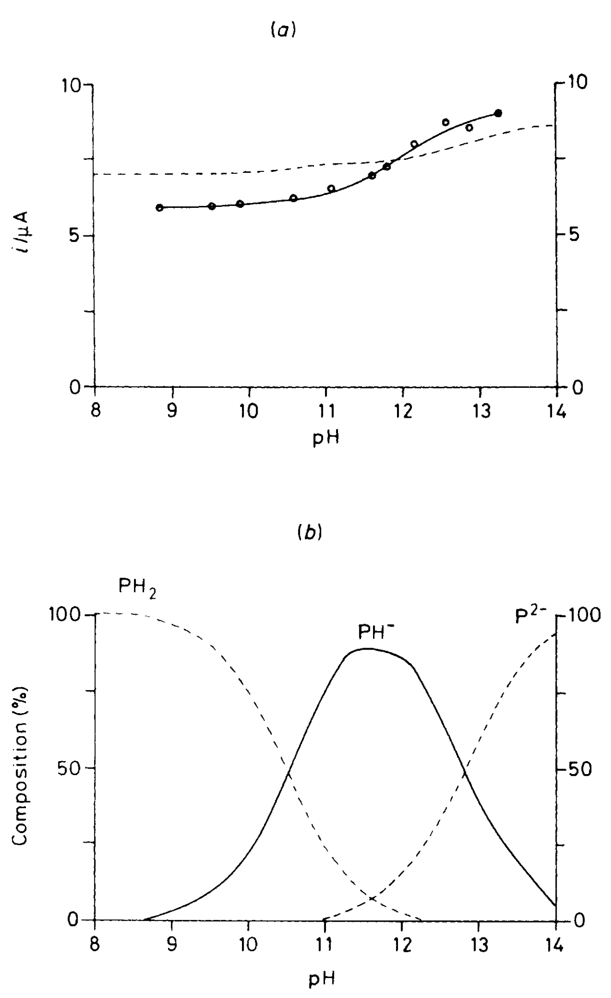
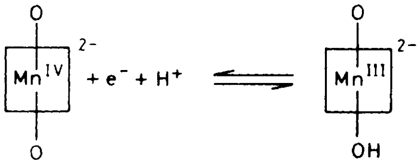


Figure 6. Effect of pH upon (*a*) calculated (- - - -) and observed (O——O) peak current and (*b*) the percentage composition of the various acid–base forms of the metalloporphyrin

pany the electron-transfer step (this requires a slope of −59 mV) [equation (16)].



$$[\mathrm{O}\text{-}\mathrm{Mn^{IV}}\text{-}\mathrm{O}]^{2-} + e^- + H^+ \rightleftharpoons [\mathrm{O}\text{-}\mathrm{Mn^{III}}\text{-}\mathrm{OH}]^{2-} \qquad (16)$$

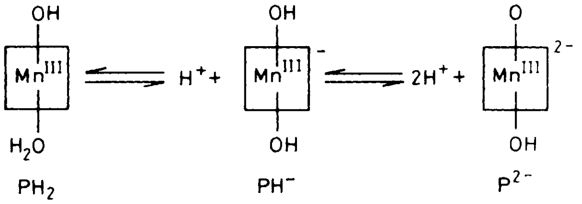
These findings are consistent with the known p*K* transitions [1] for $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ (p*K* = 10.5 and *ca.* 12.8) and $[\mathrm{Mn^{IV}(tmpyp)}]^{4+}$ (p*K* = 10.7). However, it should be noted that $\mathrm{Mn^{IV}}$ porphyrins have limited stability in aqueous solution, especially as the pH is lowered. Also, it is known that the $\mathrm{Mn^{IV}}$ porphyrins undergo efficient dimerisation, forming μ-oxo-dimers, but the time-scale for this process is unknown.[1]

Figure 6(*a*) shows a plot of pH *vs.* the peak current (i_p) as determined by cyclic voltammetry for constant scan rate and concentration of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$. Throughout the pH range 9—14 the ratio of peak currents for anodic and cathodic scans remained at 1.00 ± 0.08 but the magnitude of i_p was dependent upon pH. The maximum i_p was found at pH > 12.5. Decreasing the solution pH resulted in a decrease in i_p until, at pH < 9, the peak could not be resolved from the baseline. For a quasi-reversible redox process, the peak current is given by [19] equation (17), where C_0 refers to the

$$i_p = (2.69 \times 10^5)AD^{\frac{1}{2}}v^{\frac{1}{2}}C_0K(\Lambda,\alpha) \qquad (17)$$

concentration of electroactive material and $K(\Lambda,\alpha)$ is a measure of the reversibility of the process. This latter term is a function of the transmission coefficient α and Λ, where [20] $\Lambda = k^0/D^{\frac{1}{2}}(nF/RT)^{\frac{1}{2}}v^{\frac{1}{2}}$. Thus, the observed relationship between i_p and pH may be explained in terms of C_0, k^0 and/or α being pH dependent. In fact, it is clear that C_0 must be pH dependent since we are concerned with several acid–base equilibria for both reactants and products and it is unlikely that these various species would show identical electrode activity. Also, the cyclic voltammetry studies showed that, at constant scan rate and total concentration of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$, there was an increase in the peak separation as the solution pH was lowered so that k^0 appears to decrease with decreasing pH.

Experiments were performed to measure the pH dependencies for C_0, α, and k^0. From the known p*K* values, the pH profile for each of the various acid–base forms of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ was constructed [Figure 6(*b*)]. Cyclic voltammetry and r.d.e. methods were used to determine k^0 whilst α was obtained from the r.d.e. studies (Table 2). It is seen that α remains independent of pH throughout the range of interest with an average value of 0.58 ± 0.05. However, the intrinsic electrochemical rate constant k^0 depends markedly upon pH and decreases from 3.3×10^{-3} cm s^{-1} at pH 14 to 3.9×10^{-4} cm s^{-1} at pH 10.5. Although the r.d.e. method is expected to give more reliable estimates of k^0, the values obtained from the two sets of experiments are in close agreement. In most cases, these k^0 values represent averages of several individual rate constants, each of which describes the redox process for a particular acid–base form. The individual rate constants can be determined from the C_0 values given in Figure 6(*b*) and the k^0 values collected in Table 2. Thus, if we represent the various acid–base forms of $[\mathrm{Mn^{III}(tmpyp)}]^{4+}$ by the symbols given in equation (18), then we find that the electrochemical rate constants for oxidation of $\mathrm{PH_2}$, $\mathrm{PH^-}$, and $\mathrm{P^{2-}}$ are 4×10^{-4}, 5×10^{-4}, and 4×10^{-3} cm s^{-1} respectively. For oxidation of $\mathrm{P^{2-}}$ the redox process approaches a fully reversible reaction with $K(\Lambda,\alpha) = 0.97$, whilst oxidation of $\mathrm{PH_2}$ approaches the totally irreversible case with $K(\Lambda,\alpha) = 0.78$. That such a large difference in k^0 can be induced simply by passing through acid–base equilibria is rather surprising. For oxidation of $\mathrm{P^{2-}}$ there is a single proton change accompanying electron transfer whereas oxidation of both $\mathrm{PH^-}$ and $\mathrm{PH_2}$ involves a two-proton change and this extra proton transfer seems to be responsible for the dramatic variation in k^0.



$$\underset{\mathrm{PH_2}}{[\mathrm{HO}\text{-}\mathrm{Mn^{III}}\text{-}\mathrm{H_2O}]} \rightleftharpoons H^+ + \underset{\mathrm{PH^-}}{[\mathrm{HO}\text{-}\mathrm{Mn^{III}}\text{-}\mathrm{OH}]^{-}} \rightleftharpoons 2H^+ + \underset{\mathrm{P^{2-}}}{[\mathrm{O}\text{-}\mathrm{Mn^{III}}\text{-}\mathrm{OH}]^{2-}} \qquad (18)$$

With α and k^0 evaluated from the r.d.e. studies, equation (17) allows calculation of a pH profile for i_p and this is shown as the dashed curve in Figure 6(*a*). There is reasonable qualitative agreement between calculated and observed curves but the actual i_p values are much more dependent upon pH than expected from the calculation. We are unsure why this

Table 2. Electrochemical oxidation of $[Mn^{III}(tmpyp)]^{4+}$ in aqueous solution

pH	$k^0/10^{-3}$ cm s^{-1} (c.v.)	$k^0/10^{-3}$ cm s^{-1} (r.d.e.)	α (r.d.e.)
14.1	—	3.31	0.55
13.3	—	1.12	0.54
12.9	1.05	—	—
12.6	0.92	—	—
12.5	—	0.95	0.63
12.3	0.85	—	—
12.0	0.72	—	—
11.8	—	0.63	0.58
11.7	0.52	—	—
11.4	0.34	—	—
11.0	—	0.51	0.60
10.6	0.37	—	—
10.5	—	0.39	0.55
9.9	—	0.43	0.57
8.8	—	0.41	0.59

discrepancy exists but it could be associated with the poor stability of Mn^{IV} porphyrins in aqueous solution at $pH < 12$.

A limited number of experiments were performed with $[Mn^{III}(tspp)]^{4-}$ and the results were similar to those described above. Thus, oxidation of $[Mn^{III}(tspp)]^{4-}$ at pH 14 was a facile process ($E_{\frac{1}{2}} = 0.32$ V *vs.* n.h.e., $k^0 = 7 \times 10^{-3}$ cm s^{-1}) and the degree of reversibility was very high. Throughout the range $7 < pH < 12$, $E_{\frac{1}{2}}$ varied by −115 mV per pH unit and the actual $E_{\frac{1}{2}}$ values were similar to those found for $[Mn^{III}(tmpyp)]^{4+}$. From these oxidation studies it appears that the porphyrin ligand has little influence upon the $E_{\frac{1}{2}}$ values, unlike the situation found for the reduction studies. As such, it is important that generalisations raised from electrochemical experiments with diamagnetic water-soluble metalloporphyrins [9-11] are not extrapolated to paramagnetic metalloporphyrins.

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