J. Chem. Soc., Faraday Trans. 1, 1986, **82**, 3215–3231

Decay of High-valent Manganese Porphyrins in Aqueous Solution and Catalysed Formation of Oxygen

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Manganese(III) porphyrins ($Mn^{III}P$) are easily oxidised to the corresponding $Mn^{IV}P$ in alkaline aqueous solution. At $pH < 5$ the oxidation product is a $Mn^{III}P$ π-radical cation. These oxidised metalloporphyrins have limited stability in water and they revert to the original $Mn^{III}P$ upon standing in the dark. The rate and mechanism of this inherent reduction process depends upon pH, with lower pH giving the higher rates. The inherent reduction appears to involve disproportionation and rearrangement of the $Mn^{IV}P$ but it does not lead to formation of molecular O_2. Addition of colloidal $RuO_2 \cdot 2H_2O$, a good O_2-evolving catalyst, has a pronounced effect upon the reduction process. The oxidised metalloporphyrin is bound to the catalyst particles by electrostatic forces, and at $pH < 11$ the bound material decays more slowly than the free compound. For $8 < pH < 11$, decay of the bound metalloporphyrin involves oxidation of water to O_2, but the yield of O_2 is much less than the stoichiometric value.

Previous papers[1–4] have described the redox equilibria established between the various oxidation states of the central manganese ion sited within the porphyrin ring. The stable form is the manganese(III) porphyrin ($Mn^{III}P$), but it is easily reduced to the corresponding $Mn^{II}P$. This latter species is stable only in alkaline solution ($pH > 8$) and in the absence of O_2. Oxidation of $Mn^{III}P$ forms the corresponding $Mn^{IV}P$, which has limited stability and is reduced back to the original $Mn^{III}P$ upon standing in the dark even at pH 14.[5] Several research groups[6–9] have shown that the rate of this reduction process increases with decreasing pH. Actual reduction rate constants have been published only for the Mn^{IV}/Mn^{III} haematoporphyrin couple[9], where it has been reported that the side-chain provides the electrons necessary for the reduction of the central metal ion.[7] In this paper we report kinetic parameters associated with the decay of various $Mn^{IV}P$ obtained by derivatisation of the *meso*-tetraphenylporphyrin class.

The process under investigation is of interest because of the possible involvement of manganese in green-plant photosynthesis. Much speculation exists about whether or not a manganese complex functions as the natural water oxidation catalyst. If it does then surely it is a high-valent manganese complex that is the active catalyst. Here we give particular attention to the possible oxidation of water to O_2 by $Mn^{IV}P$ with and without an added redox catalyst.

Experimental

Manganese(III)tetrakis(4-sulphonatophenyl)porphyrin (sodium salt) ($Mn^{III}TSPP$), manganese(III)tetrakis(4-carboxyphenyl)porphyrin (sodium salt) ($Mn^{III}TCPP$), manganese(III) tetra(4-pyridyl)porphyrin ($Mn^{III}TPyP$) and manganese(III) tetrakis(*N*-methyl-4-pyridyl)porphyrin (chloride salt) ($Mn^{III}TMPyP$) were prepared and purified as described before[10] or purchased from Midcentury Chem. Co. All other materials were of the highest available purity and were used as received. For the pulse-radiolysis studies, water was obtained freshly from a Millipore Milli-Q system. For the stopped-flow and membrane polarographic detector studies, water was deionised and doubly distilled from a Fisons quartz still. It was then redistilled from alkaline permanganate to ensure that no reducing impurities remained. In all cases water was used within a few hours of final purification. The pH was adjusted by addition of the appropriate buffer; HCl/NaCl $pH < 4$; NaH_2PO_4/Na_2HPO_4 $4.5 < pH < 9.0$; $Na_2B_4O_7/KOH$, $8.8 < pH < 10.8$; KOH $pH > 11$. Where possible, the concentration of buffer was 10^{-3} mol dm^{-3} and all kinetic measurements were made at a fixed ionic strength of 0.05 mol dm^{-3}. Colloidal $RuO_2 \cdot 2H_2O$ was made as before.[11]

The general conditions used in the pulse-radiolysis experiments have been described in detail.[4,12] Pulses of 8 MeV electrons from an ARCO-LP-7 linear accelerator were usually of 10 ns duration with doses (300–600 rad) that produce $(2\text{–}4) \times 10^{-6}$ mol dm^{-3} radicals from water. An electronic shutter and the proper interference filters were used to protect the reaction solution from undue photolysis by the analysing light. Dosimetry was performed with N_2O-saturated KSCN solutions.[13] Aqueous solutions of the $Mn^{III}P$ [(5×10^{-6})–10^{-4} mol dm^{-3}] containing KBr (10^{-2} mol dm^{-3}) at the required pH were saturated with N_2O before irradiation. The course of reaction was followed by optical absorption and the resultant signals were averaged.[12]

Stopped-flow experiments were performed with an Applied Photophysics or a Durrum instrument (dead-times 2 ms). Solutions of the $Mn^{III}P$ (4.5×10^{-6} mol dm^{-3}) in water containing buffer and sufficient Na_2SO_4 to give a total ionic strength of 0.05 mol dm^{-3} were mixed with an aqueous solution of Br_2 (2×10^{-4} mol dm^{-3}) at the same pH and ionic strength. Again, the course of reaction was followed by absorption spectroscopy and decay kinetics were analysed by iterative computer fitting to pseudo-first-order processes.

At $pH > 12$ oxidation of a $Mn^{III}P$ can be achieved by addition of the (electron equivalent) stoichiometric amount of NaOCl.[1] The product is sufficiently stable to be used as a reactant in further stopped-flow experiments. Thus $Mn^{IV}P$ was prepared by stoichiometric oxidation of the corresponding $Mn^{III}P$ at pH 13 and mixed in the stopped-flow instrument with an aqueous solution containing acid and/or buffer. The rate of decay of $Mn^{IV}P$ was followed at 430 nm. In all the stopped-flow experiments the reported rate constants were the average of at least three independent measurements.

Concentrations of dissolved O_2 were monitored with a purpose-built membrane polarographic detector (m.p.d.)[14] and were displayed on a x–t chart recorder. Aqueous solutions of the $Mn^{III}P$ (2×10^{-5} mol dm^{-3}) at pH 13 were oxidised within the reaction chamber of the m.p.d. by addition of the (electron-equivalent) stoichiometric amount of NaOCl; and the solution was purged with O_2-free N_2. An aliquot of N_2-purged acid and/or buffer was added to lower the pH and the concentration of evolved O_2 measured. Measurements were repeated at least 5 times at each pH value. In related experiments, the $Mn^{III}P$ solution was thoroughly purged with N_2 within the chamber of the m.p.d. and the required amount of N_2-purged Br_2 or NaOCl solutions added *via* a septum. Again, the change in concentration of dissolved O_2 was measured.[14] Blank experiments were made in all cases. These measurements consisted of repeating the above O_2 determinations in the absence of each of the reactants. Operating the m.p.d. in its most sensitive mode gives a baseline drift of *ca.* 3 mm h^{-1}. Injection of N_2-saturated water does not perturb the baseline, but injection of sufficient O_2-saturated water to give a final O_2 concentration of 5×10^{-7} mol dm^{-3} corresponds to a 22 mm deflection on the chart recorder. The risetime for this deflection is *ca.* 15 s.

Experiments involving colloidal $RuO_2 \cdot 2H_2O$ were made by identical procedures to those outlined above. In all cases the colloidal catalyst was mixed with the aqueous solution of the $Mn^{III}P$ before the experiment.

Results and Discussion

Oxidation of Manganese(III) Porphyrins

In alkaline aqueous solution (pH > 12), an $Mn^{III}P$ is readily oxidised to the corresponding $Mn^{IV}P$, which possesses reasonable stability under such conditions.[1,5] Oxidation can be achieved with a wide variety of oxidants, including H_2O_2, $K_3Fe(CN)_6$, $KMnO_4$, NaOCl, $KBrO_3$ and $Na_2S_2O_8$, and rate constants for the oxidation step have been reported.[2] Identical oxidations proceed under pulse-radiolytic conditions using Br_2^- as oxidant.[4] Electrochemical studies[15] have shown that the redox potential for one-electron oxidation of an $Mn^{III}P$ increases with decreasing pH throughout the range $7 < pH < 14$. This effect is manifest in the rate constant for oxidation of a given $Mn^{III}P$ as a function of pH. Thus, with Br_2^- as oxidant, the bimolecular rate constant for oxidation of the various $Mn^{III}P$ (k_{ox}) undergoes[4] an approximate tenfold decrease upon lowering the pH from 13 to 7. Even so, oxidation with Br_2^- under pulse-radiolytic conditions in neutral solution is fast and the formation of $Mn^{IV}P$ is quantitative.[4]

Using Br_2 as oxidant, k_{ox} for oxidation of $Mn^{III}TMPyP$ was measured as a function of pH using the stopped-flow technique:

$$2Mn^{III}P + Br_2 \rightarrow 2Mn^{IV}P + 2Br^-. \tag{1}$$

At a constant ionic strength of 0.05 mol dm^{-3}, k_{ox} varied considerably with pH, giving values of 1×10^2, 4×10^5 and 1.5×10^7 $dm^3\ mol^{-1}\ s^{-1}$, respectively, at pH 7, 9 and 11. These large changes are due to hydrolysis of Br_2 at alkaline pH:

$$3Br_2 + 3OH^- \rightleftharpoons BrO_3^- + 5Br^- + 3H^+. \tag{2}$$

As a consequence of such changes, electrostatic forces between the reactants and the redox potential of the oxidant vary over a wide range so that changes in the observed k_{ox} values cannot simply be ascribed to changes in the structure of the $Mn^{III}P$.

In the present investigation we are concerned with decay of the $Mn^{IV}P$, and it is important that the oxidation step is complete well before decay begins. In the pulse-radiolysis experiments,[4] the formation reaction is complete well within 100 μs of the pulse, so that decays occurring on the millisecond timescale can be followed without complication. Chemical oxidations performed at pH > 12 require only stoichiometric amounts of oxidant, and the product lives for at least many minutes.[1,5] Again, there are few problems associated with such studies. At lower pH the rate of oxidation with Br_2 is slower and excess oxidant must be used. For the stopped-flow studies the concentration of $Mn^{III}P$ was 4.5×10^{-6} mol dm^{-3}, and for $8.2 < pH < 12.0$ it was necessary to use a Br_2 concentration of 2.5×10^{-5} mol dm^{-3} to ensure that oxidation was complete before the onset of decay. At pH 7 a large excess of Br_2 was needed to achieve oxidation, and this precluded meaningful measurement of decay kinetics. Thus, the stopped-flow studies were restricted to pH > 8.2. Even in this range the decay kinetics will be distorted because of the excess of Br_2 present.

Absorption spectra recorded for the $Mn^{IV}P$ product formed at $7 < pH < 14$ showed no obvious differences apart from the known p*K* transitions[1] which occur at *ca.* 7.5 and 10.5. However, pulse-radiolytic oxidation of various $Mn^{III}P$ at pH < 3 gave[4] a product with an absorption spectrum markedly different from that characteristic of $Mn^{IV}P$[1] [see fig. 7D in ref. (4)]. The strong absorption found[4] around 650–700 and 490 nm suggested that the product was a metalloporphyrin π-radical cation. Addition of sufficient HNO_3

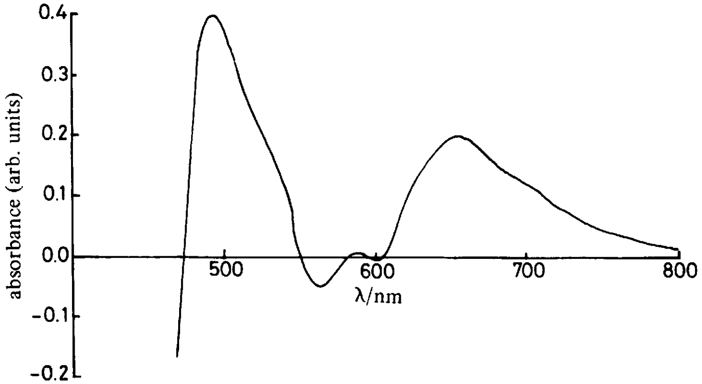


Fig. 1. Differential absorption spectrum of $Mn^{III}TMPyP^+$ as formed by adding sufficient HNO_3 to a solution of $Mn^{IV}TMPyP$ at pH 13 such that the final pH falls to 2.2.

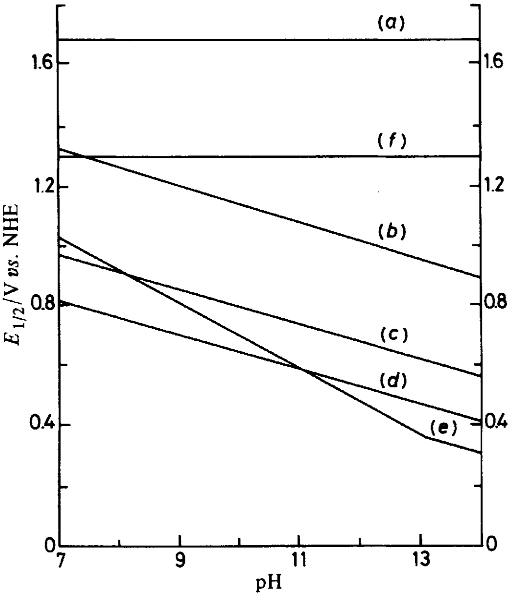


Fig. 2. Energy-level diagram showing the pH dependence of the various redox couples used in this work. The $Mn^{IV}/Mn^{III}TMPyP$ data are taken from ref. (15) and the other redox potentials have been taken from standard textbooks. The half-reactions involved are: (*a*) $Br_2^- + e = 2Br^-$; (*b*) $ClO^- + 2H^+ + 2e = Cl^- + H_2O$; (*c*) $RuO_4 + 4H^+ + 4e = RuO_2 + 2H_2O$; (*d*) $O_2 + 4H^+ + 4e = 2H_2O$; (*e*) $Mn^{IV}TMPyP + e = Mn^{III}TMPyP$; (*f*) $Mn^{III}P^+ + e = Mn^{III}P$. The redox potential for process (*f*) has not been measured in water and the value given is that determined for $Mn^{III}TPP$ in CH_2Cl_2 solution as ref. (2).

to a solution of $Mn^{IV}P$ prepared at pH 13 to give a final pH of 2 gave a transient absorption spectrum similar to that found in the pulse-radiolysis experiments (see fig. 1). Thus at low pH the oxidising equivalent seems to be centred on the porphyrin ligand rather than on the central Mn ion. This is to be expected, since the redox potential[15] for the Mn^{III}/Mn^{IV} couple increases by 118 mV per pH unit upon decreasing the pH below 10, whereas the redox potential for oxidation of the porphyrin ring should be independent of pH (fig. 2). Consequently, high pH favours formation of $Mn^{IV}P$ and low pH favours formation of the π-radical cation. The transition point depends on the porphyrin structure and is at a higher pH for TMPyP than for TSPP:

$$\begin{tikzcd} & \mathrm{Mn^{(III)}P^{+}} \\ \mathrm{Mn^{(III)}P + oxidant} \arrow[ur, "\mathrm{pH} < 5"] \arrow[dr, "\mathrm{pH} > 5"'] & & (3) \\ & \mathrm{Mn^{(IV)}P}\ . \end{tikzcd}$$

Oxidation of Manganese(IV) Porphyrins

It is known[2] from chemical studies performed with MnTCPP that oxidation with NaOCl at pH 14 results in formation of $Mn^{V}TCPP$. This was confirmed by pulse-radiolysis experiments in which $Mn^{IV}P$ was formed chemically by oxidation with Br_2 at pH 11–14 and then oxidised further with Br_2^- formed in the pulse:

$$\mathrm{Mn^{IV}P + Br_2^- \rightarrow Mn^{V}P + 2Br^-} \qquad (4a)$$

or

$$\mathrm{Mn^{IV}P + Br_2^- \rightarrow Mn^{IV}P^+ + 2Br^-}. \qquad (4b)$$

The $Mn^{III}P$ was chemically oxidised in a mixing chamber just before entering the cell. In the radiolysis cell Br_2^-, produced by the electron pulse, oxidised the $Mn^{IV}P$. This oxidation was very rapid and the rate constants for oxidation of the various $Mn^{IV}P$ are collected in table 1. The differential absorption spectra for oxidation of the $Mn^{IV}P$ are shown in fig. 3–5. The spectra observed in the case of MnTCPP and MnTSPP at pH 14 [fig. 3(*a*) and 4(*a*), respectively] exhibit a very sharp absorption band at *ca.* 430 nm, along with other bands around 550–600 nm. By comparison with the published[2] spectra of $Mn^{IV}TCPP$ and $Mn^{V}TCPP$, these spectra are assigned to the corresponding $Mn^{V}P$. However, as the pH is decreased, oxidation of $Mn^{IV}TCPP$ [pH 13, fig. 3(*b*)] and $Mn^{IV}TSPP$ [pH 11, fig. 4(*b*)] results in formation of products having broad absorptions around 500 and 600 nm. These products are more characteristic of metalloporphyrin π-radical cations than high-valence metalloporphyrins.[16–18] $Mn^{IV}TMPyP$ seems to be oxidised to the π-radical cation even at pH 14 (fig. 5). The structure of these species will be discussed further in a later section.

Decay of $Mn^{V}P$

The products of oxidation of $Mn^{IV}P$ decay relatively quickly. The first half-lives derived from the pulse-radiolysis experiments (table 1) vary from 60 ms for MnTSPP to 4 ms for MnTMPyP, both at pH 14. The oxidised form of the TMPyP complex is found to be always less stable than that of the TSPP derivative. In the present case, the nature of the oxidation products is also different, *i.e.* $Mn^{V}TSPP$ and $Mn^{IV}TMPyP^+$. Further details on the structure and mechanism of decay of these species are given below.

Decay of $Mn^{IV}P$

As discussed above, oxidation[4] of $Mn^{III}P$ at pH < 5 results in formation of the corresponding $Mn^{III}P^+$ rather than the $Mn^{IV}P$. It is not possible to oxidise the $Mn^{III}P$ at pH < 5 by chemical methods, but pulse-radiolytic oxidation[4] with Cl_2^- proceeds smoothly at pH 3. Also, addition of acid to an aqueous solution of $Mn^{IV}P$ prepared at pH 13 so that the final pH falls to < 5 leads to intermediate formation of $Mn^{III}P^+$. The π-radical cation decays fairly slowly, the kinetics giving a reasonable fit to a

Table 1. Rate constants for the oxidation of various $Mn^{IV}P$ by Br_2^- radicals and the first half-lives for the oxidation products at that pH

porphyrin	pH	[KBr] /mol dm^{-3}	$k_4/10^8$ dm^3 mol^{-1} s^{-1}	$t_{\frac{1}{2}}$/ms
$Mn^{IV}TSPP$	14	0.10	11	60
	12.9	0.01	6.0	20
	11.1	0.01	7.8	—
$Mn^{IV}TCPP$	14	0.10	18	4
	12.9	0.01	16	4
$Mn^{IV}TMPyP$	14	0.01	4.5	4

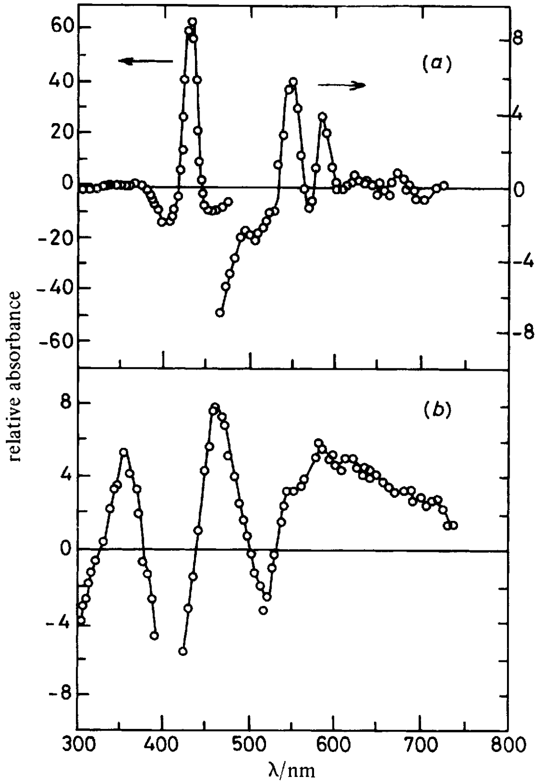


Fig. 3. Differential absorption spectra observed upon the one-electron oxidation of $Mn^{IV}TCPP$ with Br_2^- in N_2O-saturated aqueous solution. (*a*) KBr (0.1 mol dm^{-3}), KOH (1.0 mol dm^{-3}), recorded 0.5–0.7 ms after the electron pulse; (*b*) KBr (0.01 mol dm^{-3}), KOH (0.1 mol dm^{-3}), recorded 50–200 μs after the electron pulse.

first-order process. For a given porphyrin, the rate of decay is independent of the initial concentration of $Mn^{III}P^+$, ionic strength and presence of dissolved O_2. Measurements made at pH 1.8 showed that the first-order decay rate constant depended upon the nature of the porphyrin periphery groups. For example, k_{red} values of 300 ± 8, 34 ± 8, 60 ± 10 and 100 ± 12, respectively, were obtained with MnTMPyP, MnTPyP, MnTSPP and MnTCPP. In all cases, the rate of decay of $Mn^{III}P^+$ measured at 430 nm agreed well with the rate of formation of $Mn^{III}P$ measured at 470 nm.

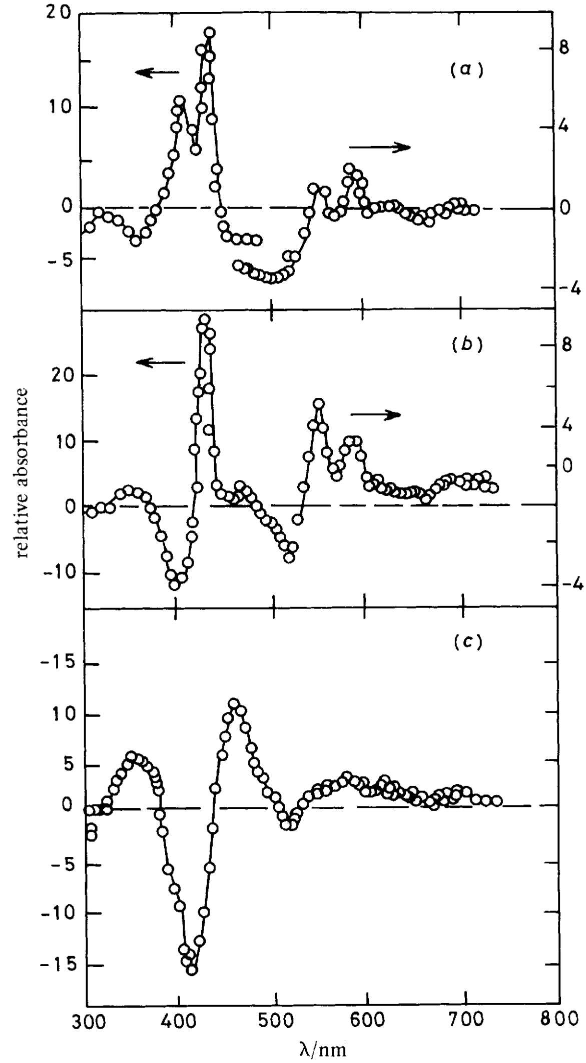


Fig. 4. Differential absorption spectra observed upon the one-electron oxidation of $Mn^{IV}TSPP$ by Br_2^- in N_2O-saturated aqueous solutions. (*a*) KBr (0.1 mol dm^{-3}), KOH (1.0 mol dm^{-3}), recorded 80–140 μs after the electron pulse; (*b*) KBr (0.01 mol dm^{-3}), KOH (0.1 mol dm^{-3}), recorded 160–280 μs after the electron pulse; (*c*) KBr (0.01 mol dm^{-3}), pH, 11.1, recorded 0.5–0.8 ms after the electron pulse.

The mechanism for reduction of the π-radical cations, under such conditions, is far from clear. Relative to π-radical cations derived from diamagnetic metalloporphyrins,[19, 20] $Mn^{III}P^+$ is fairly stable, and the observed dependence upon periphery group is consistent with known trends.[19] Experiments made with an m.p.d. showed that the reduction step does not involve oxidation of water to O_2. More probably, $Mn^{III}P^+$ reacts with trace impurities in the solution, undergoes disproportionation to form a π-dication,[21] or adds a hydroxide ion at the *meso* position.[22]

At pH 13, quantitative oxidation[1] of $Mn^{III}P$ can be achieved by addition of the stoichiometric amount of NaOCl or $NaBrO_3$. The $Mn^{IV}P$ product is sufficiently stable ($t^{1/2} > 2$ h) for its reactions to be studied by conventional techniques.[5] Thus, stopped-flow studies performed with $Mn^{IV}TMPyP$ showed that quantitative reduction occurred upon

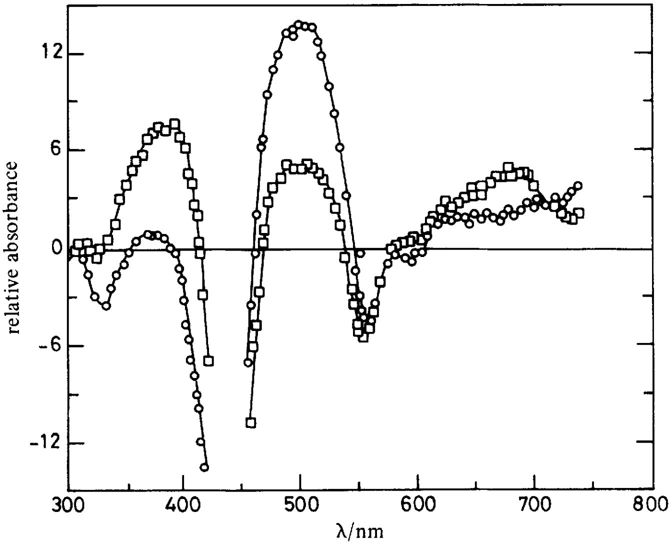


Fig. 5. Differential absorption spectra observed upon the one-electron oxidation of $Mn^{IV}TMPyP$ by Br_2^- in N_2O-saturated aqueous solution containing KBr (0.1 mol dm^{-3}) and KOH (1.0 mol dm^{-3}). Spectra recorded □, 10–25 μs and ○, 0.2–0.3 ms after the electron pulse.

mixing with H_2S ($k_{red} = 2.8 \times 10^4$ dm^3 mol^{-1} s^{-1}) or benzhydroquinone ($k_{red} = 2.0 \times 10^3$ dm^3 mol^{-1} s^{-1}):

$$2Mn^{IV}P + H_2X \rightarrow 2Mn^{III}P + 2H^+ + X. \quad (5)$$

Even in the absence of an added reductant, $Mn^{III}P$ is re-formed upon standing in the dark overnight, although there is some loss (*ca.* 10%) of porphyrin. The kinetics for this inherent reduction were found to be complex. Approximating the decay rate of $Mn^{IV}TMPyP$ to a pseudo-first-order process gave $k_{red} = (2.5 \pm 1.0) \times 10^{-3}$ s^{-1}, which would correspond to a bimolecular rate constant for reduction by water of $(4.5 \pm 1.8) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}.

Lowering the pH of the bulk solution by addition of buffer or performing the oxidation at pH < 13 leads to a marked increase in the rate of decay of the $Mn^{IV}P$ product. Throughout the range 11 < pH < 14, the decay kinetics were complex and the decay rates were slow. Decay profiles recorded at 430 nm (decay of $Mn^{IV}P$) and 470 nm (return of $Mn^{III}P$) were similar, showing that the principal decay process involved reduction of $Mn^{IV}P$ to $Mn^{III}P$, although there was *ca.* 10% overall loss of porphyrin in each case.

Fig. 6 gives some typical traces showing the decay of $Mn^{IV}TMPyP$ at different pH, as monitored at 430 nm using stopped-flow techniques with bromate as the oxidant. Bleaching of the porphyrin is evidenced by the observation that the final absorbance falls below the initial baseline. This effect is more pronounced at higher pH. The decay profiles give poor fits to second-order kinetics and better fits to first-order processes. A first-order fit to the decay profile obtained at pH 12.5 is given as an insert to fig. 6. Analysis of the decay data by an iterative fitting procedure gave first-order rate constants for reduction of $Mn^{IV}TMPyP$ of 0.029, 0.019 and 0.014 s^{-1} at pH 11.3, 11.9 and 12.5, respectively (each rate constant being the average of at least three independent measurements). Reduction rate constants measured for the other $Mn^{IV}P$ showed a similar trend with pH but were generally slower. For example, at pH 12.5 k_{red} values of 3×10^{-3}, 1×10^{-3} and 1×10^{-3}, respectively, were obtained with $Mn^{IV}TPyP$, $Mn^{IV}TSPP$ and $Mn^{IV}TCPP$. As mentioned above, the oxidised phenylporphyrins are more stable than the analogous pyridylporphyrins.

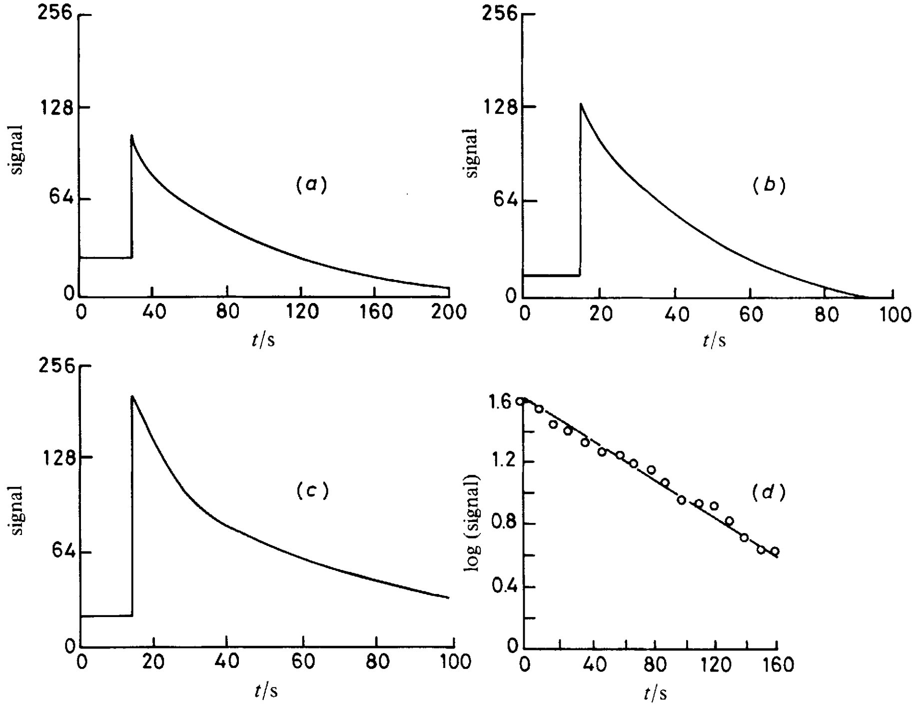


Fig. 6. Inherent decay of $Mn^{IV}TMPyP$ at different pH as measured at 430 nm after stopped-flow formation with Br_2. (*a*) pH 12.5, (*b*) pH 11.9, (*c*) pH 11.3. Trace (*d*) shows an attempted fit to first-order kinetics for the decay profile observed at pH 12.5.

Oxidation of $Mn^{III}P$ in aqueous solution between pH 5 and 11 results in formation of the corresponding $Mn^{IV}P$. There is no spectroscopic evidence to show that the oxidation product is dimeric, although the absorption spectra are quantitatively and qualitatively similar to those obtained for the $Mn^{IV}P$ at pH > 11. Pulse-radiolysis experiments have not resolved an absorption change that could be due to dimerisation, but such changes might be small. Consequently, the structure of the oxidation product is not clear, but it is possibly monomeric. Other high-valent metalloporphyrins are known[23-26] to favour formation of μ-oxo dimers at higher pH, so that the observed pK transition found around pH 10–11 might reflect both changes in the state of axially bound water molecules and the changeover from monomer to dimer.

Measurements made with $Mn^{IV}TMPyP$ showed that decay of the oxidised species occurred by two well resolved, first-order steps throughout the range $7 < pH < 11$ (fig. 7). As before, monitoring at 430 and 470 nm gave similar profiles, suggesting that $Mn^{III}TMPyP$ is re-formed in two separate steps.

The first-order rate constant observed for the fast step in the reduction reaction (k_1) is pH dependent, as shown in fig. 8 and table 2. For $Mn^{IV}TMPyP$ k_1 shows a non-linear dependence upon pH (the other porphyrins show similar behaviour). At pH < 5, k_1 refers to reduction of $Mn^{III}P^+$ whilst at pH > 11 the fast (k_1) and slow (k_2) steps cannot be resolved. There is a clear increase in k_1 upon decreasing the pH below 11, suggesting that the μ-oxo dimer undergoes a pK transition at this pH. Earlier work,[1] relying on absorption spectroscopy, reported a pK for $Mn^{IV}TMPyP$ of *ca.* 10.5. The kinetic measurements infer that the protonated species, with its higher redox potential (fig. 2), disproportionates faster than the basic form. This pK transition might involve dissociation of the μ-oxo dimer into monomeric $Mn^{IV}P$. In this case it is necessary that the monomer is reduced faster than the dimer.

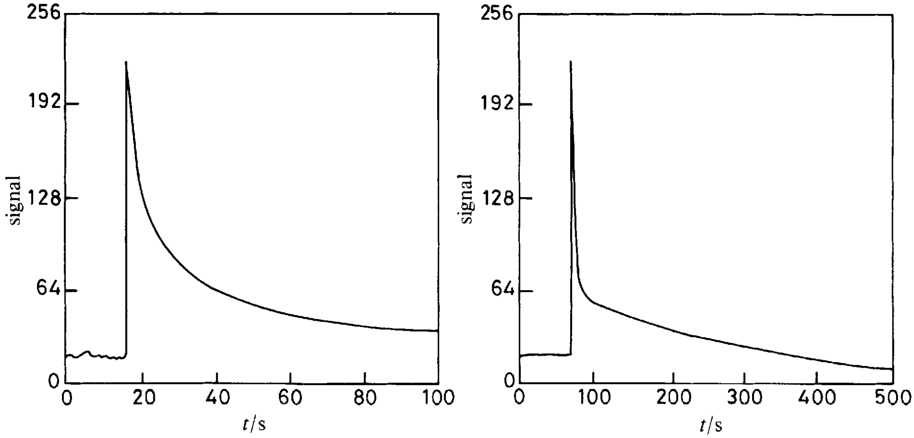


Fig. 7. Typical profile for decay of $Mn^{IV}TMPyP$ at 430 nm following stopped-flow formation with Br_2 at pH 10.6.

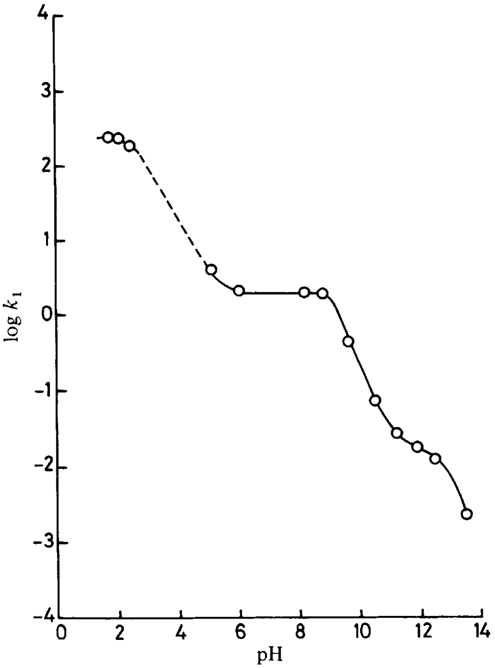


Fig. 8. Plot of log k_1 *vs.* pH for decay of $Mn^{IV}TMPyP$ as measured at 430 nm following stopped-flow formation with Br_2. Each point is the average of at least three independent measurements.

Within the limited amount of data, it appears that k_2 shows no pH dependence throughout the range $7 < \text{pH} < 11$. However, the magnitude of k_2 does depend upon the nature of the porphyrin ring, as shown by the data in table 2.

Detailed experiments performed with the m.p.d. showed that the inherent decay of various $Mn^{IV}P$ in water at $2 < \text{pH} < 13$ did not result in measurable yields of O_2. On the basis of such studies, we calculate that if O_2 is formed as a reaction product (and

Table 2. Rate constants for reduction of various $Mn^{IV}P$ in aqueous solution at pH > 7 and of $Mn^{III}P^+$ at pH < 7[a]

	k/s^{-1}		
pH	TMPyP	TSPP	TPyP
1.8	300	60	34
2.2	280	70	10
3.7	—	—	8
5.1	4.2	1.0	6.5
7.1	—	0.03	0.024
8.2	2.2 (0.010)	—	0.014 (0.003)
8.8	2.3	0.009 (0.002)	0.010 (0.002)
9.4	0.42 (0.011)	0.007 (0.002)	0.012 (0.002)
10.6	0.085 (0.008)	—	0.007 (0.002)
11.3	0.029	0.004	0.005
11.9	0.019	—	0.005
12.5	0.014	0.001	0003
13.0	—	—	0.001

[a] At pH > 11 and pH < 7 the decay profile was fitted to a single exponential process but for 7 < pH < 11 the decay kinetics required a two-exponential fit corresponding to k_1 and k_2. The numbers in parenthesis refer to k_2.

it is not consumed by reaction with $Mn^{II}P$) then its yield must be < 10% of the total expected from the stoichiometric oxidation of water:

$$4Mn^{IV}P + 2H_2O \rightarrow 4Mn^{III}P + 4H^+ + O_2. \qquad (6)$$

In separate experiments it was shown that both $Mn^{III}P$ and $Mn^{IV}P$ are able to induce decomposition of H_2O_2:

$$2H_2O_2 \rightarrow 2H_2O + O_2. \qquad (7)$$

but extensive loss of the porphyrin occurs. Thus, formation of H_2O_2 has not been confirmed in our experiments.

Mechanisms of Decay

Previous work[2] has suggested, on the basis of magnetic susceptibility measurements and absorption spectroscopy, that the $Mn^{IV}P$ formed at pH 13 exists in the form of a μ-oxo dimer:

$$PMn^{IV}—O—Mn^{IV}P. \qquad (8)$$

Assuming that the oxidation product is indeed a μ-oxo dimer, the most likely mechanism for the reduction process involves disproportionation within the dimer, explaining the observed first-order kinetics:

$$PMn^{IV}—O—Mn^{IV}P \rightarrow Mn^{III}P + Mn^{IV}P^+ \text{ (or } Mn^{V}P). \qquad (9)$$

As mentioned earlier, the preference for formation of $Mn^{V}P$ or $Mn^{IV}P^+$ depends upon the nature of the porphyrin periphery groups and upon pH. In most cases, the disproportionation product is expected to be the $Mn^{IV}P^+$. This species is fairly short-lived ($t_{1/2} \approx$ 10 ms at pH 13) and it decays to the original $Mn^{III}P$:

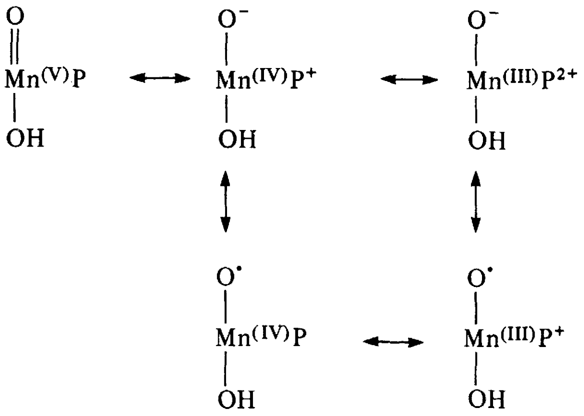
$$Mn^{IV}P^+ + 2H_2O \rightarrow Mn^{III}P + H_2O_2 + 2H^+. \tag{10}$$

The poor stability of the $Mn^{IV}P^+$ product shows that the rate-determining step in the reduction of the $Mn^{IV}P$, under such conditions, is the primary hydrolysis of the μ-oxo dimer.

Previous workers[8,9] have shown that the inherent decay of manganese(IV) haematoporphyrin results in formation of peroxide. We did not identify H_2O_2 as a reaction product in our systems, but in control experiments it was found that H_2O_2 bleached the porphyrin ring. Thus the observation that the inherent reduction of an $Mn^{IV}P$ involves some overall loss of porphyrin is consistent with the formation of H_2O_2. Studies performed with a m.p.d. showed that the reduction process did not result in formation of O_2.

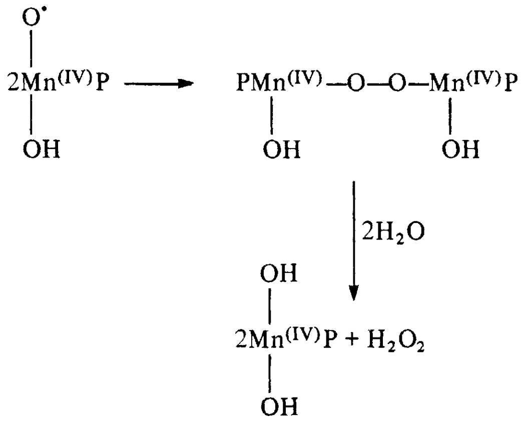
Decay of $Mn^{IV}P$ at $7 < pH < 11$ occurred by two first-order steps, again consistent with a mechanism involving disproportionation within the dimer. If the $Mn^{IV}P$ does not exist predominantly as a dimer at $pH < 11$, then we assume that it equilibrates rapidly with a small percentage of dimer which disproportionates. To account for the slow step in the re-formation of $Mn^{III}P$ it is necessary that the $Mn^{IV}P^+$ is reduced to $Mn^{III}P$ more slowly at $pH < 11$ than observed in the pulse-radiolysis experiments at $pH > 11$. This is certainly the case with other metalloporphyrin radical cations,[19, 20] but we could not confirm it for $Mn^{IV}P^+$ because the poor stability of $Mn^{IV}P$ at $pH < 12$ prevents its use as a reactant in the pulse-radiolysis set-up.

The products of disproportionation [reaction (9)] formulated as $Mn^{V}P$ or $Mn^{IV}P^+$ may exist in several forms:



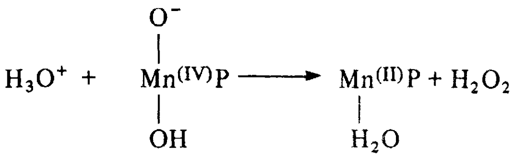
(11)

While the form favoured at very high pH is written as $Mn^{V}P$, recent work[27] has proposed an alternative assignment as $Mn^{IV}P$ with the extra oxidising equivalent centred on an axially coordinated oxygen. Whatever the real nature of this species, it is known from the pulse-radiolysis studies that it is stable only at very high pH. Lowering the pH (to < 14 for MnTMPyP or < 13 for MnTSPP) favours formation of $Mn^{IV}P^+$ (fig. 2). It is possible that lowering the pH further favours formation of $Mn^{III}P^{2+}$, but there is no evidence for such a product in our experiments. The formulation of the high-valent MnP as $^{\bullet}OMn^{IV}P$ provides a direct route for formation of hydrogen peroxide *via* a peroxo dimer:[28]



$$2\,\mathrm{Mn^{(IV)}P}(\mathrm{O^{\bullet}})(\mathrm{OH}) \longrightarrow (\mathrm{OH})\mathrm{PMn^{(IV)}{-}O{-}O{-}Mn^{(IV)}P}(\mathrm{OH}) \xrightarrow{2H_2O} 2\,(\mathrm{OH})\mathrm{Mn^{(IV)}P}(\mathrm{OH}) + H_2O_2 \qquad (12)$$

A two-electron change, involving intermediate formation of a $Mn^{II}P$



$$H_3O^+ + (\mathrm{O^-})\mathrm{Mn^{(IV)}P}(\mathrm{OH}) \longrightarrow \mathrm{Mn^{(II)}P}(H_2O) + H_2O_2 \qquad (13)$$

$$\mathrm{Mn^{(II)}P} + \mathrm{Ox} \longrightarrow \mathrm{Mn^{(III)}P} + \mathrm{Red} \qquad (14)$$
$$(\mathrm{Ox} = O_2,\ H_2O_2 \text{ or } \mathrm{Mn^{(IV)}P})$$

is a possible alternative to the above one-electron scheme. However, the characteristic absorption spectrum[1] of $Mn^{II}P$ has not been observed, even as a transient, and the presence of O_2 has no effect upon k_2. Furthermore, $Mn^{II}P$ undergo acid-catalysed demetallation[29] and, although this reaction is fairly slow at pH > 5, we might have expected to detect some demetallated porphyrin.

Catalysed Decay of Mn^{IV}TMPyP

A series of stopped-flow experiments was performed to investigate the influence of redox catalysts upon the decay kinetics of Mn^{IV}TMPyP. Experiments were made in two ways. First, chemical oxidation of Mn^{III}TMPyP was achieved by addition of the stoichiometric amount of bromate at pH 13. The resultant solution was mixed with acid and/or buffer containing a known concentration of colloidal Pt or $CoSO_4$. Decay of Mn^{IV}TMPyP was measured as a function of the concentration of added catalyst at a particular pH. Throughout the range $2 < \mathrm{pH} < 13$ neither colloidal Pt ($[\mathrm{Pt}] < 2 \times 10^{-4}$ mol dm^{-3}) nor $CoSO_4$ ($[\mathrm{Co^{2+}}] < 5 \times 10^{-2}$ mol dm^{-3}) had any observable effect upon the rate of decay of Mn^{IV}TMPyP. In the second set of experiments, buffered aqueous solutions of Mn^{III}TMPyP containing various concentrations of colloidal $RuO_2 \cdot 2H_2O$ were mixed with aqueous solutions of Br_2 at the same pH. Again, the rate of decay of Mn^{IV}TMPyP was measured as a function of the concentration of added catalyst. The decay profiles were analysed in terms of pseudo-first-order reactions by iterative computer fitting.

As found with the inherent uncatalysed decay, reaction with the catalyst led to re-formation of the original Mn^{III}TMPyP. At pH 11 to 13, addition of colloidal

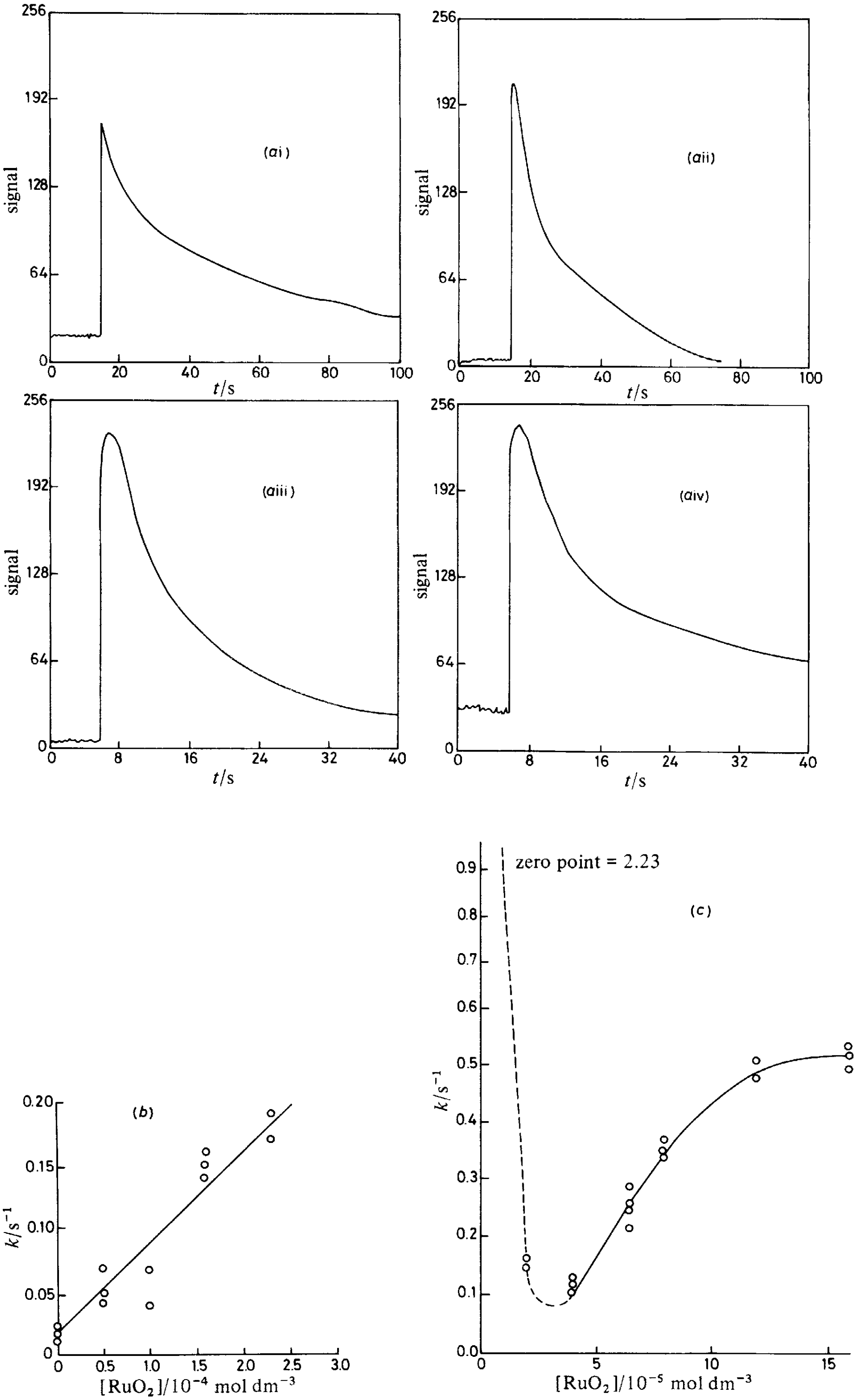


Fig. 9. For legend see opposite.

$RuO_2 \cdot 2H_2O$ resulted in a small but significant increase in the rate of decay of Mn^{IV}TMPyP. Typical decay profiles obtained in the presence of various amounts of catalyst are shown in fig. 9(*a*). Throughout this limited pH range there appears to be a linear correlation between the pseudo-first-order decay rate constant (k_{red}) and the concentration of added $RuO_2 \cdot 2H_2O$, as shown by fig. 9(*b*).

However, careful study of the experimental records shows that colloidal $RuO_2 \cdot 2H_2O$ does more than simply increase the rate of decay of Mn^{IV}TMPyP. In the presence of catalyst, the absorbance at 430 nm observed immediately after mixing [fig. 9(*a*)] is higher than found in the absence of $RuO_2 \cdot 2H_2O$. Also, high concentrations of catalyst seem to retard the rate of oxidation of Mn^{III}TMPyP. These findings suggest that the positively charged metalloporphyrin is bound to the negatively charged colloid surface by electrostatic forces. Such adsorption would inhibit oxidation with bromate owing to Coulombic repulsion and also prevent dimerisation of Mn^{IV}TMPyP. Under such conditions the oxidised metalloporphyrin would be a surface-bound, monomeric Mn^{IV}-TMPyP, which is expected to have a higher molar extinction coefficient than the μ-oxo dimer.[30] With lower concentrations of $RuO_2 \cdot 2H_2O$ there is not enough colloid surface for complete binding and Mn^{IV}TMPyP will be distributed as surface-bound monomer and non-adsorbed μ-oxo dimer. The observation that the rate of decay of Mn^{IV}TMPyP increases in the presence of colloidal $RuO_2 \cdot 2H_2O$ can then be explained in two ways. Either the surface-bound monomer has a higher inherent k_{red} than the μ-oxo dimer, or monomer and/or dimer can abstract an electron from the colloid. Over the pH range 11–14, the measured[15] redox potential for the Mn^{IV}/Mn^{III}TMPyP couple suggests that water oxidation is unlikely (fig. 2), and studies with the m.p.d. failed to detect O_2 as a reaction product. Therefore, reduction of Mn^{IV}TMPyP under these conditions does not appear to involve oxidation of water to O_2. Consequently, the most likely explanation for the observed increase in k_{red} upon adding colloidal $RuO_2 \cdot 2H_2O$ is that adsorbed, monomeric Mn^{IV}TMPyP shows a higher inherent decay rate than does the corresponding μ-oxo dimer at that pH.

At pH < 11, the presence of colloidal $RuO_2 \cdot 2H_2O$ also has an effect upon the rate of reduction of Mn^{IV}TMPyP to Mn^{III}TMPyP, as shown by fig. 9(*c*). The data given refer to pH 8.2, but similar plots were found at pH 8.8, 9.6 and 10.6. Even allowing for the large experimental uncertainty involved in such measurements, the relationship between k_{red} and concentration of catalyst is not linear. In fact, addition of low concentrations of catalyst appear to slow down the rate of reduction, whilst further additions of $RuO_2 \cdot 2H_2O$ lead to an increase in k_{red} until a plateau is reached. In each case, the presence of *ca.* 2×10^{-4} mol dm $^{-3}$ catalyst seems to give the maximum k_{red}, although the final value is not as high as found in the complete absence of catalyst. (Unfortunately, the concentration of colloid is limited to *ca.* 3×10^{-4} mol dm^{-3} because of light absorption and precipitation.) As for pH > 11, the rate of oxidation of Mn^{III}TMPyP becomes slower in the presence of catalyst, suggesting adsorption of porphyrin onto the colloid surface. However, the magnitude of the absorbance at 430 nm observed immediately after mixing does not change systematically with increasing concentration of catalyst. This infers that the oxidation product is monomeric Mn^{IV}T-MPyP with and without catalyst.

At pH < 11, adsorbed Mn^{IV}TMPyP seems to be reduced at a slower rate than the

Fig. 9. (*a*) Typical decay traces observed at 430 nm following stopped-flow oxidation of Mn^{III}TMPyP at pH 11.3 in the presence of colloidal $RuO_2 \cdot 2H_2O$. Concentration of colloid; (i) 0, (ii) 1.0, (iii) 1.6 and (iv) 2.3×10^{-4} mol dm^{-3}. (*b*) Plot of pseudo-first-order rate constant for decay of Mn^{IV}TMPyP as a function of the concentration of added $RuO_2 \cdot 2H_2O$. (*c*) Plot of the pseudo-first-order rate constant for decay of Mn^{IV}TMPyP at pH 8.2 as a function of the concentration of added $RuO_2 \cdot 2H_2O$.

non-adsorbed form, possibly reflecting a change in mechanism. Under the conditions of the stopped-flow experiments, the concentration of MnP was 4.5×10^{-6} mol dm^{-3}. The plateau region observed at *ca.* 2×10^{-4} mol dm^{-3} $RuO_2 \cdot 2H_2O$ corresponds[11] to a colloid particle concentration of *ca.* 5.4×10^{-7} mol dm^{-3}. Of the 3700 molecules of $RuO_2 \cdot 2H_2O$ that comprise a single particle, *ca.* 20% are located on the surface. Thus, the onset of the plateau region corresponds to some 10% occupancy of the surface. Dilution of the surface-bound metalloporphyrin does not affect k_{red}. Increasing the concentration of surface-bound MnP by lowering the concentration of colloid leads to a decrease in k_{red}. Lowering the concentration of colloid even further results in only partial binding of the MnP. At high ratios of MnP to colloid, the porphyrin will be held weakly at sites more remote from the colloid surface since all the preferred sites will be filled. Under such conditions, there is a distinct decrease in k_{red}. This latter finding implies that adsorbed Mn^{IV}TMPyP decays, at least partially, by abstracting an electron from the colloid particle. The measured redox potential[15] shows that water oxidation is thermodynamically possible at pH < 11 (fig. 2), and studies performed with the m.p.d. showed that small amounts of O_2 were formed in the presence of $RuO_2 \cdot 2H_2O$.

Oxidation of Mn^{III}TMPyP at pH 8–13 was achieved by addition of NaOCl solution (fig. 2). The final concentration of NaOCl was limited so as to give 95% conversion of Mn^{III}P into Mn^{IV}P. This involved stoichiometric addition at pH > 11 but a sixfold excess at pH 8. Monitoring the reaction with the m.p.d. showed that no O_2 was evolved during the inherent reduction of Mn^{IV}TMPyP. This finding confirms the studies made with bromate as oxidant. However, addition of colloidal $RuO_2 \cdot 2H_2O$ (2×10^{-4} mol dm^{-3}) prior to oxidation with NaOCl resulted in formation of small amounts of O_2 throughout the range $8 < \mathrm{pH} < 11$. For an initial Mn^{IV}TMPyP concentration of 5×10^{-5} mol dm^{-3}, concentrations of evolved O_2 of 0.9, 1.1, 1.2 and 0.6×10^{-6} mol dm^{-3}, respectively, were obtained at pH 10.6, 9.4, 8.8, and 8.2. Thus the optimum pH seems to be around 9, where the yield of evolved O_2 is *ca.* 10% of the stoichiometric amount. No O_2 was detected at pH > 11 or in experiments conducted at pH 8–11 if either porphyrin, catalyst or NaOCl was omitted.

This work has provided the first example of water oxidation by a MnP, although it appears that an active redox catalyst is necessary for O_2 evolution to be observed. Thus, the MnP itself is not able to mediate water oxidation despite its wide range of available oxidation states. In the absence of the added catalyst, water is probably oxidised to H_2O_2, which attacks the porphyrin. Such findings suggest that the active O_2-evolving catalyst in green-plant photosynthesis is not a MnP, although it could be a manganese containing enzyme. Furthermore, the poor efficiency for O_2 liberation together with the narrow pH range over which O_2 formation occurs seem to preclude the use of a MnP as a relay in water-splitting systems. As a consequence, it appears that the next step in the design of an effective O_2-evolving photosystem is to find ways to stabilise strongly oxidising metalloporphyrin radical cations.

We thank Dr R. E. Huie for the use of his stopped-flow instrument and P. Ouellette for technical assistance with the stopped-flow experiments. This work was supported by the S.E.R.C., G.E. (Schenetady) and the Office of Basic Energy Sciences of the U.S. Department of Energy through contracts to N.B.S. and N.D.R.L.

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment are necessarily the best available for the purpose.

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Paper 6/116; *Received* 15*th January*, 1986