Relevance of the reaction of a manganese(III) chelate with hydroxide ion to photosynthesis: Reaction of hydroxide ion with 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) in ligating and nonligating solvents

(photosystem II S_4 state/water oxidation)

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ABSTRACT The reaction of HO^- with 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) chloride [(TMP)Mn^{III}(Cl)] in ligating solvents (CH$_3$CN, dimethyl sulfoxide, pyridine) results in formation of (TMP)Mn^{II} ($\approx 10^6$ M^{-1}·s^{-1}), which in a slower reaction is converted to a product whose structure is suggested to be that of a porphyrin manganese(III) peroxo dimer. Admittance of O_2 at any time during these reactions leads to formation of the manganese(III) peroxo (TMP)Mn^{III}(O$_2$)$^-$. In nonligating solvents [CH$_2$Cl$_2$, (CH$_3$)$_2$CO], the reaction of HO^- with (TMP)Mn^{III}(Cl) yields (TMP)Mn^{IV}(OH)$_2$.

We report observations on reactions of chelated manganese with HO^- that may be relevant to current speculations about the mechanism of O_2 evolution in the oxygenic photosystem. Briefly, it is suggested that the light reaction raises the S_0 state of the photosystem II to the S_4 state of oxidation, and the latter carries out a four-electron oxidation of two water molecules to provide molecular oxygen (1). The S_4 state is believed to be composed of an array of two manganese(IV) and two manganese(III) species (2, 3). Important chemical mechanisms that are not well understood include oxidation of H_2O by S_4, which must involve the coupling of two oxygen atoms to provide O_2, and the generation of O_2 from H_2O_2 at the S_2 state (4).

Although the manganese ions of the S states are not present as manganese porphyrins, we have chosen to use a porphyrin as a reporter chelating agent since the position of λ_{max} of the Soret band of manganese porphyrins is characteristic of the oxidation state of the manganese. Herein we report observations on the redox reactions that accompany the reaction of HO^- with 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) [(TMP)Mn^{III}(x)].

MATERIALS AND METHODS

Absorption spectra and changes in absorbance with time were recorded on a Cary 118 spectrophotometer modified by addition of an OLIS data acquisition unit or a Perkin-Elmer 533 fast-scanning UV-vis spectrophotometer. The stopped-flow spectrophotometer contained a rapid-scan Harrick monochrometer and OLIS computer interface. 5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphinatomanganese(III) chloride [(TMP)Mn^{III}(Cl)] and 5,10,15,20-tetrakis-(2,4,6-trimethylphenyl)porphinatomanganese(II) [(TMP)Mn^{II}] were synthesized as described (5). 4′-(Imidazol-1-yl)-acetophenone (Fluka) was purified by repeated recrystallization from CH$_2$Cl$_2$/hexanes. Tetra-n-butylammonium hydroxide [(n-Bu)$_4$N$^+$HO$^-$] (Aldrich, 1 M solution in methanol) was used. 18-Crown-6 (Aldrich) was recrystallized twice from acetonitrile and dried under vacuum. Methylene chloride was purified in the manner described (6). Pyridine was distilled over calcium hydride prior to use. Dimethyl sulfoxide, acetone, and methanol were stored over 4A molecular sieves. Acetonitrile (Burdick and Jackson) was used as received from the supplier.

All spectrophotometric measurements were performed at $30 \pm 0.2°C$. Anaerobic reactions were carried out by use of spectrophotometers housed in a nitrogen atmosphere or by use of Thunberg cuvettes.

RESULTS AND DISCUSSION

We describe reactions of (TMP)Mn^{III}(Cl) with HO^- in organic solvents that do (CH$_3$CN, dimethyl sulfoxide, pyridine) and do not [CH$_2$Cl$_2$, (CH$_3$)$_2$CO] ligate the manganese(III) porphyrin. Delivery of HO^- to the reaction solutions has been made by addition of aliquots of 1 M solutions of (n-Bu)$_4$N$^+$HO$^-$ in methanol. Reactions were carried out in the absence and presence of O_2.

The spectral changes accompanying the addition of HO^- to solutions of (TMP)Mn^{III}(Cl) can be associated with changes in the oxidation state of the manganese porphyrin. Assignments of oxidation states of products are based on comparisons of UV/vis spectra to spectra of manganese porphyrin species of known oxidation state. Thus, when the porphyrin is *meso*-tetraphenylporphyrin (TPP) or TMP, the positions of the Soret bands are as follows: Mn(II) (7–10), 432–448 nm; Mn(III) (10–14), 463–490 nm; Mn(IV) (8, 13, 15, 16), and Mn(V) (13, 14, 19–21), 415–426 nm. Notable exceptions are [(TPP)Mn^{III}(O$_2$)]$^-$ with Soret λ_{max} at 446 nm (10, 14) and the low-spin complexes [(TPP)Mn^{III}(CN)$_2$]$^-$ with λ_{max} 435 nm (11) and [(TPP)Mn^{III}(Im)$_2$]$^-$ (Im, imidazolate ion) with λ_{max} 451 and 408 nm (11).
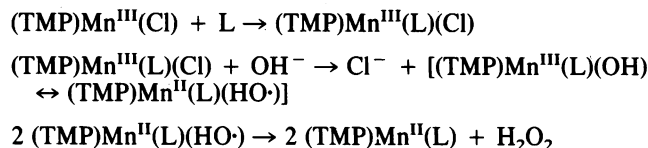
The reaction of (TMP)Mn^{III}(Cl) (478 nm) with HO^- in the absence of O_2 can be placed into two classes depending on whether the solvent is ligating or nonligating. For ligating solvents, the manganese(III) porphyrin is reduced to a manganese(II) porphyrin. In nonligating solvents, the manganese(III) porphyrin is converted to a mixture of manganese-(III) and manganese(IV) porphyrins.

Reaction of (TMP)Mn^{III}(Cl) (1.13×10^{-5} M) with HO$^-$ (2×10^{-4} M) in Ligating Solvents. In acetonitrile, only the spectrum of manganese(II) porphyrin (λ_{max} = 446 nm; ε_{max} = 2×10^5 M^{-1}·cm^{-1}) can be detected 20 ms after mixing. From the initial concentrations of reactants, the minimum

rate constant is 10^6 M$^{-1}\cdot$s^{-1}. A possible mechanism is shown in Scheme I, where ligation of HO$^-$ is followed by one-
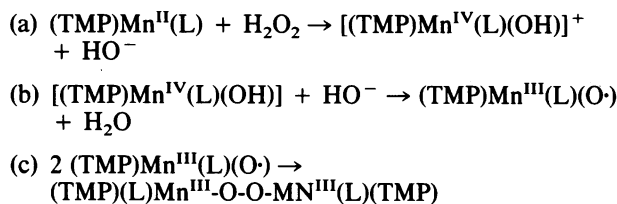
$$(TMP)Mn^{III}(Cl) + L \rightarrow (TMP)Mn^{III}(L)(Cl)$$

$$(TMP)Mn^{III}(L)(Cl) + OH^- \rightarrow Cl^- + [(TMP)Mn^{III}(L)(OH) \\ \leftrightarrow (TMP)Mn^{II}(L)(HO\cdot)]$$

$$2\ (TMP)Mn^{II}(L)(HO\cdot) \rightarrow 2\ (TMP)Mn^{II}(L) + H_2O_2$$

Scheme I

electron reduction of manganese(III). This reduction is dependent on the prior coordination of solvent (L) to (TMP)-Mn^{III}(Cl) as an axial ligand. Such a reaction is also observed in the coordinating solvents dimethyl sulfoxide and pyridine [λ_{max} of the Mn(II) species is 444 nm in dimethyl sulfoxide and 447 nm in pyridine]. The role of the solvent as a ligand is demonstrated by experiments in the nonligating solvent CH$_2$Cl$_2$ in the presence of the ligand 4'-(imidazol-1-yl)acetophenone (4 $\times$ 10^{-4} M), where a manganese(II) porphyrin is formed.

Precedent for the reduction of (TMP)Mn^{III}(Cl) by HO$^-$ is the observation (22) of the reduction of (TPP)Fe^{III}(Cl) by HO$^-$ in pyridine. For the latter, a possible mechanism of HO$^-$ attack upon the coordinated pyridine with electron transfer to the iron has been proposed. Sawyer and coworkers have also shown (23) that the oxidation potential for HO$^-$ in CH$_3$CN shifts from +0.35 V to −0.59 V upon addition of transition metal complexes, which include (TPP)Mn^{III}(Cl). This lowering of oxidation potential is proposed to be associated with stabilization of the HO$\cdot$ product by metal ion ligation through formation of a dπ-pπ covalent bond.

In the reactions of Scheme I, HO$^-$ is oxidized to HO$\cdot$. If this is so, then the HO$\cdot$ must be converted to a species with an appreciable lifetime. This species could be hydrogen peroxide formed by bimolecular self-reaction of HO$\cdot$ (10^{10} M$^{-1}\cdot$s^{-1} in H$_2$O; ref. 24). The necessity for a long-lived oxidant follows from the observation that after the reduction of (TMP)Mn^{III}(Cl) to manganese(II) porphyrin there occurs in a slower reaction the formation of a species (Fig. 1), which may be assigned the structure of a manganese(IV) porphyrin (λ_{max}, 411 nm in CH$_3$CN and 414 nm in dimethyl sulfoxide). The reactions of Scheme II provide a plausible rationalization of this finding. The requirements of Schemes I and II are that under anaerobic conditions the oxidation equivalents obtained in the reduction of the manganese(III) porphyrin to a manganese(II) porphyrin (Scheme I) are used in the oxidation of one-half the manganese(II) porphyrin to a manganese(IV)

(a) $(TMP)Mn^{II}(L) + H_2O_2 \rightarrow [(TMP)Mn^{IV}(L)(OH)]^+ + HO^-$

(b) $[(TMP)Mn^{IV}(L)(OH)] + HO^- \rightarrow (TMP)Mn^{III}(L)(O\cdot) + H_2O$

(c) $2\ (TMP)Mn^{III}(L)(O\cdot) \rightarrow (TMP)(L)Mn^{III}$-O-O-Mn^{III}(L)(TMP)

Scheme II

porphyrin. In both CH$_3$CN and dimethyl sulfoxide solvents, the decrease in A_{445} attributable to manganese(II) porphyrin and increase in A_{411} attributable to manganese(IV) porphyrin (k_{obs} = 10^{-2} s^{-1}) continues until the ratio of A_{445}/A_{411} is ≈0.7.

In the absence of O$_2$, the reaction mixtures of manganese(II) and manganese(IV) species are reasonably stable. There does occur, however, a very slow reaction (k_{obs} = 10^{-4} s^{-1} when [HO$^-$] = 3.0 $\times$ 10^{-3} M) to provide a stable species with Soret absorbances at 448 nm (ε = 200,000 M$^{-1}\cdot$cm^{-1}) and 403 nm (ε = 66,000 M$^{-1}\cdot$cm^{-1}) in CH$_3$CN. We postulate that this product is [(TMP)(L)Mn^{III}-O]$_2$. The observed Soret bands (448 and 403 nm) are to be expected if the manganese(III) of such a species were of low spin (10). The same species is formed on reaction
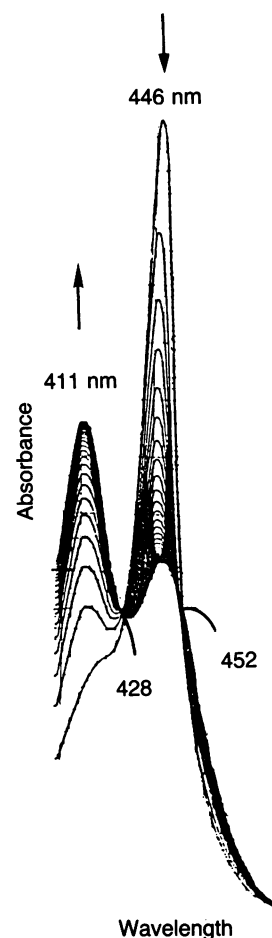

FIG. 1. Spectral changes observed upon addition of (n-Bu)$_4$N$^+$HO$^-$ (3 $\times$ 10^{-3} M) to (TMP)Mn^{III}(Cl) (8.5 $\times$ 10^{-5} M) in CH$_3$CN. Spectral scans are at 5-min intervals.

of (TMP)Mn^{III}(Cl) with K$^+$O$_2^{-\cdot}$ in acetonitrile (Fig. 2). Although no such peroxide species of a manganese(III) porphyrin has been reported, similar peroxo-bridged intermediates have been postulated to exist in iron porphyrin (25) and cobalt porphyrin systems (26). It is most interesting to note that the proposed peroxide species of Scheme II, [(TMP)(L)Mn^{III}-O]$_2$, is generated in the absence of O$_2$.

Further evidence in support of an intermediate HO$\cdot$ (Scheme I) is provided by a comparison of the stability of the generated (TMP)Mn^{II}(L), where L is pyridine solvent, in comparison to L being dimethyl sulfoxide and CH$_3$CN. Pyridine reacts with HO$\cdot$ with a rate constant of 3.0 $\times$ 10^9 M$^{-1}\cdot$s^{-1} (27). Hence, given the concentration of pyridine solvent mixture to [(TMP)Mn^{II}(L)] any generated HO$\cdot$ would be effectively trapped, preventing further reaction of the manganese(II) species. Indeed, upon reaction of (TMP)Mn^{III}(Cl) (1.6 $\times$ 10^{-5} M) with 2.0 $\times$ 10^{-4} M HO$^-$ in pyridine, only one species, (TMP)Mn^{II}, is observed (Fig. 3) even after many hours. In contrast, when dimethyl sulfoxide or CH$_3$CN is used as solvent, the manganese(II) species gives way to other reaction products within seconds. In the latter solvents, the reactivity (25) and lifetime of HO$\cdot$ are much greater than in pyridine.

In CH$_3$CN or dimethyl sulfoxide solvent, addition of O$_2$ at any time to the reaction solutions that provide the transformations of Scheme II results in the very slow (k_{obs} = 10^{-4}–10^{-5} s^{-1} depending on the time of O$_2$ addition) but clean (isosbestic points, 382, 437, 454, 511, 538, 546, 583, 601, and 620 nm; Fig. 4) formation of (TMP)Mn^{III}(O$_2$)$^-$. Both Groves (14), using (TMP)Mn^{III}(Cl) in CH$_3$CN, and Valentine (10, 28), with (TPP)Mn^{III}(Cl) in dimethyl sulfoxide or tetrahydrofuran, have demonstrated that O$_2^{-\cdot}$ reacts with manganese(III)
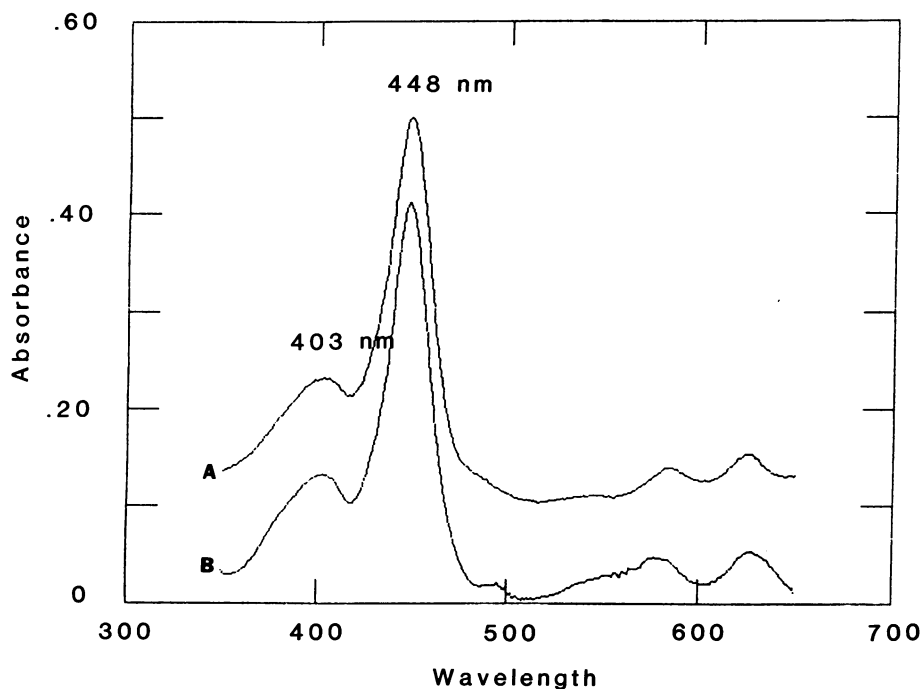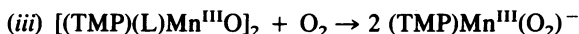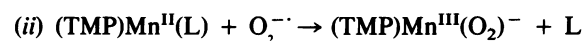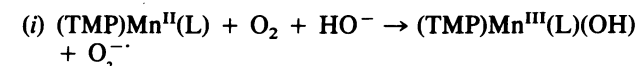
FIG. 2.   Trace A, spectrum of $[(TMP)Mn^{III}O]_2$ generated by reaction of $(TMP)Mn^{III}(Cl)$ with a saturated solution of KO_2 and 18-crown-6 in CH_3CN solution. Trace B, identical spectrum generated by reaction of $(TMP)Mn^{III}(Cl)$ with HO^- in CH_3CN solvent.

porphyrins to provide a manganese(II) porphyrin, which on reaction with another $O_2^{-\cdot}$ forms $[(Porph)Mn^{III}(O_2)]^-$. We have synthesized $[(TMP)Mn^{III}(O_2)]^-$ from $(TMP)Mn^{III}(Cl)$ in CH_3CN by addition of a saturated solution of KO_2 and 18-crown-6 in CH_3CN and shown that its spectrum was identical to that obtained on reaction of $(TMP)Mn^{III}(Cl)$ with HO^- in CH_3CN and dimethyl sulfoxide in the presence of O_2. When $(TMP)Mn^{III}(O_2)^-$ is generated under anaerobic conditions by the reaction of $O_2^{-\cdot}$ and $(TMP)Mn^{III}(Cl)$ it decomposes to form a species identical to the one we have tentatively labeled as $[(TMP)Mn^{III}(L)O]_2$. Addition of either HO^- or $O_2^{-\cdot}$ regenerates $(TMP)Mn^{III}(O_2)^-$.

Possible mechanisms for the formation of $(TMP)Mn^{III}-(O_2)^-$ (Scheme **III**) could be by either (*ii*) reaction of

(*i*) $(TMP)Mn^{II}(L) + O_2 + HO^- \rightarrow (TMP)Mn^{III}(L)(OH) + O_2^{-\cdot}$

(*ii*) $(TMP)Mn^{II}(L) + O_2^{-\cdot} \rightarrow (TMP)Mn^{III}(O_2)^- + L$

(*iii*) $[(TMP)(L)Mn^{III}O]_2 + O_2 \rightarrow 2\ (TMP)Mn^{III}(O_2)^-$

Scheme **III**

manganese(II) porphyrin species with $O_2^{-\cdot}$ or (*iii*) the reaction of the peroxo-dimer with O_2. If reaction of the peroxo-dimer
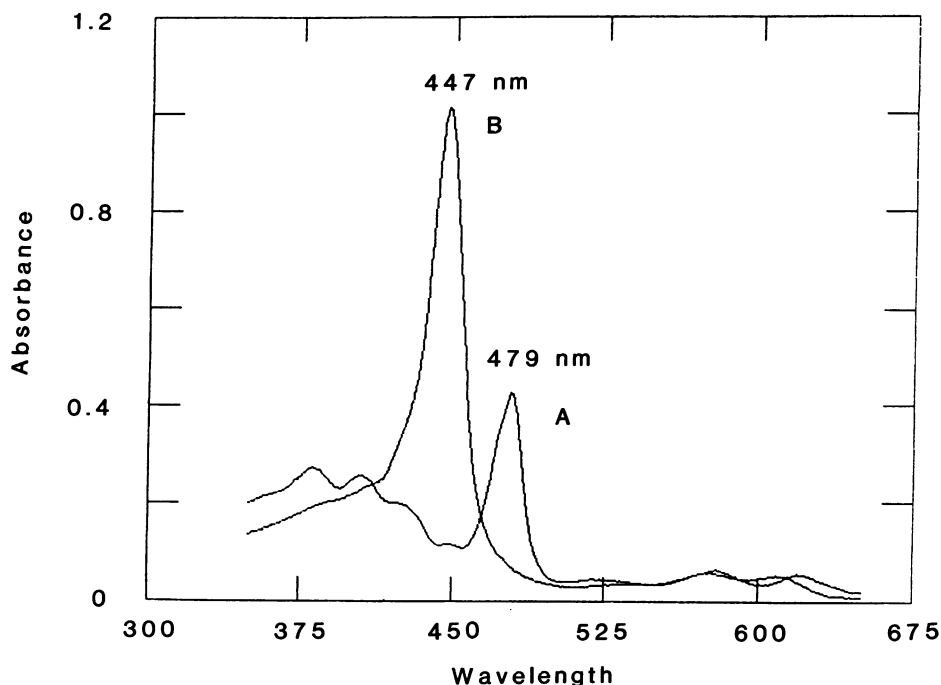

FIG. 3.   Trace A, spectrum of $(TMP)Mn^{III}(Cl)$ (4.0×10^{-5} M) in pyridine. Trace B, spectrum in the presence of $(n\text{-}Bu)_4N^+HO^-$ (8.2×10^{-2} M).
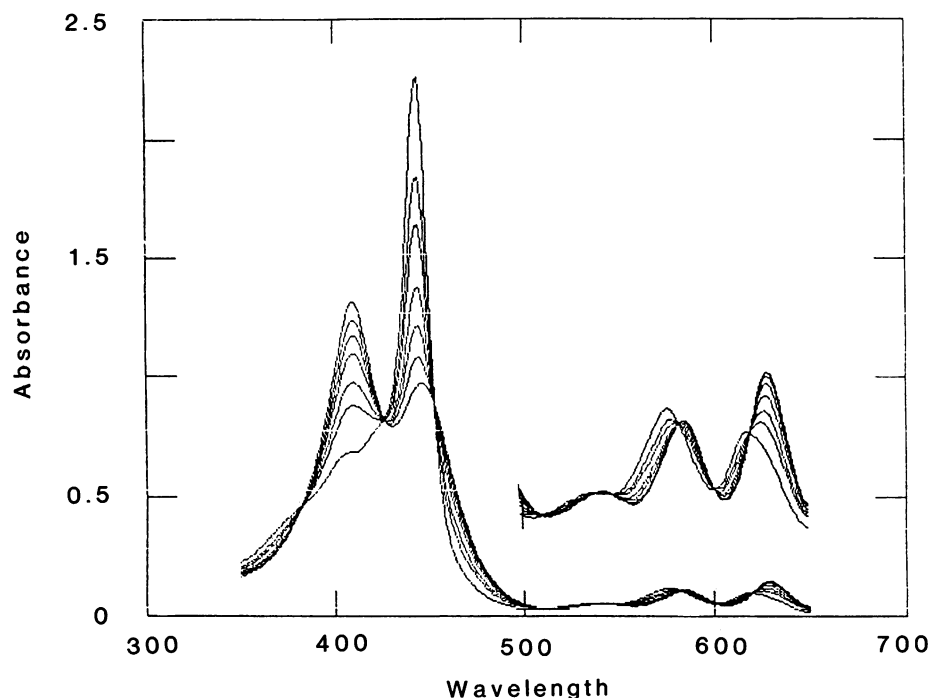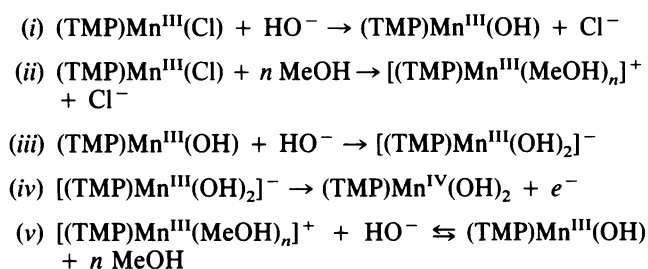
FIG. 4. Spectral changes resulting from addition of air to a CH_3CN solution of $(TMP)Mn^{III}(Cl)$ (1.2×10^{-4} M) and $(n\text{-}Bu)_4N^+HO^-$ (3.0×10^{-3} M). All peaks and isosbestic points are identified in the text.

$[(TMP)(L)Mn^{III}O]_2$ with O_2 were reversible, it would explain the observation of this species in the reactions of $(TMP)Mn^{III}(Cl)$ with O_2^- in CH_3CN.

Reaction of $(TMP)Mn^{III}(Cl)$ with HO^- in Nonligating Solvents. Anaerobic addition of HO^- to a solution of $(TMP)Mn^{III}(Cl)$, in CH_2Cl_2 or $(CH_3)_2CO$, yields a mixture of manganese(III) ($\lambda_{max} = 472$ nm) and manganese(IV) ($\lambda_{max} = 424$ nm) species. In CH_2Cl_2 with $[(TMP)Mn^{III}(Cl)]_i = 1.7 \times 10^{-6}$ and $[HO^-]_i = 2.0 \times 10^{-4}$ M, the reaction is seen to be complete in <20 ms. These results may be explained in terms of Scheme IV.

(*i*) $(TMP)Mn^{III}(Cl) + HO^- \rightarrow (TMP)Mn^{III}(OH) + Cl^-$

(*ii*) $(TMP)Mn^{III}(Cl) + n\,MeOH \rightarrow [(TMP)Mn^{III}(MeOH)_n]^+ + Cl^-$

(*iii*) $(TMP)Mn^{III}(OH) + HO^- \rightarrow [(TMP)Mn^{III}(OH)_2]^-$

(*iv*) $[(TMP)Mn^{III}(OH)_2]^- \rightarrow (TMP)Mn^{IV}(OH)_2 + e^-$

(*v*) $[(TMP)Mn^{III}(MeOH)_n]^+ + HO^- \leftrightarrows (TMP)Mn^{III}(OH) + n\,MeOH$

Scheme IV

The exchange of chloride ligand for hydroxide in the first step must be extremely fast. The ratio of manganese(III) to manganese(IV) formed in the subsequent steps can be controlled by variation of the amount of methanol {0.08–9.0 M, 8×10^2- to 9×10^4-fold excess over $[(TMP)Mn^{III}Cl]_i$} in the reaction solution. With less methanol, more manganese(IV) is formed relative to manganese(III). This observation, coupled with the lack of change in the oxidation state of $(TMP)Mn^{III}(Cl)$ in neat MeOH on addition of HO^-, is in accord with formation of $[(TMP)Mn^{III}(MeOH)_n]^+$ preventing ligation with HO^-. Aside from the importance of the mass action with increase in MeOH on increasing the solvation of the manganese(III) porphyrin, the solvation of HO^- by MeOH decreases the latter's nucleophilicity.

The one-electron oxidation of manganese(III) catechol with HO^- (29) provides a precedent for reaction *iv* of Scheme IV. We find the species assigned the structure

$(TMP)Mn^{IV}(OH)_2$ to decompose in the presence of acid or O_2. This is similar to the observations of Hill and coworkers (8) when working with authentic $(TPP)Mn^{IV}(OMe)_2$. Attempts to identify the one-electron acceptor in reaction *iv* have been unsuccessful. This is not surprising given that the concentration of the $(TMP)Mn^{IV}(OH)_2$ product is $\approx 10^{-6}$ M.

The differing reaction chemistry in ligating and nonligating solvents may be explained by the availability of both axial positions of manganese(III) porphyrin in nonligating solvent. Thus, in nonligating solvents, the formation of $[(TMP)Mn^{III}(OH)_2]^-$ is possible, whereas in ligating solvents, the opposite face of the porphyrin is occupied by solvent, $(TMP)Mn^{III}(L)(OH)$, and the ligation of a second HO^- is inhibited.

CONCLUSIONS

This investigation establishes that one-electron oxidation of water by a manganese(III) porphyrin occurs if the ligated water molecule is first dissociated to HO^-. The formation of manganese(II) porphyrin by this process is only observed when HO^- can occupy one axial coordination site, the other axial coordination site being occupied by a ligating solvent molecule. The product formed by HO^- oxidation possesses a lifetime greater than anticipated for HO·. A likely candidate is hydrogen peroxide formed by the diffusion-controlled self-reaction of two HO· species (Scheme I). A peroxide is also proposed to be formed on reaction of hydrogen peroxide with a ligated manganese(IV) species (Scheme II). The oxidation of HO^- and proposed coupling of oxygens to provide peroxide species are believed to be relevant to the chemistry of photosystem II.

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