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**CHEMISTRY OF A HIGH OXIDATION LEVEL
MANGANESE PORPHYRIN IN AQUEOUS SOLUTION**

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DISCLAIMER

CHEMISTRY OF A HIGH OXIDATION LEVEL MANGANESE PORPHYRIN

IN AQUEOUS SOLUTION

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Abstract

Manganese(III) tetrakis(N-methyl-4-pyridyl) porphyrin chloride (Mn(III)TMPyP$^+$) and other water-soluble manganese(III) porphyrins undergo facile one-electron electrochemical or chemical oxidation in alkaline solution. Best available evidence indicates that the final oxidized species is a manganese(IV) μ-oxo dimer, PMn^{IV}-O-^{IV}MnP^{2+}. This same species is also produced by the reaction of Mn(II) porphyrin and oxygen. The Mn(IV) μ-oxo dimer has limited stability in water returning to 90-94% of the original Mn(III) porphyrin. The rate of this reaction is pH dependent with faster rates at lower pH. Oxygen is not produced during this reduction process. Rather the reaction involves an unusual disproportionation in which a small percentage of the porphyrin macrocycles supply multiple electrons to reduce the remainder of the oxidized dimer. It was also found that the manganese(IV) dimer reacts rapidly with water-soluble olefins in similar fashion as observed in aprotic solvents. A mechanism for the disproportionation reaction is discussed

with a rate-determining step involving rearrangement of charge within the symmetric dimer to one with both oxidation equivalents on one metalloporphyrin unit, viz., $PMn^{IV}-O-^{III}MnP^{+\cdot}$ or $PMn^{III}-O-^{III}MnP^{++}$. This species undergoes nucleophilic attack by water or hydroxide, producing an isoporphyrin or bilirubin type molecule which has many olefinic bonds capable of reaction with remaining Mn(IV) μ-oxo dimer. Since coordination by OH^- to the manganese center favors the higher manganese(IV) oxidation level, the pH dependence of the dispro-portionation is justified by favoring rearrangement within the dimer to a porphyrin-centered oxidation.

Introduction

A number of efficient multiple-electron redox catalysts are found in natural systems. The development of homogeneous multiple-electron catalysts has proven very difficult in the laboratory. Our interest in artificial photosynthetic systems led us to consider manganese porphyrin compounds as potential oxidation catalysts to mediate the four-electron conversion of water to oxygen.[1,2] It has long been known that water-soluble manganese porphyrins that have been oxidized above the manganese(III) porphyrin level are unstable. These high valent manganese porphyrins revert to the original Mn(III) species[3] and speculation has focused on water as the reducing agent in this reaction with oxygen proposed as the product.[4]

We recently described a system[5] for the photooxidation of manganese(III) tetrakis(N-methyl-4-pyridyl)porphyrin, $Mn(III)TMPyP^+$.[6] The photooxidized product is reduced to the original $Mn(III)TMPyP^+$ in the dark and the oxidation-reduction sequence could be cycled repeatedly. Thus, this system appeared to satisfy many critical requirements of an artificial photosynthesis assembly.

This paper reports work aimed at characterizing the oxidized form of the manganese porphyrin and also examines the nature of the reduction reaction. We find that the best available evidence supports formulation of the oxidized species as a Mn(IV) μ-oxo dimer, $PMn^{IV}-O-Mn^{IV}P^{2+}$. Careful search showed oxygen was not a product of the reduction reaction. We have found that the instability of the $PMn^{IV}-O-^{IV}MnP^{2+}$ species is due to a highly unusual disproportionation reaction in which a small (4-8) percentage of the porphyrin macrocycles

supply multiple electrons (10-16 electrons each) to reduce the remainder of the oxidized Mn species. Water-soluble manganese porphyrins, therefore, are not good candidates for relays in water-splitting systems. However, we have also found that the high valent manganese porphyrin species reacts rapidly with water-soluble olefins, presumably to form epoxides.[7] Manganese porphyrin species can, therefore, be used to catalyze unusual photochemical hydrocarbon oxidation reactions.

Experimental

Manganese(III) tetrakis(N-methyl-4-pyridyl) porphyrin (chloride salt) (Mn(III)TMPyP)[+] was prepared by literature methods[8] or purchased from Midcentury Chemical Co. and further purified by chromatography. Purity was checked by elemental analysis and visible spectrum. All other materials were of the highest available purity and were used as received. Deionized water was passed through a Millipore Milli-Q system. This water was then either used immediately or was doubly distilled through an all-glass still before immediate use. Argon gas was deoxygenated by passage over BASF catalyst maintained at 150°C and then through a Nanochem Purification System (Semi Gas Systems, Inc.).

Electronic absorption spectra were taken on a Hewlett-Packard 8450A UV/visible spectrophotometer. Magnetic moments in solution were determined by the Evans method[9] using a 200-MHz Fourier transform ^{1}H-NMR instrument (UCB-200). Electrochemical measurements and experiments were made using either an IBM EC/225 Voltametric Analyzer potentiostat or a PAR Model 173 Potentiostat/Galvanostat with a Model 179 Digital Coulometer insert. A Beckman Model 322 Gradient Liquid Chromatograph System with a Model 420 Microprocessor Controller was used for HPLC analyses. Columns were Bio-Rad Aminex Ion Exclusion HPX-87A Organic Acid Column

with a micro-guard pure column and .0025 N H_2SO_4 as eluting agent or an Altech Ultrasphere ODS column with a guard column and 40% H_2O-60% CH_3CN-.1% trifluoroacetic acid as eluting agents.

Oxygen analyses were made using a Teledyne Analytical Instruments Class B-2 Micro-Fuel Cell. This device uses a lead anode (basic media) and silver-plated cathode and produces current when a gaseous component capable of oxidizing lead is present. An in-house designed and constructed current-to-voltage amplifier was used in conjunction with a recorder to monitor oxygen levels.[10] Since the lead anode is consumed the micro-fuel cell must be periodically calibrated. A typical calibration gave a detection limit of about 2×10^{-3} torr or 3 ppm oxygen. Oxygen molecules formed as a result of chemical reactions in aqueous solution must be transferred to the gaseous phase in order to be detected. The transfer rate across the phase boundary and the equilibrium between gaseous and dissolved oxygen must be taken into account in determining oxygen concentrations.

A special electrochemical reaction vessel was constructed for the oxygen experiments (Fig. la). In a typical experiment a measured number of coulombs (1.1 equivalents)was passed at a high enough potential to oxidize Mn(III)TMPyP$^+$. The current was then shut off, stirring was continued and the response of the micro-fuel cell oxygen analyzer was monitored over a sufficient period of time to allow a large percentage of the high valent manganese porphyrin to be reduced to Mn(III)TMPyP$^+$. Separate experiments established that the Mn(III)TMPyP$^+$ was indeed oxidized by these conditions and that oxygen levels were monitored through at least two half-lives of the return of oxidized manganese species to Mn(III)TMPyP$^+$.

Kinetic studies of the reduction of the high valent manganese porphyrin species were performed in the same electrochemical cell used for the oxidation. This cell was constructed of spectrophotometer cells (Fig. 1b). Stirring and temperature control were accomplished by a specially designed cell holder.[11]

Results and Discussion

Characterization of the oxidized Mn porphyrin. Oxidation of $Mn(III)TMPyP^+$ in basic aqueous solution (pH 8) can be accomplished by a number of chemical oxidants such as $NaOCl$, $KMnO_4$, $Na_2S_2O_8$ and H_2O_2. Electrochemical oxidation can also be used. The same high valent species with an absorption maximum near 420 nm is produced independent of the means of oxidation.

A novel route to the high valent species involves reaction of oxygen gas with $Mn(II)TMPyP$. Manganese(II) porphyrin species can only be produced in rigorously deoxygenated solutions. In the presence of oxygen the final stable species is a $Mn(III)$ porphyrin. Hoffman, Basolo and co-workers in a series of papers[12] describe their investigation of an intermediate oxygen-manganese porphyrin adduct species in aprotic solvents at low temperatures which they conclude is best represented by a manganese(IV)-peroxide. However, in alkaline (pH >9) aqueous solution $Mn(II)TMPyP$ (produced electrochemically or by chemical reductants) reacts rapidly with oxygen gas to produce a species with identical properties to the high valent species formed by oxidation of $Mn(III)TMPyP^+$.

Careful optical titration with known concentrations of $NaOCl$ and coulometric measurements are in agreement with a one-electron oxidation

of the original Mn(III)TMPyP$^+$ species. The oxidation could be metal-centered producing a Mn(IV) species or ring-centered to give a Mn(III) pi-cation radical species. The optical spectrum (Fig. 2) in alkaline solution is very similar to spectra published[13] for well characterized Mn(IV) porphinato species in aprotic solvents and inconsistent with spectra characteristic of Mn(III) pi-cation radical species.[14] Pulse-radiolytic oxidations of various water-soluble Mn(III) porphyrins at pH <3 give very different spectra whose characteristic features are suggestive of a metalloporphyrin pi-radical cation.[15] Furthermore, Harriman[16] found that the oxidation potential of Mn(III) porphyrins increases with decreasing pH whereas the potential of the porphyrin ring should be independent of pH. Thus high pH appears to favor formation of Mn(IV) porphyrins and low pH favors formation of the Mn(III) pi-radical cation. At high pH the Mn center is coordinated by hydroxide ion which stabilizes higher oxidation states. This is consistent with our observation that addition of the strong pi-donating ligand CH_3O^- converts a Mn(III)TPP$^{+\cdot}$ species to Mn(IV)TPP(OCH$_3$)$_2$.[14]

Various attempts in this laboratory to isolate the manganese(IV) species by lyophilization or precipitation have been unsuccessful. Harriman, et al.[17] on the basis of indirect evidence have suggested that the Mn(IV)P formed at pH 13 exists predominantly in the form of a μ-oxo dimer PMn^{IV}-O-^{IV}MnP^{2+}. We have evidence from size exclusion chromatography that strongly supports characterization of Mn(IV)P at high pH as a dimeric species. A short, 5-8 cm, column of 400 mesh polyacrylamide gel Bio-Gel P-2 (exclusion limit 1,800 daltons) was hydrolyzed with pH 9.5 borate buffer. An aliquot of a solution containing a 50:50 mole percent mixture of Mn(III)TMPyP$^+$ and the Mn(IV) porphyrin species in the

same buffer was placed on the column and eluted with the buffer. On the short column (to minimize contact of the highly oxidizing Mn(IV) species with the polyacrylamide gel) separation into bands was noted. The initial material eluting from the column was highly enriched (10:1) in the Mn(IV) porphyrin and the last fraction contained pure Mn(III)TMPyP$^+$. In control experiments mixtures of known monomeric metalloporphyrins could not be separated, and their elution behavior and retention times were similar to that of Mn(III)TMPyP$^+$ while the retention time of a Fe^{III} μ-oxo dimer[18] was similar to that of the Mn(IV) species.

There are two possible formulations for the high valent dimeric species that are consistent with a one-electron oxidation of the monomeric manganese(III) porphyrins. These are PMn^{IV}-O-^{IV}MnP^{2+} and PMn^{III}-O-O-^{III}MnP. The μ-oxo Mn(IV) dimer is favored over the Mn(III)peroxo dimer for several reasons. The visible spectrum closely resembles spectra for several well characterized Mn^{IV} μ-oxo dimers[19] isolated from aprotic solvents, and is quite different from typical Mn(III)P$^+$ spectra. The X-ray structure of species designated as a monomeric [peroxotetraphenylporphinato]Mn(III) has recently been described.[20] This species has the peroxo ligand bound in a side-on bidentate fashion and has a visible spectrum with an intense single, sharp Soret band at 437 nm,[21] which actually resembles that of a typical Mn(II) porphyrin.

The reaction of Mn(II)P and O_2 produces an identical compound to that made by oxidation of Mn(III)P. The oxidation of iron(II) porphyrins by oxygen has been thoroughly studied.[22] In that case an Fe^{III}-O_2-Fe^{III} peroxo bridge intermediate species has been detected but
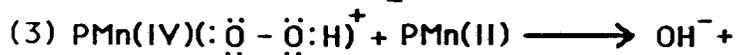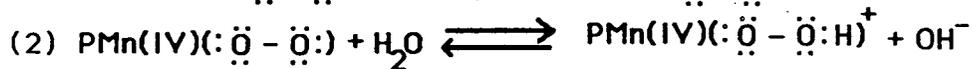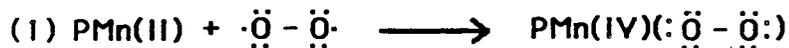
the final product is $Fe^{III}-O-Fe^{III}$. The stoichiometry in the manganese(II) porphyrin case is therefore somewhat novel, but plausible sequences can be written to produce a μ-oxo Mn(IV) dimer from Mn(II) and O_2 as well as from Mn(III) and oxidizing agents. In Scheme 1 the first intermediate species is a manganese(IV) peroxo, $PMn(IV)(O_2^{2-})$, and is similar to that proposed by Hoffman and Basolo[12] for reaction of Mn(II)TPP and O_2 in aprotic solvents. In aqueous systems this species may be protonated. The Mn(IV) peroxo intermediate is at the correct oxidation level to produce the Mn(IV) μ-oxo dimer if it reacts with a Mn(II)P. Alternatively, in a unimolecular sequence the next step might involve loss of OH^- to give a manganese(VI) oxo species. Reaction of a $Mn^{VI}=O$ and a PMn(II) then yields the μ-oxo Mn(IV) dimer.

Reactions of $PMn^{IV}-O-^{IV}MnP^{2+}$ in Aqueous Solution. The high valent dimer has limited stability in aqueous solutions and reverts to the original Mn(III)P upon standing. The obvious question is the identity of the reducing agent, and speculation has centered on water with oxygen proposed as a possible final product.[4] We did a number of control experiments involving extensive pre-electrolysis of the water-buffer solutions and used different sources and purification schemes for the Mn(III)TMPyP$^+$ compound. The course of the Mn(IV) μ-oxo dimer to Mn(III)TMPyP$^+$ reaction did not change by these precautions and eliminates extraneous impurities as the reducing agent.

Water as the reducing agent. A careful examination for oxygen as a product was performed. A trace oxygen analysis utilizing a micro-fuel cell was set up. The Mn(III)P was oxidized electrochemically and oxygen levels were monitored during several half-lives of the return of the Mn(IV) dimer to Mn(III)P$^+$. No evidence for significant oxygen
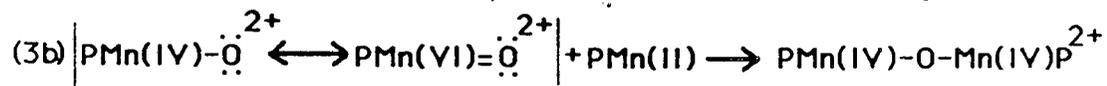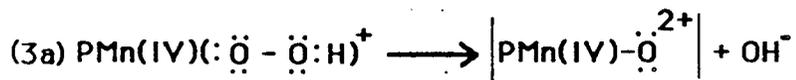
FORMATION OF Mn^{IV}-μ- OXO DIMER

by oxygen and PMn(II)

(1) $PMn(II) + \cdot\ddot{O} - \ddot{O}\cdot \longrightarrow PMn(IV)(:\ddot{O} - \ddot{O}:)$

(2) $PMn(IV)(:\ddot{O} - \ddot{O}:) + H_2O \rightleftharpoons PMn(IV)(:\ddot{O} - \ddot{O}:H)^+ + OH^-$

(3) $PMn(IV)(:\ddot{O} - \ddot{O}:H)^+ + PMn(II) \longrightarrow OH^- +$ ⌐

‑ ‑ ‑ ‑ ‑ ‑ ‑ ‑ ‑ ‑ Or ‑ ‑ ‑ ‑ ‑ ‑ ‑ ‑ ‑ │ ‑ ‑ ‑ ‑

From (2)

(3a) $PMn(IV)(:\ddot{O} - \ddot{O}:H)^+ \longrightarrow \left|PMn(IV)-\ddot{O}^{2+}\right| + OH^-$

(3b) $\left|PMn(IV)-\ddot{O}^{2+} \longleftrightarrow PMn(VI)=\ddot{O}^{2+}\right| + PMn(II) \longrightarrow PMn(IV)-O-Mn(IV)P^{2+}$

or by oxidation of $PMn(III)^+$

(a) $PMn(III)^+ + Ox \longrightarrow PMn(IV)^{2+} + Ox^-$

(b) $PMn(IV)^{2+} + H_2O \longrightarrow PMn(IV)-\ddot{O}:H^+ + H^+$

(c) $PMn(IV)-\ddot{O}:H^+ + PMn(IV)^{2+} \longrightarrow H^+ +$ ⌐

production was found, and control experiments on the sensitivity of the analysis indicated that an upper limit of 5% of the overall

PMn^{IV}-O-$^{IV}MnP^{2+} \longrightarrow$ .2 Mn(III)P$^+$ reaction could produce oxygen. These results agree with a recent report[23] using a different analytical method where again no evidence for oxygen production was found.

<u>Loss of optical density during reduction reaction.</u>   Repetitive scans of the visible spectrum as the high valent dimer reverts to Mn(III)P show five well developed isobestic points (Fig. 2). Even with concentrated solutions the isobestic points below 500 nm are maintained and less than 1% of the total optical density could be due to colored intermediates as the reduction of PMn^{IV}-O-$^{IV}MnP^{2+}$ to Mn(III)P$^+$ occurs. The highest intensity line (Fig. 2) is the spectrum taken after 96 hours which is more than 10 half-lives of the reaction under the experimental conditions. This represents 94% of the original intensity and more protracted waiting did not yield a higher absorbance. Repeated experiments with different means of oxidation of Mn(III)P$^+$ or with repeated oxidation- return sequences using the same sample gave similar results with a range of 90 to 94% return to original intensity levels. The rate of the return is dependent on pH with faster rates at low pH. Experiments were done in which Mn(III)P$^+$ was oxidized electrochemically at pH 10.5 (NaCl as electrolyte) and the pH was adjusted to 4.0 by addition of HCl. After correction for the small dilution factor the percentage return still fell in the 90-94% range even though the rate was ca. 100 times faster.

The degradation of the porphyrin chromophore could occur during the oxidation to the PMn^{IV}-O-$^{IV}MnP^{2+}$ species or could be the result of an unusual disproportionation reaction with each degraded porphyrin ring

supplying multiple electrons (9-16) to reduce the remainder of the oxidized species. The observation that the loss of porphyrin is independent of the chemical oxidant used for Mn(III)P$^+$ is an argument against oxidative degradation. In our electrochemical apparatus, constant potential electrolysis of Mn(III)TMPyP$^+$ could be accomplished to greater than 90% completion (E = 0.9 v relative to S.C.E.; pH 11.5, phosphate buffer) in less than 20 minutes. In several experiments under the same condition the potential was maintained for 100 minutes during which the current fell to low but not zero levels. Even with these prolonged oxidative conditions the return to original Mn(III)P$^+$ intensities was in the range 88 to 92%. Thus the great majority of the loss of MnP must occur during the reduction step PMn^{IV}-O-^{IV}MnP^{2+} $\longrightarrow$ 2 Mn(III)P$^+$.

Reaction with olefins. Further evidence against oxidative degradation was supplied by experiments involving addition of an oxi- dizable substrate. There are numerous reports[7] in the literature of manganese porphyrins catalyzing the epoxidation of olefins and hence serving as synthetic model systems for cytochrome P-450. These studies involve reaction in aprotic solvents, with no analogous observation reported for water-soluble manganese porphyrins. In our experiments Mn(III)TMPyP$^+$ was first oxidized electrochemically and then a 100-fold or greater excess of 3-butene-1-ol or maleic acid was added (at the same buffered pH 9.1 as the manganese porphyrin). The reduction to the original Mn(III)TMPyP$^+$ was greatly accelerated and 99 to 100% of the original optical density was achieved. This result establishes that the porphyrin macrocycle is degraded during the reduction of the Mn(IV) dimeric

species to Mn(III) and provides suggestions regarding the mechanism of the disproportionation reaction.

HPLC chromatography. Further confirmation of the unusual dispro-portionation process was provided by HPLC analysis before and after the return of the Mn(IV) μ-oxo dimer to Mn(III)P. An aliquot of a freshly prepared solution of Mn(III)TMPyP^{+} in either phosphate or borate buffer was injected into an HPLC column. With an organic acid column all positive ions were trapped in a guard column and the chromatogram of the original mixture showed only a peak for the buffer components. Another injection was made immediately after electrochemical oxidation; this chromatogram exhibited no new peaks. Then a series of injections was made during the time that the high valent dimer to Mn(III) monomer reaction was occurring. Several new peaks appeared which increased in size as the reaction proceeded. Since no organic matter other than the porphyrin was originally present, this implies that a disproportionation occurs involving electron oxidation of a small percentage of the por-phyrin macrocycles and a single-electron reduction of Mn(IV) to Mn(III).

One neutral organic product of the porphyrin oxidation was iden-tified as maleimide by coelution experiments. Many of the expected products of extensive oxidation of a tetra(N-methyl-4-pyridyl)porphyrin macrocycle in aqueous solution would carry a positive charge due to the N-methylpyridinum moiety. These products would be trapped in the cation exchange guard column used with the organic acid column to prevent the manganese porphyrin from contaminating the column. Comparable experi-ments with an ODS column and gradient H_2O-CH_3CN elution revealed a number of other peaks due to oxidative degradation of the porphyrin but were poorly resolved. Attempts at building up larger concentration of

organic products by sequential electrochemical oxidations of the same sample were complicated by the observation that the chromatogram pattern was altered after the second oxidation step. This indicates that at least some of the disporportionation products were susceptible to subsequent oxidation. This complication was even more pronounced when chemical oxidants such as OCl^- were used. However, identification of maleimide as a product is adequate confirmation of the main features of the disproportionation reaction.

Kinetics of reduction reaction. As might be expected the kinetics of the multiple electron disproportionation reaction are complicated. The rate is pH dependent, with faster rates at lower pH. Simple first order or second order plots of the decrease in absorbance at 424 nm (disappearance of dimer) or of the increase in absorbance at 462 nm (appearance of monomer) do not give straight lines over the entire course of the reaction (pH buffered with 0.1 M sodium phosphate). For 8 <pHK 12 plots of $\ln \dfrac{(A_t - A_\infty)}{(A_o - A_\infty)}$ are reasonably straight over the last 30% of the reaction, but the plots show curvature to slower rates in the initial stages.

Mechanism. A mechanism for the multiple electron disproportionation reaction must be consistent with several observations including no detectable build-up of colored intermediates and must accommodate the increase in rate as pH decreases. Our observation that the Mn(IV) μ-oxo dimer species reacts fairly rapidly with water-soluble olefinic compounds offers a possible explanation to the observation of good isosbestic points throughout the course of the reaction. Once a specific porphyrin macrocycle has undergone the first oxidation process -- the rate-determining step -- and resonance stabilization has been lost,

that moiety, either an isoporphyrin or an opened bilurubin type molecule, is able to undergo facile, successive oxidations remaining with Mn(IV) μ-oxo dimer acting as the oxidizing agent.

The initial degradation of the porphyrin would produce highly colored species but as long as subsequent reactions with remaining Mn(IV) dimer are fast compared to the first step no detectable colored intermediates will appear. The observed isosbestic points will not occur at the wavelength where the molar absorptivity coefficients of the dimer, Σ_D, and monomeric product, Σ_M are related by $\Sigma_D = \frac{1}{2}\Sigma_M$ as is the usual case but rather where $\Sigma_D = \alpha\frac{1}{2}\Sigma_M$ and α is the decimal fraction of the total return of the chromophore (0.90 to 0.96).

The ultimate organic products must be small segments of the original TMPyP macrocycle and the observation of maleimide as one of these species fits this scheme. Other products might be acids, ketones, aldehydes or alcohols derived from pyrrole or the N-methylpyridinium moiety.

The initial attack on a specific porphyrin would be the rate-determining step by the above argument. A recent report[23] on the stability of manganese porphyrins in aqueous solution suggests that hydrogen peroxide is first produced which then bleaches the porphyrin. Detectable quantities of hydrogen peroxide are not present at the end of the reaction. However, we find that excess hydrogen peroxide does in fact cause loss of absorbance in the Soret region, but with a significant build-up of intermediates with absorbance in the 650 to 750 nm region. Even when a high concentration of manganese porphyrin was oxidized electrochemically there was no observable increase in absorbance at these longer wavelengths as the Mn(IV) dimer was reduced.

Also, when a less than stoichiometric amount of peroxide is added to Mn(III)TMPyP$^+$ oxidation to the Mn(IV) μ-oxo dimer occurs smoothly. These observations argue against a mechanism involving a first step that produces H_2O_2 and Mn(III)TMPyP$^+$.

A possible rate determing first oxidation step involves internal rearrangement in the dimer from a symmetrical charge distribution PMn^{IV}-O-^{IV}MnP, to one where oxidation equivalents are centered on a porphyrin ring: PMn^{IV}-O-Mn^{III}P$^{+\cdot}$ or PM^{III}-O-Mn^{III}P^{++}. These species with ring-centered oxidation would be susceptible to nucleophilic attack by water or hydroxide. Thus the initial product would be an epoxide or a dihydroxy species which would undergo further oxidation.

An explanation can be offered along these lines of the pH dependence of the rates with faster rates at lower OH$^-$ concentrations. As noted above, OH$^-$ coordination to the Mn stabilizes the Mn(IV) oxidation level. As pH is lowered water replaces OH$^-$ and rearrangement within the Mn(IV) dimer to species with Mn(III) and porphyrin ring-centered oxidation would be favored.

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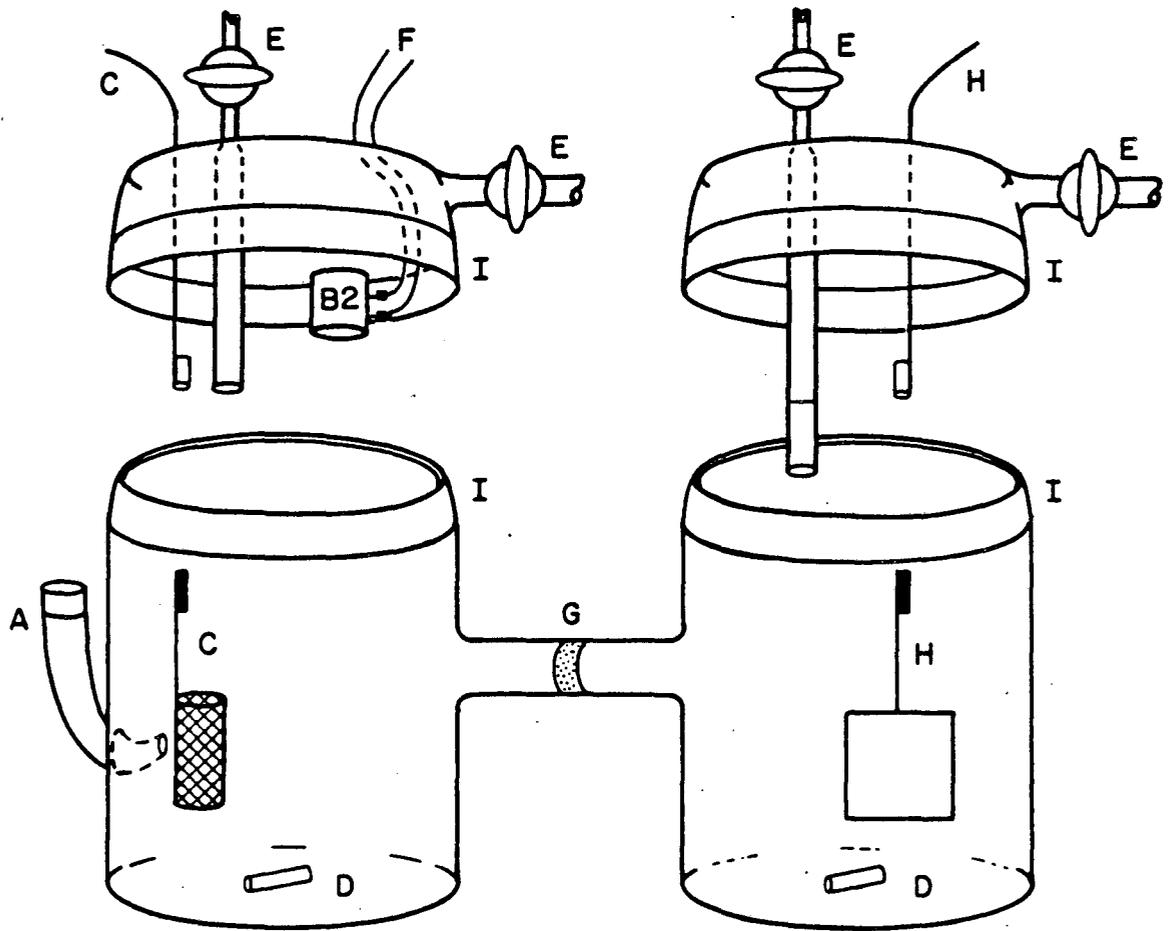
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Figure Captions

Figure 1a. Reaction Vessel for Electrochemical Oxidation of $Mn(III)TMPyP^+$ and O_2 Detection. (A) side tube for SCE reference electrode; (B2) Teledyne Micro Fuel Cell for O_2 analysis; (C) Pt mesh working electrode and lead; (D) Stir bars; (E) Stopcocks for deaeration; (F) Leads for microfuel cell; (G) Medium glass frit; (H) Pt foil counter electrode and lead; (I) Ground glass joints.
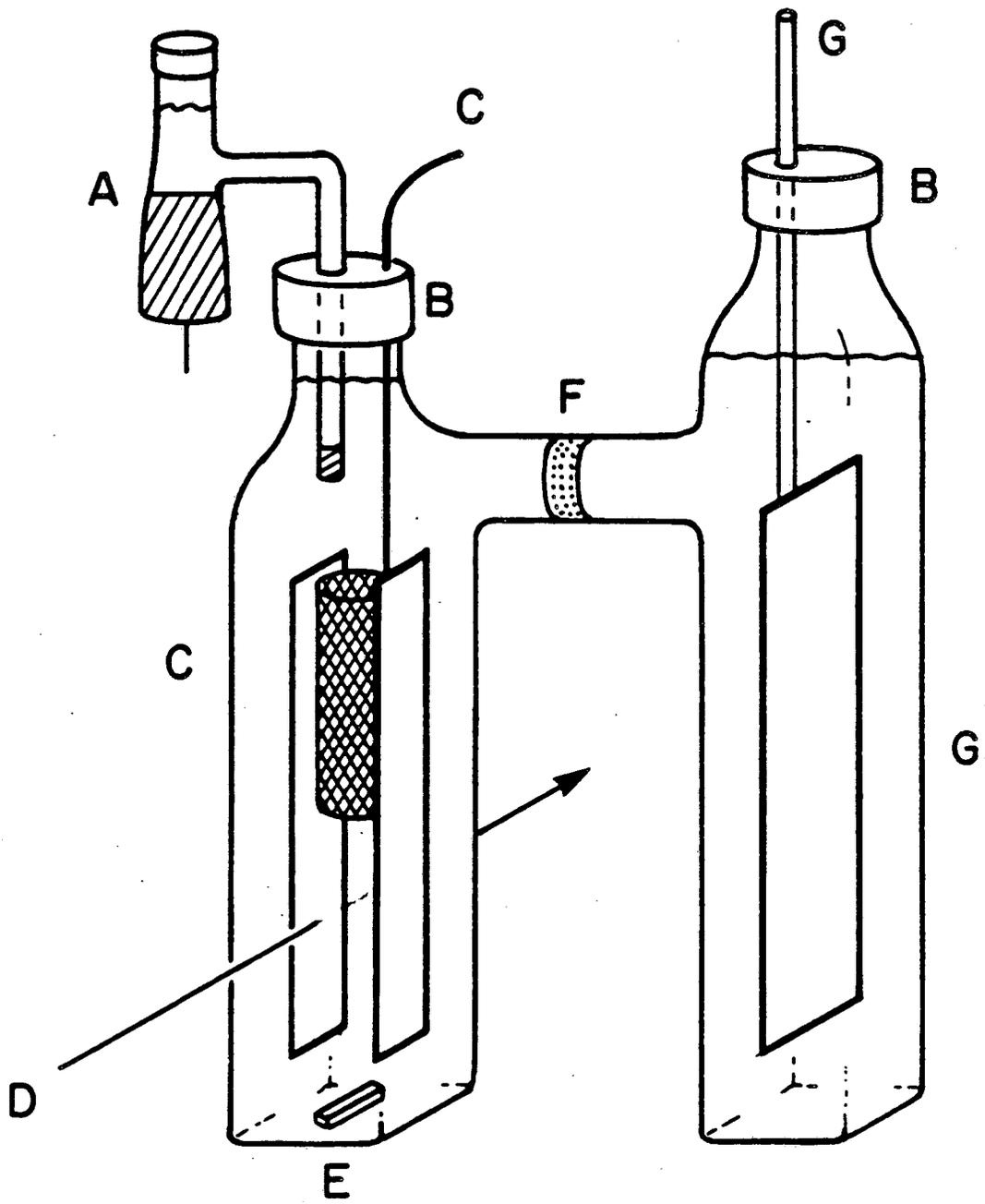
Figure 1b. Spectroelectrochemical Cell. (A) SCE reference electrode; (B) Rubber septa; (C) Pt mesh and foil working electrode and lead; (D) Light path of spectrophotometer; (E) Micro stir bar; (F) Medium glass frit; (G) Pt foil counter electrode and lead.

Figure 2. Visible Spectra. (1) Spectrum of oxidized Mn porphyrin, λ_{max} 420 nm with 10% remaining Mn(III)P; (2) Spectrum of $Mn(III)PTMPyP^+$; T = 25°C, 0.1 $\underline{M}$ sodium phosphate, pH = 9.1. (2) 50 min; (3) 100 min; (4) 200 min; (5) 400 min; (6) 800 min; (7) 1600 min; (8) 96 hrs.
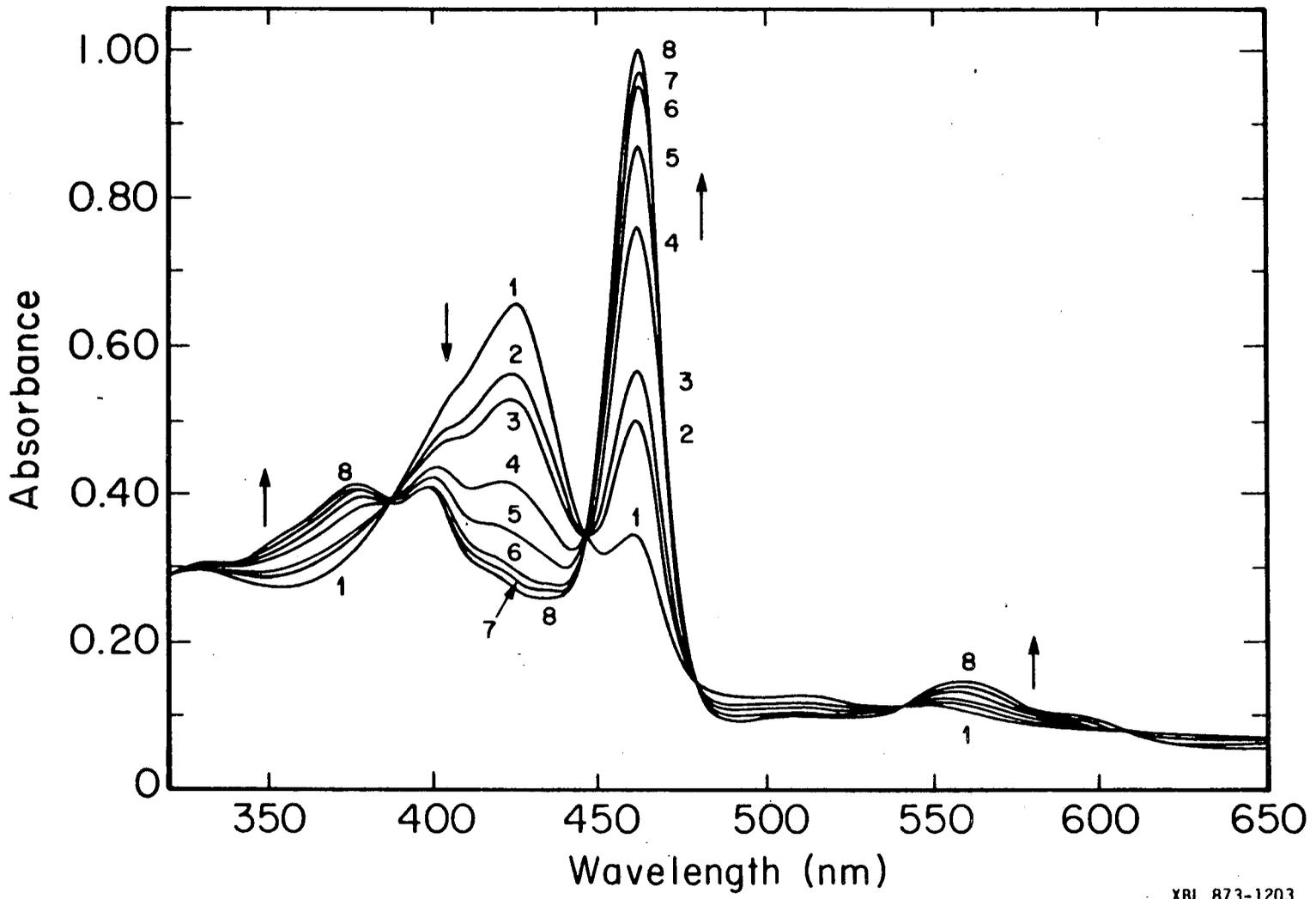
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Fig. 1a

A

C

B

G

B

F

C

G

D

E

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Fig. 1b

Fig. 2

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