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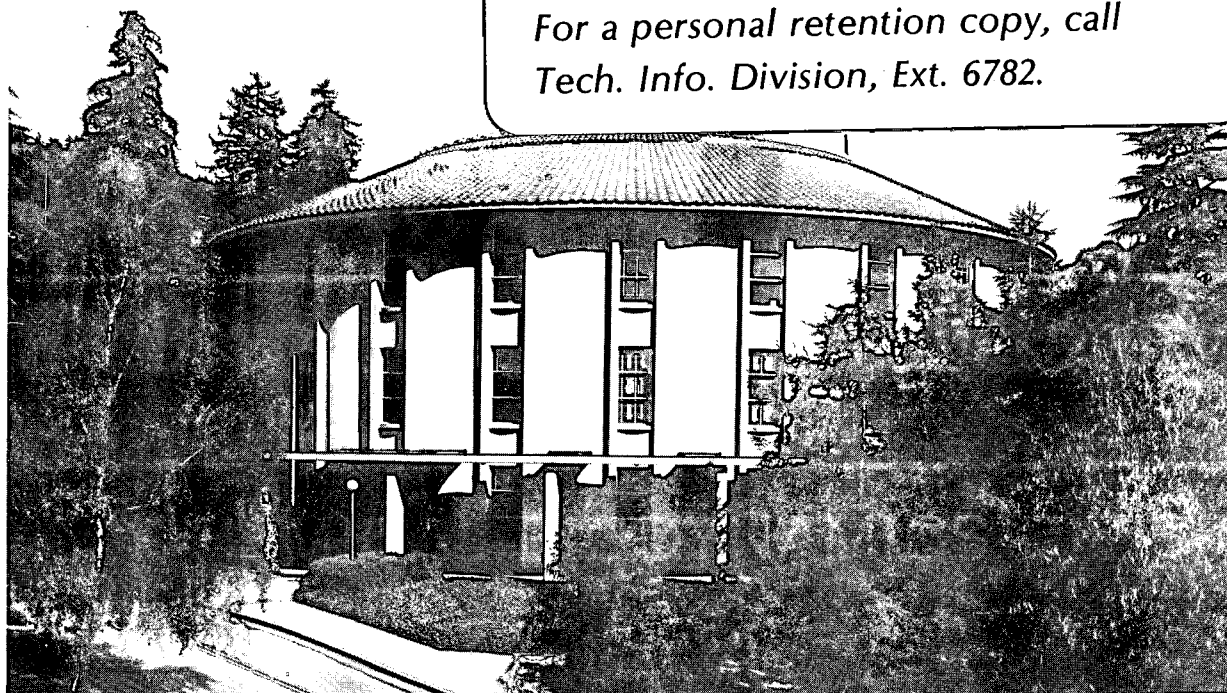
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SURFACTANT MANGANESE COMPLEXES AS MODELS FOR THE  
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R. Wohlgemuth, J.W. Otvos, and M. Calvin

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SURFACTANT MANGANESE COMPLEXES AS MODELS  
FOR THE OXIDATION OF WATER

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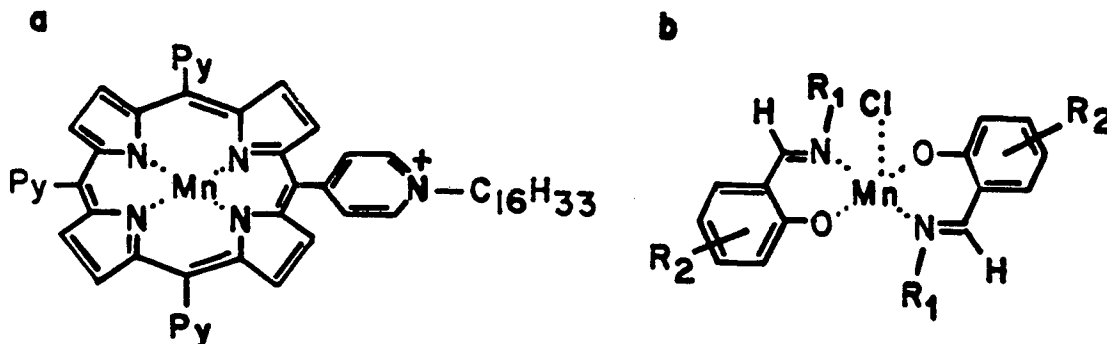
ABSTRACT

Surfactant manganese complexes have been studied spectroscopically and electrochemically as models for the catalysts involved in the photooxidation of water to produce oxygen. Evidence has been obtained for the participation of the suggested redox cycle  $Mn^{II}$  to  $Mn^{III}$  to  $Mn^{IV}$  and back to  $Mn^{II}$  with the evolution of oxygen.

1. INTRODUCTION

Both in natural and artificial photosynthetic systems, water oxidation into molecular oxygen and protons plays an important role in the utilization of the photoregenerated oxidizing power. (See e.g. P. Joliot, B. Kok, 1975; R. Humphry-Baker et al., 1982). A catalyst (or a system of catalysts) is required to couple the photoproduction of oxidizing equivalents to the 4-electron oxidation of water. In the case of natural systems the exact molecular nature of this catalyst (or system of catalysts) is still unknown, but there is little doubt that manganese is an essential component (see J. Amesz, 1983). Despite this importance only a few classes of synthetic manganese complexes have been studied, among those the porphyrin-(M. Calvin, 1965; A. Harriman, G. Porter, 1980; N. Carnieri, et al., 1982; C. L. Hill, F. J. Hollander, 1982); phthalocyanin (A.B.P. Lever et al., 1981; M. M. Morrison, D. T. Sawyer, 1977; R. R. Gagne, et al., 1981); quinone-(M. W. Lynch et al., 1981); gluconate-(M. E. Bodini, D. T. Sawyer, 1976); polyhydroxy-(K. D. Magers, et al., 1978, B. U. Naig, G. C. Dismukes, 1983). We have chosen to study surfactant derivatives of the manganese porphyrin (Structure 1a) and Schiff base complexes (Structure 1b) for

two reasons: (1) A change in the oxidation state of the manganese atom can be easily followed by UV-VIS spectrophotometry and (2) the hydrocarbon tail(s) on the ligand(s) allows us to anchor the molecule in a membrane vesicle or a micelle, while the manganese could still be located near the interface



Structure 1a MnTyP-C<sub>16</sub> Py = pyridyl Structure 1b MnSB-2Cl<sub>2</sub>

R<sub>1</sub> = n-dodecyl

R<sub>2</sub> = 3-fluoro

Since surface-attached redox systems have been widely used in catalytic and electrochemical fields (K. D. Snell, A. G. Keenan, 1979), it seemed worthwhile to make use of the hydrophobic part of our surfactant manganese complexes and confine them to a hydrophobic electrode surface like carbon.

## 2. EXPERIMENTAL SECTION

### 2.1. Preparation and characterization of the complexes

5-(1'-hexadecylpyridinium-4'-yl)-10,15,20-tris(pyridyl)-porphine manganese perchlorate (Structure 1a) was synthesized from the tetrapyrrolylporphine by alkylation, isolation of the monoalkylated porphine and subsequent manganese incorporation (Y. Okuno et al., 1980). The Schiff base complexes (Structure 1b) have been prepared from the corresponding substituted salicylaldehydes by condensation with the amine,

isolation of the free ligand and complexation with  $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$  in methanol (T. Matsushita et al., 1981). The purity of the complexes was checked by TLC, elemental analysis and spectrophotometry. While the UV-VIS absorption spectrum of the Mn-porphyrin derivative allows us to find out that the oxidation state of the manganese atom is +III, magnetic susceptibility measurements have been done to conclude that in case of the manganese Schiff base complexes (R. Wohlgemuth, manuscript in preparation). Electron impact mass spectra of the manganese Schiff base complexes confirmed the molecular weights

## 2.2 Electrochemistry

The potentials of all electrochemical experiments have been controlled by an IBM Potentiostat EC/220 and the response function either directly plotted on a Hewlett-Packard XY recorder or alternatively sent to a VAX computer. The cell was a standard three electrode cell equipped with a glassy carbon (W. E. Van der Linden, J. W. Dieker, 1980) working electrode ( $0.19 \text{ cm}^2$ , IBM), a platinum wire counterelectrode and a silver/silver chloride reference electrode. All electrochemical experiments were conducted under an atmosphere of argon. Millipore water which was glass distilled to remove organic trace impurities was used, and  $0.1 \text{ M KH}_2\text{PO}_4$  (pH 7.0) served both as buffer and electrolyte.  $1.25 \times 10^{-8}$  mol of the Mn-complex in organic solution (typically  $\text{CHCl}_3/\text{MeOH}=1/1$ ) was deposited drop by drop on the glassy carbon electrode, letting the solvent evaporate. The working electrode was then put in a high vacuum chamber for two hours. Before each experiment the glassy carbon electrode has, in addition to the normal cleaning procedure for the whole cell, been treated with finely powdered aluminum oxide and after that washed again with glass-distilled water until no further change in the cyclic voltammogram of the water could be observed (typically about  $2 \mu\text{A}$  current change between +1.0 and -1.0 V).

## 3. RESULTS AND DISCUSSION

The cyclic voltammograms of Fig. 1 show the characteristic irreversible wave on the anodic side of the the manganese tetrapyrridylporphyrin derivative (Fig. 1a) and the manganese Schiff base complex with  $R_1 = n$ -dodecyl (Fig. 1b). These steady-state cyclic voltammograms, which are reached after a few cycles, are diagnostic of a catalytic reaction mechanism:



If  $k$  is much bigger than  $nF/RT$  times the sweep rate, one expects the cyclic voltammogram to have the shape of Fig. 1 on the anodic side (R. S. Nicholson, I. Shain, 1964). The peak on the cathodic sides corresponds to oxygen reduction with the given Mn-complex-coated glassy carbon electrode and is always bigger on the first scan. The position of this peak can also shift slightly from the first scan until the steady state is reached. The long-term stability of the manganese surfactant porphyrin complexes is excellent, while the manganese Schiff base complexes undergo hydrolysis at the C=N bond (Wohlgemuth et al., manuscript in preparation).

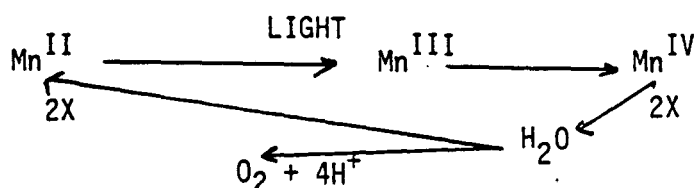
Because of the greater stability of the porphyrin compound its oxidation properties were studied further. We observed a large catalytic wave at +1.25 volts on the oxidation sweep and no  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{III}}$  reduction appears on the reduction sweep. This suggests that two  $\text{Mn}^{\text{IV}}$  species, which are produced in the oxidation sweep, are capable of cooperatively oxidizing water to produce oxygen and return to the  $\text{Mn}^{\text{II}}$  state. This cooperative possibility is related to the fact that most flat molecules tend to form stacked crystals. This is especially true of porphyrins in which the metal centers frequently lie in relatively close proximity to each other in such stacks, whether they be normal or tilted.

We therefore performed a long-term oxidation experiment on the manganese porphyrin coated on the glassy carbon electrode to determine directly the possible participation of  $\text{Mn}^{\text{II}}$  species in what appeared to be an oxidation step from  $\text{Mn}^{\text{III}}$  to  $\text{Mn}^{\text{IV}}$ . First, the  $\text{Mn}^{\text{III}}$  species, which is the stable form in air, is placed on the glassy carbon

electrode in a very thin layer, as previously described. It is then maintained at a controlled oxidation potential of +1.25 volts in a 0.1 M phosphate buffer at pH 8. After the passage of a high multiple of the equivalents of manganese placed on the electrode, the manganese porphyrin is carefully eluted off the electrode anaerobically and its spectrum taken (Fig. 2). The presence of the shoulder at 440 nm indicates the presence of some  $\text{Mn}^{\text{II}}$  porphyrin in the product. Upon the introduction of oxygen to the methanolic solution the spectrum reverts to the original  $\text{Mn}^{\text{III}}$  with its peak at 460 nm. The control spectrum confirming that this is the case is shown in Fig. 3 in which the original  $\text{Mn}^{\text{III}}$  porphyrin is coated on the electrode and then dissolved off without any electrolysis to show it is quantitatively recoverable. An estimate of the amount of  $\text{Mn}^{\text{II}}$  present after electrolysis indicates that it would be of the order of 10% of the total manganese.

Presumably the amount of  $\text{Mn}^{\text{II}}$  that builds up in the solid surface of the coated electrode will depend upon many variables. Among them would be the rate at which the oxidizing  $\text{Mn}^{\text{IV}}$  reverts to  $\text{Mn}^{\text{II}}$  with evolution of oxygen which, in turn, depends upon the rate of oxidation relative to the rate of oxygen evolution. All the variables would be subject to a variety of parameters including pH, the thickness of the layers and other matters which have not yet been investigated.

These results are consistent with the original concept of S. R. Cooper and M. Calvin, 1977: That is, that the participation of two manganese atoms through a redox cycle leads to evolution of oxygen and, therefore, that complexes containing at least two manganese atoms would have to be constructed to be stable as binuclear complexes in the solution environment in order for the system to work successfully as a photochemical device. It is conceivable that a surfactant monomer distributed on the surface of the vesicle or micelle might have sufficient lateral mobility to act cooperatively in this manner provided the photochemical system could be so arranged as to produce the photo-oxidized manganese species at the interface and at a pH at which it would be stable as a manganese complex of any oxidation number. This concept is shown diagrammatically:





Electrochemical studies of such organized assemblies may contribute an important clue.

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## Figure Captions

FIGURE 1 Cyclic voltammogram of Mn-complexes coated on glassy carbon electrode; sweep rate 50 mV/sec, initial potential + 1.25 V (vs. Ag/AgCl). (a) MnTPyP-C<sub>16</sub>. (b) MnSB-C<sub>12</sub>, R<sub>2</sub> = 3-Fluoro

FIGURE 2 Absorption spectra of surfactant Mn-porphyrin after controlled potential electrolysis on glassy carbon electrode

FIGURE 3 Absorption spectrum of surfactant Mn-porphyrin before controlled potential electrolysis on glassy carbon electrode

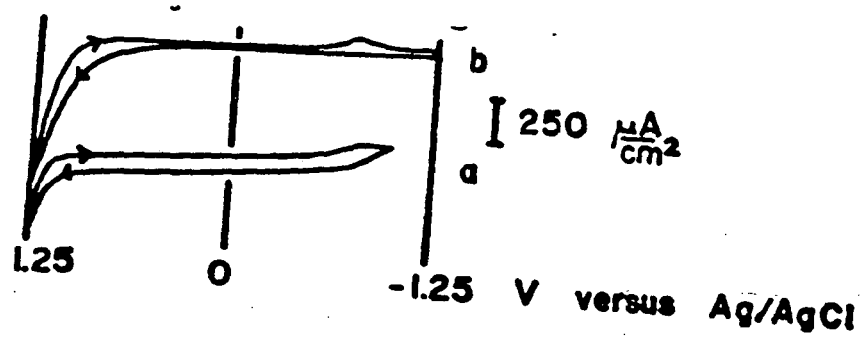
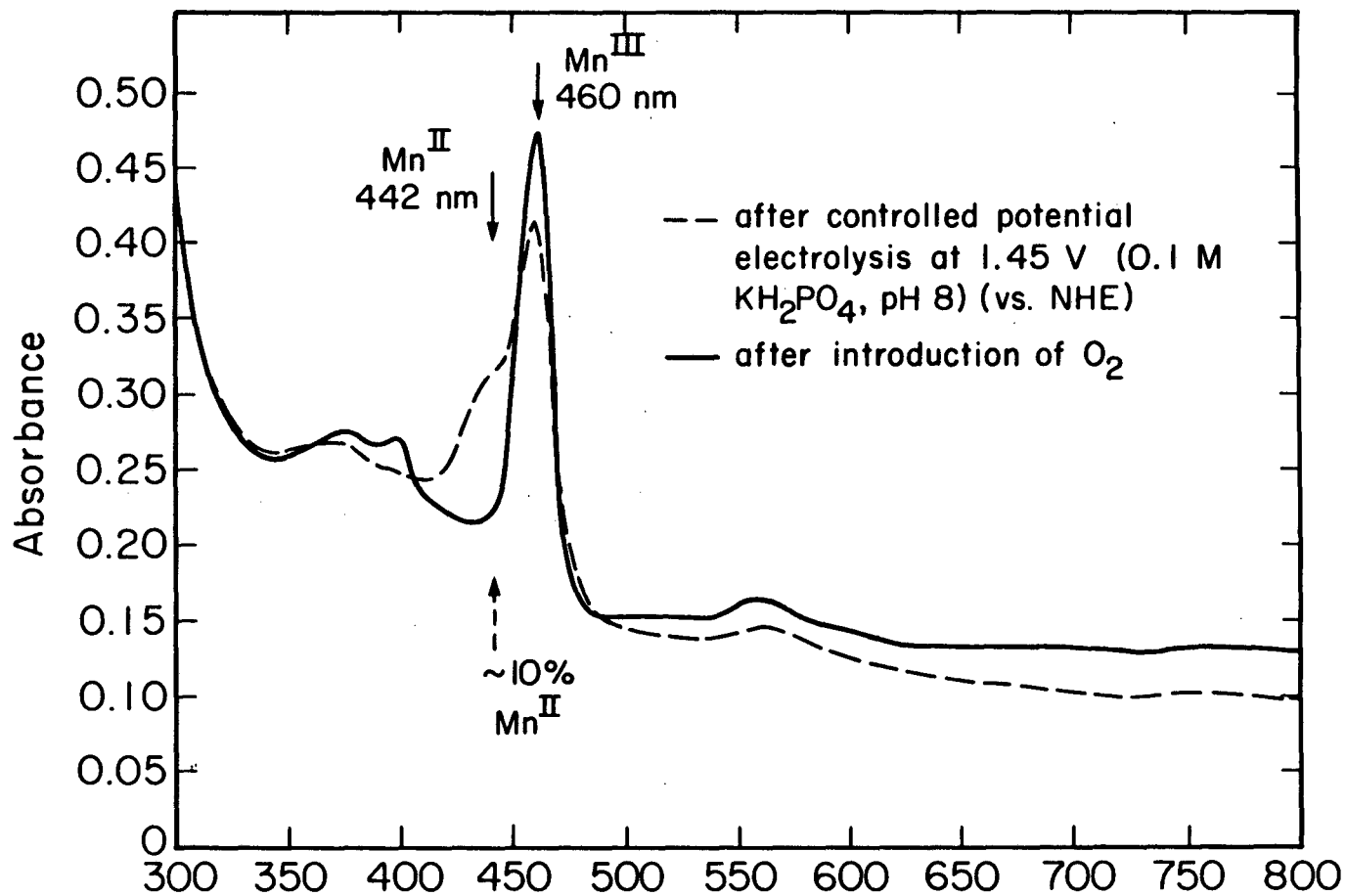


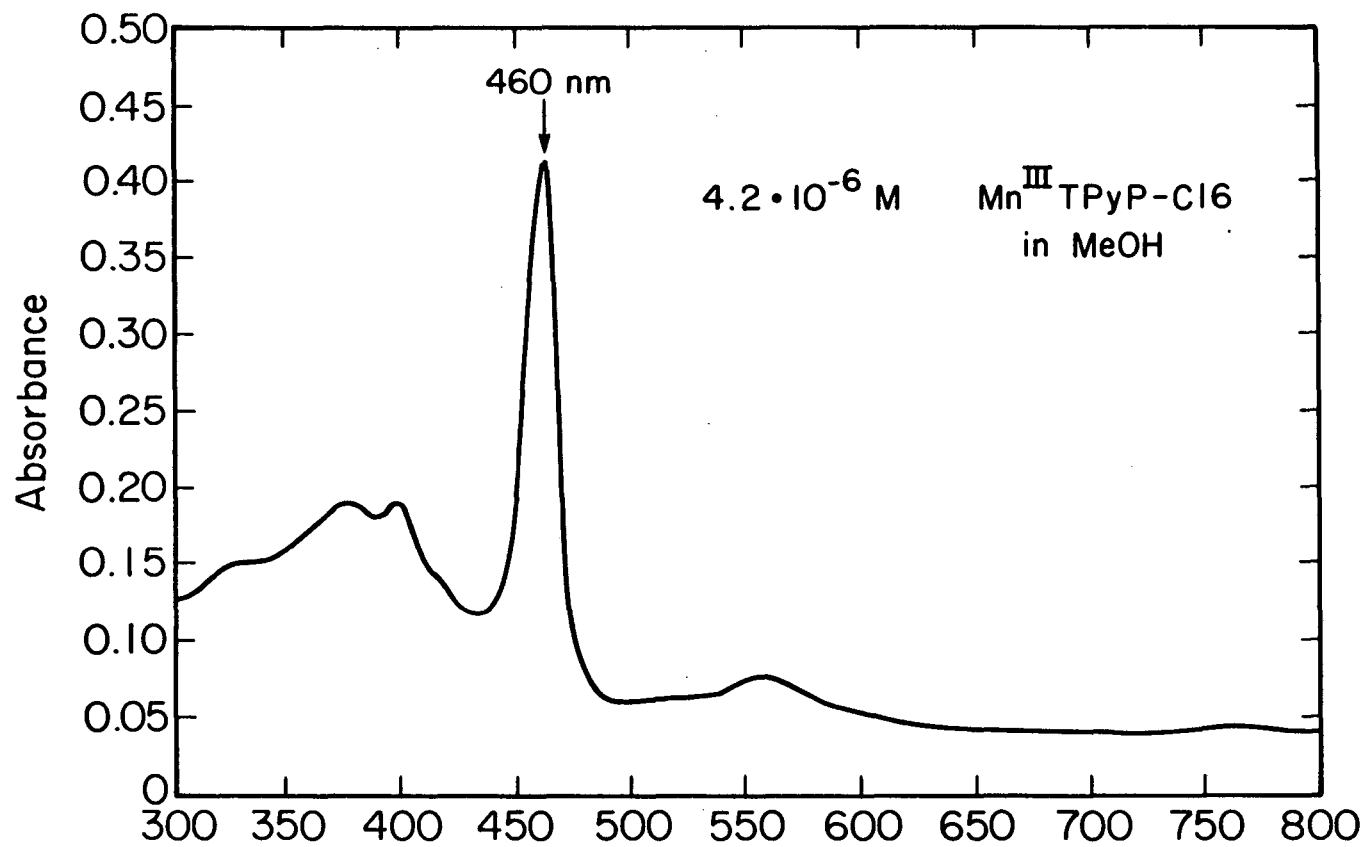
FIGURE 1



Absorption spectra of surfactant manganese porphyrin after controlled potential electrolysis on glassy carbon electrode

XBL 8311-4603

FIGURE 2



Absorption spectrum of surfactant manganese porphyrin before controlled potential electrolysis on glassy carbon electrode

XBL 8311-4602

FIGURE 3

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