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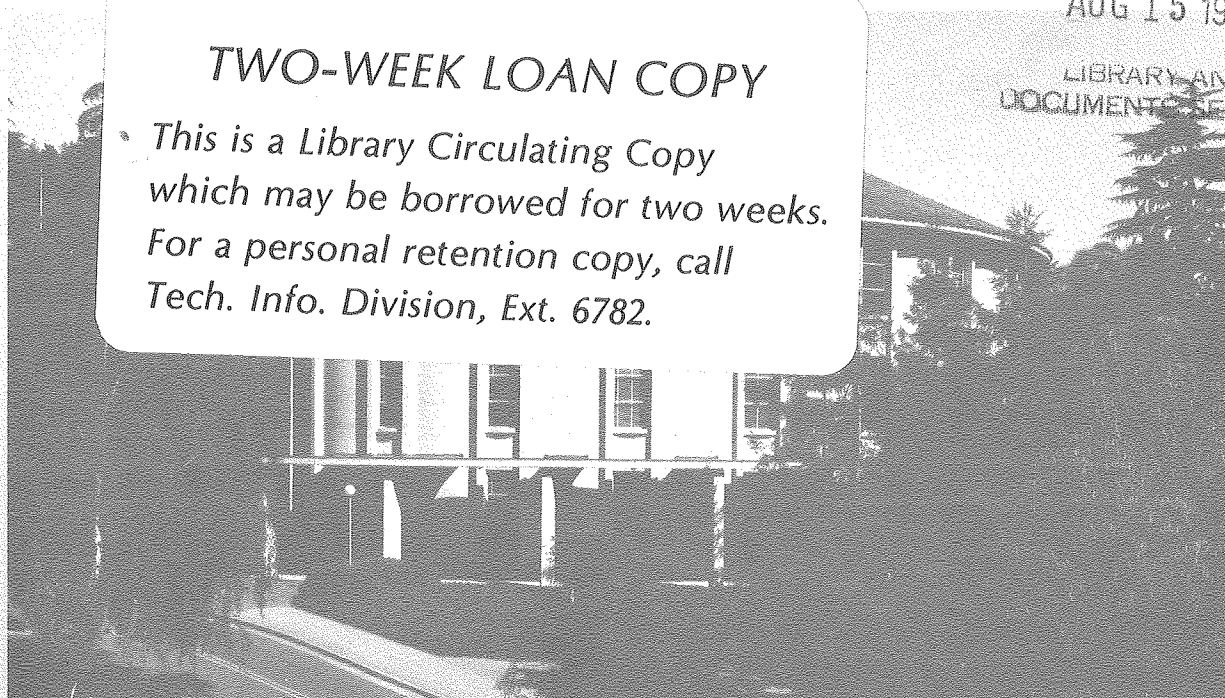
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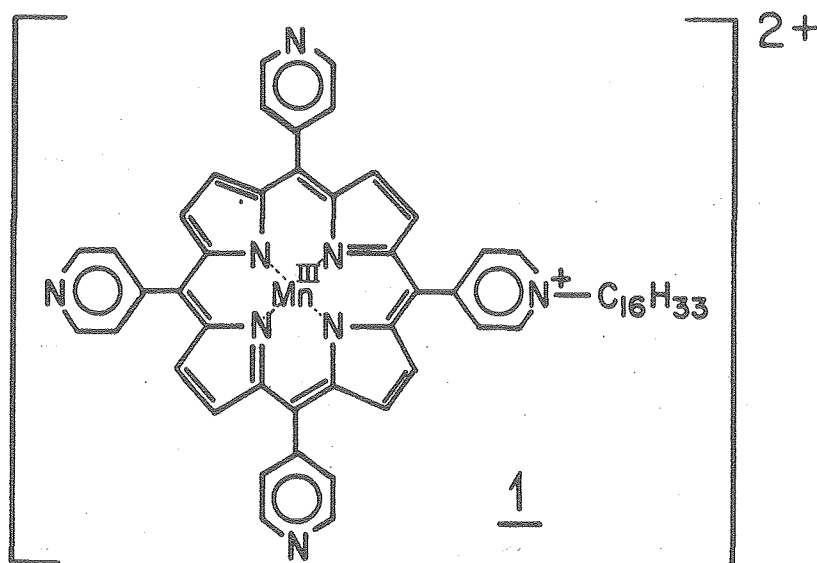
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## PHOTOINDUCED TRANSFER OF OXYGEN FROM WATER:

### AN ARTIFICIAL PHOTOSYNTHETIC SYSTEM

The photoinduced splitting of water into hydrogen and oxygen has evoked great interest in recent years as a means for energy storage and fuel production.<sup>1-4</sup> Photoinduced reduction of water to hydrogen, using visible light, has been described using heterogeneous<sup>5-8</sup> or homogeneous<sup>9</sup> catalysts. However, the complementary part involving the oxidation of water to oxygen is required in order to create a cyclic artificial "photosynthetic" fuel system. The major difficulty associated with the photooxidation of water involves the requirement for a four electron transfer to produce oxygen. A stepwise one-electron oxidation of water is unfavorable due to the implied formation of active hydroxyl radicals. Very recently, it has been reported that  $\text{RuO}_2$  can serve as a heterogeneous charge storage catalyst for oxygen production.<sup>10,11</sup> On the basis of our limited knowledge about natural photosynthesis, in which manganese ions play an important role in oxygen evolution,<sup>4</sup> synthetic manganese complexes, and in particular dimeric complexes, have been proposed as potential catalysts for oxygen production.<sup>12</sup> So far, efforts directed toward this goal have been unsuccessful.<sup>13-15</sup> Consequently, using a manganese complex, we attempted to perform a photoinduced oxidation of water whereby the active oxygen is transferred to a trapping substrate. In such a way, the requirement for a dimerization process to evolve molecular oxygen<sup>4,2</sup> is avoided. We wish to report a photoinduced redox cycle sensitized by a manganese porphyrin, 5-(4'-hexadecylpyridinium)-10,15,20-tri(4'-pyridyl)-porphinatomanganese(III) (1) (abbreviated to Pn-Mn<sup>III</sup>)<sup>16</sup> in which the resultant reaction is the oxidation of water and trapping of the single oxygen atom by a substrate (triphenylphosphine).



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The investigated system consists of a homogeneous mixture containing methanol (2.75 ml), aqueous phosphate buffer (0.25 ml, pH 4.5, 0.36M), Pn-Mn<sup>III</sup> ( $9 \times 10^{-6}$  M), methylviologen ( $MV^{2+}$ ,  $1.5 \times 10^{-3}$  M), and triphenylphosphine ( $PPh_3$ ,  $3.25 \times 10^{-2}$  M). Illumination of the solution, sealed in a cuvette under a nitrogen atmosphere, with a 900-W xenon arc lamp filtered through a cupric sulfate solution ( $330 \text{ nm} < \lambda < 560 \text{ nm}$ ) results in the formation of methylviologen radical cation ( $MV^{\cdot+}$ ) as well as changes in the absorption pattern of the porphyrin. The new Mn-porphyrin spectrum,  $\lambda_{\text{max}} = 435 \text{ nm}$  ( $\epsilon = 1.7 \times 10^5$ );  $570 \text{ nm}$  ( $\epsilon = 1.5 \times 10^4$ );  $615 \text{ nm}$  ( $\epsilon = 9 \times 10^3$ ), is consistent with the formation of Pn-Mn<sup>II</sup>. Chemical reduction of Pn-Mn<sup>III</sup> with  $NaBH_4$  results in similar

spectral changes, and the assignment is further supported by published spectra of other meso-substituted manganese(II) porphyrins.<sup>17,18</sup> Further illumination of the mixture results in a continuous reduction of  $MV^{2+}$  to its radical cation ( $MV^{\dot{+}}$ ). The production of  $MV^{\dot{+}}$  is monitored spectrometrically<sup>19</sup> and the rate of production is displayed in Fig. 1a. Excluding triphenylphosphine from the system results in a considerable decrease in the rate of  $Pn-Mn^{III}$ -to- $Pn-Mn^{II}$  conversion as well as in the rate of  $MV^{\dot{+}}$  production (Fig. 1b). Thus, triphenylphosphine plays a central role in the photosensitized reduction of  $MV^{2+}$ . Comparison of the sensitizer concentration ( $9 \times 10^{-6} M$ ) with the amount of  $MV^{\dot{+}}$  produced ( $1.4 \times 10^{-4} M$ ) indicates a mechanism in which the sensitizer is recycled. Introduction of air into the cuvette reoxidizes  $MV^{\dot{+}}$  to  $MV^{2+}$  and  $Pn-Mn^{II}$  to  $Pn-Mn^{III}$ . The visible absorption spectrum of the aerated sample reveals no change in the initial concentration of  $Pn-Mn^{III}$ . Thus, the sensitizer is preserved quantitatively in the redox cycle. On the basis of the rate of  $MV^{2+}$  reduction an approximate quantum yield of  $MV^{2+}$  reduction of 0.01 is calculated.

The formation of  $MV^{\dot{+}}$  together with  $Pn-Mn^{II}$  implies that triphenylphosphine is oxidized in a redox cycle. Since neither  $Pn-Mn^{III}$  nor  $Pn-Mn^{II}$  oxidizes  $PPh_3$ , while  $Mn^{IV}$ -porphyrins do oxidize  $PPh_3$  (vide infra), and because of the high oxidation potential of  $Mn^{IV}$ -porphyrins<sup>20</sup> we propose the mechanism outlined in Scheme 1 as a possible pathway for the photochemical redox cycle. In this cycle,  $MV^{2+}$  is involved in two photochemical steps. Initially, photoexcited  $Pn-Mn^{III}$  reduces  $MV^{2+}$ , producing  $Pn-Mn^{IV}$ . The oxidizing agent thus formed oxidizes water and the active oxygen so produced as  $Pn-Mn$ -Oxide is transferred to  $PPh_3$  to produce  $Pn-Mn^{II}$  and triphenylphosphine oxide. Recently reported oxygen transfer reactions to triphenylphosphine using organometallic oxo-complexes<sup>21-23</sup> support the intermediary formation of a manganese oxide. It should be noted that the proposed use of Mn-Porphyrins in oxygen production<sup>12</sup> is based



on a pathway similar to the one described in Scheme 1, except that the intermediary Pn-Mn-oxide is expected to dimerize to a binuclear peroxide. In the present case, triphenylphosphine provides an alternative pathway by scavenging the proposed Pn-Mn-oxide through an oxygen transfer reaction. The following evidence supports the proposed redox cycle:

(a) The luminescence of Pn-Mn<sup>III</sup> in alcohol glass at 77°K is quenched by MV<sup>2+</sup>, thus implying an oxidative quenching of the sensitizer whereby the intermediary Pn-Mn<sup>IV</sup> is formed. Consequently, we find that the rate of reduction of Pn-Mn<sup>III</sup> to Pn-Mn<sup>II</sup>, monitored spectroscopically, depends on MV<sup>2+</sup> concentration (Figure 2).

(b) The appearance of triphenylphosphine oxide shows that an oxygen transfer to the trap has been accomplished. To accumulate the oxidation product, an alternative route for the subsequent reoxidation of MV<sup>+</sup> is required.

The reduction potential for the MV<sup>2+</sup>/MV<sup>+</sup> couple (-0.44 V)<sup>19</sup> is adequate for reduction of water at pH 4.5. Indeed, MV<sup>+</sup> reduces water to hydrogen in the presence of Pt or PtO<sub>2</sub> as catalysts.<sup>5,7</sup> Hence, a mixture containing 10 ml of methanol, 1 ml of phosphate buffer (0.03 M) (pH 4.5), MV<sup>2+</sup> (1.6 x 10<sup>-3</sup> M), triphenylphosphine (94.3 mg, 3.3 x 10<sup>-2</sup> M), and Pn-Mn<sup>III</sup> (1 x 10<sup>-5</sup> M) was illuminated while being stirred in a sealed flask under nitrogen in the presence of 2.2 mg of PtO<sub>2</sub> (Adams catalyst). No formation of MV<sup>+</sup> was observed, although the porphyrin was reduced to Pn-Mn<sup>II</sup>, suggesting that MV<sup>2+</sup> was being recycled. After two hours of illumination, 32 mg of triphenylphosphine oxide (32% yield) were isolated. The high turnover number of about 1000 on Pn-Mn reveals that a photoinduced cycle whereby an oxygen transfer from water to the trapping substrate has been accomplished.

Finally, in an independent experiment, we were able to show that a  $\text{Mn}^{\text{IV}}$ -porphyrin is indeed capable of oxidizing  $\text{PPh}_3$  in a two-electron oxidation process. In this experiment,  $\text{Mn}^{\text{III}}$ -TPP-acetate dissolved in benzene was oxidized to  $\text{Mn}^{\text{IV}}$ -TPP by  $\text{Na}_2\text{S}_2\text{O}_8$  and KOH solubilized by the aid of 18-Crown-6 ether. Addition of  $\text{PPh}_3$  to the  $\text{Mn}^{\text{IV}}$ -TPP solution resulted in a quantitative reduction to  $\text{Mn}^{\text{II}}$ -TPP.

The major importance of our proposed cycle is that coordinated water is oxidized photochemically. As this reaction can be coupled to hydrogen generation, the system may be considered as an artificial photosynthetic unit. The possibility for oxygen transfer to substrates other than triphenylphosphine is of considerable interest. Indeed, we find that substituting an olefin, e.g. cyclohexene, for the triphenylphosphine results in similar behavior, i.e. enhanced rates of reduction of  $\text{Pn-Mn}^{\text{III}}$  and  $\text{MV}^{2+}$  compared to the system without added oxygen acceptor. Other oxygen traps which function similarly on these rates are iodobenzene and phthalic acid. We believe that such oxygen transfer processes might be important in developing fuel sources (hydrogen) coupled to the production of useful oxygenated products. A further possibility rests on the utilization of the oxygenated products as a precursor for a subsequent catalytic evolution of oxygen. The possibility of initiating photosensitized oxidation of organic substrates using manganese porphyrins as well as the mechanism elucidation are now being explored. Furthermore, the results encourage continued search for binuclear manganese complexes as catalysts for oxygen production.

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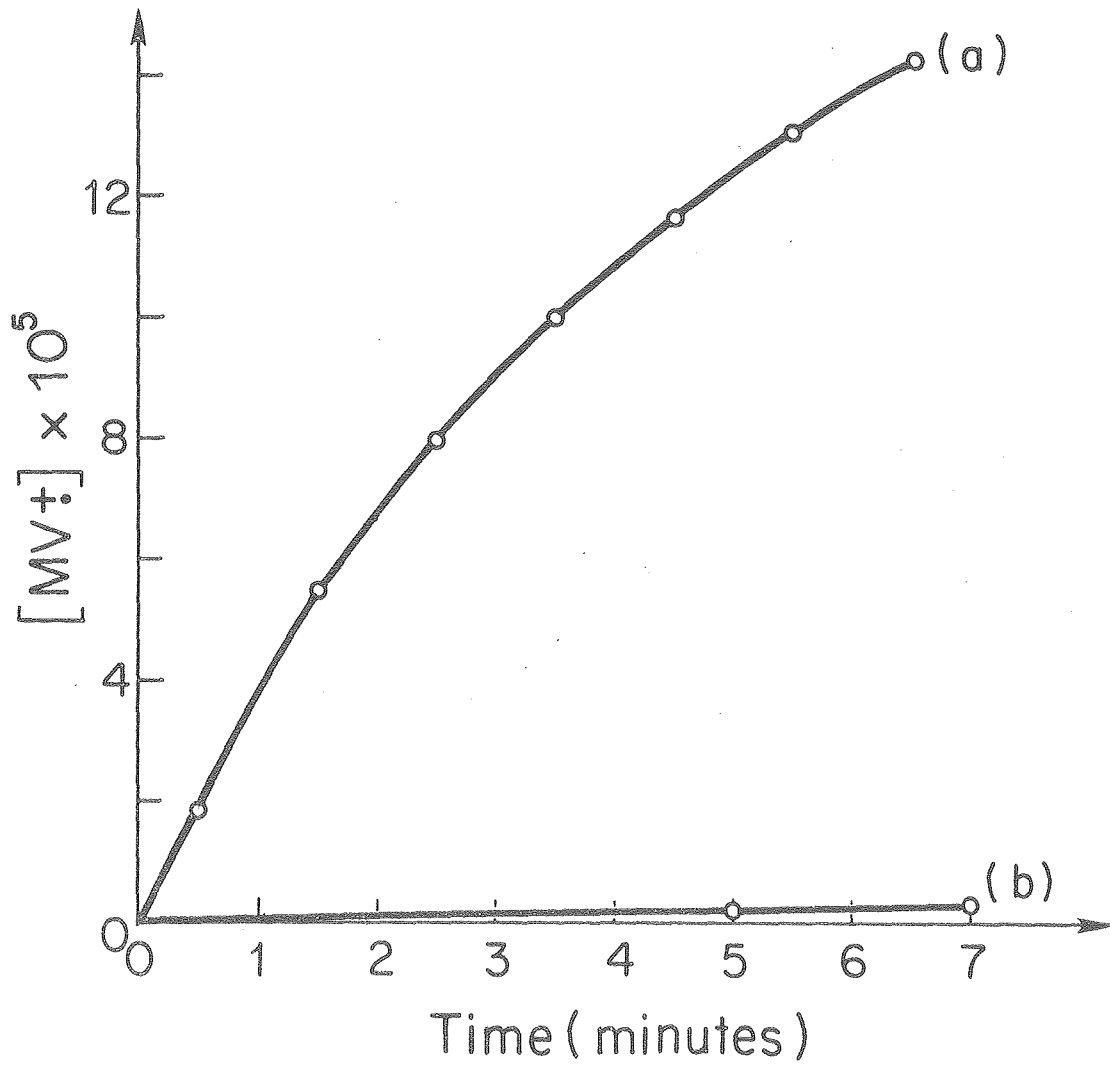
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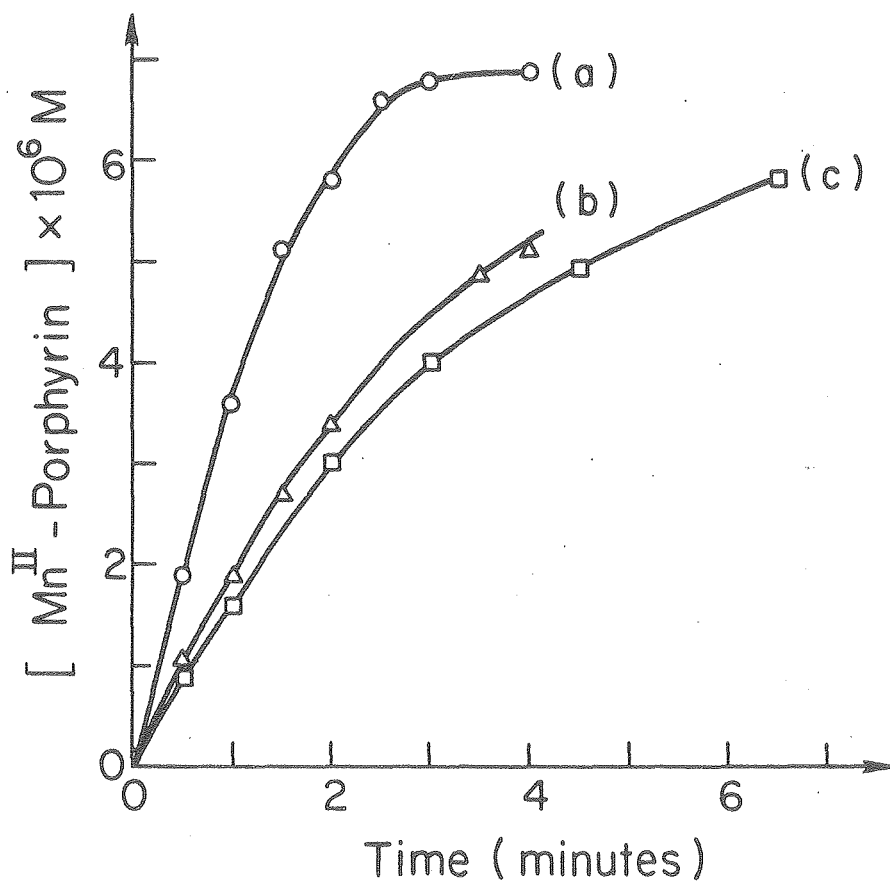
Figure Captions

- Figure 1: Methylviologen radical production as a function of cumulative illumination time: (a) with  $\text{PPh}_3$ ,  $3.25 \times 10^{-2} \text{ M}$ , (b) without  $\text{PPh}_3$ . Initial concentrations:  $[\text{MV}^{2+}] = 1.5 \times 10^{-3} \text{ M}$ ;  $[\text{Pn-Mn}^{\text{III}}] = 9 \times 10^{-6} \text{ M}$ .
- Figure 2:  $\text{Mn}^{\text{III}}$ -porphyrin photoreduction: dependence on methylviologen concentration.  $\bigcirc$ ,  $[\text{MV}^{2+}] = 9.0 \times 10^{-4} \text{ M}$ ;  $\triangle$ ,  $[\text{MV}^{2+}] = 4.8 \times 10^{-4} \text{ M}$ ;  $\square$ ,  $[\text{MV}^{2+}] = 2.4 \times 10^{-4} \text{ M}$ . Initial concentrations of  $\text{Mn}^{\text{III}}$ -porphyrin ( $0.7 \times 10^{-5} \text{ M}$ ) and  $\text{PPh}_3$  ( $7.5 \times 10^{-3} \text{ M}$ ) were the same in all three runs. In this experiment light intensity was attenuated with a neutral density filter to 18% of that used in data of Figure 1.



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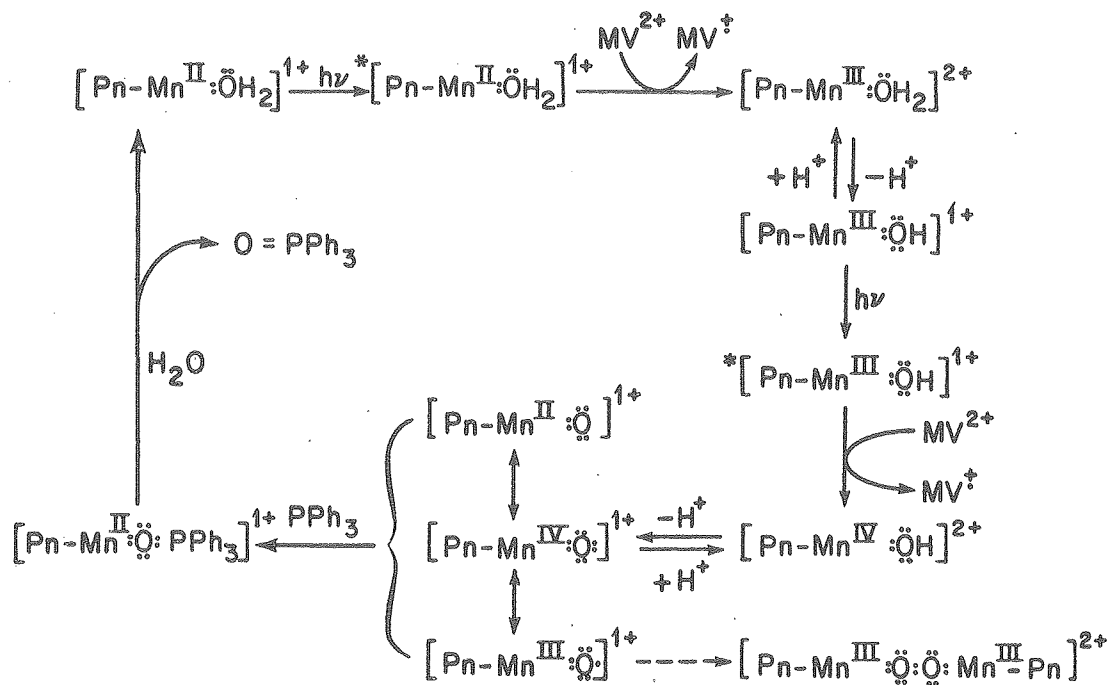
Figure 1 Willner et al.



XBL795-4772A

Figure 2 Willner et al.





XBL 796-4863

Scheme 1 Willner et al.