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Authors
Wohlgemuth, R.
Otvos, J.W.
Calvin, M.

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ENVIRONMENTAL INFLUENCES ON THE PHOTO-OXIDATION OF MANGANESE BY A
ZN-PORPHYRIN SENSITIZER

(Artificial Photosynthesis/Charged Membranes/Surfactant Manganese Complex)

Roland Wohlgemuth, John W. Otvos and Melvin Calvin

Lawrence Berkeley Laboratory and Department of Chemistry,
University of California, Berkeley, CA 94720

Abbreviations:

ZnTPyP-C\textsubscript{16} - (5-[[1'-hexadecylpyridinium-4'-yl]-10,15,20-tris[4'-pyridyl]-21H,23H-porphine]-zinc perchlorate

MnTPyP-C\textsubscript{16} - Bromo-aquo-(5-[[1'-hexadecylpyridinium-4'-yl]-10,15,20-tris[4'-pyridyl]-21H,23H-porphine]-manganese perchlorate

PVS - N,N'-bis(sulfonato-n-propyl)-4,4'bipyridyl (propylviologen sulfonate)

DMPB - 1,2-dimyristoyl-glycero-3-phospho-D,L-glycerol, sodium salt

egg PGG - egg-phosphatidyl-DL-glycerol, which contains a mixture of phosphatidylglycerol with different fatty acid chains

DMPC - 1,2-dimyristoyl-sn-glycero-3-phosphocholine

DMPA - 1,2-dimyristoyl-sn-glycero-3-phosphate, disodium salt

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Abstract: The photosensitized oxidation of a membrane-bound Mn(III)-tetrapyrindylporphyrin derivative by a Zn-tetrapyrindylporphyrin derivative, which is confined to the membrane, has been achieved in negatively charged membranes consisting of phosphatidylglycerol or phosphatidic acid. At the same time, the zwitterionic electron acceptor, propylviologen sulfonate (PVS\(^0\)), is reduced in the aqueous phase. The same reaction cannot be obtained with zwitterionic or cationic membranes. Neither does this photosensitized reaction take place in a homogeneous solution with Mn(III)-tetrapyrindylporphyrin and Zn-tetrapyrindylporphyrin. These results show that the organization of donor, sensitizer and acceptor at an appropriately selected interface allows reactions which would not otherwise occur in homogeneous solutions.
INTRODUCTION

Light-driven chemical reactions that are capable of storing part of the photon energy in the form of stable intermediates are becoming increasingly important.\textsuperscript{1-6} The photochemical splitting of water to oxygen and hydrogen is an example of such a reaction and has been extensively studied over the past few years. (For a review, see ref. 7 or 8.) So far, cyclic systems for that reaction have been based on a (micro)heterogeneous approach where sensitizer, primary donor and acceptor do not diffuse freely with respect to one another, but are organized in a certain way to promote the photogenerated charge separation and to retard the back-reaction of primary products.\textsuperscript{8} Nature itself makes use of this kind of arrangement in the electron transfer chain of photosynthetic membranes. Much effort has gone into the simulation of the reduction half of the process,\textsuperscript{1,2,13,14,15} using sacrificial donors, but comparatively few studies have focussed on the oxidation side.\textsuperscript{10-13}

In this paper, we investigate the possibility of oxidizing Mn(III)-systems photochemically with the aid of a sensitizer and stabilizing the oxidized form for a sufficient time in order to observe it. Manganese in its oxidation state of +4 or higher has been of interest for a long time in oxidation and dehydrogenation reactions in organic chemistry.\textsuperscript{16-22} In photosynthesis as well, nature (according to the Kok scheme), seems to make use of a Mn(IV)-compound when oxygen is evolved from chloroplasts under illumination by the sun.\textsuperscript{23,24} Although the precise nature of the manganese environment is not yet known, direct observations of the Mn in the chloroplasts have shown the average oxidation state without illumination to be between +2 and +3.\textsuperscript{25,26} Based on these studies, a bridged Mn-dimer was suggested\textsuperscript{*} and found to be

\textsuperscript{*} (See also Reference 1)
consistent with the model of Wydrzynski and Sauer.\textsuperscript{27} In addition, Wang\textsuperscript{28} proposed a mechanism of water oxidation promoted by mononuclear manganese(IV).

The easiest way to photo-oxidize Mn(III)-porphyrins would be to excite them directly and to transfer an electron to a suitably chosen acceptor, e.g., a quinone, as described by Harriman and Porter.\textsuperscript{30,31} There are, however, many factors that count against the use of manganese porphyrins as photosensitizers, one of them being the short excited state lifetimes,\textsuperscript{32} which play a decisive role in the efficiency as long as we have to let the reactants diffuse together. Another way of creating oxidized Mn-compounds photochemically (see Fig. 1) is to separate the function of absorbing the photons from the species to be oxidized.\textsuperscript{33}

The position of the absorption maximum depends very much on the oxidation state of the Mn\textsuperscript{29} and allows us to assess the extent of a redox reaction from a simple spectrophotometric measurement. Porter\textsuperscript{30} suggested that in order to overcome the rapid back-transfer of the electron from the reduced acceptor to the oxidized photosensitizer, the manganese complex should be linked permanently to the photosensitizer. So far, however, no effort to construct such a compound has been undertaken, as far as we know. We have chosen instead to decrease the back-reaction between the reduced acceptor and oxidized photosensitizer by (a) organizing the Mn-compound and the photosensitizer on a membrane interface while the acceptor resides in the aqueous phase (see Fig. 2), and (b) making the membrane interface negatively charged and using a zwitterionic acceptor (PVS\textsuperscript{0}) whose reduction product is then repelled from the membrane.
Fig. 1. Basic arrangement of photosensitizer A, electron donor (Mn$^{\text{III}}$ complex) and electron acceptor A used in this approach to photo-oxidize the Mn$^{\text{II}}$ complex
Fig. 2  Organization of the electron donor D and the photosensitizer S at a negatively charged membrane-water interface, with a neutral electron acceptor A in the aqueous phase
MATERIALS AND METHODS

Materials: The Zn-photosensitizer, 5-(1-hexadecylpyridinium-4-yl)-10, 15,20-tris-[4-pyridyl]-21H,23H-porphine-zinc perchlorate as well as the donor, bromo-(5-[hexadecylpyridinium-4-yl]-10,15,20-tris[4-pyridyl]- 21H,23H-porphine)-manganese perchlorate, were prepared according to ref. 34. The purity was checked by HPLC on a Rheodyne NH₂ column in CHCl₃/MeOH at 95:5. PVS was prepared in the following way: A mixture of 4,4'-bipyridine dihydrate (7 mmol, ALDRICH) and 1,3-propanesultone (70 mmol, ALDRICH, 97%) was heated for 10 minutes to 100°C, then cooled and mixed with 15 ml MeOH (MALLINCKRODT, AR). The suspension was stirred for 24 hrs at room temperature, then filtered and washed three times with a total of 20 ml MeOH. Elemental analysis: Calc. (for C₁₆H₂₀N₂S₂O₆·H₂O): C, 45.93, H, 5.26, N, 6.70, S, 15.31. Found: C, 45.99, H, 5.04, N, 6.42, S, 15.32. The ¹H-NMR spectrum in D₂O is as expected.

sn-phosphatidyl-DL-glycerol sodium salt, both dimyristoyl- and egg derivatives, were purchased from CALBIOCHEM, while 1,2-dimyristoyl-sn-glycero-3-phosphate disodium salt and 1,2-dimyristoyl-sn-glycero-3-phosphocholine were from R. Berchtold, Biochemical Laboratory (Mattenhofstr.34, 3007, Berne, Switzerland).

Vesicle Preparation: Three µmol of the phospholipid were mixed with the long chain Zn-sensitizer, ZnTPyP-C₁₆, and the donor MnTPyP-C₁₆ in MeOH/CHCl₃ at 1:1. The solution provides adequate mixing of the components. The solvent is then removed, first with a stream of N₂, then with high vacuum for 2 hrs. Usually a reference sample which does not contain the donor is prepared in exactly the same manner. After drying, 3 ml of ion exchanged (Milli-Q System) and twice distilled water was added, the suspension sonicated for 10 min at a temperature above phase transition, and finally 0.5 ml of 10⁻² M PVS solution added (pH 7). This produces the system shown in Fig. 3.
Apparatus: The illumination was performed after the vesicle suspension was transferred to an oxygen-tight cuvette equipped with glass stopcocks, a teflon stirring bar and a septum. It was deaerated by repeated evacuation and flushing with argon. The collimated beam of a 1000W xenon lamp (operating at 25 V, 40 A) passed through 10 cm water. An interference filter with a transmission maximum at 430 nm and 10 nm full width at half-maximum selected the photons. The cuvette was in a water bath at room temperature and had a magnetic stirring bar. The incident photon flux, as checked with Reinecke salt actinometry and by direct measurement with the EG&G photometer in conjunction with a B1669 flat filter and an OD-4 neutral density filter was $3.1 \times 10^{-6}$ (E/min-cm²). Absorbance spectra were measured on an HP-8450 spectrophotometer. The flash photolysis system is described elsewhere.

RESULTS AND DISCUSSION

Fig. 3 shows the system in the case of an egg PG vesicle. It illustrates that the donor, MnTPyP-C₁₆, and sensitizer, ZnTPyP-C₁₆, are distributed in both layers of the membrane and that the acceptor, PVS, which was added after the vesicles had been formed, is on the outside of the vesicle.

Illumination of this system at 430 nm (Soret band of the ZnTyP-C₁₆) results in the disappearance of MnIII TP yP-C₁₆ and the formation of a new peak at $\lambda = 424$ nm, characteristic for MnIV TP yP-C₁₆. The presence of kosbestic points shows that MnIII is converted quantitatively to
Fig. 3  Single unilamellar vesicle (SUV) with a diameter between 200 and 500 Å (prepared by sonication) and the indicated ratio between phospholipid (egg-PG, DMPG, DMPA or DMPC), electron donor (MnTPyP-C16) and photosensitizer (ZnTPyP-C16) of 86:3:1, with the electron acceptor (PVS) added only on the outside of the vesicle.
Mn$^{IV}$. In about 30 minutes, Mn$^{III}$TPyP-C$_{16}$ can be completely oxidized to the Mn$^{IV}$ compound. The fact that Fig. 4 does not show a large absorption for PVS$^{-}$ can be understood in terms of the small concentration of the donor, which produces PVS$^{-}$ stoichiometrically. By increasing the donor concentration, PVS$^{-}$ can indeed be observed and the ratio between the decrease in Mn$^{III}$ concentration and the increase in PVS$^{-}$ is approximately 1:1.

Elimination of the PVS from the system results in no change in the absorption spectrum of the donor when the system is illuminated in the manner described above. If the membrane is constituted of DMPG or DMPA instead of egg-PG, but otherwise the same conditions used, the system responds in the same way as before, giving the Mn$^{IV}$TPyP-C$_{16}$. On the other hand, if DMPG is replaced by DMPC, which has the same phase transition temperature but a zwitterionic headgroup, and all other components (donor, sensitizer, acceptor) present under the same conditions, illumination does not give any change in the starting absorption spectrum of Mn$^{III}$TPyP-C$_{16}$. Furthermore, when Mn$^{IV}$ in the membrane is treated with chloroform-methanol, which dissolves the membrane, the Mn$^{IV}$ disappears.

Finally, we have looked at the corresponding homogeneous system, wherein the porphyrin analogues without the C$_{16}$ have been used, and it turned out that illumination of the Zn-sensitizer produced no photo-oxidation of Mn$^{III}$.

** The oxidation of the Mn$^{III}$ on the inside surface as well as on the outside could be a result of electron exchange across the membrane between Mn$^{III}$ and Mn$^{IV}$, or, possibly, of PVS$^{0}$ diffusion through the membrane. Also, the manganese porphyrin itself may move through the membrane in a flip-flop mechanism.
Fig. 4  Difference spectra of system I (3x10^{-5} M Mn^{III}TPyP-C_{16}; 10^{-5} M ZnTPyP-C_{16}; and 10^{-3} M PVS in an egg-PG vesicle) vs. system II (10^{-5} M ZnTPyP-C_{16} and 10^{-3} M PVS in an egg-PG vesicle) after subsequent 5 minute illumination at 430 ± 5 nm at 31 x 10^{-6} E/min-cm² light intensity
An examination of Fig. 5 brings up the question of why the \( \text{Mn}^{IV} \text{TPyP-C}_{16} \) is so stable. The entire set of experiments suggests that the back-reaction between the oxidized Zn-sensitizer and the reduced PVS is dramatically retarded in the case of a negatively charged membrane. This is indeed true, as illustrated in Fig. 6, where on a millisecond time scale no decay of PVS\(^-\) is observed at all. It might, however, not be a purely electrostatic effect, because the alkyl chain on the Zn-sensitizer might pull it further into the membrane, making access of reduced PVS, and therefore back-electron transfer, more difficult. Similar effects have been found with a surfactant ruthenium sensitizer in micelles and membranes.\(^{39,40}\) The unusual fact that the \( \text{Mn}^{IV} \) can be prepared at pH 7, while in homogeneous solution \( \text{Mn}^{IV} \) is stable only at pH\(\geq11\)\(^{29}\), may be an advantage for the use of \( \text{Mn}^{IV} \) as an oxidant.

CONCLUSIONS

We have achieved the photochemical production of an oxidized \( \text{Mn}^{III} \text{TPyP-C}_{16} \) by having the donor and sensitizer in a negatively charged membrane, while the neutral electron acceptor was in the aqueous phase. The oxidized species is probably stabilized in the membrane by one or both of two effects: (1) The negative surface charge attached to the polar head group of each phospholipid molecule slows down back-reaction with the reduced acceptor, and (2) the inaccessibility of the Mn, buried in the membranes, to the reduced electron acceptor further shields it from reaction.
Fig. 5  Model for the photo-oxidation of Mn\textsuperscript{III}TPyP-C\textsubscript{16} with the Zn-porphyrin sensitizer
Fig. 6  Flash photolysis experiment (pulsed dye laser using Coumarin 450, see also ref. 37) of ZnTPyP-C16 incorporated into egg-PG membranes and PVS (see system II in Fig. 3) using the transient absorbance change at $\lambda = 602$ nm as detection technique
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References

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