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QUANTUM CAPTURE AND REDOX STORAGE

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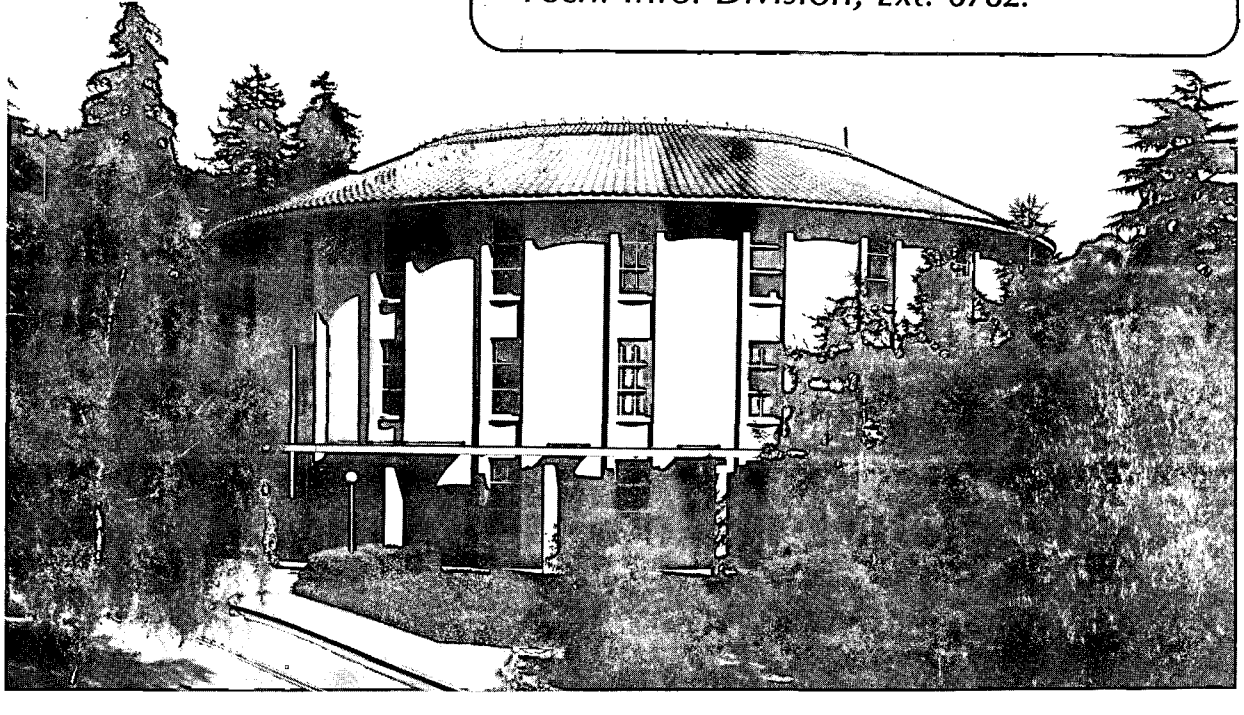

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QUANTUM CAPTURE AND REDOX STORAGE

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ABSTRACT

A review is presented of the efforts to achieve artificial photosynthesis by electron transfer across phase boundaries using vesicle systems, particle systems and special catalysts for oxygen and hydrogen production. Future efforts will be concerned with the development of different particle systems for electron transfer and methods for the photochemical reduction of carbon dioxide to various useful compounds.

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INTRODUCTION

Artificial photosynthesis is a process that mimics the principles of green plant photosynthesis with a totally synthetic device that will capture the quanta from the sun and store them as stable chemicals.[1,2] The problem involves devising a system in which the short-lived energy of a sensitizer can be stored in some stable chemical form, usually by the transfer of an electron from one point to another nearby point. If energy is to be stored after electron transfer, the system must be in a higher energy state than it was in before, otherwise, the products of the electron transfer reaction will have a tendency to back-react.

The green plant has evolved over several million years the ability to accomplish these reactions with a high degree of efficiency. Our problem is to use our knowledge of green plant quantum conversion to construct an entirely synthetic device that will be successful in splitting the water molecule to yield hydrogen (reductant) and oxygen (oxidant). It is anticipated that the process of artificial photosynthesis will one day fulfill the ultimate needs of modern society for liquid and gaseous fuels as the supplies of ancient photosynthesis become exhausted.

A good bit is already known about the storage process in green plants. In order to run the photosynthetic carbon cycle, the details of which have already been elucidated, light quanta from the sun must be captured. We know that the light is absorbed by green plant chlorophyll

in the chloroplasts and produces a long-lived excited state lasting a few milliseconds which, in turn, induces electron transfer to an acceptor. A "hole", or positive charge, appears on one side of a membrane (such as the natural membrane in chloroplasts) and a negative charge on the other, with a slow back reaction because the charges are on opposite sides. The negative charge eventually gives rise to reducing power for the carbon dioxide and the positive charge eventually gives rise to oxidizing power, with the final formation of oxygen. This result suggests that the membrane itself is unsymmetrical. How does that charge separation across the membrane occur and what do we know about it?

DESIGN OF VESICLE SYSTEM

It seems to me that the principal thing that the green plants have learned to do is to transfer electrons across phase boundaries. There are two phase boundaries in the system, one between the water and oil layer of the membrane on the inside and the second between the oil and the water layer on the outside.[3] We undertook to demonstrate electron transfer through a bilipid membrane, which the biochemists have long known as an easily constructed liposome.[4]

We constructed a bilipid membrane from a natural or synthetic phospholipid. By sonicating the particles in water, the bilipid membranes would close into small vesicles which are membrane hollow spheres with water on the inside and water on the outside. The size of the actual vesicle, which was measured by several different methods, is about 500 A in diameter and about 40 A thick.[5] It is possible to place photosensitizers on each side of the bilipid membrane to facilitate the transfer of an electron through the membrane and thus separate the oxidizing power from the reducing power.[6]

The sensitizer in the green plant is chlorophyll, a porphyrin ring with a long phytol tail. The porphyrin head is in the hydrophilic part and the phytol tail is the hydrophobic part. The chlorophyll acts as a surfactant dyestuff, that is, something that will find its way to the interface between the lipid and the water. If the sensitizer is made up

simultaneously with the phospholipid vesicle, the surfactant dyestuff will automatically lodge itself right at the interface: the hydrophilic head will be at the interface between the water and the oil with the hydrophobic tail in the oil.

We have used two different types of surfactant dyestuffs. One is a synthetic porphyrin with four mesopyridine rings. If a long-chain hydrocarbon is placed on one of the pyridine rings it will be a surfactant dyestuff. For the acceptor we have used an analog of paraquat which traps the electrons from the excited sensitizer. The usual acceptor molecule has two positive charges. When it has two negative charges also, the molecule itself is neutral. When one electron is placed into the system, one of the positive charges is destroyed, leaving two negative charges; that one thus becomes a net negative ion. This fact may play a role in the charge separation process.

The components of the system (shown in Figure 1) consist of tris-bipyridyl +2 ruthenium with the two tails on one bipyridyl which will bond at both lipid surfaces of the vesicles. On the inside of the vesicle, a donor substance is placed as a sacrificial donor which could reduce +3 ruthenium to +2 ruthenium and itself be irreversibly oxidized;[7] this is a method of providing electrons on the inside of the vesicle. The acceptor molecule, heptylviologen, a viologen with two 7-carbon tails, is placed on the outside of the vesicle. We wanted a few of the molecules to reside in the membrane, that is, to be distributed between the water layer on the outside and the membrane.[8,9]

When the light is turned on, the +2 ruthenium becomes excited and reaches a long-lived triplet state, long-lived enough to find one of the viologen molecules in the membrane and reduce it to heptylviologen cation radical. If the heptylviologen in the bulk solution could be reduced in a large amount, it would be possible to show that the electrons have come from the inside of the vesicle and have passed through to the outside. The cofactors are heptylviologen as acceptor, surfactant ruthenium bipyridyl as sensitizer, zinc ion on the outside of the membrane and ethylenediaminetetraacetic acid as donor on the inside. The

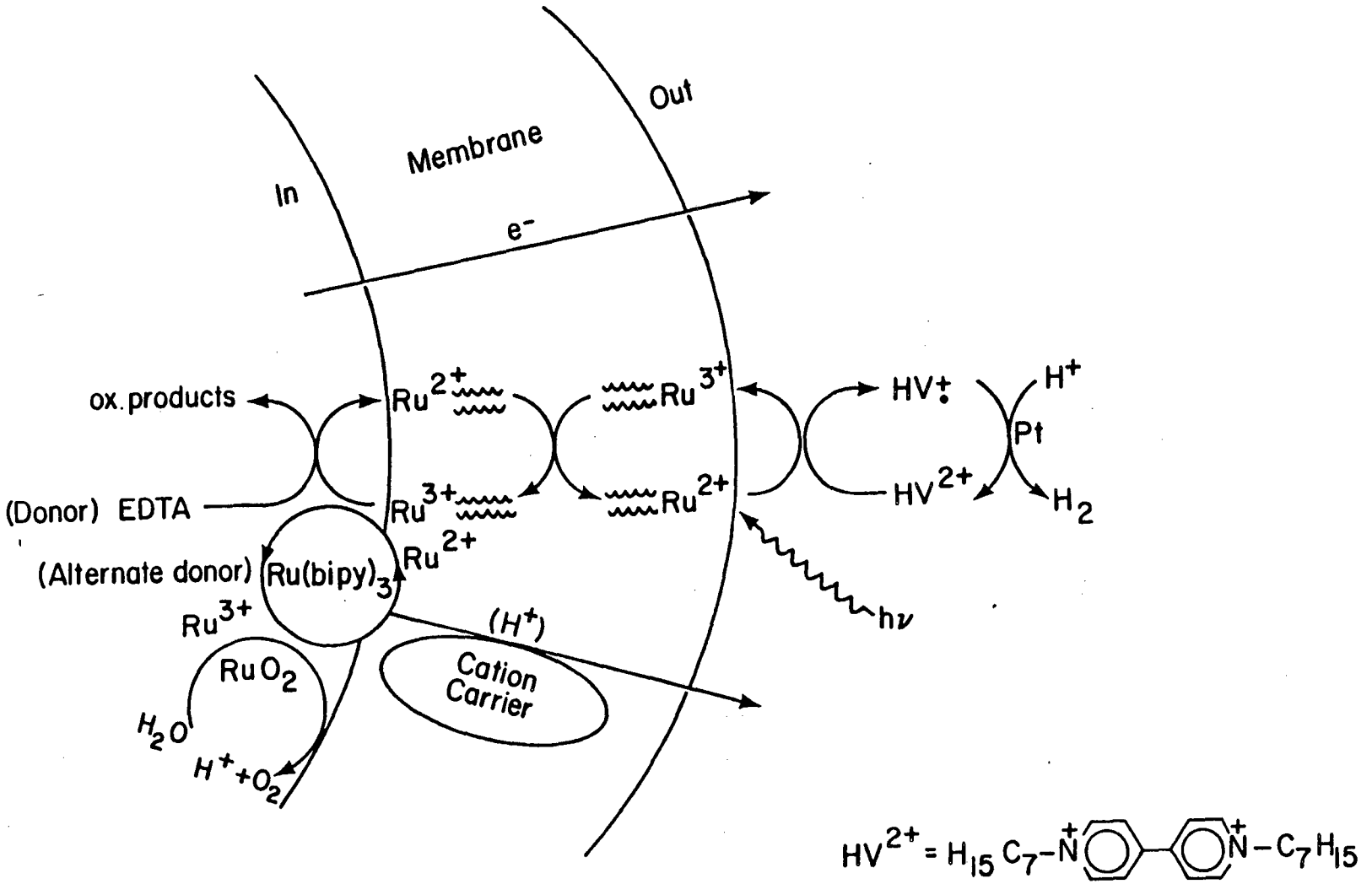

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Figure 1. Scheme for photosensitized electron transfer across a lipid vesicle wall

viologen is reduced in a very short time, in very large amounts compared to the amount of ruthenium in the vesicle. The viologen which is reduced corresponds to the amount of EDTA inside. We thus have evidence that electrons on the inside must have passed through the membrane to the outside. The process is as follows: The light excites the +2 ruthenium which reduces viologen on the outside of the vesicle; the +2 ruthenium goes to the +3 state on the outside. On the inside of the vesicle there is +2 ruthenium. The inside and outside of the vesicle are less than 40 A apart. There is a possibility that the electron from the +2 ruthenium inside the vesicle can tunnel across the 40 A membrane into the +3 ruthenium on the outside, reduce it back to the +2 ruthenium on the outside and itself become +3 ruthenium on the inside of the vesicle. The +3 ruthenium surfactant on the inside can then oxidize the +2 ruthenium bipyridyl in the water layer to +3 ruthenium in the water layer which can oxidize the water on ruthenium oxide or cobalt oxide catalyst.

We have therefore created a complete system which depends on the passage of the electron through the membrane by a tunnelling phenomenon between the ruthenium atoms, one on each side of the membrane, with no quinone carriers.

MANGANESE CATALYSTS FOR OXYGEN PRODUCTION

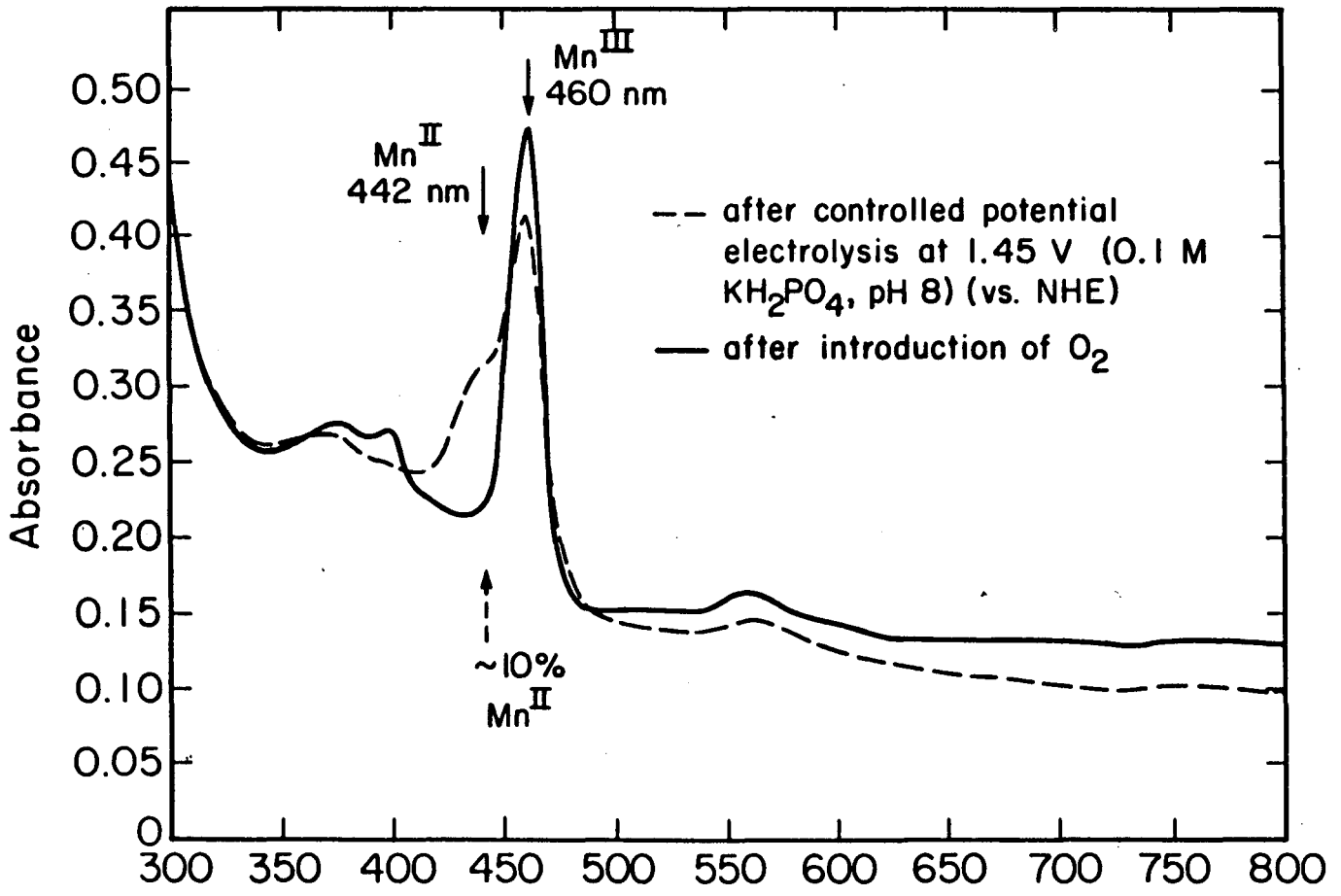
In green plants the catalyst for the oxygen side is some kind of manganese compound, and we know the acceptors for the hydrogen production side are iron-sulfur compounds. The problem now is to construct suitable synthetic compounds to perform both the reduction and oxidation reactions.

In plants manganese is involved in the conversion of water to molecular oxygen, a process which proceeds via the transfer of four electrons. The fact that four electrons are required to go from water to oxygen and the fact that it has been shown that manganese has been involved in that process led us to suppose that the manganese involved

was at least a dimer, consisting of two manganese ions which were passing between two oxidation states, +2 manganese and + 4 manganese.[10,11]

If manganese atoms act together through two electron changes, then the total charge is four electrons. If such a manganese dimer, or higher polymer, could be synthesized to perform this reaction, it should be possible to construct a soluble synthetic catalyst for making molecular oxygen.

We undertook an electrochemical examination of the stable and readily available manganese porphyrin compounds in the solid state to see what the redox behavior might actually be with the manganese atoms in close proximity in a crystal even if not in a single molecule.[12] A surfactant manganese porphyrin, MnTPPyP-C_{16}, was spread carefully on the surface of a glassy carbon electrode arranged in a cyclic voltammeter.. The electrode is cycled through a oxidation potential above +1.5 volts and down to a reduction potential of -1.0 volt. The results indicate that there is a very deep wave as the reaction goes oxidation in the presence of manganese, meaning that the oxidation is not of the manganese alone but is a catalytic oxidation of the water. The current is much greater than the amount of manganese present. When the current sweeps back, there is no +4 manganese to be reduced to +3 manganese; it is already at the +2 manganese level and a trace of oxygen. We oxidized the coated electrode at a controlled potential, about +1.25 volts. At this point, the manganese should have been oxidized from the +3 state to the +4 state. We then dissolved the manganese off the electrode and examined the absorption spectra (Figure 2). The results of the control experiment, in which the manganese is placed on the electrode and dissolved off without further modification, are also shown in Figure 2. The spectrum of the compound that is dissolved off the electrode which has been oxidized at + 1.25 volts is mostly +3 manganese (460 nm)), but the hump at 442 nm in Figure 2 is +2 manganese. When air is blown through this finally dissolved system, the +2 manganese ($\sim$10% of the total) is immediately oxidized to +3 manganese, quantitatively equivalent to the starting material.



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

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Figure 2

We have demonstrated that the oxidation of +3 manganese results in the production of some +2 manganese which is what the previous theory implied. Presumably the amount of +2 manganese 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 +4 manganese reverts to +2 manganese with the 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, thickness of the layers and other matters which have not yet been investigated.

These results suggest that the original concept is correct: That is, the participation of two manganese atoms through a redox cycle leads to evolution of oxygen. Therefore, binuclear complexes containing at least two manganese atoms would have to be constructed to be stable in the solution environment in order for the system to perform successfully as a soluble 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 photooxidized manganese species at the interface at a pH at which would be stable as a manganese complex of any oxidation number. Electrochemical studies of such organized assemblies may contribute an important clue.

We then set out to oxidize manganese on the surface of a vesicle on the assumption that lateral mobility in the vesicle would permit cooperation of two manganese porphyrin molecules to generate oxygen, shown diagrammatically in Figure 3. We started this effort by constructing a surfactant zinc porphyrin and a surfactant manganese porphyrin, both of which can move about laterally quite easily in the membrane. We then tried to demonstrate the oxidation of manganese by sensitizing the reaction mixture with zinc porphyrin, which would be the analog of chlorophyll. The experimental results indicated this system might be correct.[13] The difference spectra of the manganese and zinc porphyrin system, and that of the zinc porphyrin and propylviologen

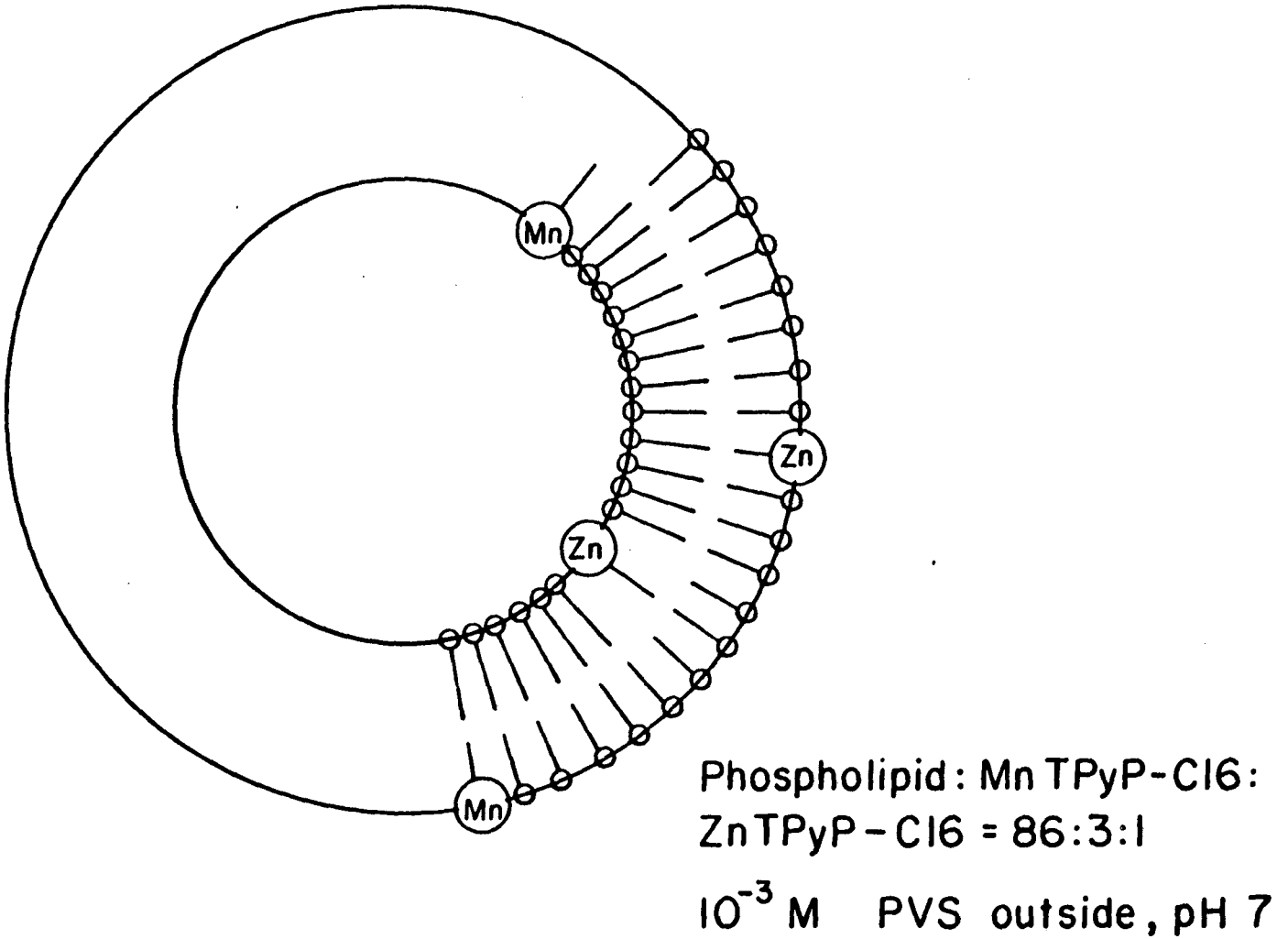

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Figure 3. Single unilamellar vesicle with a diameter between 200 and 500 A, prepared by sonication and indicated ratio between phospholipid and photosensitizer of 86:3:1 with the PVS added on the outside of the vesicle

sulfonate, seemed to indicate that we had succeeded. However, one of the absorption peaks (420 nm) is that of a free porphyrin and not of the +4 manganese as we had first supposed. We are not sure how that 420 nm peak came to exist. Either the +3 manganese was oxidized to +4 manganese, and two of them came together to give oxygen, in which case the +4 manganese would go down to the +2 manganese level. It turns out that at pH 6 the +2 manganese ion is immediately ejected from the porphyrin molecule with the result that free porphyrin is formed.

An alternative possibility would be the direct photochemical reduction of +3 manganese porphyrin to + 2 manganese porphyrin, followed by its decomposition. Since thee are three times as many manganese atoms as zinc atoms in the membrane, the zinc porphyrin cation radical would have to be reduced and recycled to achieve this result.At the moment what might reduce the zinc cation radical in that case is undertain. It remains for future flash photolysis experiments to determine the actual sequence of results and the method of preventing direct electron transfer from excited zinc porphyrin to +3 manganese porphyrin to produce +2 manganese porphyrin (if it occurs) by competition from other, more plentiful, acceptors.

PARTICLE SYSTEMS

It occurred to us that it might be possible to use a surface potential to achieve charge separation without having the charge go across a membrane boundary.[14,15] It is possible to arrange the system in such a way that the surface potential of the interface will be the controlling factor in the efficiency of electron transfer if the right particles are used with the correct charge distribution and proper structure of donors/acceptors/sensitizers. We chose silica particles which are highly negatively charged to test this idea, performing the experiments at pH 9 to be sure that the positive sensitizer is closely attached to the negatively charged surface.[16] Thus, back reaction of the two materials which should go energetically back downhill may be prevented (Figure 4).

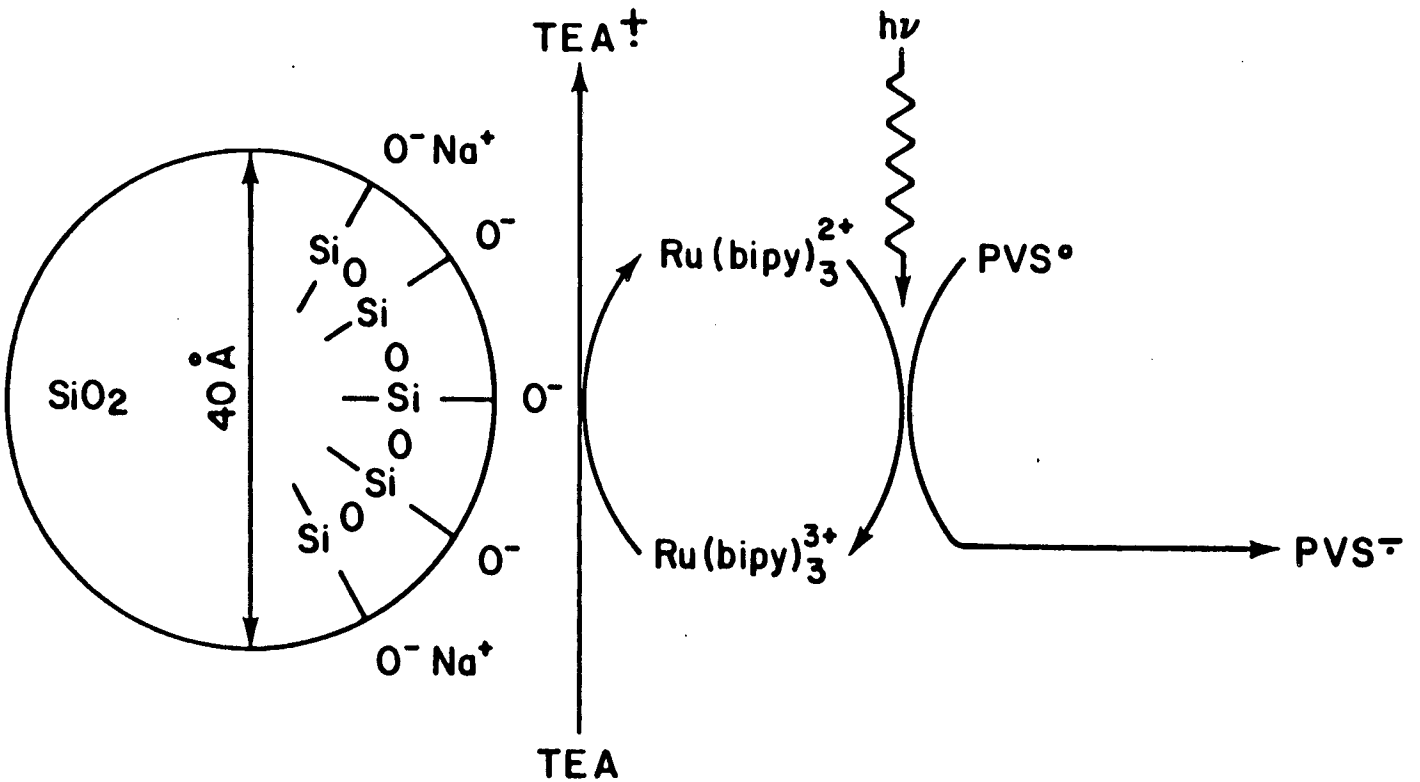

Figure 4. Schematic function of SiO_2 particles in separating photoproducts

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There is now a way to use negatively charged surfaces of different surface potential, and by careful adjustment of the particles to modify the back reaction. In another experiment with the same type of system we learned that it is not possible to reduce ferricyanide, with three negative charges, on silica alone; when propylviologen sulfonate (zero net charge)is added to the mixture, the reaction goes forward. This is a shuttle system, with a cationic sensitizer and an initially neutral shuttle, to take the electrons from triethanolamine, for example, and deposit them on the ferricyanide negative ion which cannot approach the silica particle. The shuttle system is much more efficient than the sum of the two separate systems, i.e. silica particles plus propylviologen sulfonate plus ferricyanide vs. silica particles and ferricyanide or silica particles and PVS. The experimental results indicate a synergistic effect because the propylviologen sulfonate is regenerated very rapidly (Figure 5).

It is possible to move electrons from a highly negative environment to an environment of lower negative surface potential to make hydrogen and oxygen. The surface potential can be adjusted at will, thus controlling the approach of the particles to the surface. This new type system would contain two different particles which, with proper catalysts, can produce molecular oxygen and, through the use of a shuttle system, molecular hydrogen. The system can be used in two separate vessels, connected by a diffusion barrier which will not allow the negatively charged particles to cross.

In the system described above the back reaction between oppositely charged photoproducts was slowed down by the addition of a charged interface in the form of colloidal silica particles. In order to maintain a high charge density on the silica surface, the pH of the solution must be 9 or greater. Reduced PVS radical cannot be used to produce hydrogen at a pH greater than 7. In order to maintain a high charge density at a pH value where hydrogen production is possible, a surface with ionizable groups with a significantly lower pK was necessary, e.g., the sulfonate group.[17] As sulfonated colloial particles were not readily available, we began to study the effect of the linear, water soluble

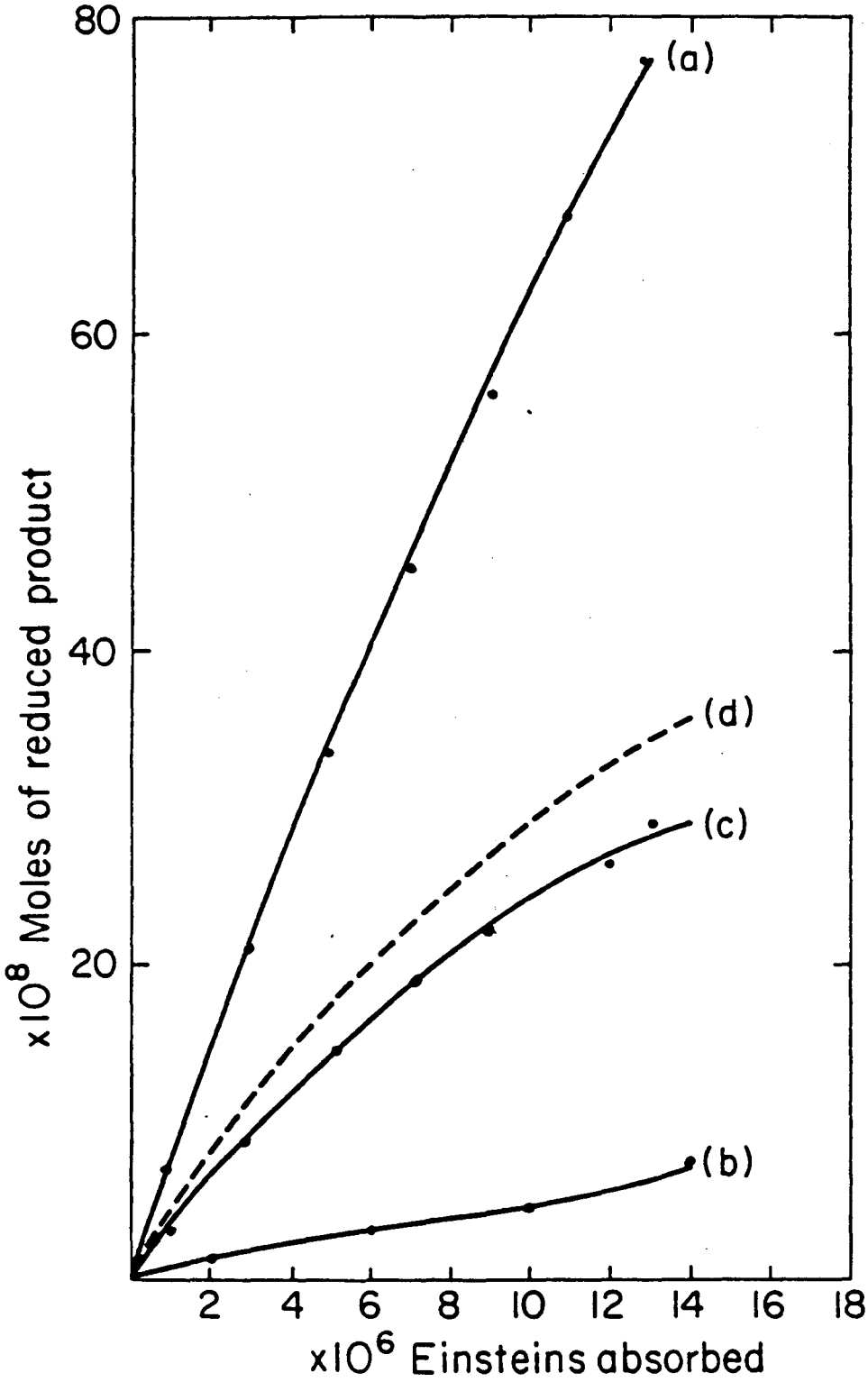

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Figure 5 Formation of reduced products in the heterogeneous system containing 0.2% SiO_2 as a function of light absorbed showing synergism of PVS^0 shuttle. (a) complete system, (b) system containing sensitizer with ferricyanide only, (c) system containing sensitizer with PVS^0 only, (d) calculated sum of (c) + (b)

polyelectrolyte, poly(styrene sulfonate)[PSS] on the back reaction between oxidized $ZnTMPyP^{5+}$ and propylviologen sulfonate radical cation. Polyelectrolytes have been shown to decrease the rate of reaction between oppositely charged species.[18] The sulfonate groups of the polyelectrolyte remain charged even under acidic conditions. Changes in the absorption spectrum of $ZnTMPyP^{4+}$ upon the addition of PSS indicate a strong binding of $ZnTMPyP^{4+}$ to the anionic PSS.

In continuous photolysis experiments at pH 9.8, using $ZnTMPyP^{4+}$ as photosensitizer, PVS^{0} as electron acceptor and triethanolamine as a sacrificial electron donor, the addition of PSS resulted in a twofold increase in quantum yield,, which compares poorly to the 38-fold increase upon the addition of silica particles. Flash photolysis experiments using $ZnTMPyP^{4+}$, PVS and PSS with no sacrificial donor at pH 5 show that the back reaction between $ZnTMPyP^{5+}$ and PVS^{-} is indeed decreased by a total of 25 in the presence of PSS. Unexpectedly, however, these experiments show that the forward reaction between the cation porphyrin and neutral (but zwitterionic) PVS is also decreased significantly relatively to solutions containing no polyelectrolyte. Preliminary electrochemical measurements of the peak current density of PVS reduction in the presence of PSS indicate that there may be some association between the PVS and PSS. Further investigations are in progress.

Sulfonated polystyrene microspheres of 2000 A diameter (Figure 6) have been prepared by the addition of a chlorosulfonic acid/PCl_3 mixture to a crosslinked styrene/divinyl benzene copolymer prepared by emulsion copolymerization. Continuous and flash photolysis experiments using these particles are currently underway[16] .

PHOTOCHEMICAL REDUCTION OF CARBON DIOXIDE

One important desideratum of artificial photosynthesis would be the photoinduced reduction of carbon dioxide to various, more useful compounds.It is very difficult to activate CO_2 or to complex it as a

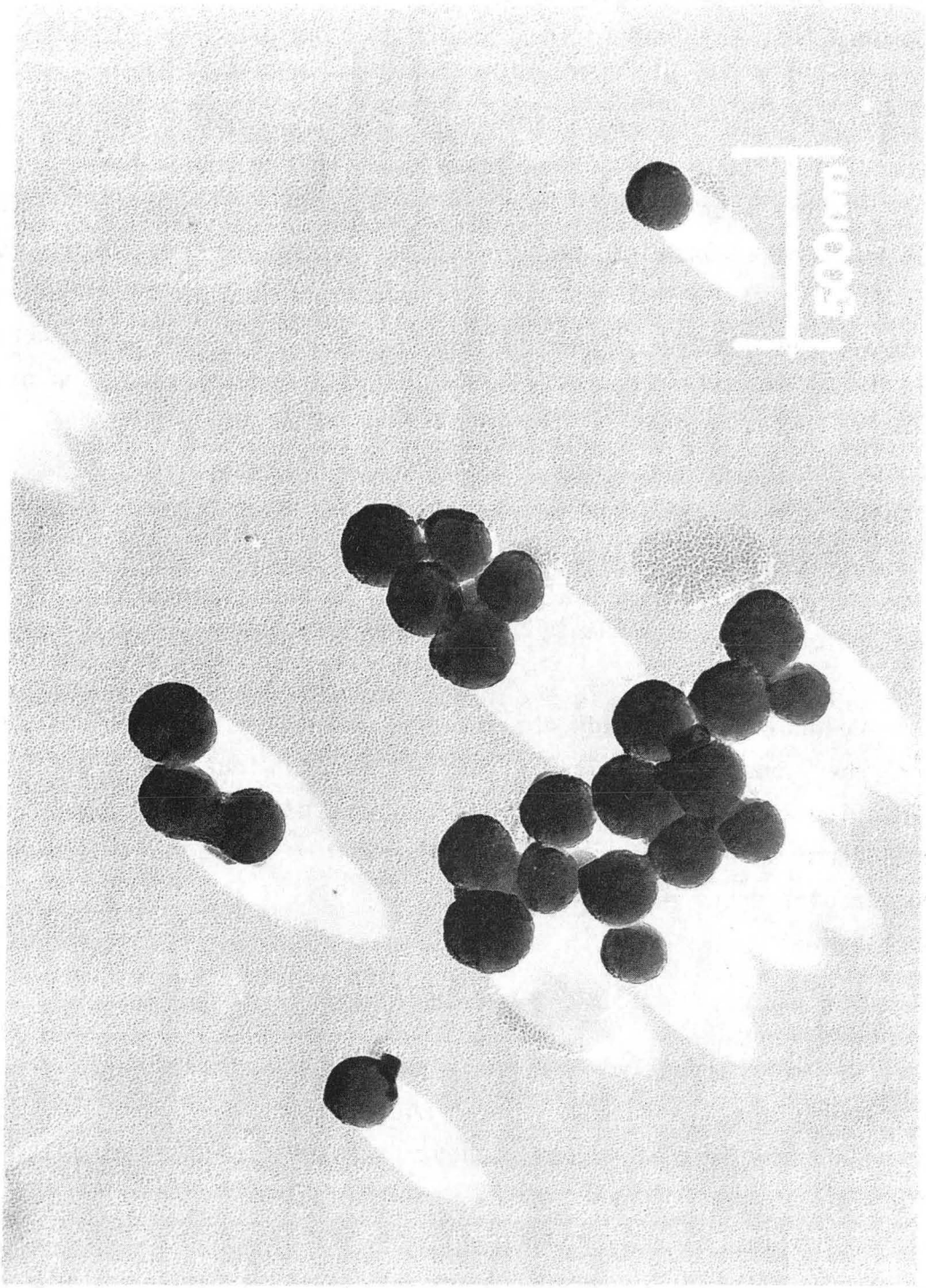

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Figure 6. Electron micrograph of sulfonated polystyrene microspheres of 2000 A diameter

ligand to transition metal compounds. Recently, however, information has appeared that may lead to the acomplishment of CO_2 reduction.

Certain methanogenic bacteria, that is, those that catalyze the reduction of CO_2 to CH_4 have been known to require nickel in order to grow. It has been found in Methanobacterium thermoautotrophicum that the active enzyme contains two nickel atoms per protein in the unusual oxidation state of +3 nickel. Also, certain classes of nickel complex exist, such as complexes with peptides, thiolate and macrocyclic ligands, that have redox potentials adequate for the reduction of CO_2 to CO and could, therefore, serve as biomimetic models. Indeed some of these complexes have been shown to catalyze electrochemical CO_2 reduction.[19] If these nickel compounds, or some similar ones, can be photoreduced with the aid of a sensitizer such as porphyrin, we would have the ingredients of a CO_2 system. Numerous electron donors could then be considered as ultimate reducing agents for the process.

We would first study the known nickel complexes electrochemically, and when one with suitable properties is found its photochemical reduction would be attempted. The overall process would be the photochemical reduction of CO_2 with visible light to CO or any of a number of reduced organic products.

CONCLUSION

We are currently involved with: (a) Construction of a suitable stable binuclear (probably surfactant) manganese or ruthenium catalyst to generate molecular oxygen without decomposition; (b) establishment of electron transfer over thick membranes; and (c) production of microparticles of polystyrene which have been sulfonated to create a material which will behave like silica but at a lower pH. Also, we are attempting to find catalysts to bind carbon dioxide, which will catch the electron(s) from the photochemical reaction and reduce carbon dioxide through formic acid, formaldehyde and oxalic acid, ultimately to achieve methanol as our desirable final product.

REFERENCES

1. M. Calvin. Acc. Chem. Res. 11, 369 (1978); Energy Res. 3, 73 (1979); Faraday Soc. Disc. 70, 383 (1980); Photochem. Photobiol. 37, 349 (1983); Can. J. Chem. 61(3), 83 (1983).

2. J. S. Connolly (ed). "Photochemical Conversion and Storage of Solar Energy", Academic Press, New York (1981). J. P. Bolton and D. O. Hall. Ann. Rev. Energy 4, 353 (1979).

3. J. H. Fendler. Acc. Chem. Res. 13, 7 (1980).

4. A. D. Bangham. Biol. Cell. 47, 1 (1983).

5. David E. Baker. Energy Interactions and Phospholipid Vesicles. M.S. Thesis, University of California, Berkeley, June 1982. LBL 14673.

6. N. J. Turro, M. Gratzel and A. M. Braun. Angew. Chem. Int. Ed. Eng. 19, 675 (1980).

7. T. Ohsako, T. Sakamoto and T. Matsuo. Chem. Lett. (Japan), 1675 (1983).

8. W. E. Ford, J. W. Otvos and Melvin Calvin. Nature, 272, 507 (1978).

9. W. E. Ford, J. W. Otvos and Melvin Calvin. Proc. Natl. Acad. Sci. U.S.A. 76, 3590 (1979).

10. S. R. Cooper and Melvin Calvin. J. Am. Chem. Soc. 99, 6623 (1977). S. R. Cooper, G. C. Dismukes, M. P. Klein and Melvin Calvin. J. Am. Chem. Soc. 100, 7138 (1978).

11. O. Bortolini and B. Meunier. J. Chem. Soc. Chem. Commun. 1983, 1364.

12. R. Wohlgemuth, J. W. Otvos and Melvin Calvin; to be published.

13. R. Wohlgemuth, J. W. Otvos and Melvin Calvin. Proc. Natl. Acad. Sci. U.S.A. 79, 5111 (1982).

14. I. Willner, C. Laane, J. W. Otvos and Melvin Calvin. ACS Symp. Series 177, 71 (1982).

15. J. Kiwi, K. Kalyanasundarm and M. Gratzel. Structure and Bonding, 49, 39 (1982).

16. I. Willner, J. W. Otvos and Melvin Calvin. J. Am. Chem. Soc. 103, 3203 (1981).

17. N. Ise, T. Okubo and S. Kunigi. Acc. Chem. Res. 15, 171 (1982).

18. T. Casti, J. W. Otvos and Melvin Calvin; to be published.

19. A. J. Thomson. Nature, 298, 602 (1982).

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