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ARTIFICIAL PHOTOSYNTHESIS

M. Calvin

June 1986

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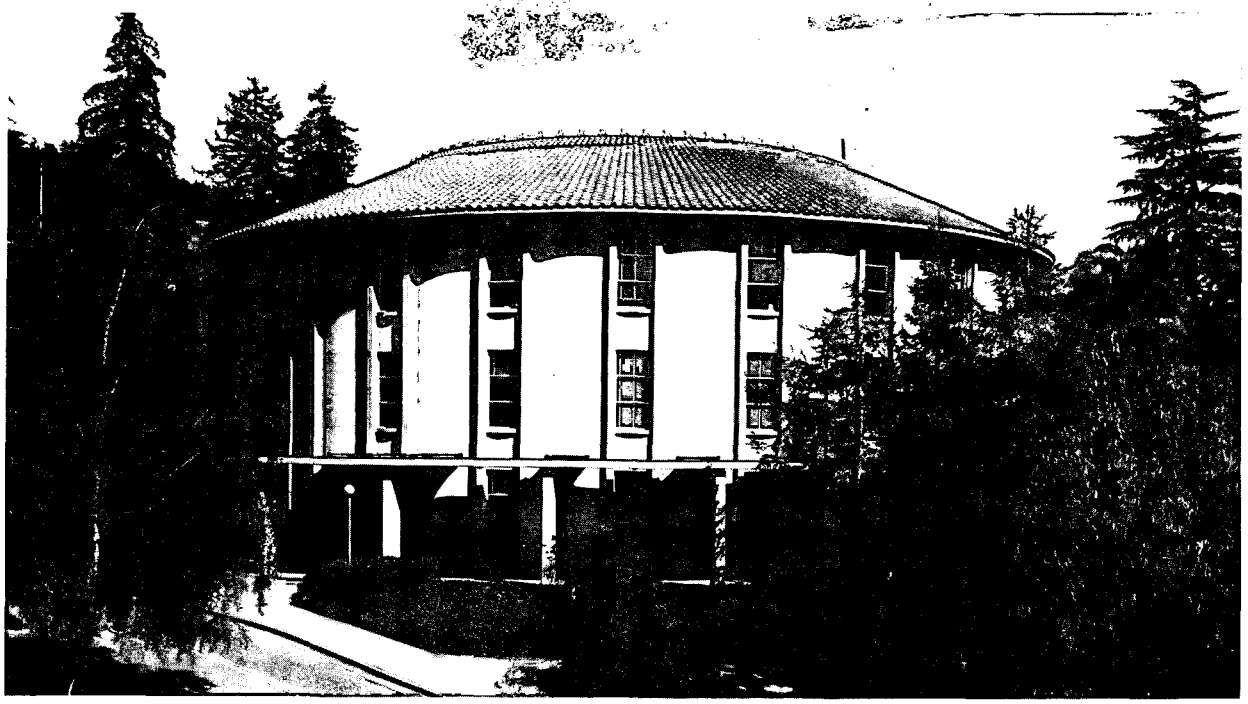

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ARTIFICIAL PHOTOSYNTHESIS

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ABSTRACT

The principal factor enabling green plants to convert incoming visible quanta into some stable chemical form long enough to do secondary chemical reactions for storage involves the separation of charge across a phase boundary (e.g., membrane-water). The positive charge, or hole, ultimately is used to generate oxygen from water by electron withdrawal and the negative charge is ultimately used to reduce carbon dioxide. In our synthetic system, at least in its first phase, we are concerned with the conversion of the negative charge to hydrogen (later to reduce carbon dioxide) and the positive charge to oxygen or possibly some oxidized products otherwise difficult to obtain. The first step requires not only the stabilization of the excited state to some extent but more importantly the stabilization of the produced charge separation. The final result of this effort will be to produce a device in which the reduction and the oxidation steps are contained either in separate parts of the device or separated by a membrane which keeps the ultimate reduction and oxidation productions from back reacting.

Presented at the 41st Northwest Regional Meeting of the American Chemical Society, Portland, Oregon, June 14, 1986.

INTRODUCTION

In examining the natural photosynthetic process it seemed that the basic physical phenomenon which allows the green plant to be the best converter of solar quanta that exists today is the fact that it has evolved a system of photoelectron transfer which involves the transfer of an electron across a phase boundary of some type. When we began this work about fifteen years ago all we really knew was that the various constituents of the electron transfer system were situated on a membrane in such a way that the electron transfer occurred across that membrane from one water phase into an oil phase and then again into another water phase. That seemed to us to be the essential feature which allowed the plant to convert quanta into stored chemical energy relatively efficiently.[1-3]

There are a number of ways in which such a system can be assembled. The simplest way is to use the surface potential of a semiconductor between the solid and the liquid phase as the device for separating the charge.[4] In fact, that was the first way we undertook to solve this problem in the laboratory. It seemed, however, that we should be more imaginative and try to find at least partially self-organizing systems which would provide a phase boundary (oil-water phase boundary) related in some way to the natural one.

Just recently it has been possible to observe enough detail of structure of the natural system in which that electron transfer occurs in nature to give us information as to how we might construct a synthetic system which would do this, in other words, mimicking more closely the natural process of quantum conversion.[5]

RESULTS AND DISCUSSION

When we began this investigation all we knew was that the system was primarily a membrane, and in and on that membrane were various constituents which allowed the electron to be transferred through it. The evidence for that was in several forms, including electron micrographs of the physical structure of the natural photosynthetic apparatus in its various layers, indicating protein components that were extruded on two sides of the membrane and having different appearances. This led us to the notion that the electron transfer took place through that membrane. The essential features of the process involve the absorption of two quanta, leading to the transfer of an electron from a manganese catalyst on one side of the membrane, finally leading through ferredoxin on the other side to the reducing power which runs the CO_2 reduction cycle. It was not a very far fetched notion to suppose that we could construct a system which would somehow simulate this arrangement, particularly in a self-organizing system. In this photosynthetic electron transfer scheme there are two sensitizers present, and on one end of the system there is a series of catalysts which permit the hole, left behind, to take electrons from water and generate oxygen. At the other end there is another series of electron transfer catalysts which can be intercepted before they reach CO_2, and hydrogen can be generated from the ferredoxin or NADPH. However, it did not seem necessary to try

to reproduce synthetically the entire electron transfer scheme, and the easiest thing to do would be to find the membrane, the sensitizers and the catalysts on each side which would produce oxygen or some intermediate oxidant on one side and hydrogen or some intermediate on the other side which might eventually be used to reduce CO_2. That was the essential feature that we endeavored to reproduce.

The first task was to find sensitizers, either donors or acceptors which would automatically find their way into a membrane. Chlorophyll, after all, is a surfactant dyestuff, but it is not a very satisfactory molecule to work with in this instance. For a device which we wanted to be totally synthetic we should use a synthetic surfactant sensitizer. The basic structures of the compounds we used are shown in Figure 1. The ruthenium tris-bipyridyl shown here, for example, does not exhibit surfactant properties until one places on one of the positions of one bipyridyl (usually the position para to the nitrogen) a carboxyl group on each side of a bipyridyl and then treats the carboxyl group in such a way as to make a long chain amide from it. By doing this for one of the three bipyridyl groups it is possible to obtain a surfactant $Ru(bipy)_3$ sensitizer/ In the case of the porphyrin, one can get organic-soluble sensitizers, or one can get water-soluble cations or water-soluble anions. If one of the pyridinium groups of tetrapyridyl porphyrin has a long chain attached (C_{16} or C_{18}) we would then have a surfactant porphyrin as well. We did prepare compounds of this type for use in our photochemical studies. For electron acceptors we used the general structure of bipyridinium compounds, such as propylviologen sulfonate (PVS), a neutral dipolar molecule which becomes negative upon addition of an electron to give the free radical of the bis-pyridinium monoanion ion.

Experiments to determine photosensitized electron transfer across a membrane (such as a lipid vesicle wall) were performed[6-8], and the scheme for this process is illustrated in Figure 2.[2]. The ruthenium sensitizer with the two tails finds it way to both sides of the membrane. Initially, we used purified natural phospholipid to make a vesicle. (Thirty years ago when vesicles of this type were first made by a British physiologist, A. D. Bangham, they were called liposomes. When I first heard of them I tried to call them "bangasomes", after Dr. Bangham, but he did not approve of that, so the term liposomes was used for many years. Gradually the physical chemists took over this concept and these hollow spheres are now called vesicles, for obvious reasons.)

Originally phospholipid from, for example, egg lecithin dissolved in an organic solvent which is miscible with water was used, and then this solution was injected into the water. Vesicles can be made from any two tailed surfactant lipid, either natural or synthetic. The phospholipid, of course, is not water soluble and tends to come out of the water as a bilayer. If the mixture is violently shaken, the bilayer rolls up into hollow spheres; they are double membranes, which are microspheres of the order of 500 A diameter (20-40 A thick). The membrane in Figure 2 is made in the fashion I have just described, and if this is done in the presence of the surfactant dye, the dye will lodge on both sides of the membrane. The details of where it lies have not been determined specifically to find the depth at which such a

surfactant dye might be found in a membrane. In general, they are on the surface with the tails projecting into the bilipid membrane and the heads near the water surface of the membrane, on both sides of it.

The electron acceptor (in this case heptylviologen, HV) is on one side of the membrane (in this case, outside). If colloidal platinum is placed on the outside of the membrane, together with the viologen we could get molecular hydrogen generated from the semireduced viologen. On the other side ofthe membrane we needed a donor which would ultimately take electrons from water. We have not yet found that donor in a homogeneous condition, but in a heterogeneous situation, including $Ru(bipy)_3^{2+}$ plus ruthenium dioxide, the colloidal RuO_2 micro solid is a very good catalyst for accmulating four electrons which it can do by taking the electrons from water, the electrons being removed by the oxidized ruthenium bipyridyl in a water-soluble condition. The colloidal ruthenium oxide when reacting with $Ru^{+3}(bipy)_3$, will produce molecular oxygen. We thus have developed the surfactant sensitizer, the acceptor catalyst, and the donor catalyst system. As a beginning, we used a sacrificial donor--ethylenediaminetetraacetic acid (EDTA)--to demonstrate electron transfer through the membrane.

The size of the vesicles which we made from phospholipids (phosphatidyl choline, for example) is about 500 A in diameter and the thickness of the phosphatidyl choline bilayer is about 40 A, with the subtraction, of the $Ru^{2+}(bipy)_3$ heads at about 15 A each. It turned out that it was not necessary to have present either the quinone or the borane cation-carrier in order for the electron to be transferred through the membrane. The heptylviologen distributes itself between the external surface of the membrane and the water layer. The methylviologen does not go at all into the surface. Since electron transfer and exchange is more rapid to the surface heptylviologen than to the water methylviologen, the reaction proceeds most rapidly then (Figure 3). If the the heptylviologen is not used and we used only methylviologen which does not distribute between the lipid and the water, the reaction goes more slowly.

Here we have the evidence that the electron does indeed get transferred from the inside of the membrane, where the EDTA (which does not permeate the membrane) is the electron donor, to the methylviologen on the outside of the membrane which is the electron acceptor.[9] When this reaction is done in the absence of the membrane the only time it works is when EDTA is present in the same phase (water) as the electron acceptor viologen. Keep in mind that the distance across the membrane through which the electrons hop, i.e., between the two rutheniums on the opposite sides of the membranes, is something less than 40 A because of the penetration of the membrane by the ruthenium heads.

Recently a very nice experiment was performed which measured the rate of electron transfer between two sites separated by fixed and known distance of saturated hydrocarbon (Figure 4).[10] This shows a molecule in which one can vary the distance between the donor and the acceptor. It turns out that when this molecule is flashed with a 5 picosecond pulse you get a cation radical at the naphthalene end, an anion radical at the

cyanoethylene end, and a huge dipole which is measurable with a quantum conversion value of 1 for all the distances shown. The rate at which the electron and hole recombine through the saturated rigid system was measured. The center-to-center distance is plotted in nanoseconds on the abscissa against the lifetime of the charge separated state produced by the flash. The logarithm of the lifetime increases linearly with the distance, and at 20 A, a little bit shorter than what we believe to be the distance between the two ruthenium heads in the viologen layer, the lifetime is 500 nanoseconds. This data confirms the fact that it is quite easy to to achieve the electron transfer across such a bilipid membrane as we did in our experiments. The demonstration of the electron transfer across the bilipid membrane can be taken as an experimental fact.

The problem now is to devise catalysts for both sides. The acceptor and the catalyst for the reduction side of the reaction are well established; the viologen radical with colloidal platinum as the catalyst will produce molecular hydrogen using a $Ru(bipy)_3^{2+}$ sensitizer with a Ni(II) cyclam catalyst.[11] On the other side of the membrane, as shown in Figure 2, we used a sacrificial donor (EDTA), but we also know it is possible to have the reaction proceed using water-soluble $Ru^{+2}_{+3}(bipy)_3$ and colloidal ruthenium oxide. When the ruthenium goes to Ru^{+3} in the water layer it has the potential to make oxygen slowly, and in the presence of the solid catalyst ruthenium oxide the oxygen is made very efficiently. Putting the entire sequence together, however, is difficult, because one way or the other a colloidal material is required inside of the vesicle, which is difficult. Using either the platinum or ruthenium oxide it would be necessary to place a colloidal material inside the vesicle.

Therefore, a great deal of time has been spent in searching for homogeneous materials which will perform the same functions, i.e., homogeneous catalysts that will produce hydrogen or homogeneous catalysts that will produce oxygen. There is a soluble binuclear platinum compound which apparently can, when it is reduced, produce molecular hydrogen.[12] The homogeneous oxygen catalyst, on the other hand, is less easily visualized. While it is true that apparently some of the bipyridyl complexes seem to be able to produce molecular oxygen, it is not a very clean reaction and not unambigous,[13] since the oxygen was identified only by means of cyclic voltammetry and the question of the homogeneity or heterogeneity of the catalyst remains. More recently a trinuclear ruthenium complex has been identified[14] as a homogeneous catalyst with direct measurement of oxygen itself.

We continued to search for additional homogeneous catalysts and our choice was guided by the fact that in the case of natural photosynthesis the catalyst for oxygen production is some kind of a manganese compound.[15] We may now have some clue as to how a manganese porphyrin might work as a catalyst for this reaction, as shown in Figure 5 which shows some of the chemistry of a manganese porphyrin.[16] The stable oxidation number of the manganese in a porphyrin in air under ordinary conditions, whether it is in water or organic solvent, whether it is tetramethylpyridyl or tetraphenyl, is Mn^{+3}. Manganese can be

photochemically oxidized with various agents to get an oxidized form which has the absorption peak at 424 nm. The Mn^{+3} can be reduced by borohydride to the Mn^{+2} state which has an absorption spectrum at 440 nm, as opposed to 476 nm which is Mn^{+3}. We have, therefore, defined the three oxidation states of manganese, by their absorption peaks. We find that when the Mn^{+3} is oxidized to Mn^{+4}, or reduced to Mn^{+2} and oxygen added, the Mn_{424} compound results; this Mn_{424} is ultimately unstable and the compound goes back to Mn^{+3}. At first we thought it must be generating some kind of an oxidized water, but we have so far been unable to find the oxygen.

The structure of the oxidized manganese could be either the oxy-Mn^{+4} or the μ-oxo dimer of the Mn^{+4} as shown in Figure 5. The identity of the Mn_{424} compound is determined by the absorption peak and seems to be the μ-oxo-dimer on the basis of its molecular weight as determined by gel filtration. The factors determining the return to the Mn^{+3} have not yet been established in all details. Figure 6 shows the absorption spectra of the three manganese compounds which are very easily distinguishable in aqueous solutions. This data indicates that the various oxidation states of the manganese are easily distinguishable optically and also that they can be dealt with individually. Figure 7 shows the absorption spectra of several other molecules used together with the manganese compounds in a variety of photochemical experiments. These spectra are used in the determination of the kinetics of the oxidation changes.

The next question was to determine whether or not it would be possible to photooxidize the manganese. This was done through an photooxidation to the $Ru^{+3}(bipy)_3$ which will oxidize the Mn^{+3} to Mn^{+4}. The schematic diagram of this system is shown in Figure 8 where the photoinduced oxidation of the manganese porphyrin took place in homogeneous solution, with the $Ru^{2+}(bipy)3$ as the photosensitizer and $Co(NH3)5Cl^{2+}$ [chloropentamminecobalt(II) chloride] as the electron acceptor.[17] The reaction oxidizes the manganese photochemically. The rates of the oxidation reaction as well as the back reaction are shown in Figure 9. The kinetics of oxidation were complex. The oxidized manganese tetraphenylporphyrin formed is unstable and returns to the original Mn^{+3} species almost quantitatively in about 20 hours. The spectral changes for the return are shown in Figure 9b. The formation of the oxidized manganese tetraphenylporphyrin and its reduction to the Mn^{+3} form can be cycled several times, and at least five cycles of the oxidation-reduction were monitored. At the end of each cycle about 95% of the Mn^{+3} and 100% of the $Ru(bipy)_3^{2+}$ were regenerated.

We evolved a possible route by which the Mn^{+4}_{+3} may produce oxygen from water (Figure 10), the Mn^{+4} going back to Mn^{+3} and oxygen. However, we have never seen the oxygen in this particular system. There seems to be evidence that the Mn^{+4} is such a strong oxidant that it might oxidize the porphyrin ring itself given enough time. Once the porphyrin ring is opened there are a a large number, at least 18, reducing electrons which can then reduce the remaining Mn^{+4} porphyrin molecules to Mn^{+3}, thus allowing for the 95% recovery. If an easily oxidizable substrate such as maleic acid, or 3-butenol-1 is added, the recovery of Mn^{+3} is rapid and 100%. Therefore, it will be necessary to devise systems to produce

the oxygen more rapidly so that there is not enough time to oxidize the porphyrin, or else we must stabilize the porphyrin by suitable substitution so that even with the longer reaction time the porphyrin ring will resist oxidation by the Mn^{+4}.

The actual system that we propose to use is shown in Figure 11, a unilamellar vesicle, using the surfactant ruthenium with a water-soluble manganese inside the vesicle itself and propylviologen sulfonate or heptylviologen on the outside, with bis-hexadecylphosphate (or phospholipid) for the vesicle material. It appears, however, that the manganese is such a strong oxidant that it will destroy an ordinary organic vesicle with carbon-hydrogen bonds, and so we must invent a vesicle or membrane that cannot be destroyed, such as one made of fluorinated hydrocarbon (Nafion membrane).[18] We need to construct a membrane from fluorinated hydrocarbons which will allow us to separate the reduced viologen from the oxidized manganese and perform separate reactions on either side of such a fluorinated membrane.

CONCLUSION

Considerable efforts have been made toward the goal of artificial photosynthesis, to lay the foundation for efficient and economically viable conversion of sunlight to storable high energy compounds. In order to achieve the goal of water decomposition to hydrogen and oxygen by visible light two processes must be achieved: Charge separation by electron transfer across a phase boundary followed by two different catalytic reactions to transform the separated charged into stable separated products.

A device for the photolysis of water might appear as a hollow fiber bundle[19] similar in structure to the artificial kidney. Embedded in the hollow fibers would be the redox stations through which the electrons can be moved and on the outside are the acceptors/donors and catalysts. Having transferred the electron through the membrane it would be possible to produce hydrogen on one side of the membrane and oxygen on the other. The device will ultimately have to be constructed from material which cannot be destroyed by the chemical constituents of the reaction. We are now in the process of developing membranes which will resist the oxidizing power of the Mn^{+4} porphyrin or the $Ru(bipy)_3^{3+}$.

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FIGURE CAPTIONS

Figure 1 Structures of donors/acceptors/sensitizers

Figure 2 Scheme for photosensitized electron transfer across a lipid vesicle wall

Figure 3 Cofactors in photoelectron transfer reactions across a membrane

Figure 4 Charge recombination time as a function of distance between charged centers

Figure 5 Possible structures for manganese porphyrins

Figure 6 Absorption spectra of $MnTMPyP^{n+}$ in aqueous solution

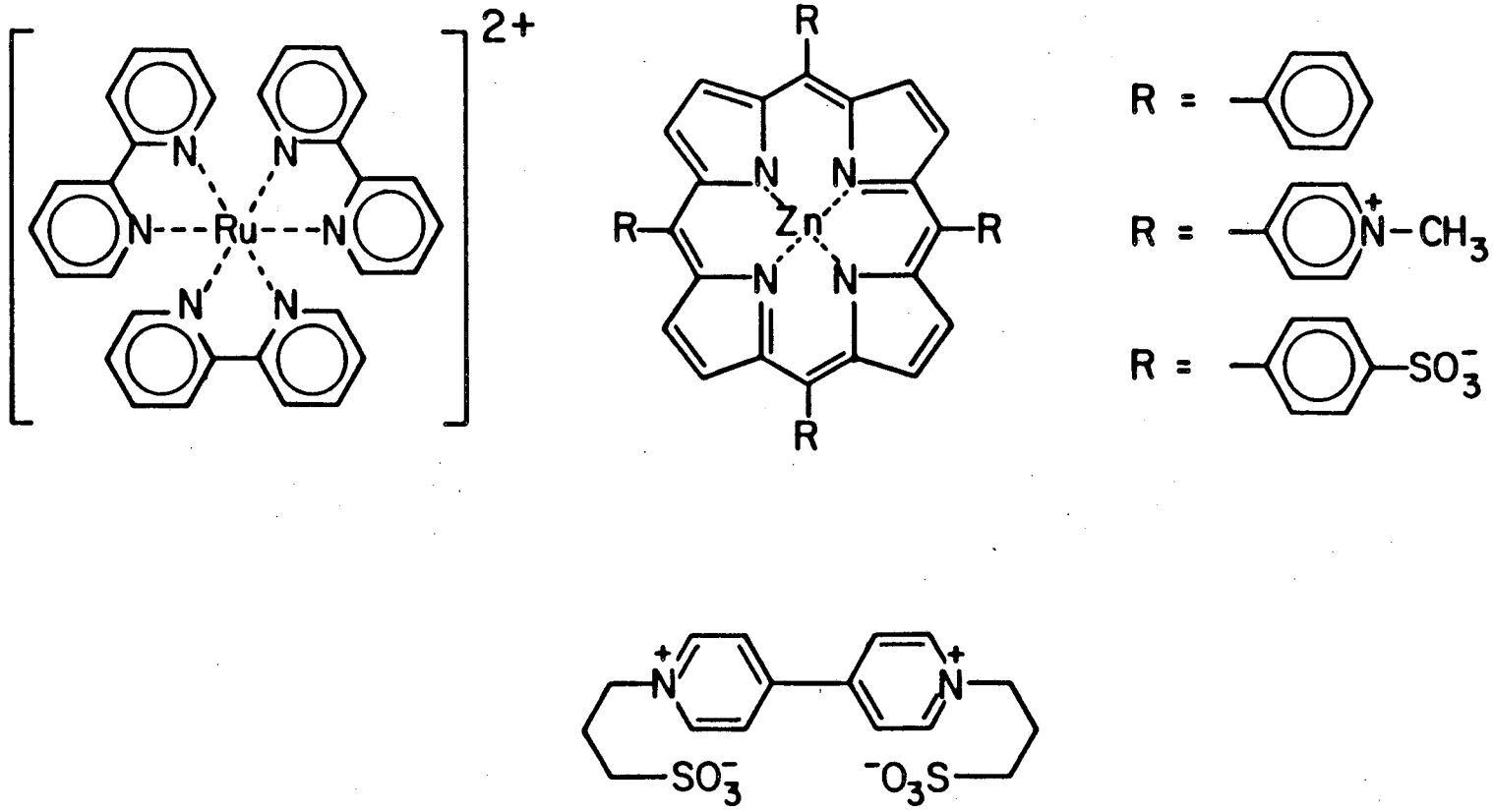
Figure 7 Absorption spectra of $MnTMPyP^{5+}$, $ZnTMPyP^{4+}$ and $Ru(bipy)_3^{2+}$ in aqueous solution

Figure 8 Schematic diagram of the arrangement used in the photoinduced oxidation of Mn^{+3} porphyrin in homogeneous. $Ru(bipy)_3^{2+}$ is the photosensitizer and $Co(NH_3)_5Cl^{2+}$ is the electron acceptor.

Figure 9 Absorption spectra observed with time of illumination in aqueous solution containing $Ru(bipy)_3^{2+}$, $Co(NH_3)_5Cl^{2+}$ and Mn^{+3}

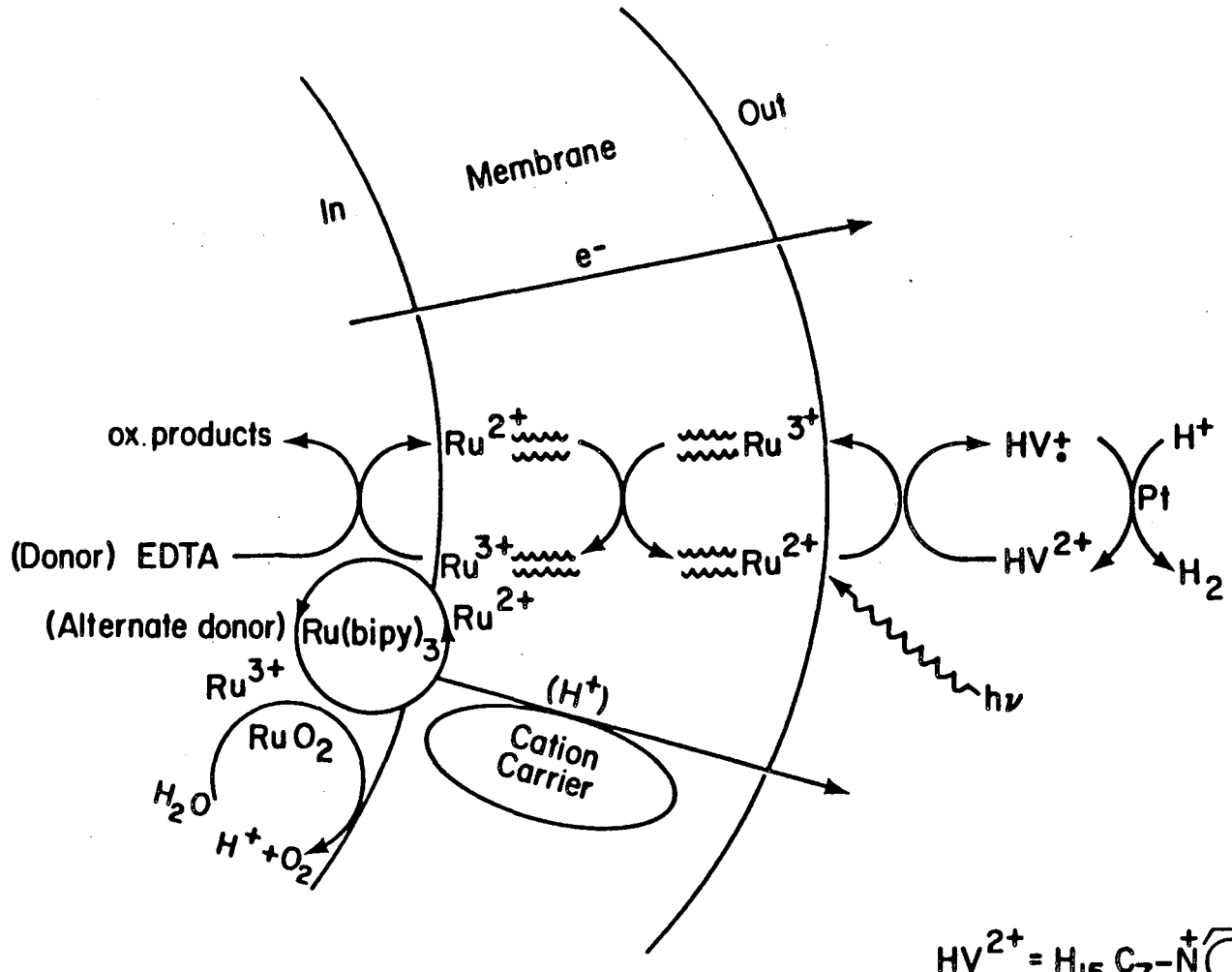
Figure 10 A possible route by which Mn^{+4} may produce oxygen from water

Figure 11 Single unilamellar vesicle



XBL 814-4530

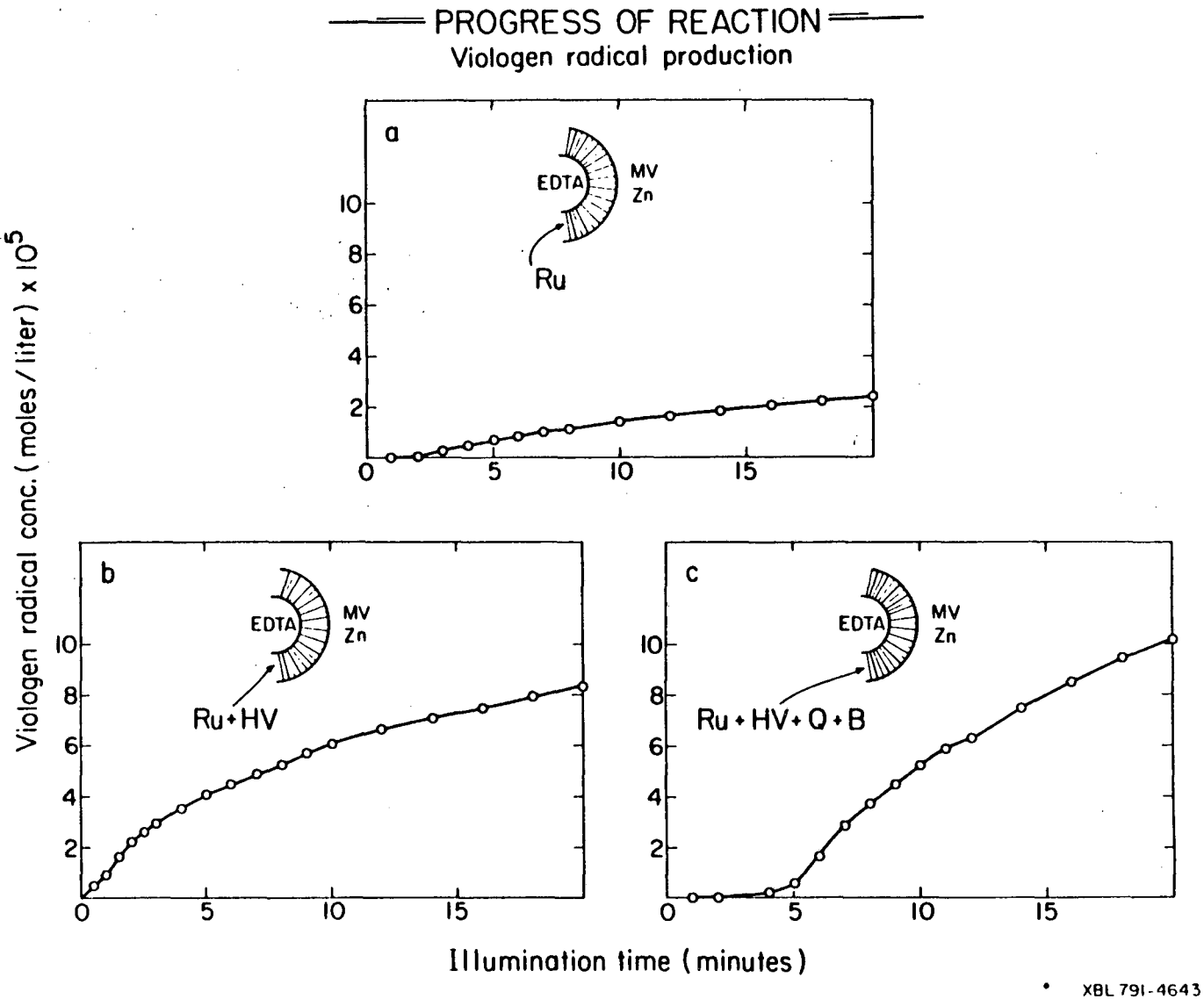
Calvin
Figure 1



$HV^{2+} = H_{15}C_7\text{-}N^{+}\text{-}C_6H_4\text{-}C_6H_4\text{-}N^{+}\text{-}C_7H_{15}$

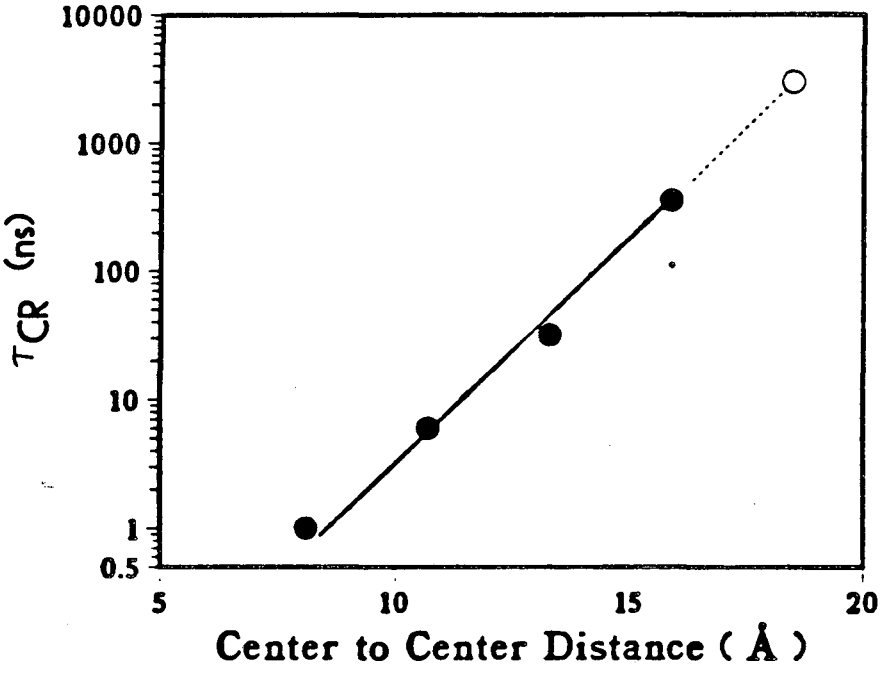
XBL 821-61

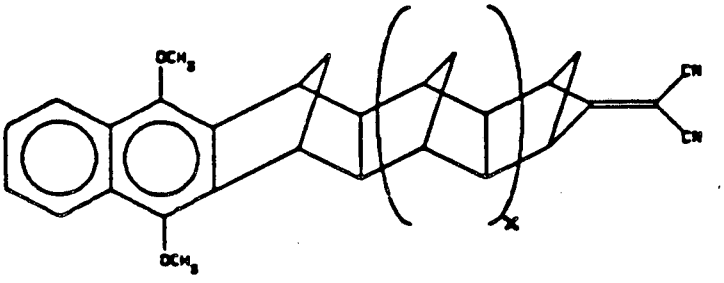
Calvin
Figure 2



Calvin
Figure 3

Charge recombination time as function of distance between charged centers



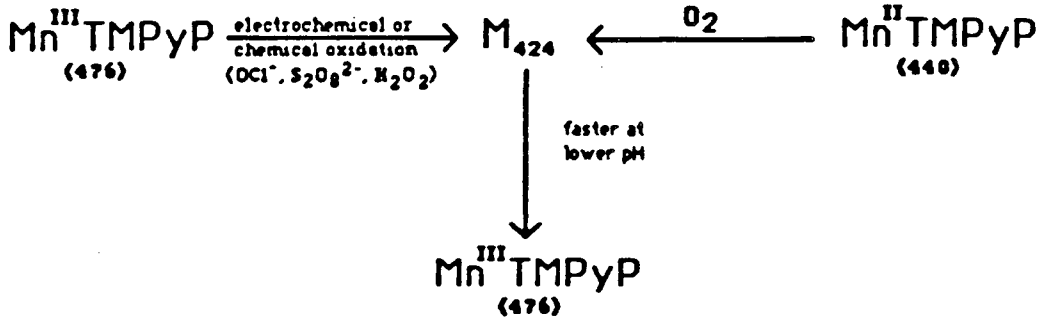


For X =	0	1	2	3	4
C - C d Å =	8.1	10.7	13.3	15.9	18.5

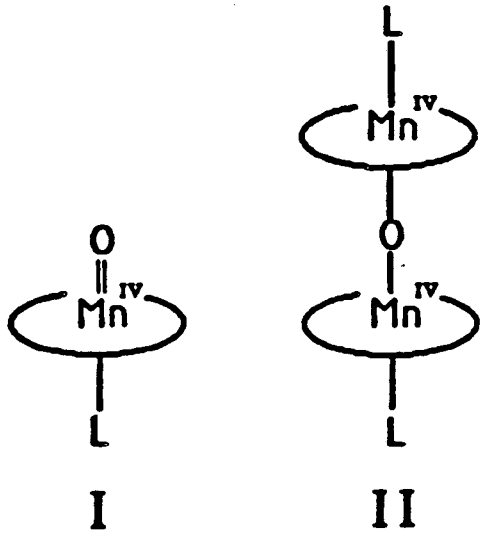
From data of Warman, J. M. et al. *Nature*, 1986, 320, 615.

XBL 865-1856

Calvin
Figure 4



Possible Structures for M_{424}

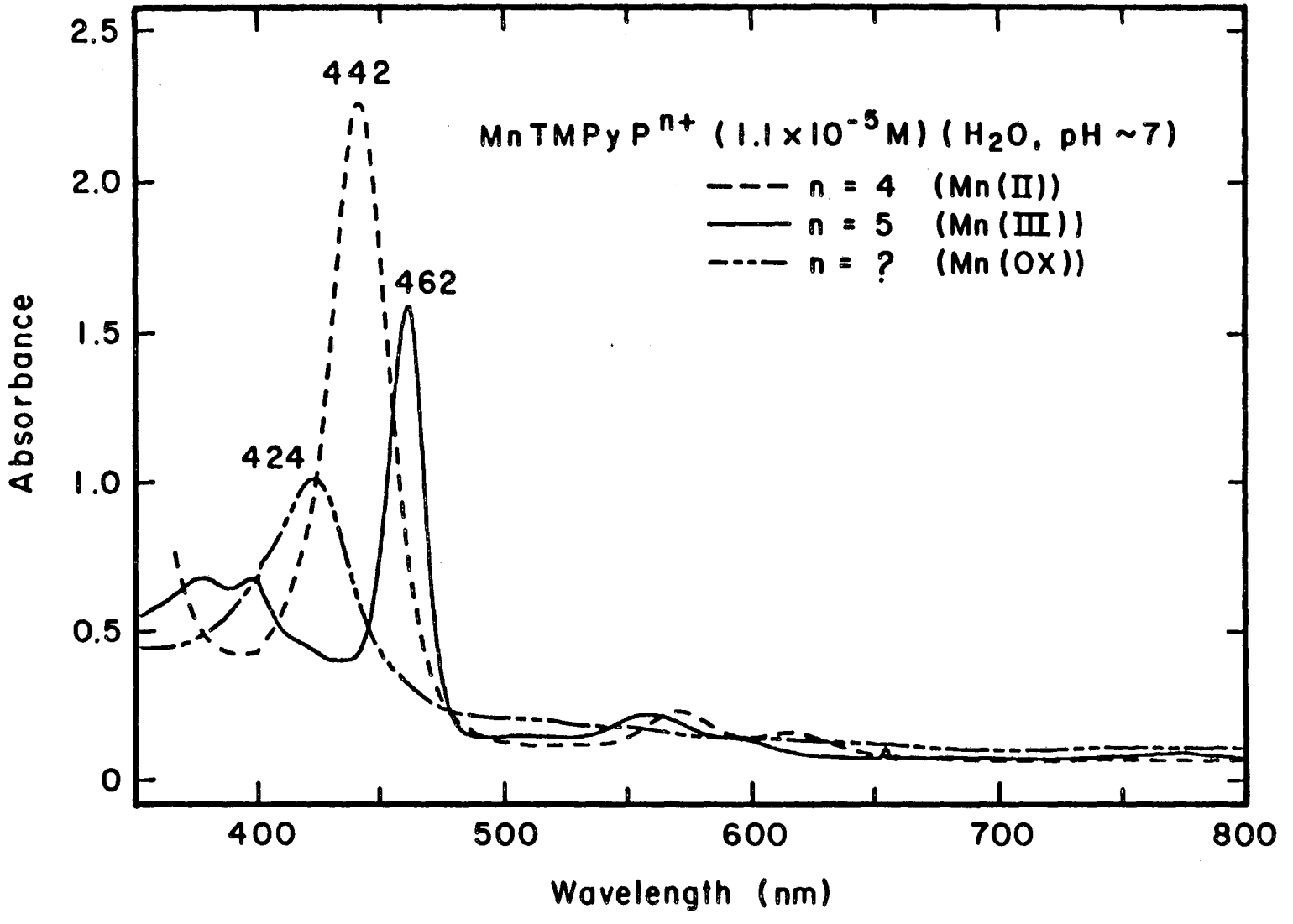


Observations:

1) One electron oxidation
2) M_{424} is a dimeric species (gel chromatography)
3) M_{424} reacts with olefinic compounds

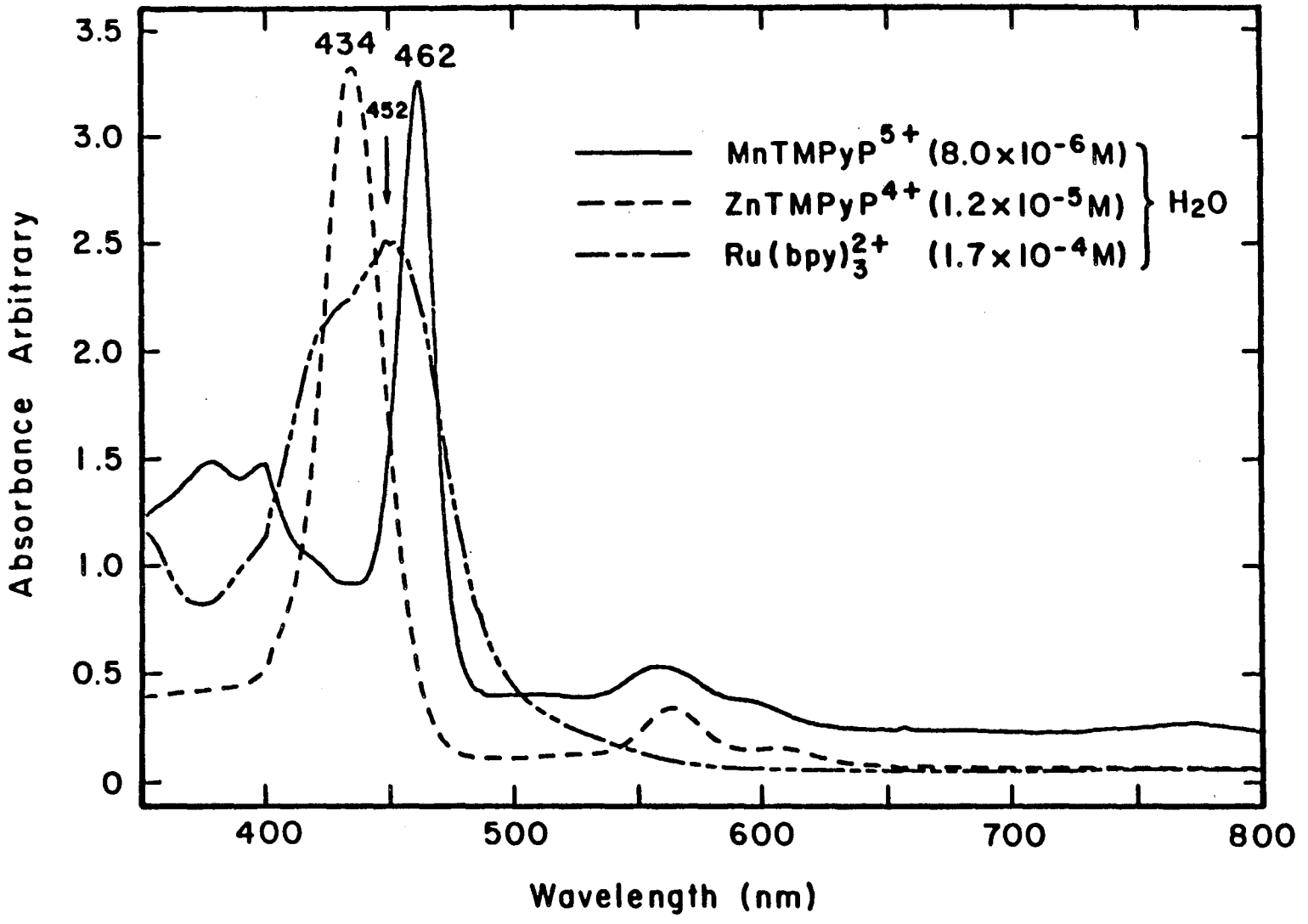
XBL 853-1622

Calvin
Figure 5



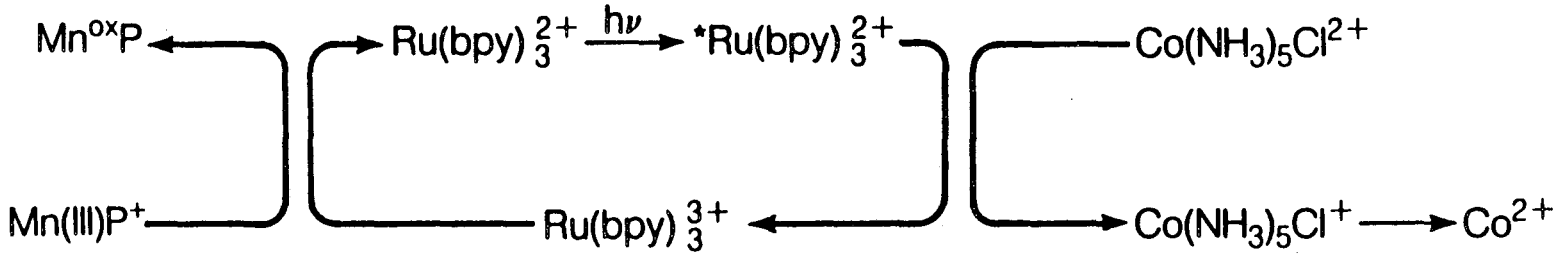
XBL 862-675

Calvin
Figure 6



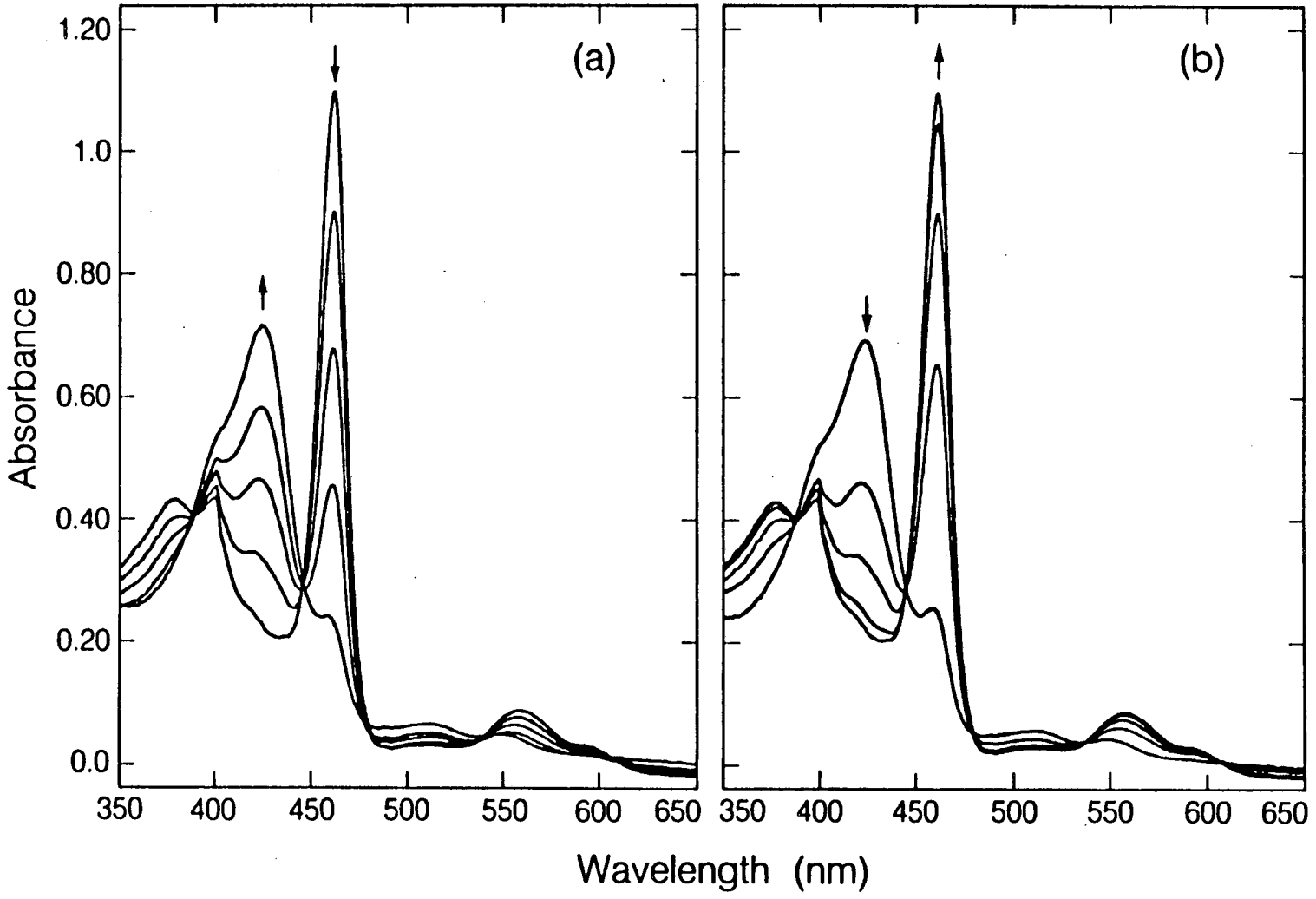
XBL 862-674

Calvin
Figure 7



XBL 8512-9045

Calvin
Figure 8



XBL 8512-9046

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Figure 9

A POSSIBLE ROUTE BY WHICH Mn^{IV} MAY PRODUCE OXYGEN FROM WATER

$$4\,Mn^{IV} + 2H_2O \xrightarrow[-4H^+]{} 2\,Mn^{IV}-O-Mn^{IV} \longrightarrow 4\,Mn^{III} + O_2$$

$$2\,Mn^{IV}-O-Mn^{IV} \longrightarrow [2\,Mn^{IV}-\ddot{O}\cdot] + 2\,Mn^{III}$$

$$\downarrow$$

$$Mn^{IV}-O-O-Mn^{IV}$$

$$\downarrow$$

$$2\,Mn^{III} + O_2$$

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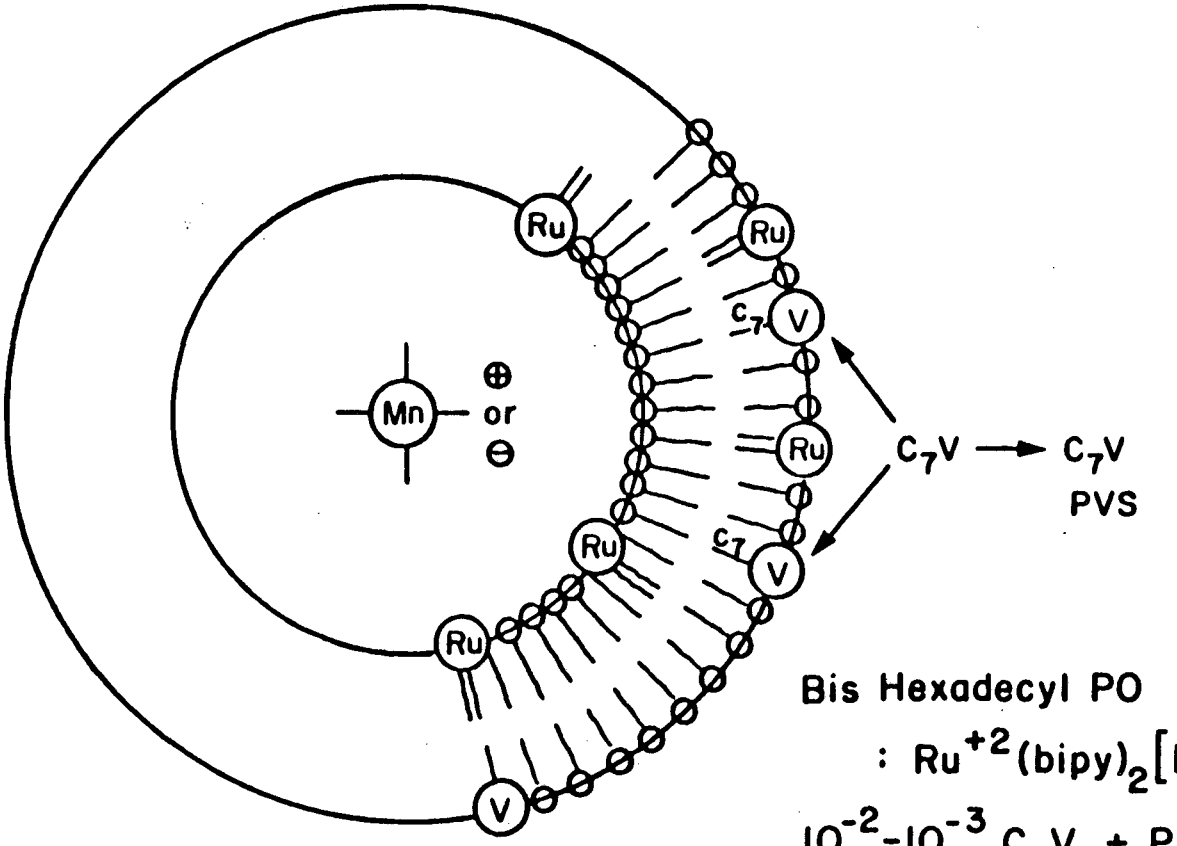
Figure 10



Bis Hexadecyl PO (Phospholipid)

: $Ru^{+2}(bipy)_2[bipy(C_{16})_2]$ (~100:1)

10^{-2}-10^{-3} C_7V + PVS outside

10^{-4} $MnP^{(+ \text{ or } -)}$ inside

pH 9-10 both sides

Single Unilamellar Vesicle

Calvin
Figure 11

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