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SYNTHETIC CHLOROPLASTS

Melvin Calvin

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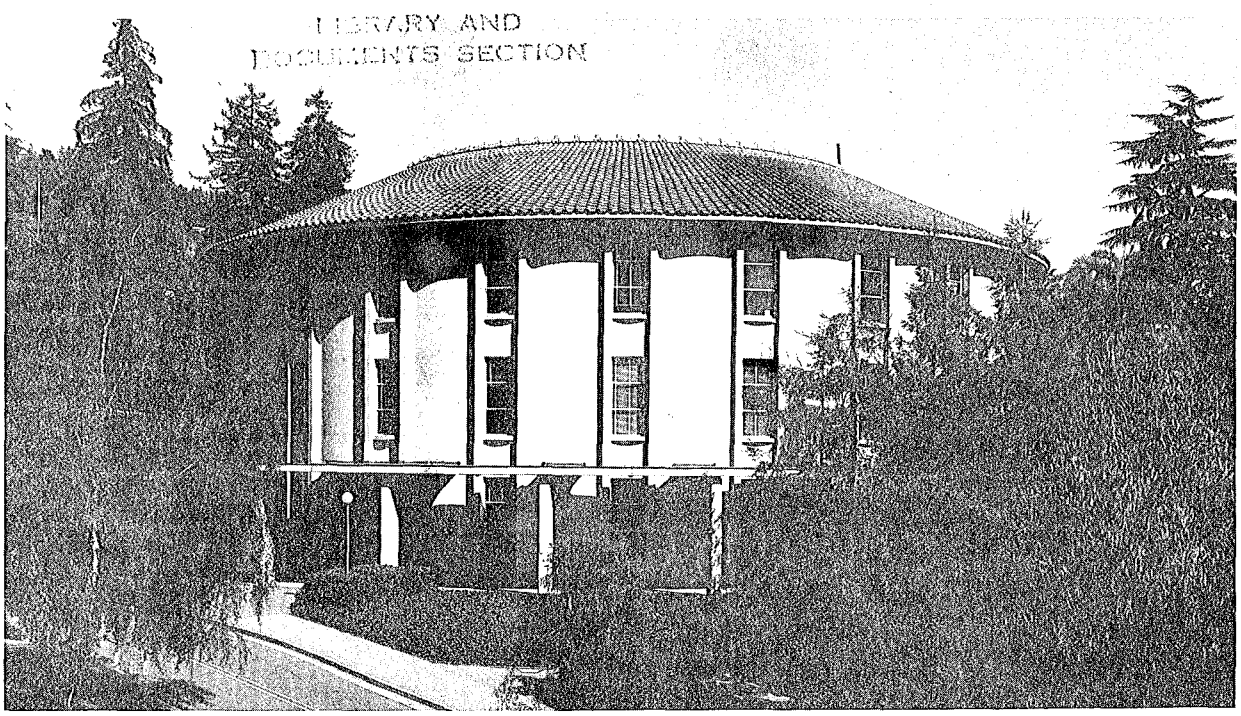

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SYNTHETIC CHLOROPLASTS

Melvin Calvin

Laboratory of Chemical Biodynamics
University of California
Berkeley, California 94720 U.S.A.

ABSTRACT

The principal function of the chloroplast is to capture solar quanta and to store them in some stable form. We are in the process of trying to construct a totally synthetic system that would simulate some of the reactions of the two photosystems which occur in natural chloroplasts.

Toward this end, we have demonstrated a number of the reactions required in separated systems. We have shown that it is possible to transfer electrons across an insulating membrane barrier with a surfactant photosensitizer. Others have shown, and we have confirmed, that it is possible to collect the two electrons necessary for the generation of molecular hydrogen on a heterogeneous catalyst suspended in water and similarly to collect the four holes on another heterogeneous catalyst suspended in water for the generation of molecular oxygen. A synthesis of some of these molecular catalysts for both these purposes is underway, with some partial success.

When these partial reactions are assembled in a system, the resulting "synthetic chloroplasts" will not resemble the natural entity in detailed construction as they will contain no protein.

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INTRODUCTION

I would like to describe to you an artificial photosynthetic system which we have been trying to construct which will achieve the essential function of the chloroplast, that is, the capture of quanta and their conversion into stable chemical form.[1-3] I know that the synthetic system will not perform in exactly the same structural fashion as the natural photosynthetic system of the green plant (the natural chloroplast). All we wish to reproduce is the function(s) of the natural system, i.e., the capture of quanta and their storage in a stable chemical form.

Recently I had occasion to encounter a rather interesting quotation which impinges on the subject. It was an editorial entitled "The Photochemistry of the Future" written by the Italian photochemist, Giocomo Ciamician, in October 1912 and published in Science.[4] This is one paragraph from that paper:

> "Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is today the greatest source of energy and wealth."

I think this statement represents a point of view which was of great importance then and is perhaps even more valid today. One last sentence from this article, by way of introduction to the subject of the present discussion, is:

> "Is fossil solar energy the only one that may be used in modern life and civilization? That is the question."

Someone recently characterized our present use of fossil solar energy as an "addiction" and the transition from coal to oil as like that from hashish to heroin. The historian Alfred B. Chandler says:[5]

> ".....I will examine how the world initially became "hooked" on fossil fuel during the first industrial revolution. I think the application of science to the process of prediction and distribution, while expanding productivity and lowering costs, increased the addiction (to fossil fuel). Recent events, by focussing on a final, and possibly fatal, dependency on fossil fuel have created a need for a third industrial revolution. I will suggest the importance of institutional arrangements in accomplishing this withdrawal from the dependency, but I won't prescribe a cure."

We have approached the problem of developing a truly synthetic system for the conversion of solar energy into stored chemical energy in a series of steps.[6,7] The best quantum converting "machine" that we know today is the green plant, with its chloroplasts, and the possible uses that we can make of that machine are already well established. We have been using that "green machine" for human energy since civilization began. We were using them during the last century as a source of fuel as well. In the early 19th century we ran our machinery on wood. With the coming of the industrial revolution we turned to coal and, finally, we gave up the "green machine" in the early 20th century for petroluem. Today, the system is going the other way again: Wood has long since been displaced by coal which, in turn, was displaced by petroleum which is now running out. Presumably the petroleum will have to be replaced by many different methods

of utilizing solar energy, with the green plant being the most common.[8] We are "going back" to the "green machine" today by converting the carbohydrate of the plant into a more useful liquid fuel by a fermentation process to make alcohol. The processes and technology for this first step are already available and in use in some areas of the world (specifically Brazil)[9] and are currently under development here in the United States.[10,11]

The second stage of this "going back" to the "green machine" involves the discovery of plants (and development of their agronomy) which carry the reduction of carbon dioxide all the way to hydrocarbons, instead of stopping at carbohydrates as most plants do.[8] There are some plants already in use commercially that can go all the way to hydrocarbon, for example the Hevea rubber tree, and we have found others which will go all the way to hydrocarbons and which will grow in the semiarid areas which are available in many places in the world. Examples of plants which produce hydrocarbons are members of the Euphorbiaceae family, which has over 2000 different species of latex-producers.

The third and final method of "going back" to the "green machine" will be to reproduce synthetically the quantum capturing and converting function of the chloroplast (7,12,12a,12b) so that we will not require either plants or the land on which to grow the plants.

We are using the green plant chloroplast as a model to guide us in the construction of efficient and useful ways of capturing and storing the quanta.[13] In general, while a sensitizer can absorb the quantum and reach an excited state, we must still find a way for that excited state energy to be stored in a permanent form. The principal way to do this is by inducing an electron transfer reaction, i.e., moving the electron from a donor system to some acceptor

system. Basically the problem is to prevent the back reaction. The system has to be adjusted in such a way that the excited energetic state that we start with does not fall back to some ground state without any storage of chemical energy.

The green plant has long since learned how to perform these energy-efficient capturing and converting reactions which take place in the lamellae of the chloroplasts. An electron micrograph of such lamellae is shown in FIGURE 1 and you can see that the lamellae are constructed of a collection of membranes with two distinct types of surfaces. One membrane surface is characterized by a distribution of rather large particles and another surface is characterized by a distribution of much smaller protein particles. The membrane appears to have two sides, between which the quantum conversion occurs. The details of what is occurring in the plant chloroplast are not absolutely known at the present time, but a simplified representation of what is known about the photosynthetic electron transfer scheme (the so-called Z-scheme) is shown in FIGURE 2. We see that there are two quanta involved which, by their successive acts, move an electron from a donor water molecule through two successive quantum acts to reach a level approaching that of molecular hydrogen. Thus, the electron is moved in two successive steps from a level in which it exists in water to a level something above that of molecular hydrogen. These two quantum acts (so called I and II) may take place on those two protein molecules on each side of the membrane. This is the kind of physical and chemical model that has guided us in the design of our artificial photosynthetic system.[13]

EXPERIMENTAL AND RESULTS

In order to simulate the natural quantum conversion act in the green plant we constructed an insulating membrane, placed somewhere between the two quantum acts, which would allow the two steps to take place on opposite sides of such a membrane. This rather naive concept is a simplified method of reducing the natural photosynthetic quantum conversion act to a level where it might be synthetically reproduced. The diagrammatic representation of this photoelectron transfer scheme is developed in Figures 3 and 4. The bilipid membrane is represented by phospholipid molecules on either side, and on one side is a donor system and on the other side an acceptor catalyst. There are two sensitizers, one on each side of the membrane (labeled photosystem I and photosystem II). The electron is taken from a water molecule on the left-hand side of the membrane by the first quantum act. It falls back part way and then is taken by the second quantum act up to the level of molecular hydrogen and injected into the acceptor catalyst. One could try to construct such an artificial flat membrane on a solid or liquid surface; a number of people are doing this with some degree of success.[14,15] It seemed to us, however, that we could achieve this kind of a system by constructing vesicles. This entity was invented by a biochemist (biologist) named Bangham,[16] who took phospholipids from cells, cleaned them up, and after having removed most of the excess protein and other extraneous matter, he achieved a fairly pure phospholipid substance. By shaking the phospholipid violently in a water medium, Bangham was able to form a vesicle which he called a "liposome" because he was using the lipids of the cells. These liposomes were in various forms, one of which was a simple bilipid membrane sphere. By bilipid I mean two layers of phospholipids, tail to tail, in which the surface tension and surface properties of the lipids and the water were such that when the monolayer

on the water system is broken up it tends to form into spheres. This is a spontaneously formed spherical vesicle (liposome) with water on the inside and water on the outside. When this phenomena occurs in the presence of whatever substance you wish to place on the inside of the liposome, for example, in the presence of A, then A will be captured on the inside. If the sensitizer is present, it will be captured, depending on the nature of that sensitizer. We can then wash away the molecules in the water outside and place B (a separate water soluble complex) back on the outside, thus obtaining an asymmetric system.

If the vesicle were as far as we could go experimentally, we would have to perform both reactions at the same time: build up the system to do two separate phase boundary electron transfer reactions simultaneously.

The basic property of the chloroplast is its ability to transfer an electron across a phase boundary, i.e., across a water-oil boundary, and this seems to be one of the essential physical requirements. The two phase boundaries can be generated separately by making an oil droplet with a monolipid layer which is a micelle and not a vesicle, as shown in FIGURE 4. Thus, the two phase boundary reactions can be performed separately. One sensitizer can be placed on one of the oil droplets and a second sensitizer on the other oil droplet, so that the reactions could be developed separately. We have, however, done a photoelectron electron transfer through the wall of an actual vesicle across both phase boundaries.[17,19a,19b]

Catalyst Construction:

We need a catalyst (D) to obtain electrons from water, and A is an acceptor catalyst which can hand on the electrons to protons in order to generate hydrogen. What do we know about these two entities in the chloroplast? The sensitizers are clearly the chlorophyll molecules in one form or another, together

with their associated pigments, but the catalyst that leads to the hydrogen generation, on one side, and the oxygen generation, on the other side of the membrane are not so well known. Before we tried to generate the catalyst, we used a donor system which did not require water and oxygen generation, and an acceptor system which did not immediately require the generation of hydrogen. In other words, we performed "simpler" chemistry when we began this series of experiments, before trying to synthesize the hydrogen and oxygen generating catalyst as well. The natural hydrogen generating catalyst is rather well known, an iron-sulfur protein,[18] but the oxygen generating catalyst is still under investigation.[19]

Instead of using water as a donor and protons as the acceptor we used a simpler reaction which was easier to accomplish than the generation of hydrogen and oxygen from water, which is depicted in FIGURE 5, showing the oxidation of ethylenediamine tetraacetic acid (EDTA) with methyl viologen (MV) sensitized by a suitable sensitizer, which resulted in oxidation of one of the glycine groups to formaldehyde and carbon dioxide, with the simultaneous reduction of the MV to a cation monoradical.[17] This is a rather simple slightly uphill chemical reaction, which produces deep blue color as one of the reaction products. This color can be used as an indication of whether or not the reaction is "going". We used EDTA as a donor and MV as an acceptor, and instead of using water soluble ruthenium bisdipyridyl as the sensitizer we constructed a surfactant with a C_{16} tail which creates a complex which will locate at the water-oil interface. The surfactant dyestuff will occur at the water-oil interface when the vesicles themselves are created (FIGURE 6). All the components are dissolved in ethanol-diethylformamide, together with the phospholipid, and that solution is injected into 0.5 M EDTA in buffer. This,

in turn, gives rise to the vesicles which have EDTA on the outside and EDTA on the inside, and the ruthenium complex on each surface. With EDTA on both sides of the vesicle, we pass this system through a gel, which has pores too small to accept the vesicle but small enough to accept the EDTA. During gel filtration the EDTA molecules diffuse into the gel pores, and the resulting vesicles have EDTA on the inside and buffer on the outside. We now add the methylviologen (MV) to the outside of the vesicle, creating an unsymmetrical vesicle with EDTA (donor) on the inside and the acceptor (MV) on the outside. Zinc ion is added to block any leakage of EDTA from the inside of the vesicle.

Vesicle Construction:

A representation of the method of vesicle structure is shown in FIGURE 7.[12] At the beginning of the experiment, the vesicles have a thickenss of about 50 Å, a simple bilayer, two phospholipid molecules tail to tail with the ratio of phospholipid to ruthenium of about 20:1. The ruthenium is on the surface of the interface in a relatively polar environment. On the inside of the vesicle, there is the donor molecule and on the outside, the methylviologen.

It seemed to us, when the experiments were in the earlier stage of development, that there should be a carrier (FIGURE 8) to help the electrons across the membrane. Therefore, a quinone was placed in the membrane to carry the electrons through and also a proton carrier was placed in the membrane to transfer the protons. The actual-membrane structure had plastoquinone and a diborane added to it. With the quinone present, the back reaction would eventually take over since the quinone can actually carry the electron back. When the quinone and proton carrier were removed, the reaction was slower, but with very little induction period.[12a,12b]

The reason for the slowness turned out to be that neither the donor or

the acceptor were anywhere near the sensitizer during its excited state. It appeared desirable to insert something which would trap the electrons near the surface of the membrane which could then hand the electrons over to the bulk acceptor. Therefore, we used heptylviologen to be distributed between the surface of the membrane and the bulk of the solution. This provides an acceptor next to the excited sensitizer which could then transfer to viologen in the bulk of the solution very rapidly. Once the electron leaves the membrane it will not get back because of dilution in the bulk viologen.

Kinetic Experiments:

How did the electron go through the membrane? Once the excited electron is trapped by viologen, the external Ru^{+2} has become Ru^{+3}. I thought for some time that there had to be a second quantum absorbed by the internal Ru^{+2} to transfer the electron across the membrane. This would make the reaction dependent upon the square of the light intensity; one quantum would move the electron from Ru^{+2}_{ex} to viologen and the other quantum from Ru^{+2}_{int} to Ru^{+3}_{ex}. We then performed a light intensity experiment, the results of which are shown in FIGURE 9, and the reaction is linear with light intensity, showing that it is not a bimolecular (two-quantum) process but is a one-quantum process. Therefore, the transfer of the electron through the membrane is not light-dependent. The exchange reaction between Ru^{+3} on the outside of the membrane and Ru^{+2} on the inside of the membrane is very fast, and the kinetics and equations for the photoreduction of viologen are shown in Figure 10. The exchange reaction, as far as the membrane is concerned, is perfectly symmetrical, and the two rate constants are equal and in opposite directions. All the other constants can be measured separately, and then the overall reaction can be measured. From this rate of the exchange reaction can be deduced, and it is very high.

The question was then raised as to whether or not this was a mass diffusion reaction, dependent upon the rate of atoms on the outside exchanging with the ruthenium atoms on the inside of the membrane, that is an actual atomic migration or diffusion reaction. If it were, then the diffusion reaction should be independent of ruthenium concentration. If it is a diffusion through the membranes, the reaction should be unimolecular in ruthenium. However, if the exchange reaction is light-dependent, it would depend directly on the ruthenium concentration. The photoreduction kinetics are shown in FIGURE 11, which indicates that when the ruthenium concentration is increased, the rate is increased. The reaction is thus an isoelectronic exchange reaction and not a diffusion reaction. This is determined by the kinetic experiments as well as the actual rate itself.[19a,b]

We have thus demonstrated that is is possible to transfer an electron across an insulating barrier. The isoelectronic exchange is the mechanism by which an electron moves from one side of the membrane to the other, an average distance of ∿40A via a tunneling phenomenon.

Next it was necessary to develop the correct catalytic system to capture the excited electron on the outside of the membrane and eventually donate it from the inside. When Ru^{+3} is on the inside of the vesicle, we have the oxidation potential to oxidize water to oxygen, provided a catalyst is supplied. It takes four electron transfers to oxidize water to molecular oxygen.

A schematic representation for oxygen evolution from water on a solid catalyst is shown in FIGURE 12. The catalyst must be capable of accumulating the four electrons which are necessary to generate molecular oxygen and allow Ru^{+3} to oxidize water and be reduced to Ru^{+2}. This type of experiment has been performed by Grätzel[20] and others, and we discovered that platinum or

cobalt oxide could be used for the catalyst as well as ruthenium oxide.

This method accumulates four one-electron oxidation steps on the solid surface, because the Ru^{+3} bipyridyl has the potential for this type of reaction. The other end of the reaction is reduced MV (methyl viologen radical cation) which has the potential to generate molecular hydrogen from protons, again only provided there is an agent present which will allow the two electrons to accumulate, or to have some other catalyst (such as rhodium cluster) which will also allow the two electrons to accumulate in the same place.

It is, however, difficult to place a solid catalyst on the inside of a vesicle because the solid particles would have to be extremely small to be able to reside inside of the vesicle without disturbing its surface. It would be better, if possible, to learn what the natural catalyst might be for oxygen generation. We now have both catalysts and both systems developed. The potential exists to create a device which would perform the same functions as natural photosynthetic quantum conversion.

Manganese Function:

We know a good bit about the natural catalyst for oxygen generation. For example, we know that it is a manganese compound of some sort.[6,7] Many years ago, the plant physiologists had determined that when a plant is starved for manganese it fails to have the capacity to generate molecular oxygen. When manganese ion is added to the plant's environment it recovers very quickly the capability of generating molecular oxygen. Many experiments have been done to confirm that idea, i.e., that manganese is somehow involved in an essential role in the first reaction of taking an electron from water to whatever it is in the chlorophyll or other substance to which it goes.[21]

What is the nature of the manganese compound? We know the nature of the acceptor compound on the reducing side (an iron-sulfur protein), but the manganese has not been determined. This has been under investigation for many years, in our own laboratory and elsewhere. For example, it has been unequivocally demonstrated that the compound is not manganese porphyrin, rather it is a very weakly bound manganese protein of some kind.

Recently, we thought about this problem again and realized that we had been pretty naive to think it was a simple manganese porphyrin. In order to simulate the reactions in green plants, it is necessary to accumulate four electrons. The only way a manganese porphyrin could accumulate these electrons would be two electrons at one time. Originally, I thought there would be two manganese atoms in this reaction, somehow, going in oxidation number from two to three to four, and back again to two, both together in a complex which would create a control system with four electrons together.

We synthesized a number of binuclear manganese compounds containing two manganese atoms in a complex. For a while, I thought we had made molecular oxygen from one of these manganese complexes, but that was an error. As a consequence, however, we had available the binuclear manganese compounds. Then, a physical (spectroscopic) method became available to explore the nature of the manganese compound in the plant without taking the plant apart, i.e., in living, functioning chloroplast material. We found that we could use the method of extended x-ray fluorescence spectroscopy (EXAFS) to determine the presence of the manganese without interference from the rest of the plant material.

Using this spectroscopic method it is possible to use a frozen chloroplast sample, which contains about two manganese atoms per 1000 chlorophyll molecules,

and the manganese atoms alone can be examined. The interference pattern of the scattered x-rays detects only the manganese atoms and its nearest neighbors.[23] We then used the binuclear manganese compound previously synthesized as a calibrating material; the EXAFS of this compound is shown in FIGURE 13. From this spectroscopic information it is possible to deduce that in the chloroplasts there are two manganese atoms with a small distance between them. The origin (Figure 13) represents the position of one of the manganese atoms, and the second manganese atom shows an intensity peak somewhat over 2 A distant. A similar picture is observed in the chloroplasts, showing that there are at least two manganese atoms within 2.5 A of each other. The EXAFS method proved that there is at least a binuclear manganese compound present in the chloroplast material. We can say, therefore, that there are manganese atoms acting in pairs (or groups larger than pairs) in the chloroplast which can perform the same electron transfer reactions which occur in the natural material.

With that as background, we undertook to use the synthetic vesicles which we had developed[12,17] and to replace the ruthenium with a surfactant manganese compound. A general scheme for the photochemical generation of oxygen sensitized by manganese compounds is shown in FIGURE 14. This indicates that there must be two or more manganese atoms, as shown in the last reaction, acting in concert in the vesicles.

We then prepared tetrapyridyl porphyrin, the structure of which is shown in FIGURE 15. This chlorophyll analogue is a surfactant porphyrin which will lodge at the interface of the vesicle in place of the ruthenium.

In preparation for this part of the experiment, we performed a reaction in an alcohol solution where there was not an interface. The first experiments

were done with a manganese porphyrin in a homogeneous solution in methanol, a single phase. The manganese in the porphyrin, as Mn^{+3}, and the methylviologen were dissolved in a methanol solution. When the light was turned on, the MV was reduced to the viologen radical cation which seemed to be in the right direction energetically. At that point, the reaction did not appear to go backward. However, when we extracted the manganese, instead of finding Mn^{+4} (which is what one would expect), the substance turned out to be Mn^{+2}. Evidently we were exciting Mn^{+3} into an excited state, handing an electron over to the viologen which was then visible (FIGURE 16), but when the manganese was isolated it turned out to be Mn^{+2}.

The only way we could understand that result was to assume that two Mn^{+4} atoms were acting together, as shown in FIGURE 14. There you can see when Mn^{+3} is excited, and the electron is passed on to methylviologen, it leaves behind Mn^{+4}. This reacts with water to make an intermediate Mn^{+4} oxide, which can be written as an Mn^{+3} oxygen radical, two of which could come together to make a bis-Mn^{+3} peroxide. Finally, one electron from each Mn^{+3} oxide bonds would be extracted by Mn^{+3} to reduce it to Mn^{+2}, liberating molecular oxygen. Therefore we find Mn^{+2} and we should observe molecular oxygen. What appeared to happen was that a very potent intermediate oxidizing agent oxidized methanol, and the resulting reduced product was Mn^{+2}. In the absence of any other oxidizable substrate there is a very slow oxidation of methanol.

It occurred to us that we should try and synthesize a dimer, which we have since done.[24] Furthermore, we realized that a very potent incipient oxygen atom bearing only six electrons is present in the oxidized monomer. If a Lewis base is also present, having an unshared electron pair, it should be possible to hand an oxygen atom on to the base. We should then get Mn^{+2}.

Therefore, any compound that has an unshared pair of electrons, or pair of electrons capable of accepting an oxygen atom with six electrons, could be an acceptor. We first used triphenylphosphine (TPP) and the oxygen atom (on manganese) and a vacant orbital interacts with the phosphine, leaving behind Mn^{+2}; the product formed is triphenylphosphine oxide, in effect, an oxygen-transfer reaction.[25] (We are currently conducting an experiment with oxygen-18 water to show that the oxygen atom is from the water and not from some other source).

It should be possible to generate more phosphine oxide than total manganese present in this reaction by recycling the Mn compound. If a little platinum is inserted with the viologen, it is possible to generate any amount of phosphine oxide.

We have been able to perform this reaction with other acceptors, using anything with a pair of electrons that can handle the six-electron oxygen atom. We have generated the "hot" oxygen atoms with light from water, potentially a much more important reaction than generating molecular oxygen from water. The by product of the reaction from "hot" oxygen atoms is hydrogen and this is essentially free, economically.

If we examine the curves of FIGURE 16, we can see that the rate of the reaction is determined by the rate of the initial transfer of the electron from the manganese to the methylviologen.

We now have confirmatory chemical evidence that we have converted the Mn^{+3} porphyrin to Mn^{+4} oxide, the crucial intermediate, by simple chemistry. The abosrption spectra for three different manganese complexes in different oxidation states are shown in FIGURE 17: The Mn^{+3} porphyrin, the initial product; the Mn^{+2} porphyrin, the final product, and the Mn^{+4} oxide, the presumed intermediate. All of these three compounds can be synthesized separately by standard chemical reactions. For example, if Mn^{+2} tetrapyridyl porphyrin is oxidized by iodosobenzene

(an oxygen transferring agent), the Mn^{+4} oxide is the result (FIGURE 18), which shows the oxidation product by iodosobenzene on Mn^{+2} and its failure on Mn^{+3}, as well as the product of a one electron oxidant such as sodium hypochlorite, acting on Mn^{+3}. The chemical relationships are shown in FIGURE 19. We are able to oxidize the manganese porphyrins by one- and two-electron steps. Thus, when we oxidize Mn^{+2} with iodosobenzene, we get Mn^{+4}; if we try to oxidize Mn^{+3} with iodosobenzene the reaction does not go. The same product results from the Mn^{+2} and iodosobenzene, or the Mn^{+3} and sodium hypochlorite. If triphenylphosphine is added to this oxidation product, the resulting products are phosphine oxide and reduced manganese; the Mn^{+2} initially formed reacts with Mn^{+4} to give back Mn^{+3}.

DISCUSSION

We have shown photochemically, and confirmed chemically, that the Mn^{+4} oxide intermediate is indeed a "hot" oxygen atom from water. The specific photochemistry of the manganese-sensitized generation of active oxygen atoms is shown in FIGURE 20. Thus starting with Mn^{+3} and with two quanta we go to Mn^{+4} and then to the phosphine oxide, bringing back the Mn^{+2} and on to Mn^{+3} again. We have generated two reduced viologen radicals for each oxide, and the net reaction is: Phosphine plus water to yield phosphine oxide and molecular hydrogen, sensitized by manganese. Obviously, it is possible to replace the phosphine with other useful oxygen acceptors, particularly olefines, and the final product will be more useful than phosphine oxide.

It should be emphasized that what has been accomplished here is much more important than getting molecular oxygen. We have generated a "hot" oxygen atom from water--not from oxygen--with a cyclic reaction[25] by virtue of the two quanta. The results of these experiments on artificial photosynthetic

systems will be a new chemical industry, with hydrogen generation (as well as oxygen generation) from water as well. The quantum yield of this reaction is high; so far the energy yield itself is low, because the sensitizer has low light absorption.

The system we have constructed, which mimics the natural photosynthetic process of the green plant, is, perhaps, not the system we started out to construct initially. It is, perhaps, something better. The philosophy of this result has been expressed by Jack Kent (FIGURE 21) which expresses the unpredictability and interrelatedness of all of science.

A diagrammatic representation of the entire reaction is shown in FIGURE 22. At the bottom of the diagram is what appears to be a cross section of the vesicle with the manganese dimer in one of them to generate oxygen. This figure should be viewed as a cross section of a tube, and the tubes are hung between headers which enclose the space outside the fibers, in this case containing the quinone-hydroquinone couple which will transfer both protons and electrons between the two systems. The couple is similar to the quinone in the natural photosynthetic system and has the same function. Also shown in this diagram are various hydrogen generators (ruthenium, viologen, platinum).

It is possible to perform these artificial photosynthetic reactions either in hollow fibers (FIGURE 22) or in gels (FIGURE 23). These reactions could be made to occur by suspending the vesicles in the gel precursor and then causing the gel to form, either by polymerization or by temperature change. Thus the particles (vesicles) each containing the separate systems could be immobilized and coupled together by the quinone redox couple.

It is my feeling that when we finally construct the artificial system, it will be somewhat different from that depicted in Figures 22 or 23. We will

use an oxygen acceptor, instead of the manganese dimer, to create a useful oxidized product, with the hydrogen produced in the other vesicle. With our artificial system it will be possible to perform exactly the same chemical reactions which occur in the natural material.[26]

CONCLUSION

As a result of our efforts to develop artificial photosynthetic systems we have succeeded in at least designing the oxygen generating system--oxidation product as well--coupled with a hydrogen generating system. This type of "synthetic chloroplast" will probably be more useful in the chemical industry than would be one which would make ATP and other chemical components in an attempt to more closely reproduce the function of the natural chloroplast.

We have not only designed, but have succeeded in accomplishing, the two separate reactions--the oxidation (or excitation) of water and the reduction of protons--in two separate systems. It now remains to couple these two reactions in a continuing and stable manner so that the products generated at both ends of the system may be usefully coupled.

All of the efforts in this direction--in our laboratory and elsewhere--are directed to the problem of using water and sunlight for our fuel and material source in the future. Even though at the moment it is a philosophical question, we are moving in the right scientific direction in our ability to mimic the complex natural photosynthetic process by constructing artificial devices for its essential parts. The progress in recent years is encouraging.

Combining the different parts of the artificial system into one comprehensive system will certainly be accomplished in the near future. The fact that this has been achieved long ago in nature gives us encouragement that we will be able to overcome the problems as well.

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FIGURE CAPTIONS

Figure 1 Details of Chloroplast Lamellae

Figure 2 Photosynthetic Electron Transfer Scheme (Z-scheme)

Figure 3 Photoelectron Transfer Scheme (vesicle)

Figure 4 Photoelectron Transfer Scheme (micelle)

Figure 5 Photosensitized Reduction of Methylviologen by Ethylenediamine Tetraacetate

Figure 6 Vesicle Preparation

Figure 7 Diagram of Vesicle Cross Section

Figure 8 Cofactors in Photoelectron Transfer

Figure 9 Light Intensity Dependence of Photoinduced Electron Transfer

Figure 10 Kinetic Scheme for Photoreduction

Figure 11 Photoreduction Kinetics

Figure 12 Schematic Representation of Oxygen Evolution

Figure 13 EXAFS of Manganese Compounds

Figure 14 Proposed Photochemical Generation of Oxygen Sensitized by Manganese Porphyrin (General Scheme)

Figure 15 Structure of Tetrapyridyl Mn^{III} Porphyrin

Figure 16 Mn^{III} Porphyrin Photoreduction Dependence on Methylviologen Concentration

Figure 17 Visible Spectra of Manganese Complexes in Different Oxidation States

Figure 18 Spectra of Oxidation Products of Mn^{III} Tetrapyridyl Porphyrins in Iodosobenzene

Figure 19 One- and Two-Electron Oxidation of Manganese Porphyrins

Figure 20 Specific Photochemistry of Manganese-Sensitized Generation of Active Oxygen Atoms

Figure 21 King Aroo (Jack Kent)

FIGURE CAPTIONS (Page 2)

Figure 22 Schematic for Synthetic Chloroplasts: Hollow Fiber Technique

Figure 23 Schematic for Synthetic Chloroplasts: Microemulsion

Figure 1 XBB 740-7523

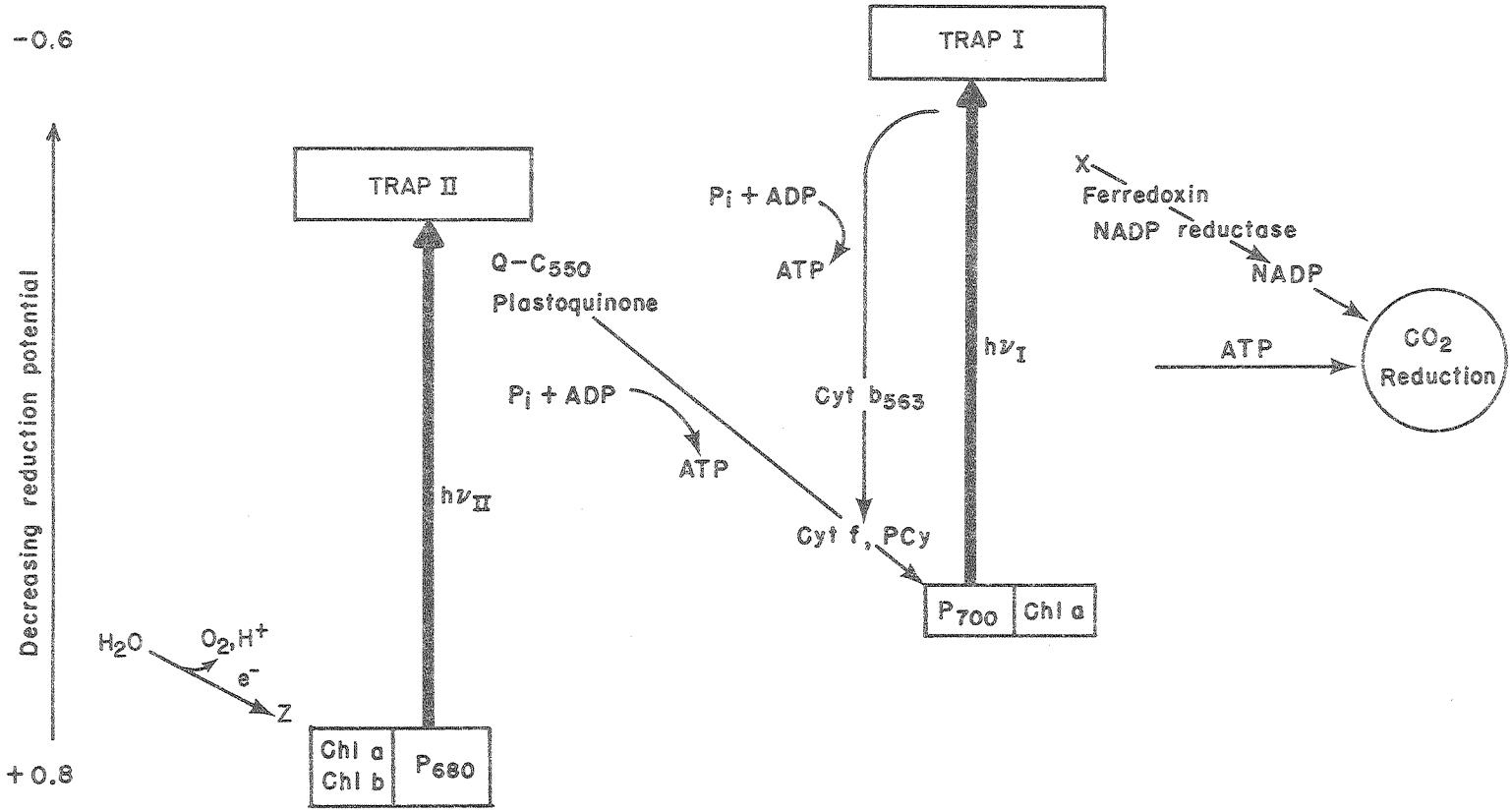

Fig. 2

XBL7410-5395 B

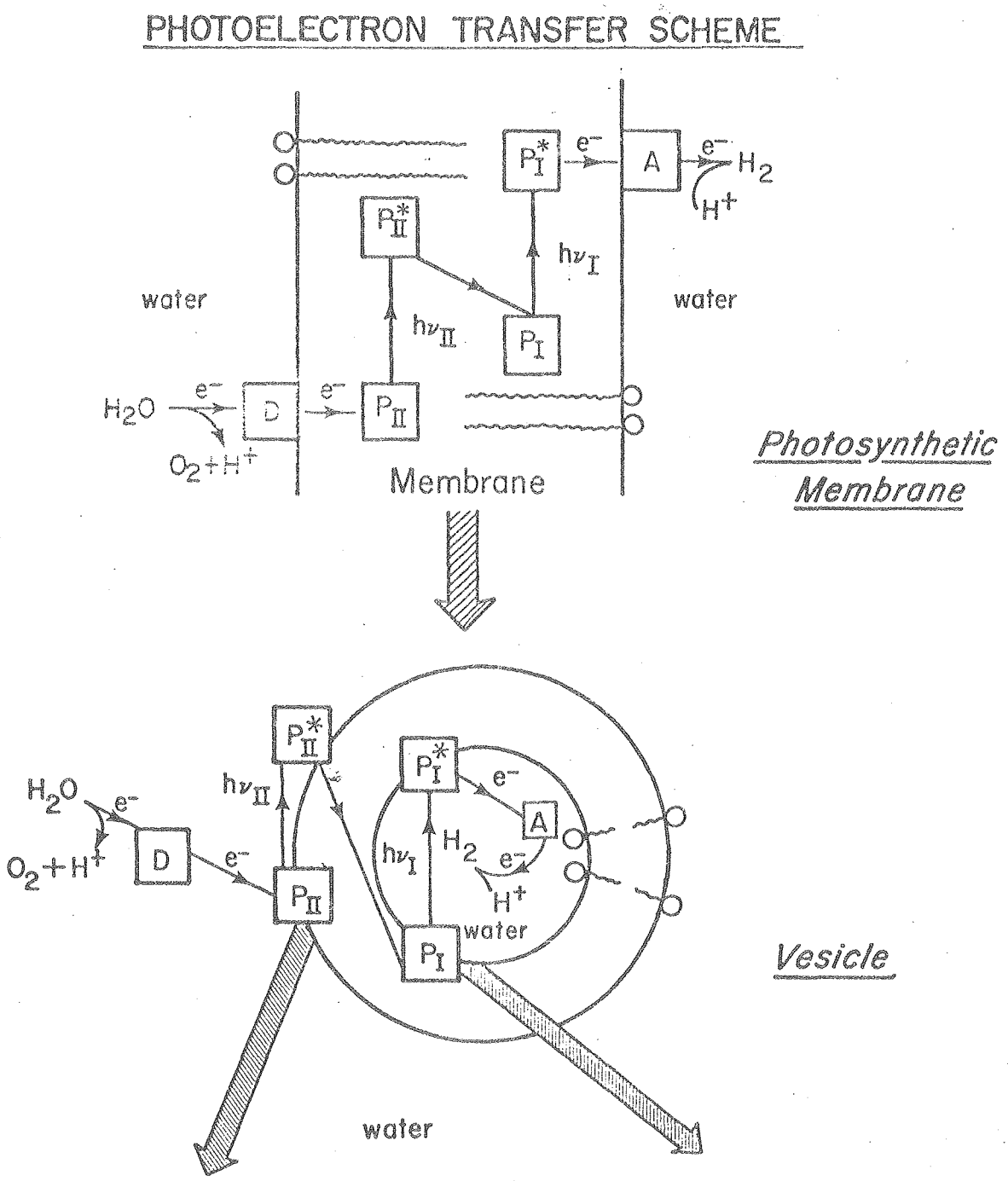
PHOTOELECTRON TRANSFER SCHEME
water
water
Membrane
Photosynthetic Membrane
Vesicle
water
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Fig. 3

PHOTOELECTRON TRANSFER SCHEME

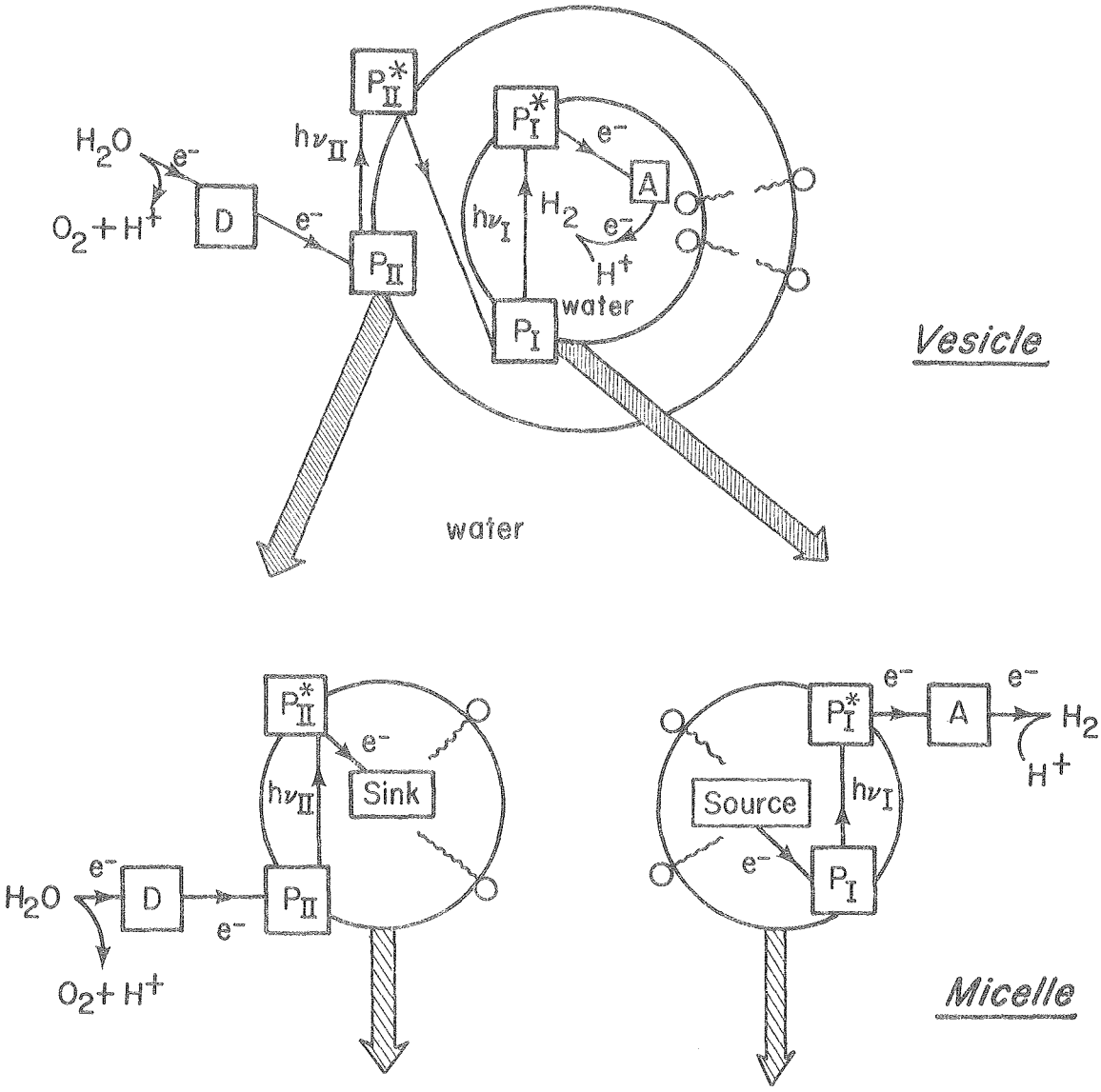
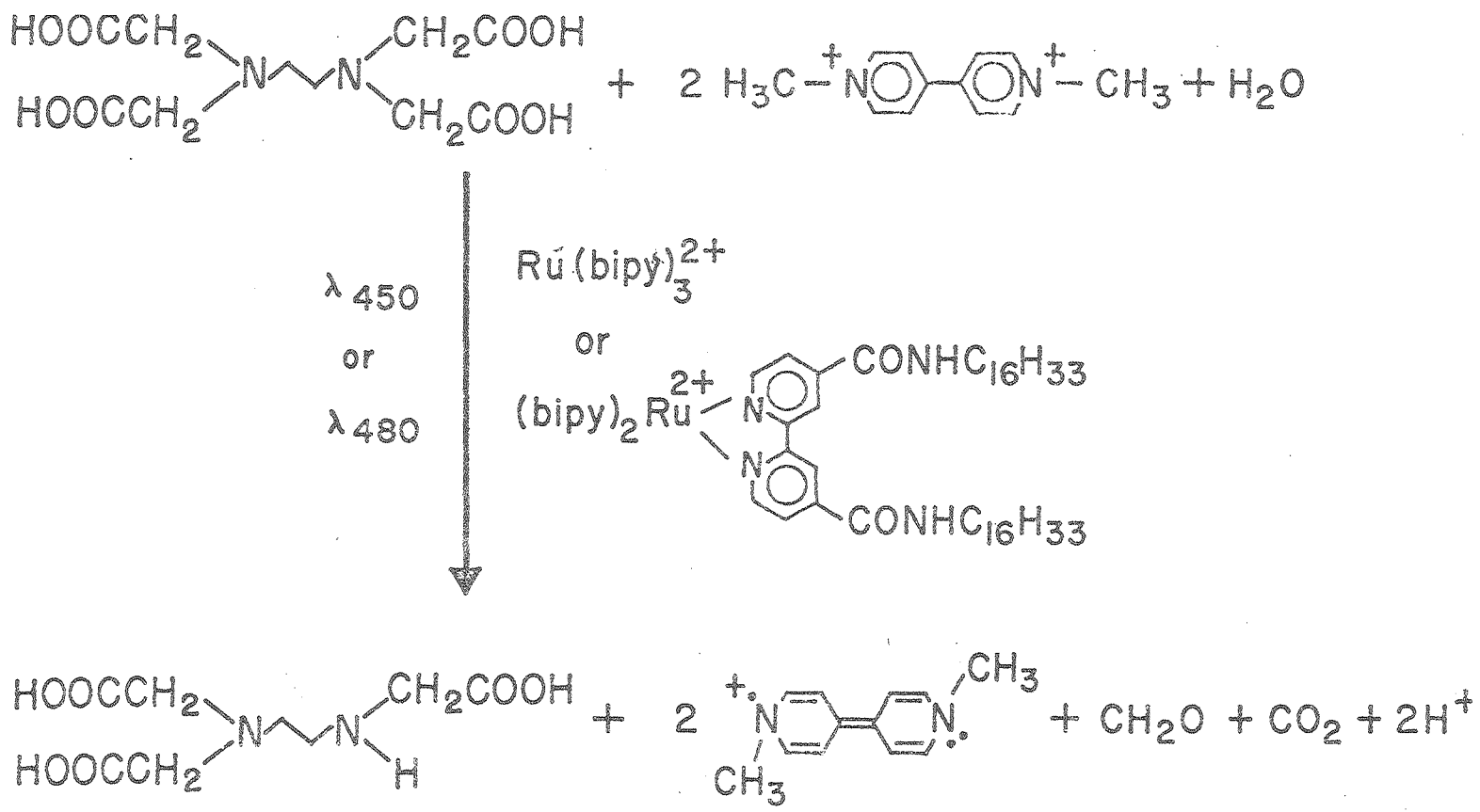


Fig. 4

XBL 774-4348

Photo-sensitized reduction of methylviologen by ethylenediamine tetraacetate



$\Delta G^\circ \sim +20$ Kcal per mole of EDTA

XBL 783 - 3829

Fig. 5

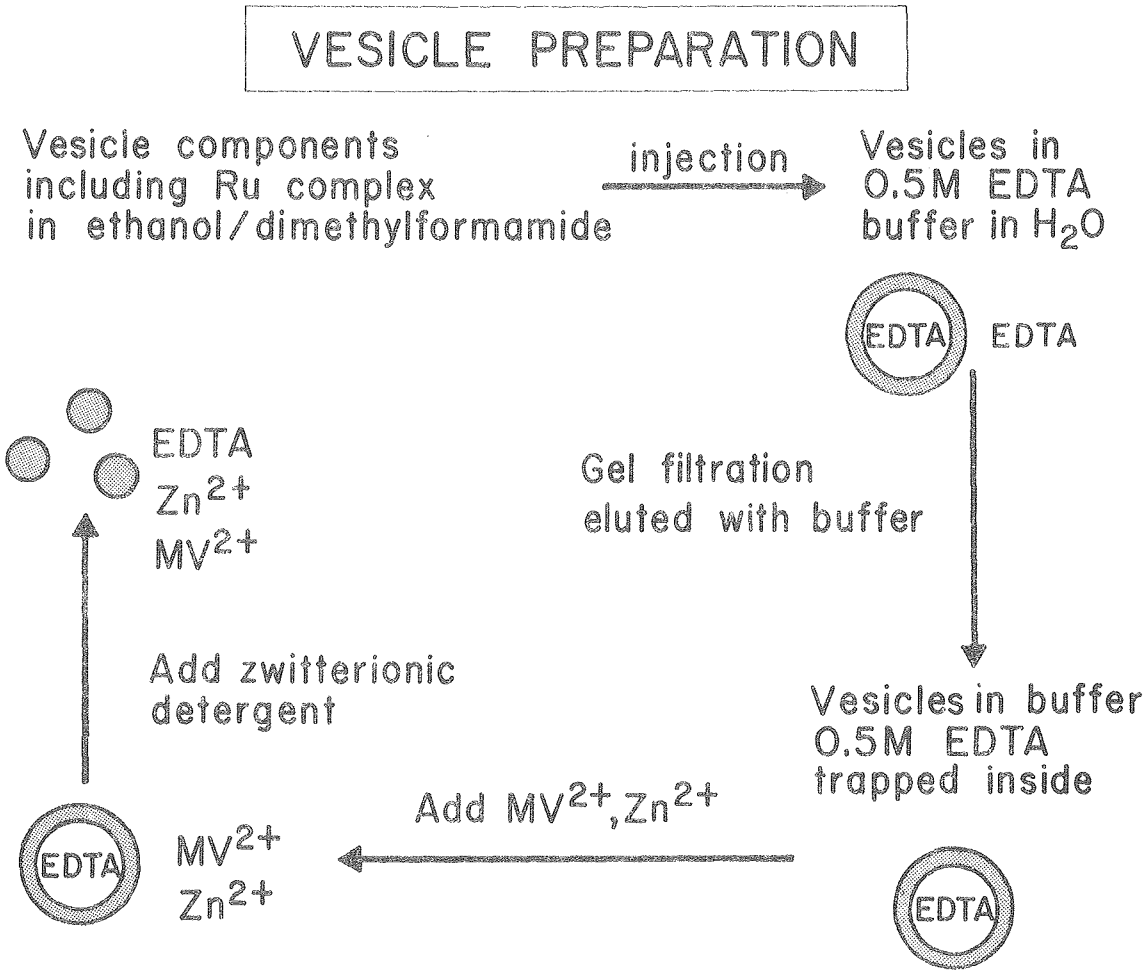


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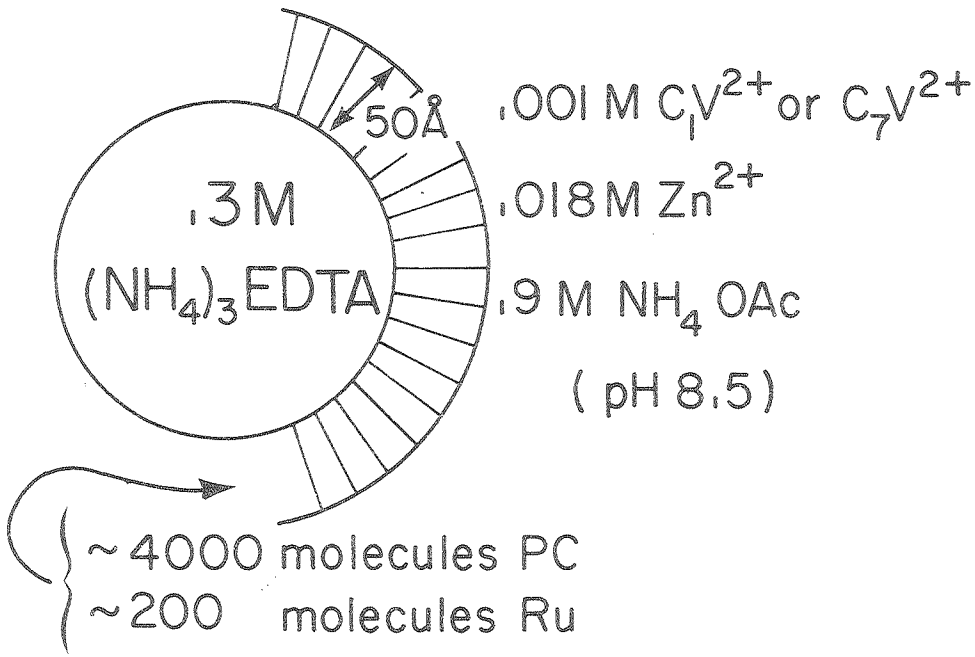
Fig. 6



XBL 793-4694

Fig. 7

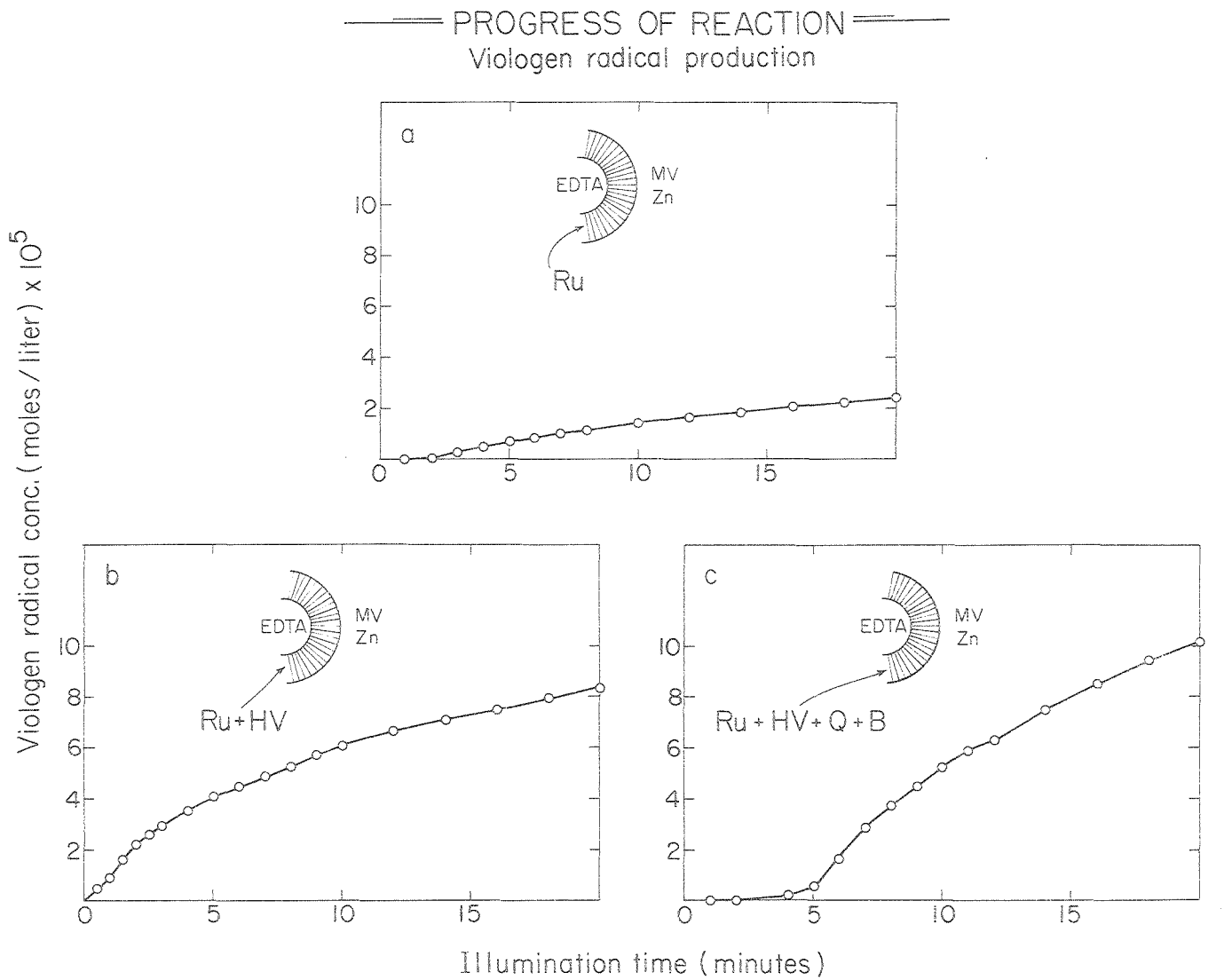
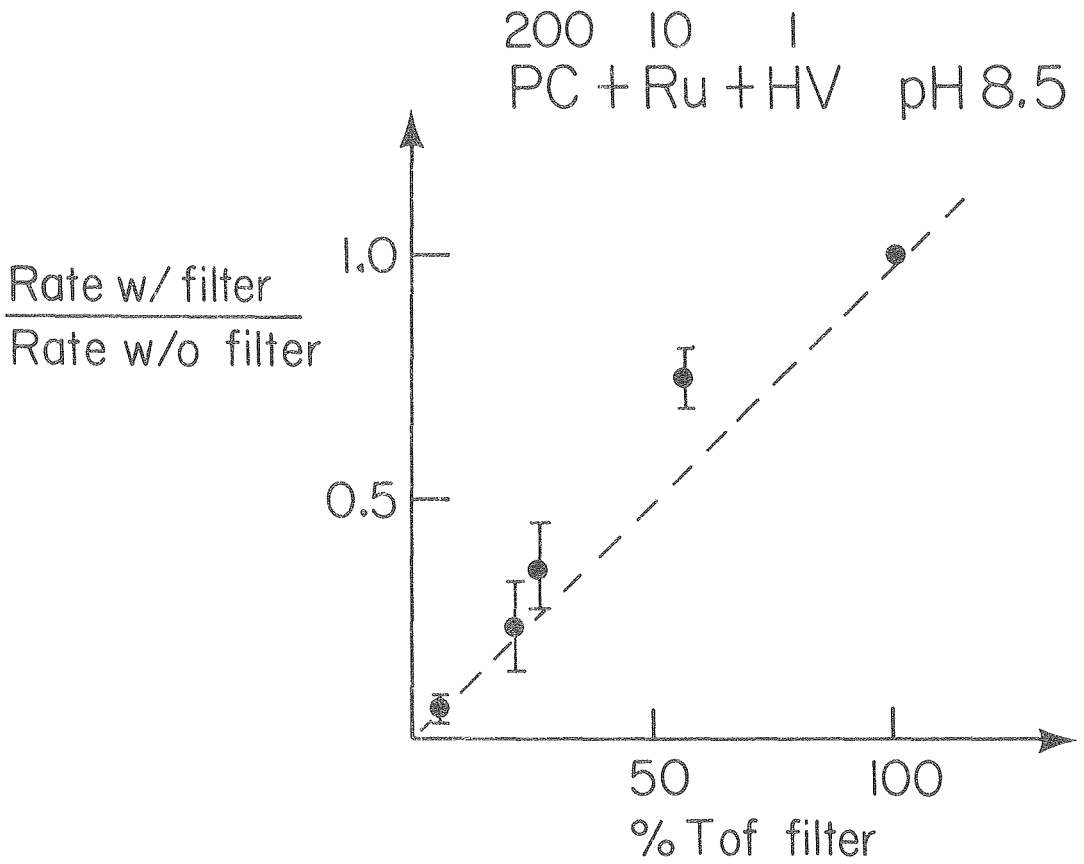


Fig. 8

XBL 791-4643



XBL 786-4031

Fig. 9

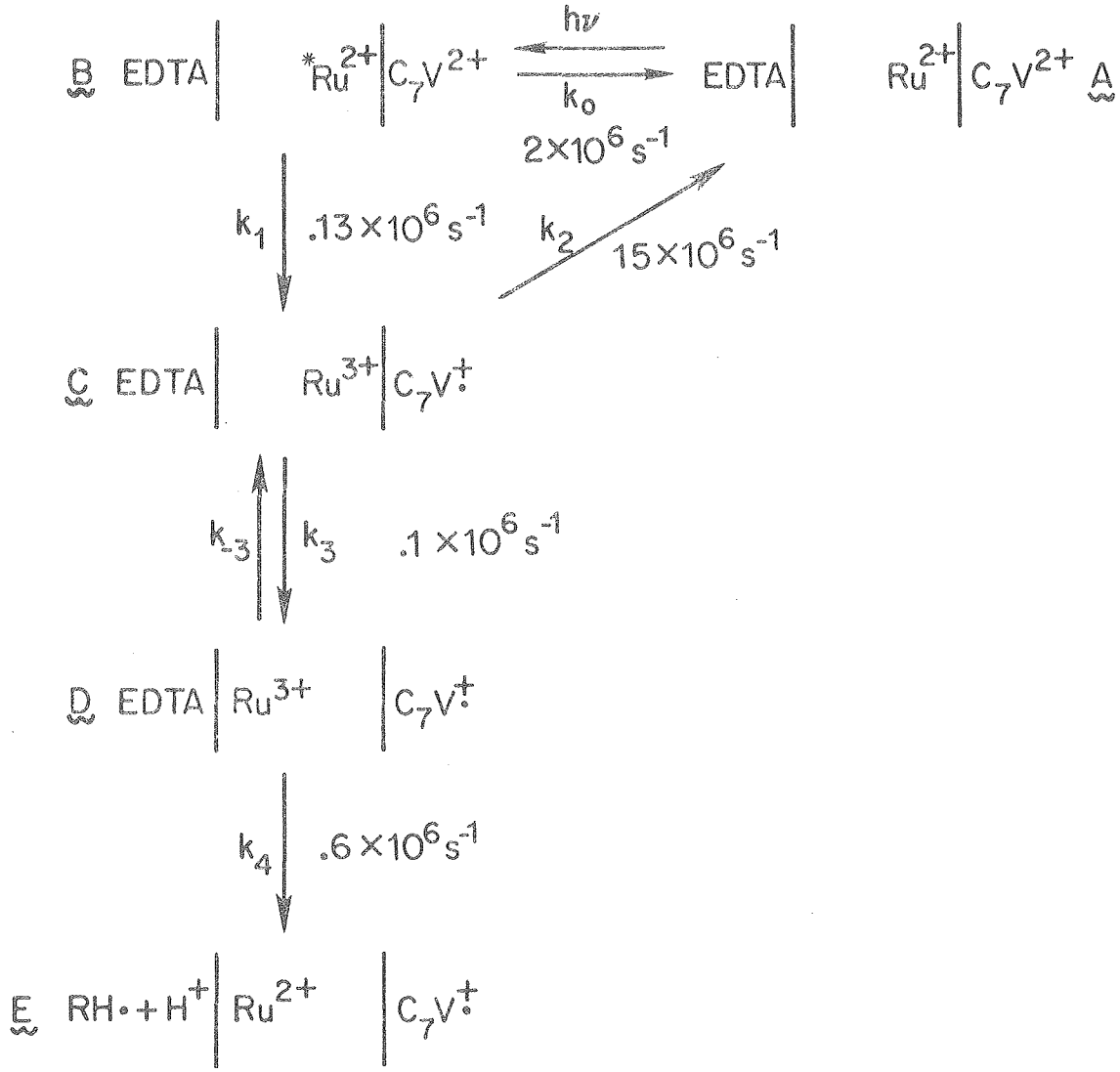


Fig. 10

XBL794-4751

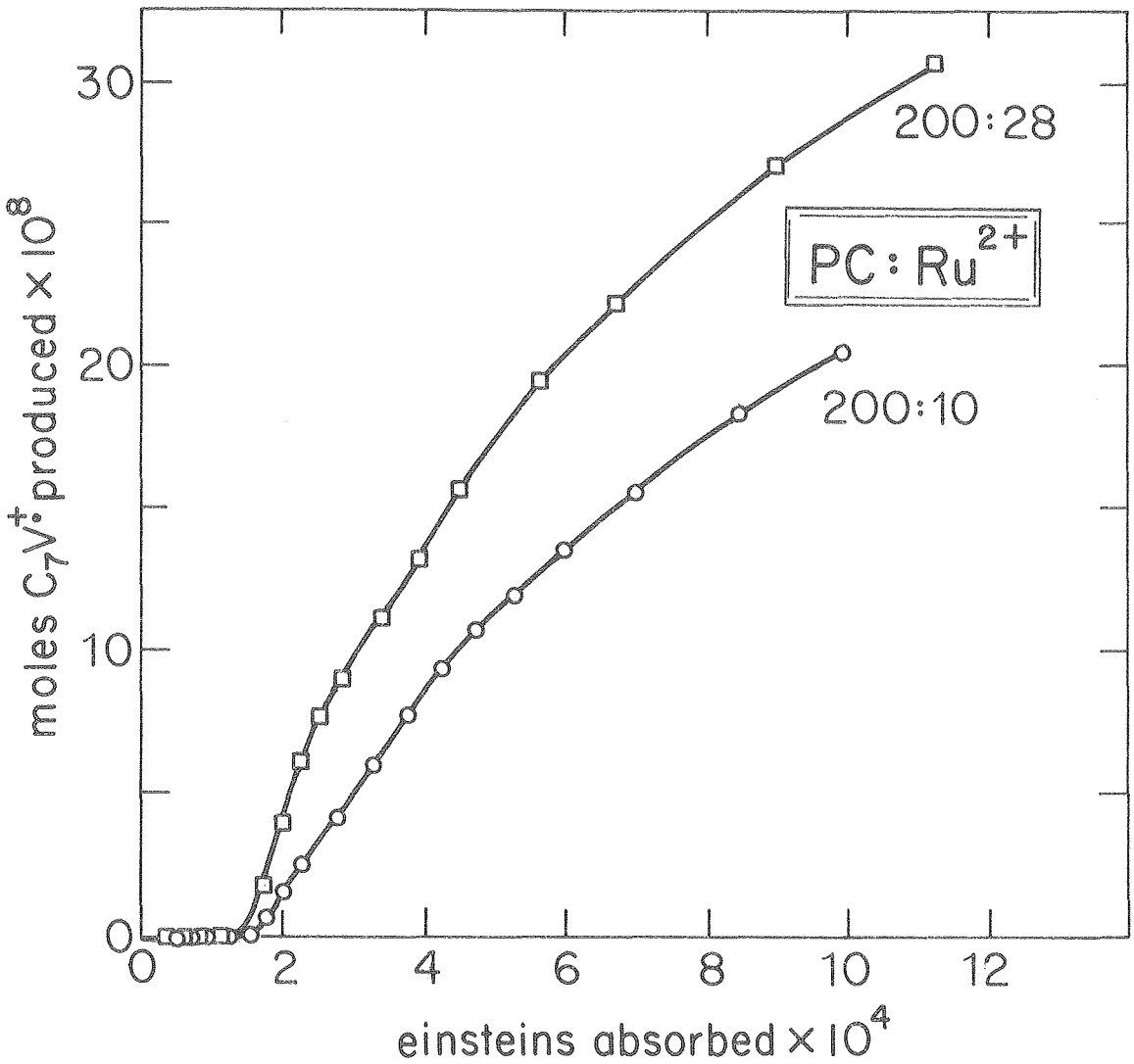


Fig. 11

XBL794-4767

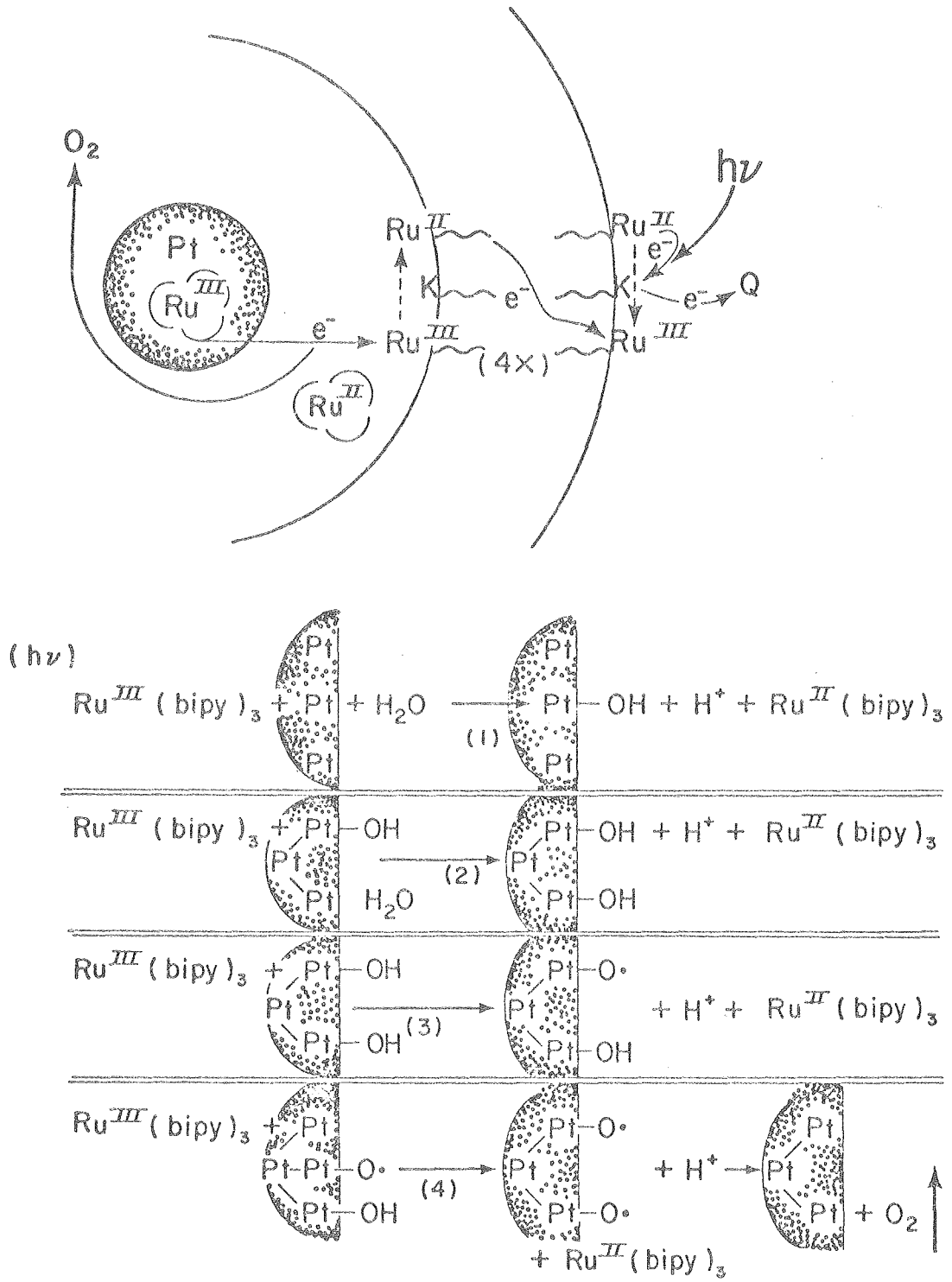


Fig. 12 Schematic for Oxygen Evolution.

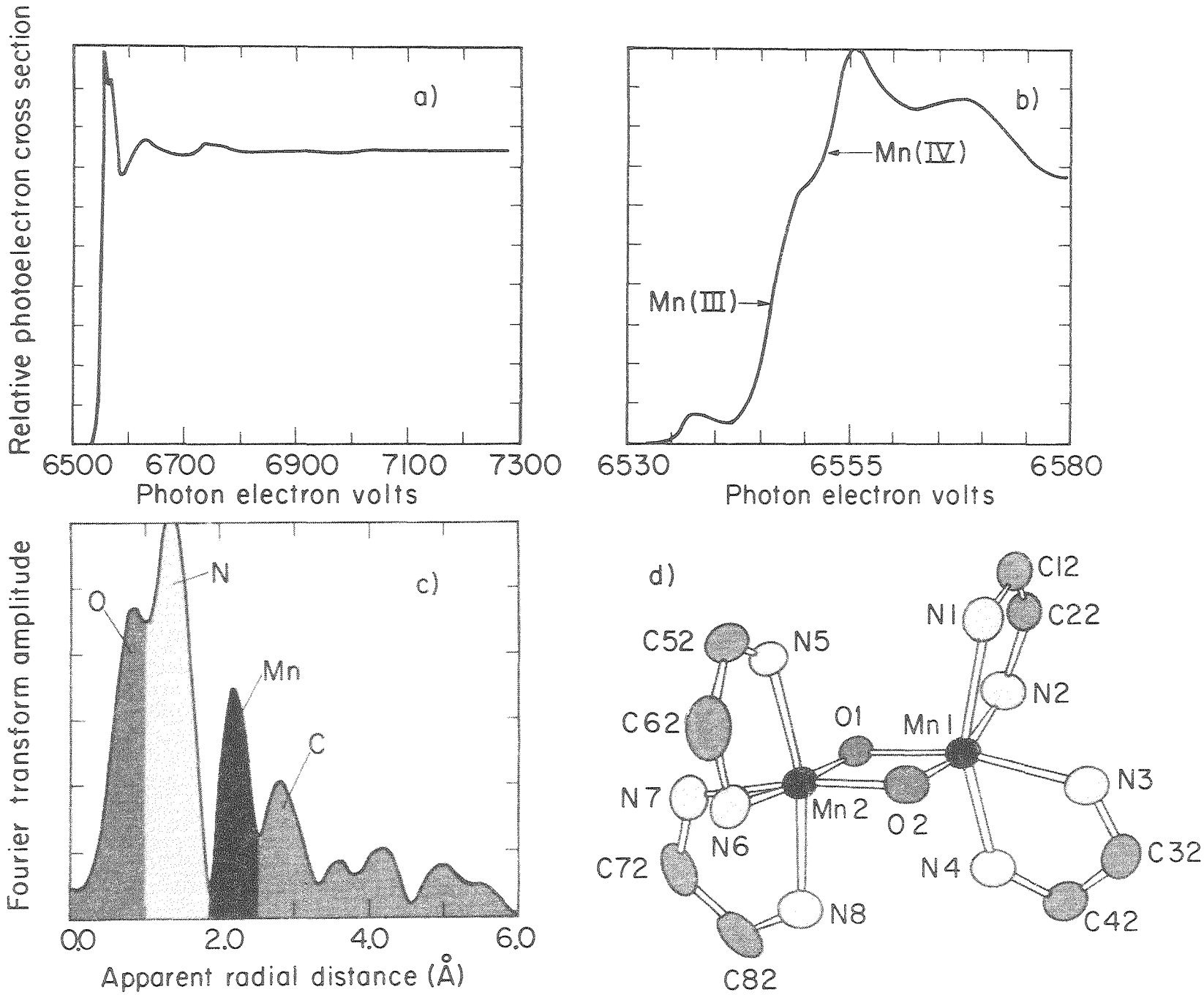


Fig. 13

CBB 786-6999

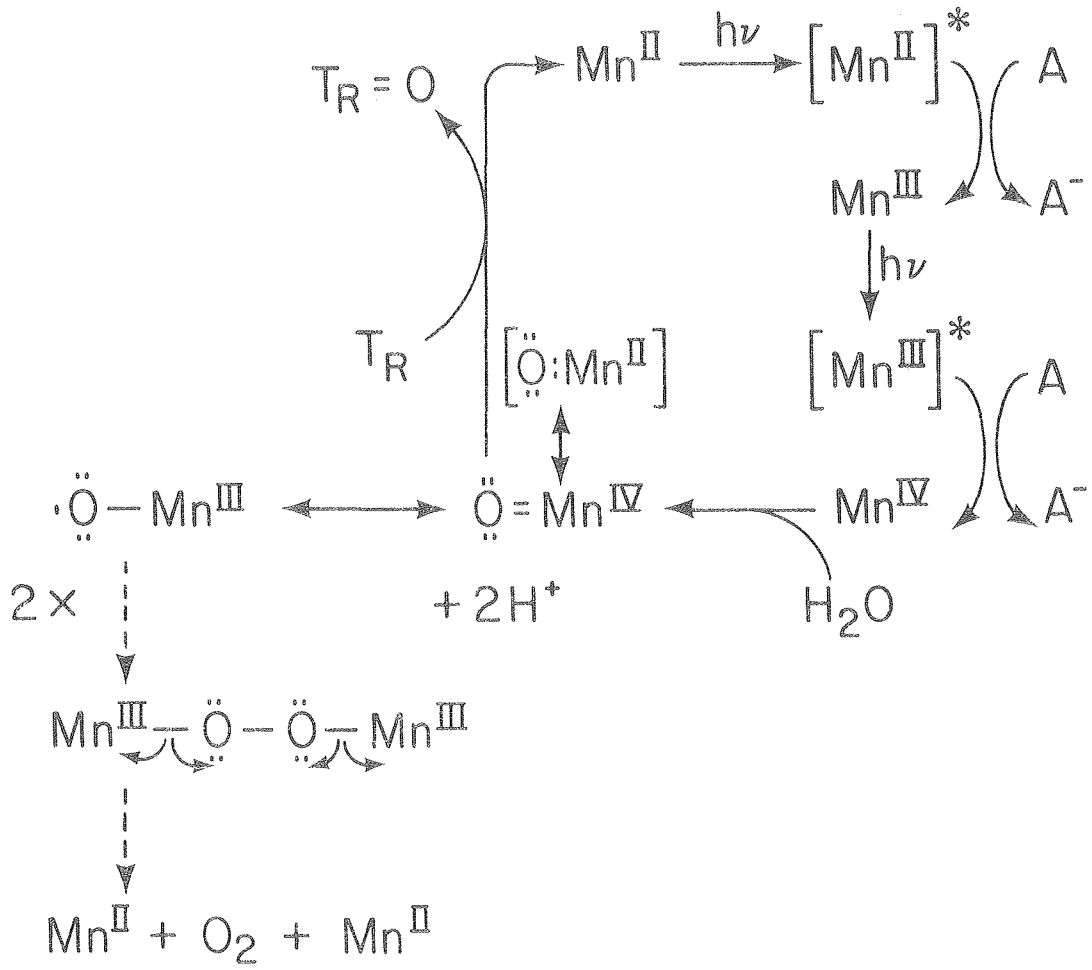


Fig. 14

XBL 802-4023A

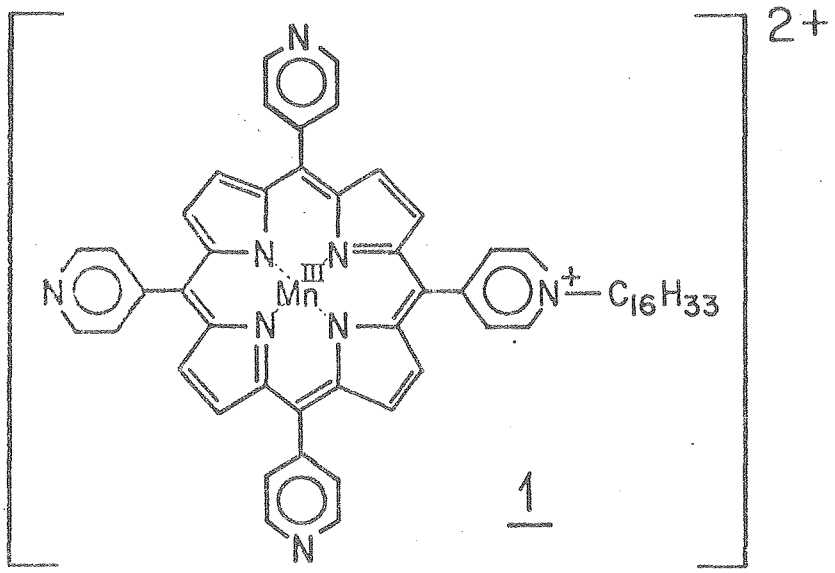


Fig. 15 XBL 796-4864

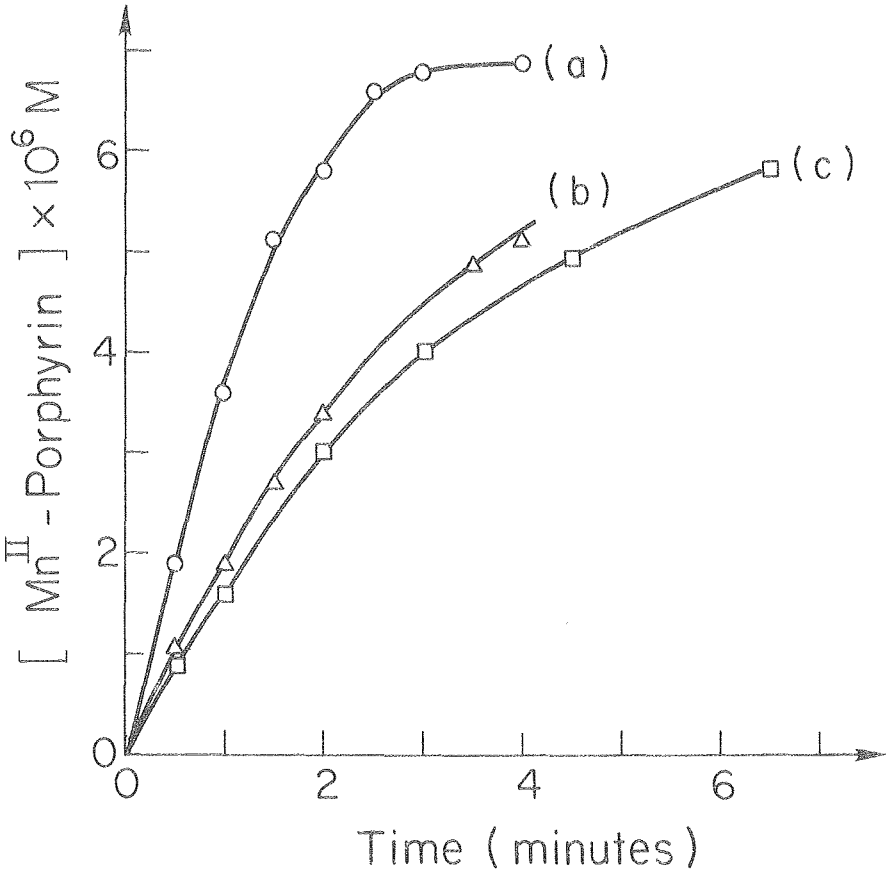


Fig. 16

XBL795-4772A

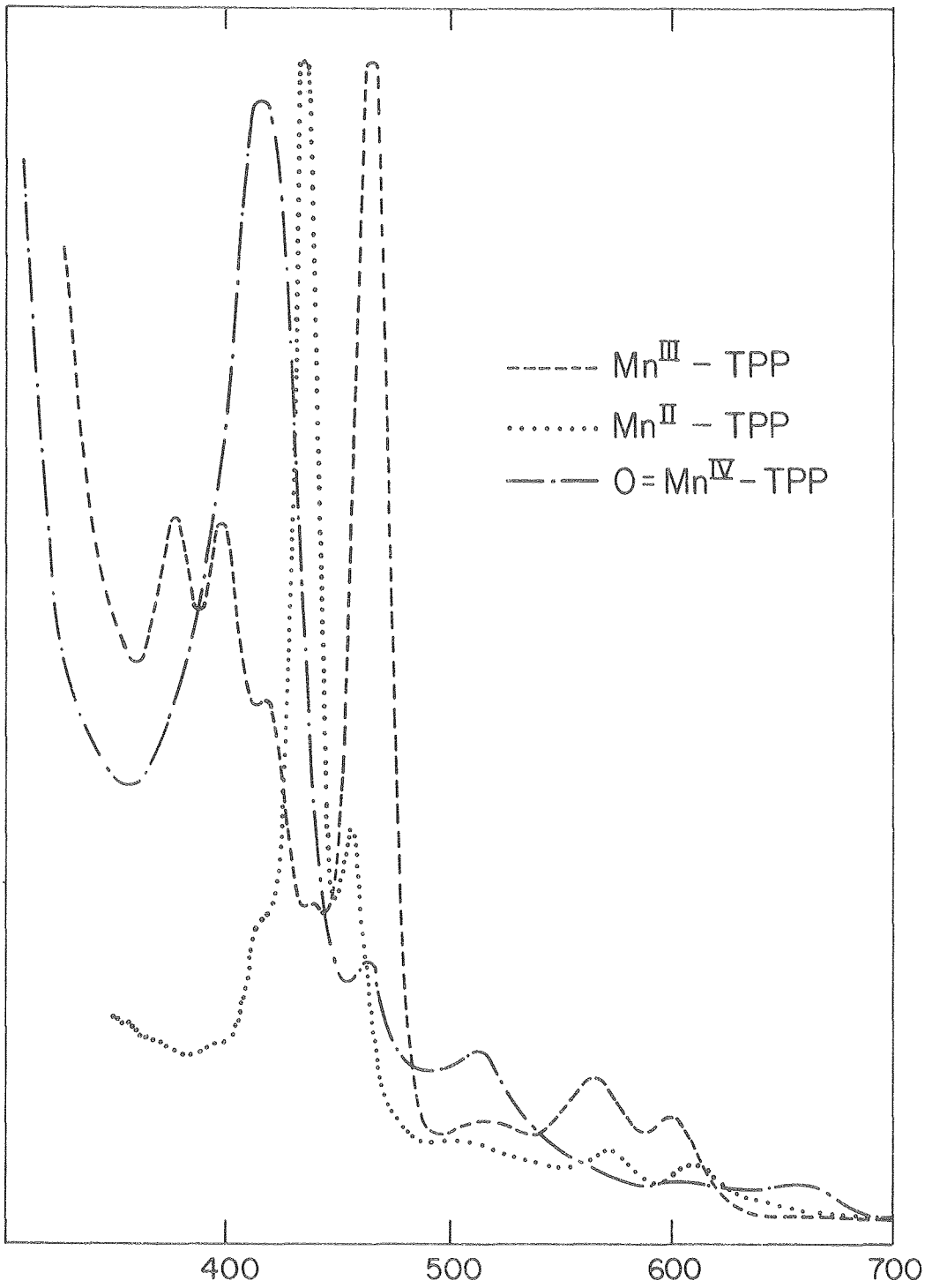


Fig. 17

XBL 802-4059

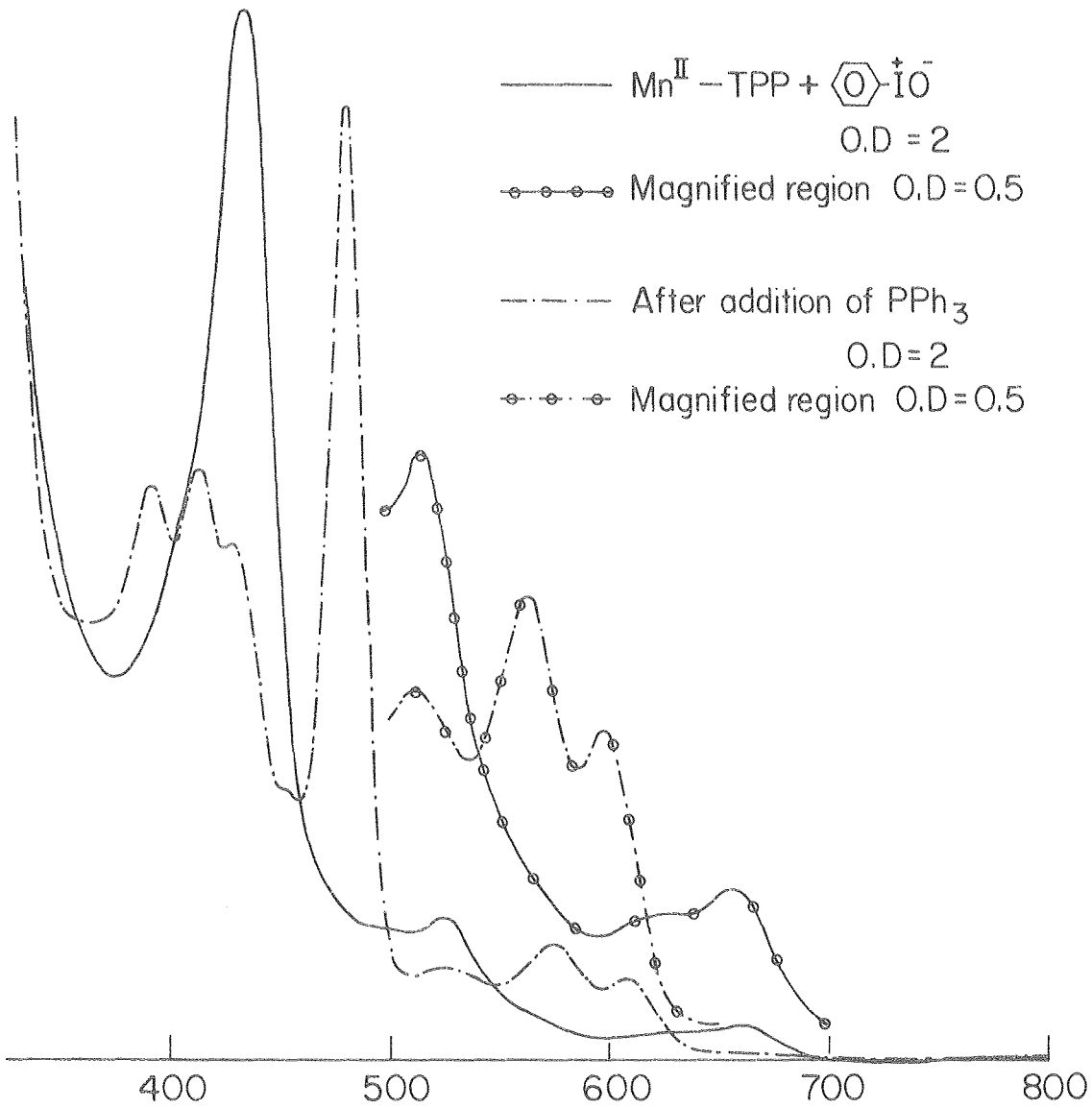
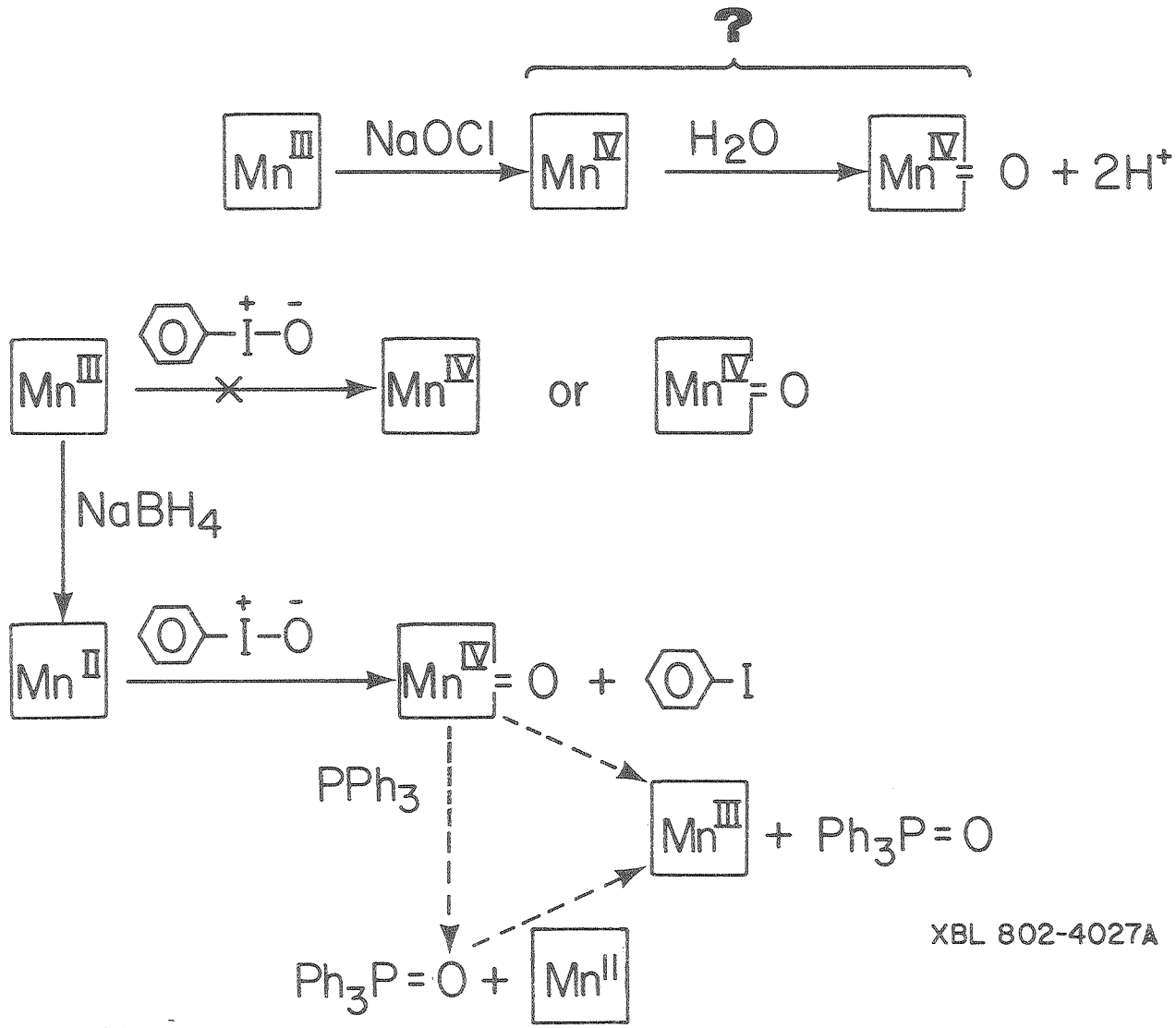


Fig. 18

XBL 802-4028



XBL 802-4027A

Fig. 19

$$2H_2O \longrightarrow O_2 + 4H^+ + 4\bar{e}$$

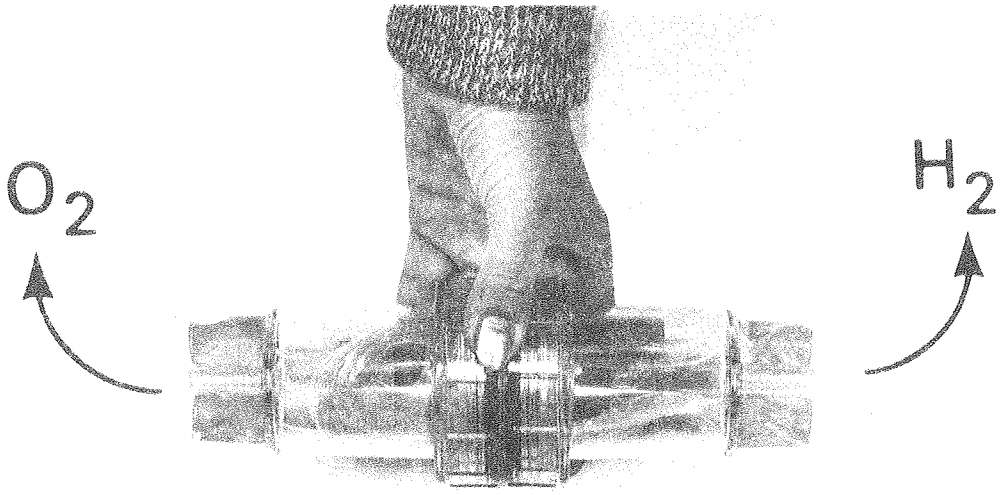
$$H_2O \longrightarrow [:\ddot{O}:] + 2H^+ + 2\bar{e}$$

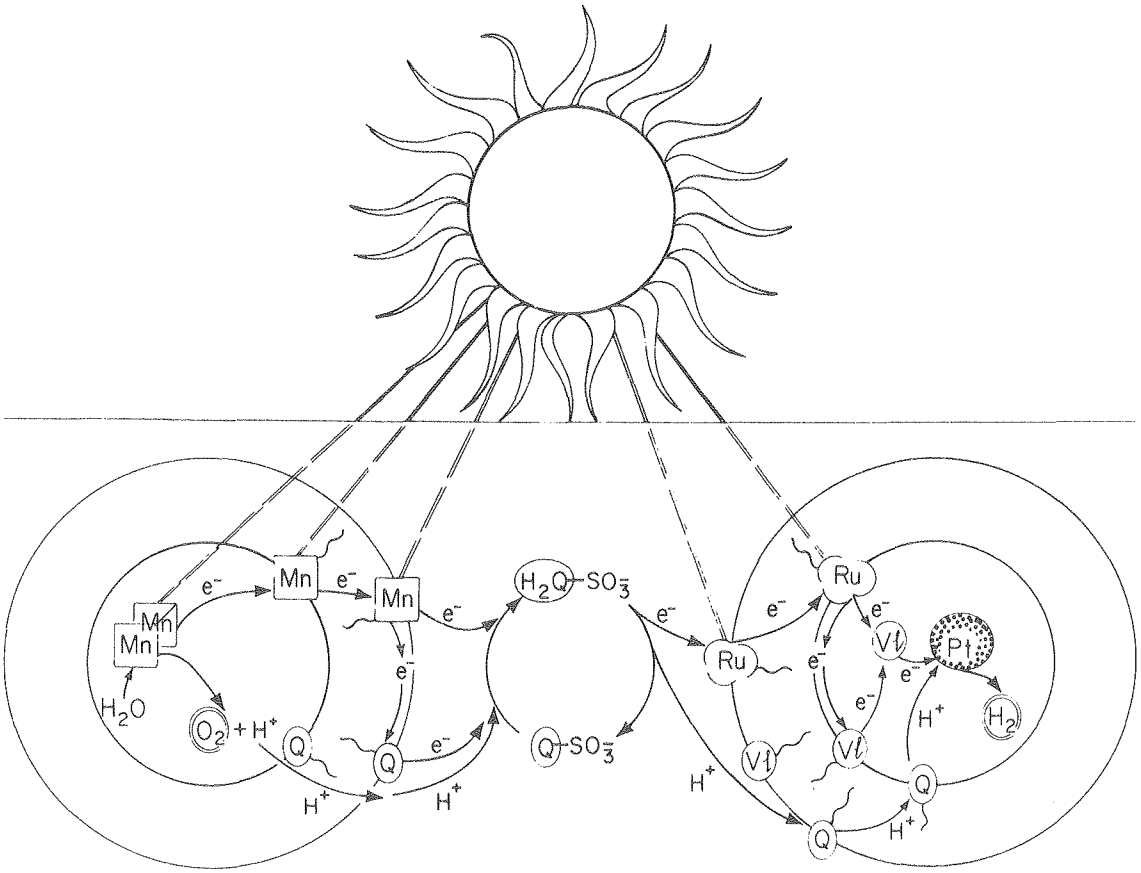
$$T_R{:} + [:\ddot{O}] \longrightarrow T_R{=}O$$

$$2 \times T_R{=}O \xrightarrow{\text{Cat.}} 2 \times T_R + O_2$$

$$T_R + H_2O \xrightarrow[(h\nu)]{S} T_R{=}O + H_2$$

Fig. 20 XBL 802-4026





Schematic for synthetic chloroplasts

Fig. 22

CBB 7810- 13629

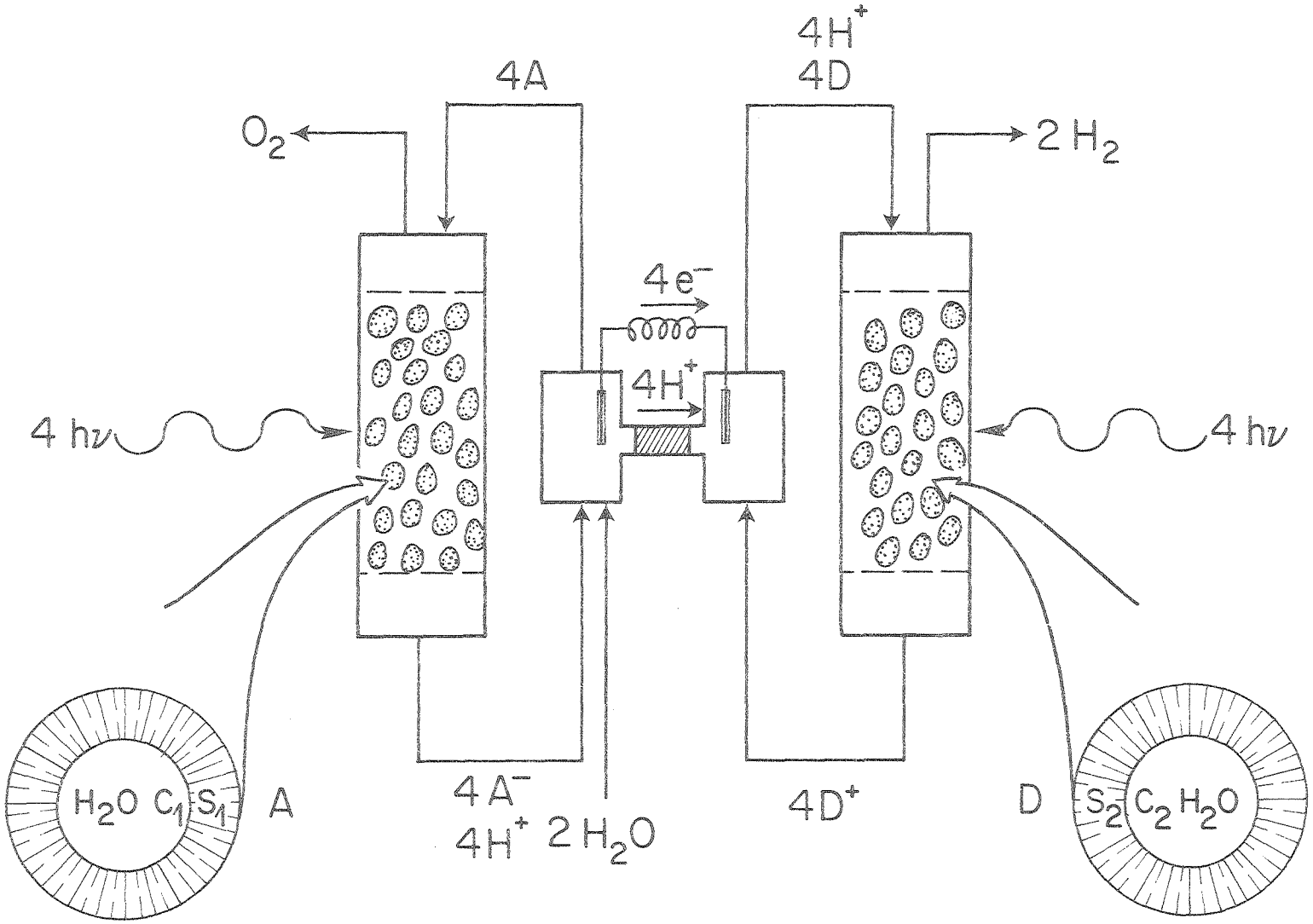


Fig. 23

XBL798-4987

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