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AND RELATED SUBJECTS

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Quantum Conversion in Chloroplasts*

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I. Introduction

In this chapter† we may not use the terms catalysis or catalysts explicitly. However, we can state at the outset that the whole photosensitive system that we are discussing is a catalytic system for converting electromagnetic energy into chemical energy. The system itself, to a first approximation, remains unchanged and, therefore, fulfills the definition of a catalyst. Within the system there are a great many individual catalytic steps, some of which are clearly defined and recognized, and others as yet less known. Yet the primary quantum conversion process involves perhaps the most important case of radiation catalysis. It is followed by the numerous catalytic steps which constitute a large chapter of the chemistry of life processes.

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One of our major interests for the past fifteen years has been the mechanism by which the green plants can convert electromagnetic energy into chemical energy. The over-all reaction by which plants do this, chemically at least, is written in the following terms:

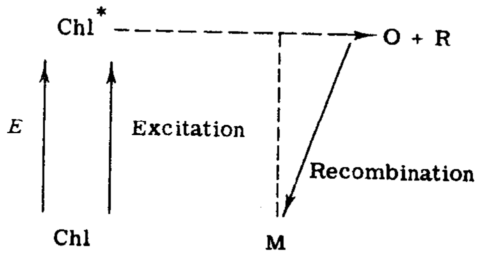
$$CO_2 + H_2O \xrightarrow{h\nu} (CH_2O)_n + O_2$$

This is the over-all process in which light is converted into chemical potential and that light is the light which is first absorbed, in most cases, by chlorophyll.

A good deal of work has gone into breaking the process of photosynthesis down into a whole series of physical and chemical steps, and I will briefly define those aspects which have led to the present subject matter. Very early in the work, the reduction of the carbon dioxide by a reducing agent to produce carbohydrate was shown to be a separate and independent reaction, independent at least of the primary light absorption and conversion process (*1*). Using radiocarbon, we have drawn a rather detailed map of the route from CO_2 to carbohydrate and a variety of other plant materials (amino acids, proteins and the like) (see refs. *2–6*; for a complete review of the path of carbon in photosynthesis, see *6a*). The other half of the process, the primary quantum conversion, was and has been for many years associated with the so-called photolysis of water. Here, we come to a matter of definition of terms. We can write the first step as the absorption of light by the chlorophyll to produce an excited chlorophyll, and the excited chlorophyll then is presumed to react with some molecule to produce two species of some sort—let us call them O and R. It is at this point that the electronic excitation is converted, at least hypothetically, into two chemical species which should have stored in them the energy corresponding to the original excitation. They should be able to liberate very nearly all of that excitation upon back reaction:

$$\mathrm{Chl} + h\nu \xrightarrow{\qquad\qquad} \mathrm{Chl}^*$$

$$\mathrm{Chl}^* + \mathrm{M} \xrightarrow{\qquad\qquad} \underset{\substack{(\mathrm{OH})\\(+)}}{\mathrm{O}} + \underset{\substack{(\mathrm{H})\\(e)}}{\mathrm{R}} + \mathrm{Chl}$$

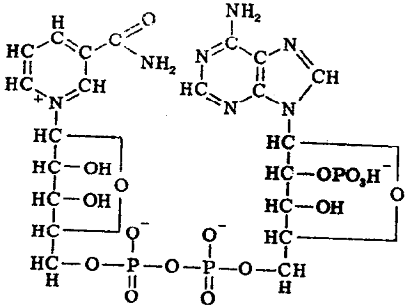


In other words, these two chemical species, O and R, whatever they are, upon recombination will liberate some quantity of energy approaching that which was originally used to create them. This can be said because the over-all efficiency of the process is relatively high as photoprocesses go. It is certainly not less than 20 to 30%, and there are those who believe it may be as high, over-all, as 60% or more. Even if we accept a number as low as 30% as the upper limit of the over-all efficiency of the quantum conversion, we require that the initial step be of very high efficiency, because in the succeeding reduction of the carbon dioxide we already know that we are not more than 80% efficient in the chemical steps. If we are going to end up with an over-all efficiency of not less than 30%, we must have a very efficient transformation in the very first step.

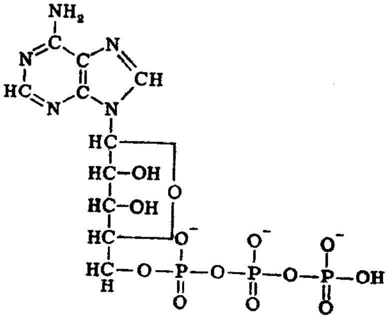
II. Energy Sources for Photosynthesis

Commonly this transformation, as I said earlier, has been written in terms of the photolysis of water. The biochemists and biologists have tended to call this molecule (M) a water molecule, and call the product O some kind of a hydroxyl radical, in an unknown form, and the product R some kind of a hydrogen atom, again in some unknown form (*7–10*). The chemists who have been working on this area, on the other hand, have tended to go one step further in their generalization and call one of the products an oxidant (O) and the other a reductant (R). But that really doesn't say much more than the other description, given by the biochemists and biologists. Still more recently, physicists have entered the picture and they have tended to write the reaction in a slightly different way, calling the reductant, the electron, and the oxidant, the "hole" (*11*, *12*, *13*). These are completely parallel representations of the energy conversion process. This is all that was meant by the statement that the primary quantum conversion process involves the photolysis of water. The ultimate result must be, as we know, generation of molecular oxygen from the oxidant (whether we call it a hole, an oxidant or hydroxyl radical in some unknown form) and generation, on the reduction side, of electrons or chemical species which can be defined as a reduced species, or a hydrogen atom bound to some particular form. The reductant will eventually be used in the reduction of carbon dioxide to produce the carbohydrate.

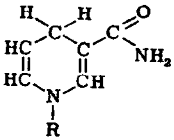
We already know from our earlier mapping of the path of carbon in photosynthesis that we need not only a reducing agent for the reduction of carbohydrate but also, in addition, a rather specific type of chemical. Since we know the exact steps for carbon reduction, we were able to define what this reducing agent is at the last stages at which it is used. It is a reduced form of pyridine nucleotide (TPNH). In addition to this molecule which carries the hydrogen, we know that we need some pyrophosphate linkage, generally in the form of adenosine triphosphate (ATP):



Triphosphopyridine nucleotide (oxidized form) (TPN^+)



Adenosine triphosphate (ATP). In adenosine diphosphate (ADP) terminal phosphate is replaced by -OH



Nicotinamide portion of TPNH (reduced TPN^+)

The pyrophosphate linkage (in ATP) is required to assist in the final reduction of the carbohydrates. We know that this molecule must also be produced somewhere in the region of the initial photochemical act.

There has been a good deal of work done which has demonstrated that both TPNH and ATP are indeed produced by the photochemical apparatus of the plant (*14*, *15*), and there has been a good deal of additional work trying to define exactly where along the chain of events—that is, on the route from the oxidant to oxygen, or from the electron (or the reductant) to carbohydrate—the polyphosphate (pyrophosphate) is produced. There is some suggestion that it may be produced as the electron (hydrogen atom, reductant) moves down from its initial high energy level. One could also conceivably produce the pyrophosphate as the "hole," or oxidant, drops down some sort of energy hill toward oxygen. Finally, there could be some recombination of the separated products through an enzymic mechanism which would give rise to pyrophosphate here as well. All three types of transformations are potential sources for the generation of a pyrophosphate linkage. There have appeared in the course of breaking down the fragments of plants, a variety of experiments in which there has been some demonstration that the recombination process works (*9*, *10*, *16*). The most popular notion currently is that most of the pyrophosphate arises along the route of the hydrogen on the way down, and some by recombination. But all three are real possibilities.

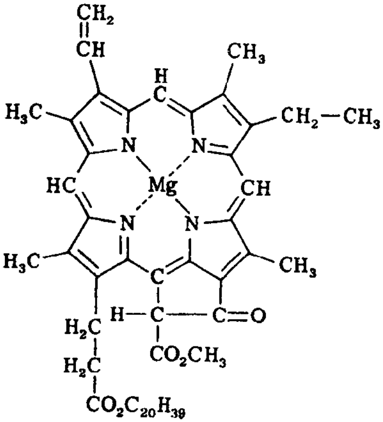
III. Photochemistry of Chlorophyll

What we are concerned with is not what happens after this primary quantum conversion act but only what the nature of the primary act (or acts) itself may be. There is a good deal of information developing in the region of the reaction following the primary process, particularly on the reducing side, and relatively little on the oxidized side yet, and some on the recombination. But it is the primary act itself that we will be concerned with here.

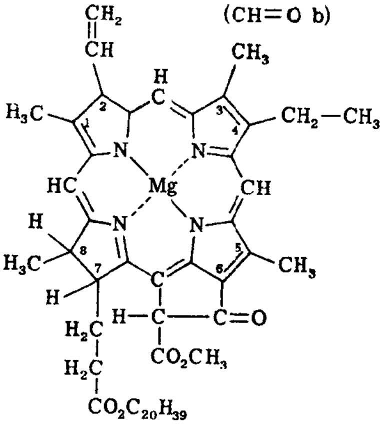
In order to see what our train of thought was over the course of the years, one should remember the structure of chlorophyll and a few things that have been done in an attempt to try and find out what the primary quantum conversion act of photosynthesis was. There are a number of peculiarities about the structure of chlorophyll which have led many chemists to suggest a number of reactions which might possibly be involved in the primary quantum conversion act.

A. PHOTOCHEMISTRY OF CHLOROPHYLL IN SOLUTION

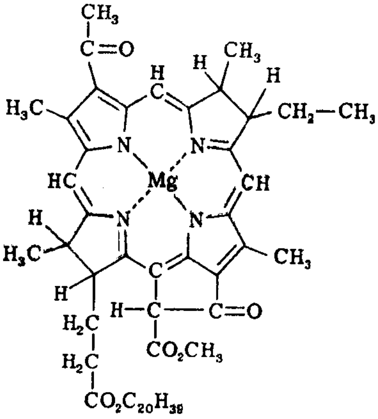
Over the past fifty years, ever since Stoll first gave us the basic notion as to what chlorophyll was like (*17*), and in the last twenty years since the structure has assumed its present form (*18*, *19*), a good many attempts have been made to study the photochemistry of chlorophyll in solution to try and find out if the nature of the primary quantum conversion act could not be worked out. For example, this author and his colleagues spent a good deal of time on the assumption that the "extra" pair of hydrogen atoms which is involved in the conversion of porphin to chlorin (ring IV) might be involved in the photochemistry, that is, chlorophyll might be functioning between the porphyrin, or protochlorophyll, and chlorophyll (*20*). In the plant in the steady state it is, of course, mostly in the form of the dihydro compound, but upon illumination it might reduce something and then the protochlorophyll so formed might pick up the two extra hydrogens from the water molecule. This is one type of reaction which has been suggested.



Protochlorophyll



Chlorophyll a (b)



Bacteriochlorophyll

Another point of great interest which has attracted considerable attention is the enolizable hydrogen on carbon atom No. 10 in the isocyclic ring. There have been a number of schemes devised and a good deal of photochemistry done with a view toward possibly using this particular reactive point as the point at which the water molecule was split, or the CO_2 molecule was reduced (*21–24*). None of this work has been very fruitful, except to give more information about the photochemistry of chlorophyll in solution. It has not, however, led to any model reaction in which anything approaching the 35 kcal, which the excited chlorophyll bears, is stored in the reaction product. In fact, as far as I know, there is not *any* photochemical reaction in solution in which a very large fraction (more than 50%, say 80 to 90%) of the energy in the excited state is stored in the immediate reaction product. This is not surprising when you to stop to think about it in retrospect. The excited state of chlorophyll stores about 35 kcal. If the products also had to have in them an appreciable fraction of this, say 30 kcal, the products cannot have a barrier for their return in the back reaction of more than this difference, whatever it is—and it cannot be very large. For this reason, the back reaction generally does take place, and one is not successful in separating the energetic products in any photochemical model in solution, with chlorophyll or any other substance for that matter.

IV. Photophysical Effects in Model Systems

A. ENERGY TRANSFER IN MODEL SYSTEMS

After spending a good many years of our own lives, as well as having looked at the efforts of many others, there occurred a concatenation of circumstances which focused our attention on quite a different point of view. The first of these resulted from the examination of the photochemical apparatus of the plant itself, shown in Fig. 1, which is an electron micrograph of a tobacco chloroplast in which all of the photochemistry occurs. The layers are roughly 60 A thick and this will give some idea of the highly ordered structure in which the photochemistry is performed. The chloroplasts contain a highly ordered array of chlorophyll and many other molecules. Figure 2 shows a still higher magnification of one of the small lamina (lamella), and one can see that they are themselves composed of small spherical molecules which are packed in some as yet hypothetical way; it looks as if they are packed together to form the lamina, one sphere on top of the other (*25*). These photographs show that we are not dealing with molecules in solution in the ordinary sense at all when we consider the photochemical apparatus.

FIG. 1. Electron micrograph of tobacco chloroplast.

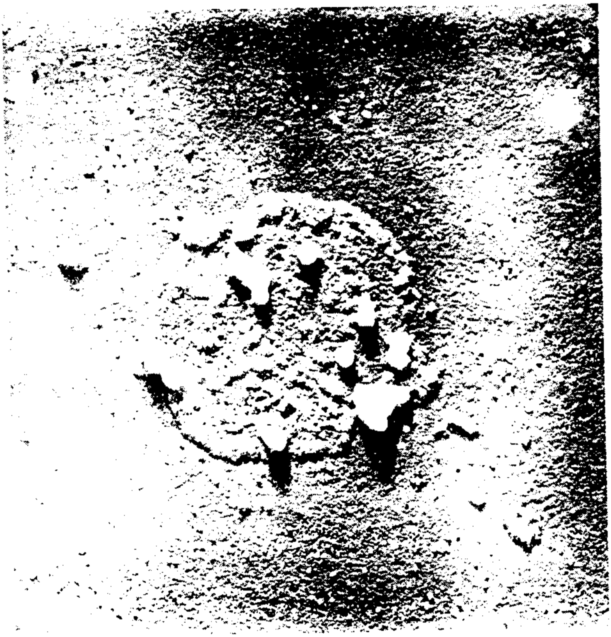


FIG. 2. Electron micrograph of frozen dried spinach sonicate showing "Quantasomes"; 880 A diameter polystyrene latex markers (25).

We are dealing with a highly ordered array of substances. What that array is on the molecular level—i.e., how the plane of the chlorin ring is located with respect to these layers or with respect to the spherical globules of which the layers seem to be composed—is still a matter of controversy and remains one of the areas which this writer would like to see the physical chemists explore. It is necessary to bridge the gap between ordinary statistical molecular behavior and individual structures that can be seen. We do not know, for example, what the arrangement of the chlorophyll molecules is in the lamellar layers. Order is, however, the major factor with which we are left.

One of the other two factors which came together some years ago and which increased our interest in this kind of work was the first report by one of my former associates, D. D. Eley of the University of Manchester, England, of the fact that an organic molecule which had some of the structural features of a porphyrin, namely, phthalocyanine, had the properties of a semiconductor (*26*). He reported the nature of that conductivity and something about the energy gaps that were involved. The third piece of general knowledge which came our way and influenced us to change our point of view in an attempt to understand this primary quantum conversion act was the description of a quantum converter made up of a solid atomic lattice. This was the silicon photobattery in which the Si lattice had in it certain impurities (atoms which had either an excess electron, or had shortage of electrons), and a suitable structure was devised which was able to convert the quantum into electrical potential with an efficiency at first of only 3%; this efficiency has since gone up to 10 to 12%.

This fact, taken together with the other two (recognition of the ordered structure of the photochemical apparatus in the plant and the development of the concepts of organic semiconductors) on top of the theoretical arguments that we have no real way of chemically separating the high energy products that must be formed, and the failure of all experimental attempts to find any, led to the supposition that perhaps the quantum conversion act was not a photochemical process at all but something more resembling the *photophysical* process which occurs in the atomic lattices (*14*, *27*, *28*). Instead of using atomic arrays to achieve the separation of products we would use an organic molecular array, of which chlorophyll was one of the principal constituents.

B. PHTHALOCYANINE AS A MODEL FOR CHLOROPHYLL ENERGY TRANSFER

In order to develop this notion we undertook the model studies which will be discussed below, the determination of the electrical and magnetic properties of organic solids. The first type of solid which was studied was phthalocyanine itself, since this was the first one that was reported by Eley. The real problem was not the conductivity of the phthalocyanine but how it might interact with other molecules that might be present in a chloroplast system—electron donors and electron acceptors corresponding to the donor and acceptor systems in the atomic lattices. We here made use of the background of organic oxidation-reduction which was available to us, both in terms of the knowledge of the nature of the oxidation-reduction reactions and also the knowledge of the nature of the interactions between donors and acceptors which has been growing steadily in the last decade. (The growth of our knowledge of the interaction of donor and acceptor molecules had one of its principal starting points here in Berkeley with the work of Hildebrand and Benesi *(29)* on iodine and benzene interactions).

C. PHOTOINDUCED CHARGE SEPARATION AND QUANTUM CONVERSION

The first thing we wanted to find out was whether or not it was possible to devise a system of donor and acceptor molecules, of which chlorophyll might be either, in which the primary quantum conversion act was not a production of molecules which themselves have to separate from each other, but rather purely a *separation of charge rather than a separation of atoms* (*28*). The charge could separate not by molecular diffusion but simply by charge diffusion. This kind of a separation process could occur much more easily and readily than the molecular diffusion process, and if there is a proper lattice arrangement of donors and acceptors, there will be a chance to achieve this kind of separation with concomitant quantum storage. Actually the work so far done has not demonstrated such a storage unequivocally, but it has been very suggestive and should be discussed further.

The systems that were used by this writer and colleagues contained one of some four or five different donor molecules—phthalocyanine, violanthrene, perylene, etc.—we found that almost any highly aromatic system could serve as a conducting matrix and phthalocyanine was only one of these. The electron acceptor systems that we used were o-chloranil (the most commonly used), iodine and tetracyanoethylene. These donor and acceptor systems were used in various combinations. A pattern of results based on a conductivity cell is shown in Figs. 3a, b, and c. It is made of aquadag electrodes on which is coated the matrix (phthalocyanine or violanthrene, as the case may be); usually the samples are sublimed onto the electrode system. On top of the matrix is placed one of the "doping" agents, one of the donors or acceptors.

In most of our work the matrices have been the donor molecules and the other part of the layer has been the acceptor molecules, which is either sublimed on top or sprayed on in a dilute benzene solution. These are the two principal ways in which the acceptor molecule is laid onto the donor.

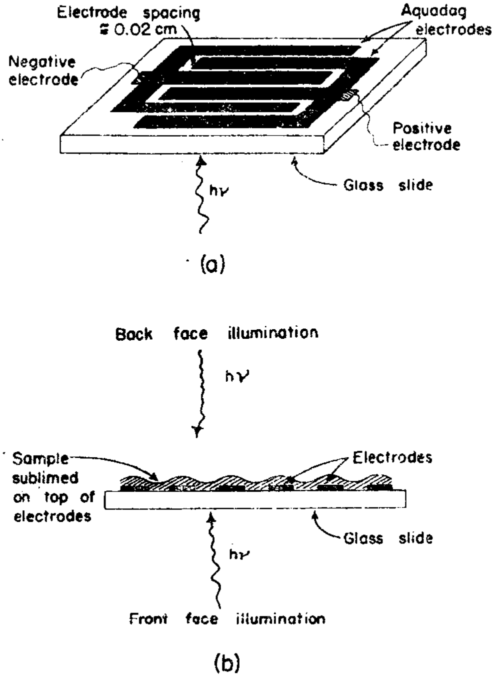


FIG. 3. Diagram of sample conductivity cells.

We have measured, in most cases, the conductivity between the electrodes, both in the dark and upon illumination, as a function of the added acceptor molecules (*30*, *31*, *32*). Figure 4 shows the results of such an experiment using phthalocyanine. You will notice that the dark conductivity of the system rises by a factor of almost one million as small amounts of electron acceptor, o-chloranil, are added to the

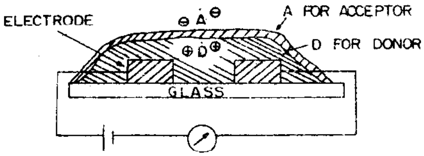


FIG. 3c. Layered donor-acceptor system.