PHOTOCHEMICAL UTILIZATION OF LIGHT ENERGY

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1. Introduction.—Nature offers us an imposing example of photochemical storage and utilization of light energy in the photosynthesis of plants. All life energy of animals, as well as the overwhelming proportion of energy man uses to heat his dwellings, smelt metals, and keep the wheels of industry turning, is derived from recent or ancient photosynthesis.

Of course, plants are not only energy converters, producing fuel, but also photochemical factories, synthesizing carbohydrates from water and carbon dioxide. These, in turn, serve as substrates for the enzymatic synthesis of all other types of food and of a variety of components of living organisms.

For his food, man still is entirely dependent on plants; but he may be approaching plants in his capacity of converting light into other, usable forms of energy. As we have heard in this symposium, solar batteries, thermoelements, or barrier layer cells can now convert sunlight into electrical energy with a yield of between 5 and 10 per cent. However, no known photoelectric or thermoelectric conversion devices are cheap enough to consider covering large areas—open fields, deserts, rooftops—with such converters to produce commercial energy.

Out of an average of \(1 \times 10^{13}\) kcal of solar energy (visible and infrared) reaching the surface of the earth (including the oceans) each second, about \(5 \times 10^{10}\) kcal, or 0.5 per cent, are stored as chemical energy by plants growing on land or floating in the ocean. (A considerable uncertainty of this estimate is caused by the limited data available on the rate of photosynthesis by phytoplankton in different parts of the world ocean.)

The efficiency of utilization, by plant-covered land areas, of the incident visible light (excluding the infrared), averaged over the annual growth period, has been estimated as of the order of 2–3 per cent. In experiments with intensely stirred algal suspensions, this yield could be raised to 5–7 per cent, and in short-time laboratory experiments, to 20–30 per cent. The assertion by O. Warburg, that the conversion yield of photosynthesis can be pushed, in manometric experiments, up to 90–100 per cent is implausible and could not be confirmed by other investigators, employing the same or a variety of other methods.

The above figures suggest that the efficiency of photosynthetic energy storage under natural conditions is determined, not by intrinsic limitations of the efficiency of the photochemical process itself, but by some secondary causes. The most fundamental of these may be the limited supply of carbon dioxide in nature. With a normal atmospheric concentration of only 0.03 per cent CO\(_2\), it is truly re-
markable that land plants can maintain a rate of about 20 mg CO₂ reduced per hour per 100 cm² of leaf surface, which is needed to produce an average conversion yield of 2 per cent. Other limitations of the over-all rate of photosynthesis are caused by enzymatic bottlenecks; these do not allow a much higher rate of photosynthesis to be reached even with an artificially increased supply of CO₂. However, these enzymatic limitations may be due to the adaptation of plants to the naturally available supply of CO₂: there would be no use for them to accumulate enzymes in amounts capable to handle much more substrate than is available under natural conditions. For the same reason, it is of no particular significance to plants (at least, to land plants) whether their pigments—in particular, chlorophyll—absorb all or only part of the available light, since the average supply of light exceeds that of carbon dioxide. (Plants living deep under water are in a different position—they often depend on the presence of additional pigments, such as fucoxanthol or phycocerythrin, to insure absorption of sufficient amounts of the dim, greenish light that reaches them.)

This suggests the possibility not only of imitating in vitro the photosynthetic performance of plants but even of improving on it by devising photochemical systems with wider spectral sensitivity and higher primary energy conversion yield, and (most importantly) without an early "light saturation," caused in photosynthesis by enzymatic "bottlenecks."

There is no reason to assume that man will never discover inexpensive photochemical systems permitting the conversion of, say, 10 or 20 per cent of incident solar energy either into potential chemical energy (such as that of an explosive gas mixture) or into electrical energy. Some such attempts have been made, using simple inorganic systems. An example is the system $2\text{NOCl} \xrightarrow{hv} 2\text{NO} + \text{Cl}_2$, studied by Daniels and co-workers. However, I intend to discuss here not these simple reactions, but the more complex ones which could be considered as analogous to the primary process in photosynthesis.

2. The Primary Photochemical Process in Photosynthesis.—The exact nature of the reaction by which light energy is first converted into chemical energy in plants remains uncertain. From indirect biochemical evidence there is a widespread inclination to believe that this reaction is two-fold, involving the reduction of a pyridine nucleotide, such as TPN, by water, the latter being oxidized to free oxygen:

$$\text{TPN} + \text{H}_2\text{O} \xrightarrow{hv} \text{TPNH}_2 + \frac{1}{2}\text{O}_2,$$

(1)

and the conversion of adenosine diphosphate into adenosine triphosphate (photophosphorylation):

$$\text{ADP} + \text{P} \xrightarrow{hv} \text{ATP},$$

(2)

where $\text{P}$ stands for "low energy," inorganic phosphate. Repeated suggestions—revived in a recent review by Stanier in the *Bacteriological Reviews*—that photophosphorylation is the only primary energy-storing reaction in photosynthesis, appear to me very implausible and unsupported by the totality of experimental evidence. It seems more plausible that photophosphorylation itself is a secondary process; it could result from partial reversal of a reaction of type (1). It is well known that in respiration, the oxidation of pyridine nucleotide produces several molecules of ATP.
It is known that TPNH₂ and ATP together can bring about (in the presence of proper enzymes) the reduction of carbon dioxide (incorporated in a carboxyl group) to the carbohydrate level.

Since the oxidation-reduction potential of the couple TPN/TPNH₂ is about \(-0.3\) volt and that of the couple \( \text{H}_2\text{O}^+/\text{O}_2 \) about \(+0.8\) volt, reaction (1) leads, under standard conditions, to the storage of \(2 \times 1.1\) ev, or about 50 kcal/mole, of free chemical energy (the factor 2 originating from the involvement of two electrons), whereas reaction (2) stores, under standard conditions, only about 10 kcal/mole.

Recently, evidence has been obtained (in our and in other laboratories) that photosynthesis involves (at least) two primary photochemical processes, sensitized by two different forms of chlorophyll \(a\). These two processes could conceivably correspond to equations (1) and (2), respectively: an oxidation-reduction, and a photophosphorylation. However, even if this be the case, reaction (2) could still result from the reversal of a process of type (1): both forms of chlorophyll \(a\) could sensitize an oxidation-reduction against the gradient of chemical potential; but one of these reactions could be reversed, with the formation of high-energy phosphate, while the products of the other could be prevented from recombination and become available for the reduction of carboxyl groups.

According to a plausible hypothesis by James Franck, the two types of chlorophyll \(a\) differ by their association with either a hydrophilic or a hydrophobic medium.

3. *Prevention of Back Reactions.*—A chlorophyll molecule excited by visible light contains about 45 kcal/mole or about 2 ev of electronic excitation energy. This is enough to transfer an electron, even from a very weak oxidant, to a very weak oxidant, since two volts span almost the whole series of oxidation-reduction potentials. The difficulty, which requires ingenious solution, lies therefore not so much in the achievement, by means of visible light, of a sufficiently endergonic oxidation-reduction reaction, as in effective prevention of the reversal of this reaction, which would lead to the loss of stored energy. In principle, this could be done in two ways—by chemical stabilization, or by physical separation of the unstable products.

The structure of the photosynthetic apparatus makes tempting the second hypothesis—that of physical separation of the intermediates. This structure is characterized by thin parallel lamellae. These are not always as neatly arranged as shown in Figure 1 (a) or (c), but they are always there, even in the most primitively organized blue-green algae (d) and photosynthetic bacteria. Each lamella probably consists of alternating layers of hydrophilic (proteidic) and hydrophobic (lipoproteidic) materials. Chlorophyll probably is located on the interfaces between hydrophilic and hydrophobic layers, forming monomolecular (or bimolecular) layers. One can imagine an excited chlorophyll molecule transferring one electron to an “acceptor” molecule in the adjacent lipoidic layer and recovering it on the other side from a proteidic layer (or vice versa). The two reaction products thus find themselves in two different phases and can undergo enzymatic stabilization, ultimately leading to their conversion into carbohydrate and molecular oxygen, without danger of immediate recombination.

It has been suggested, e.g., by Calvin, that this separation of products may be based on an electron migration similar to that occurring in crystalline photoelectric conductors. However, with a monomolecular pigment layer, all that is needed is for the electron to migrate across a single chlorophyll molecule, and this is always
possible in an aromatic ring system. No \textit{intermolecular} photoconductivity is needed in this case; and such conductivity is made unlikely by the non-crystalline nature of chlorophyll monolayers \textit{in vivo}, evidenced by the position of their absorption bands.

4. \textit{Variations of the Photosynthetic Process}.—The photochemical apparatus can be used for different variations on the general theme of photosynthesis. In one class of them, carbon dioxide is replaced by another oxidant. For this purpose, cell-free chloroplasts are best used, because the membrane of the intact cell blocks the passage of many oxidizing compounds which can otherwise participate in the reaction. The only “substitute oxidant” so far found to be usable with whole cells is benzoquinone, but with chloroplast fragments, a large variety of oxidants, such as ferric salts, quinones, and dyes have been successfully employed.
Another variation of photosynthesis is based on substitution of a different reductant for water—molecular hydrogen, hydrogen sulfide, or an organic compound, RH₂. This is the normal form of photosynthesis in bacteria; but Gaffron has shown that it can be induced, by incubation in hydrogen, also in certain algae.

All these variations affect little, if at all, the quantum efficiency of the photochemical process, or its action spectrum; but, since all substitute oxidants and all substitute reductants are stronger than CO₂ and H₂O, respectively, the amount of light energy converted into chemical energy in these varieties of normal photosynthesis is quite low or even negative. In these reactions, it is the activation energy of an otherwise sluggish reaction that is primarily or exclusively supplied by light.

5. Model Reactions in Vivo.—Reactions in vitro, which could be broadly considered as analogous to the energy-storing photochemical reaction in photosynthesis, are various light-induced oxidation-reductions against the gradient of electrochemical potential. Two additional criteria are important: (1) The reaction should be sensitized, so that the light-absorbing pigment would not be consumed but regenerated, as chlorophyll is in photosynthesis, and (2) the oxidation and reduction products should not react back immediately, dissipating the stored energy, but survive long enough to be separated.

In photosynthesis, the two final products, O₂ and \{CH₃O\}, are stable practically indefinitely. An acceptable alternative in vitro would be delayed recombination—delayed long enough to permit the conversion of a considerable part of the stored energy into some useful form, such as electrical energy.

Photochemical electron transfers against the gradient of chemical potential are common; every electronically excited molecule can be considered as a powerful reductant, able to transfer its excited electron to a reluctant acceptor—and often also as a powerful oxidant, able to take an electron away from a reluctant donor. Electrochemical and spectroscopic evidence suggests that in every "stable" light-absorbing system which contains oxidizable or reducible components, there do occur, despite apparent stability, hidden photochemical oxidation-reduction processes, immediately reversed by back reactions. The problem is to find systems which permit rapid stabilization or spatial separation of the energy-rich oxidation and reduction products. Only a few such systems have been identified and studied in some detail.

Systems involving dissolved chlorophyll or its derivatives and analogues have received particular attention. The best known is the "Krasnovsky reaction" involving chlorophyll and ascorbate dissolved in pyridine. (Other reductants, such as phenylhydrazine, can be used instead of ascorbate but give a lower quantum yield.) This system reacts according to reaction:

\[ \text{Chl. } a + \text{ ascorbate} \rightarrow \text{Chl.}a \text{ H}_2 ("\text{eosinophyll"}) + \text{dehydroascorbic acid}, \]  
\[ (3) \]

where "eosinophyll" denotes a pink compound, probably derived from chlorophyll by addition of two hydrogen atoms. (Contrary to early suggestions, it is not a free radical, since it exhibits no paramagnetic resonance.)

The normal redox potential of the couple ascorbate/dehydroascorbate is 0.0 volt; that of the system chlorophyll \( a / \text{eosinophyll} \) must be negative, because reaction (3) is reversed in the dark. How much more negative, is shown by the fact
that if riboflavin or certain other oxidants with normal potentials down to $-0.3$ volt are present, eosinophyll reduces them to the corresponding leucocompounds and is itself converted back into chlorophyll. The free-energy storage in the photo-reduction of riboflavin by ascorbate is of the order of $2 \times 0.2$ ev, or about 9 kcal per mole. According to Bannister's work in our laboratory, this reaction occurs with a quantum yield of the order of 0.2, so that the energy conversion yield (in red light) is of the order of 4 per cent.

The Krasnovsky system thus satisfies, albeit with a relatively low yield, the first two above-suggested criteria—it stores chemical energy, and it can be used for sensitization. Its products—e.g., leucoriboflavin and dehydroascorbic acid—do react back, but only relatively slowly. So far, no experiments have been made on separating these products (e.g., by distribution between immiscible solvents) or on utilizing the back reaction for the production of electric current. (However, Evstigneev did demonstrate the occurrence of a photogalvanic potential between two platinum electrodes immersed into an illuminated and a darkened zone, respectively, in a chlorophyll-ascorbate solution.)

More extensive measurements of this "photogalvanic" effect and of the electric work which can be derived from it have been made on an analogous redox system, consisting of an aqueous solution of the purple thiazine dye, thionine, and a ferrous salt, reacting according to the equation

$$\text{Thionine } + 2\text{Fe}^{++} \xrightarrow{h\nu} \text{Leudothionine } + 2\text{Fe}^{3+}$$

(4)

The reversible bleaching of this system was discovered by K. Weber, and its kinetics and its photogalvanic properties were studied by us first in 1938–1940; recently, the study of this reaction has been resumed in our and in several other laboratories. Photogalvanic potentials up to 400 mv can be easily obtained, and currents can be produced in an external circuit with a wattage equivalent to a few tenths of one per cent of the absorbed light energy. The yield of conversion to electric energy depends in this case on the ratio between the rates of the homogeneous and the heterogeneous back reaction. (The latter can be considered as a reaction catalyzed by the electrodes: electrons are conveyed, from leucothionine to ferric ions, via the electrodes and the external circuit.) To minimize this ratio, one must decrease electrolytic polarization, which depresses the concentration of the oxidation product at the anode and of the reduction product at the cathode. The electrode surface must be made large and the volume of the solution small; and effective stirring must be provided. Without stirring, the illuminated compartment is gradually enriched in Fe$^{3+}$ and the non-illuminated compartment in Fe$^{2+}$, and the pH in the two compartments becomes different.

It is easily seen that a photogalvanic system is rather similar to a solar battery, or a barrier layer cell. These, too, can be considered as oxidation-reduction systems, in which the light-absorbing layer serves as a photoelectrode, donating electrons to the dark (or transparent) layer. The direct return of the electron and its recombination with the positive hole it has left behind are delayed by a potential barrier at the interface of the two layers, so that a large fraction of the liberated electrons can be channeled back through an external circuit.

It is possible, indeed likely, that the stability and efficiency of crystalline systems in the conversion of light into electricity will never be matched by photogalvanic
systems; but one cannot be sure, and the costs per unit area are likely to be more favorable in the latter case.

We now turn to the problem of utilizing stored chemical energy by stabilization rather than by immediate conversion into electrical energy. Crystalline convertors cannot store energy, because the potential barrier against direct recombination is low, and the "condenser capacity" of the system is relatively small. One could, however, envisage photochemical systems able to store chemical energy for indefinite time, as plants do in accumulating organic matter and releasing oxygen into the air. Particularly tempting would be the production of an explosive but metastable gas mixture, such as knallgas, $\text{H}_2 + \text{O}_2$. Heidt has tried to produce knallgas photochemically from ferric/ferrous (or ceric/cerous) solutions. Light-excited ferric (or ceric) ions are able to oxidize water, e.g.,

$$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH}^{-} (\rightarrow \text{O}_2), \quad (5)$$

while excited ferrous (or cerous) ions can reduce water

$$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{H} (\rightarrow \text{H}_2) \quad (6)$$

While some evidence for the occurrence of these reactions could be adduced, the quantum yields were minimal. This may be due not to the low quantum yield of the primary photochemical processes in (5) and (6) but to the high probability of various back reactions, permitting only a very small proportion of the primary products to escape as oxygen or hydrogen gas. In this case, again, an ingenious invention is needed to separate the products and to prevent, or, at least, to limit, the back reactions between them.

The following experiment illustrates the problem. The thionine-ferrous iron reaction can be performed in a stirred water-ether emulsion (under exclusion of air). The two liquids are then permitted to separate. In the dark, the aqueous layer recovers only a little of its original coloration, while the ether layer remains colorless. If now enough methanol is added to permit mixing of the two phases, the full color returns. Obviously, much of the reduced thionine has been preserved in the ether layer, while ferric ions have stayed in the aqueous layer. Light energy, stored in this way, was released upon mixing. If two platinum electrodes are placed, one in the aqueous layer and one in the ether layer (with some methanol added to increase conductivity), a potential difference of the order of 0.3 volt is found—similar to that found between two electrodes immersed in the illuminated and the darkened zone in a homogeneous, aqueous solution of thionine and ferrous ions.

Another pertinent experiment has been recently described by Kallmann. He found that when two compartments, filled with an electrolyte such as NaCl, are separated by a thin (~10 μ thick) anthracene crystal and the latter illuminated from one side by near-ultraviolet light absorbed by anthracene, a "photovoltaic effect" results, with the illuminated side of the crystal becoming negative and the "back side" positive. If now two electrodes are placed in the two compartments and an external connection provided, a current flows across the illuminated crystal plate. It must be supported by electrons released into the electrolyte at the illuminated side (neutralizing some cations present in solution) and taken up by the crystal plate at the opposite side, neutralizing some anions in solution. (Ulti-
mately, H₂ gas should be evolved from one compartment and O₂, or Cl₂, gas from the other compartment; but no actual gas evolution has been as yet observed.) Kallmann suggested that this mechanism of water decomposition, with spatial separation of the two products, may be relevant to the photolysis of water in photosynthesis. An analogy between the thin anthracene crystal and the chlorophyll monolayers in the chloroplasts presents in fact a tempting hypothesis. Whether it is truly pertinent to photosynthesis or not, Kallmann's system illustrates the kind of "ingenious arrangement" needed to solve the problem of separating the oxidation and the reduction products of an endergonic photochemical process and thus achieve a durable storage of light energy.

PHOTOELECTRICITY

BY PAUL RAPPAPORT

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It has been seven years since groups at Bell Telephone Labs, Wright Air Development Division, and RCA Labs first worked on the solar cell. During that time the cell has changed from a scientific curiosity to the only reliable long-term power source available to our space program. Tiros, Courier, Advent, Pioneer and other satellites have used such devices satisfactorily and Vanguard has been transmitting solar-cell powered signals back to earth for three years now. In these satellites, the single crystal silicon solar cell operating as a photovoltaic device converts the sun's photon energy directly into electricity to provide the needed power.

Several papers; 1-3 have been written which review the basic principles and state of the art of solar cells so that this will not be discussed here. The silicon solar cell is fairly well developed, yielding a conversion efficiency in the 10–15% range; however, there are still a number of important research problems to be solved before the space scientists and mankind have the desired solar power source. These problems include among others reliability, lower cost, lighter weight and higher efficiency and are summarized here.

The Efficiency Problem.—For several years research has been directed to higher efficiency, especially at higher temperatures. Such materials as gallium arsenide, indium phosphide, cadmium sulfide and gallium phosphide, which theoretically should have an advantage over silicon, have not been developed to the extent necessary for this. Table 1 shows the results to date on all important photovoltaic materials.

<table>
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<tr>
<th>Material</th>
<th>Efficiency</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Silicon</td>
<td>14%</td>
<td>1</td>
</tr>
<tr>
<td>Gallium arsenide</td>
<td>&gt;10%</td>
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<tr>
<td>Cadmium sulfide</td>
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<tr>
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