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PROSPECTS OF PHOTOCHEMICAL CONVERSION

C.D. ANDRIESSE

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Abstract

This is a review of the possibilities for a direct conversion of solar energy to chemical energy. By this conversion a natural flux will be fed in an artificial reservoir, from which high-quality energy can be tapped when necessary. After discussing the chemistry of photosynthesis in plants, the structure of the pertinent 'machine' is described with emphasis on the photosynthetic membranes. Energy storage is the result of the blocking of back-reactions. Having understood essential functions of the natural membranes one can design artificial devices, of which three are discussed. They are only of academic interest. Despite the considerable progress in the realization of such structures, the stabilization of photo-charge in a product like hydrogen is not yet possible.

CONTENTS

1. WHY PHOTOCHEMICAL CONVERSION?

Any thought about the sustainability of our way of living, and indeed the chance of our survival, has to include the enormous source of solar energy.

So far, the use of solar energy is restricted to the conversion into heat or electricity, both on a very modest scale. We can store the heat, but not the electrical energy, at least not in useful quantities. Like sunlight, electricity is basically an energy flux - a power which has to be used when it is generated. This may not fit to the demand. At night, for instance, many production processes are continued. The only method for the storage of electrical energy consists of a conversion into some potential energy, either by pumping up water or by investing it in chemical bonds. We mostly use electrochemical conversion in batteries and electrolysers.

What about a direct conversion of sunlight into chemical energy? This would provide us with a renewable stock of energy which is available when we need it. The detour via photo-electrical and electrochemical conversion (for which we need solar cells and batteries or electrolysers) would no longer be necessary and the technology might be simpler and cheaper.

Nature gives us an example. The best photon-converting 'machine' we know is the green plant with its chlorophylls. Green plants synthesize in total about 10 billion tons of carbohydrates per year (3×10^5 kg s^{-1}), which is about 8 times the global energy use in 1990.

We are starting to use this 'machine' by converting, via fermentation, carbohydrates of plants into liquid fuels like methanol (a substitute for gasoline). But the limitations are severe. The average energy flux used in wood production is low (about 0.2 W m^{-2}). This means that an enormous forest is required to provide liquid fuels at the rate in which they are presently consumed; the area is about 3×10^{13} m^2, almost 4 times Brazil. If the potential energy of carbohydrates is completely extracted, 25 percent of all forests in the world would have to be harvested. If fermentation is used, the percentage goes up to 40. Harvesting only 10 percent of forest growth, however, requires already taking a step to ecological engineering. It is by no means certain that this is feasible. The introduction of fast-growing monocultures in an attempt to improve biomass yields and to achieve true 'cultivation' of energy crops is an ecological risk that requires long experience to evaluate.

A more sophisticated use of the photon-converting 'machine' consists in studying its mechanism. Some day we may understand how carbohydrates are synthesized, via reduction of carbon dioxide, and use this knowledge for our own design. Then we may grasp how photons are captured and injected in the synthesis reaction, so that we will require neither plants nor land on which to grow them.

2. NATURAL PHOTOSYNTHESIS

Plants convert sunlight into chemical energy. To state it more precisely: they use the energy of solar photons to synthesize carbohydrates from water and carbon dioxide. This process is based on two reactions between a photon (with energy [ph]) and a dissociated water molecule:

$$[ph] + (H^+ + OH^-) \rightarrow (H^+ + e^-) + OH$$

Reactions of this type give rise to transitions between energy states E_k in the plant ($k = 0, 1, 2 \ldots$ and $E_{k+1} > E_k$); it has been shown that the two pertinent transitions are from E_0 to E_1 and from E_2 to E_3. Photons are also used in the reduction of the hydroxyl radicals:

$$[ph] + OH \rightarrow e^- + OH^+$$

a reaction leading to the transition from E_1 to E_2, and:

$$[ph] + (OH^+ + OH) \rightarrow H^+ + (H^+ + e^-) + O_2$$

a reaction leading to the transition from E_3 to E_4. So 1 oxygen molecule and 4 proton-electron pairs are produced from 4 photons and 2 water molecules. The process by which the water molecules are attached and the oxygen molecule is released gives a transition from E_4 to E_0, which means that the reactions are cyclic. This 'clock' is driven by light and yields reactive pairs.

The proton-electron pairs, assisted by further photons, react in some way with carbon dioxide and give a unit of carbohydrate plus water:

$$6[ph] + 4(H^+ + e^-) + CO_2 \rightarrow [CH_2O] + H_2O$$

The simplest carbohydrate has 6 units; it is glycose $[CH_2O]_6$. Plants synthesize carbohydrates with more than 6 units which also contain metal atoms, such as phosphorus in adenosine triphosphate (ATP). Details of the last reaction are largely unknown. It needs 4 photons and ATP as catalyst, which requires 2 more photons for its synthesis. The net synthesis reaction can now be written as:

$$10[ph] + H_2O + CO_2 \rightarrow O_2 + [CH_2O]$$

where the output of 1 water molecule has been subtracted from the input of 2 water molecules.

For photons with the wavelength of 680 nm the energy input 10[ph] is 2.9×10^{-18} J; such photons are well absorbed by the plant's chlorophyll. The potential energy in a unit of carbohydrate is 0.78×10^{-18} J, so that the maximum energy-conversion efficiency is 0.78/2.9 = 0.27. This is a maximum, as most sunlight photons have a wavelength shorter than 680 nm. For really available photons the conversion efficiency would be about 0.15. Also this value is a maximum, however, for light reflection and respiration gives a considerable loss. The actual efficiency is only 0.06.

3. NATURA ARTIS MAGISTRA, OR ABOUT THE 'MACHINE'

The 'machine' which allows for this conversion is the result of 3 billion years of plant evolution. It is a structure of proteins, being polypeptides (linear polymerizations of many hundreds of amino acids) which are folded in an intricate, orderly way; they contain pigments (light-sensitive chlorophylls). This structure is unstable; it is continuously broken down and built up again in the energy flux of photons. [This feature may make it difficult to imitate nature; technological devices usually are well defined and stable.] The protein structure has various functions. One distinguishes antennas (where photons are absorbed and lead to electronic excitations), membranes (where these excitations lead to the separation and stabilization of charge) and surfaces (where these charges are exchanged in the molecular reactions by which carbohydrates are synthesized).

3.1 Antennas

Photons are captured in excitations of the chlorophyll. These excitations occur in the electron systems of these molecules at optical frequencies (of the order of 10^{15} Hz). Each reaction centre (see below) is coupled to some 100 (in exceptional cases 1000) chlorophyll molecules, so that practically any photon entering the volume of these molecules will produce an excitation. The large size of this light-harvesting system (the antenna) implies that the excitation must visit many molecules, and thus that the transfer of the excitation from one molecule to another must be easy. The transfer is as fast as 0.2 ps. [The antennas display a large variety of structure and composition; they are also highly heterogeneous, as is indicated by their absorption and emission spectra and by the spectral changes induced by pulsed excitation.]

3.2 Membranes

A special pair of chlorophyll molecules P at the inside of the antenna is able to convert the excitations in rather slow (acoustic) vibrations. These are periodic motions of the carbon- and oxygen-nuclei with respect to each other. Spectroscopic studies of P have shown that the coupling of high-frequency excitations to these low-frequency vibrational modes is special indeed, very much stronger than in monomeric chlorophylls. The vibrational motions are likely to be intramolecular in origin. They might lead to charge separation, but no one has yet found evidence for this hypothesis.

[In solar cells charge separation is achieved by the electrical field in a p-n junction. This field pushes the charges (set free by photons) faster to the collectors (on either side of the junction) than they can recombine. One may speculate that the vibrational modes in the special pair P produce alternating electrical fields which are sufficiently slow and strong to separate the charges (the above proton-electron pairs) before they can recombine. One may also speculate that the structural flexibility of P (and of any dissipative structure) plays an important role, as it will lower the barriers between states.]

The centre of a molecule of the special pair (and of any chlorophyll) is structured like porphyrin, which is a much smaller and more symmetrical molecule though. Let us describe this molecule, as we shall return to it below. Porphyrin has a square structure with a magnesium atom (Mg) in the middle and nitrogen atoms (N) at the 4 corners. In turn each N is at the corner of a pentagon, directed away from Mg, with 4 carbon atoms (C) at the other corners. The pentagons lie in the same plane as the central square so that the whole molecule is flat. It is kept flat by intermediate C bound to the C in the pentagons which are adjacent to N. Porphyrin counts therefore 1 Mg, 4 N and 20 C, whereas the open bonds of C accommodate 12 H (hydrogen atoms). In the case of chlorophyll the open bonds are filled by various hydrocarbons with at least one chain. As a result the flatness of the central structure is no longer warranted; anomalous distances between the atoms and thus degeneracy can be expected.

The special pair P is only one of the molecule-pairs of the reaction centre. The main structure of the reaction centre is a large protein complex embedded in a membrane. A number of smaller molecules, known as prosthetic (helper) molecules, are in turn embedded in the protein complex. Not only the special pairs are such prosthetic molecules, but also pheophytins, quinones and cytochromes. Their role is to chemically stabilize the charges which (somehow) have been separated by P.

A striking feature of the membrane structure is that it has a nearly perfect twofold symmetry. A reaction centre that had been rotated by 180° around its axis (the axis being perpendicular to the membrane surfaces) would nearly look like an unrotated centre. The prosthetic molecules are arranged in two spirals situated symmetrically on opposite sides of the central protein. In spite of the symmetry, the electrons seem to follow only one of these spirals during the charge separation.

After the charge separation the protons H^+ are quickly, in a few ps, transferred to the one membrane surface (let us say the top) not far from P; there they are attached to a chain of P, giving PH^+. In comparison, the electrons e^- are very slowly, in about 0.1 ms, transferred to the other surface (the bottom). They move in three fast steps (hops), but between these hops they linger at prosthetic molecules. First they hop to pheophytins, which are still close to the top, where they stay for about 100 ps. There is a chance that the electrons return to P, but the chance for a further journey is greater. As a rule the second hop is to certain quinones (Q_A) close to the bottom, where they stay for about 0.1 ms. Finally they hop to other quinones (Q_B) at the bottom.

These quinones play a key role in the charge stabilization. Quinones consist of a carbon hexagon where the corners are subsequently connected to (1) =O, (2) a chain, (3) $-CH_3$, (4) =O, (5) $-O-CH_3$ and (6) $-O-CH_3$. The chain consists of n units [-C-C=C-C-] where, to give an example, n = 10 for the reaction centre of rhodobacter sphaeroides. This so-called ubiquinone-10 is present in both the Q_A- and the Q_B-binding sites of the protein complex. In contrast to the situation at the Q_B-site, the ubiquinone-10 is strongly perturbed at the Q_A-site (being asymmetrical with anomalous distances between the C-atoms), so that it can only accept one electron. This one electron is tranferred to ubiquinone-10 at the Q_B-site. When a second electron is transferred, the ubiquinone-10 can be completely reduced to ubiquinol-10, denoted by Q_B^{--}.

This ubiquinol-10 forms a redox potential with an oxidized cytochrome. Cytochrome is a water soluble globular molecule that can drift through the membrane from PH^+ at the top to Q_B^{--} at the bottom. In this way it is able to carry protons from the special pair to ubiquinol-10, with the result that Q_BH_2 is formed. [Compare this process with the proton transfer in acid electrolytes.]

3.3 Surfaces

What follows is not well known, but it probably takes place at the (bottom) surface of the membrane with its access to the CO_2 in the air. Q_BH_2 pulls away from the membrane and triggers the later stages of photosynthesis, for which ATP and (further) photons are needed. This implies that the pertinent ATP structures at the surface are coupled to an (or the) antenna as well.

4. ON THE STORAGE EFFICIENCY

The above 'machine', being not very good at converting the available photon energy to chemical energy (the energy-conversion efficiency being 0.06), is quite good at storing the photon energy once that energy has been converted to electrical energy by a separation of charges. It depends on the chance of back-reactions, as mentioned for the electron hops from pheophytin. Hops to the quinones are by an order of magnitude more frequent than hops back to the special pair, so that 9 out of 10 hops lead to charge stabilization and 1 leads to charge loss (by the neutralization of PH^{+}).

The storage can be modeled as follows. Consider three states 0, 1 and 2. The ground state 0 can be compared with that of the special pair before excitation. The high state 1 can be compared with that of the special pair after excitation (release of an electron) or with that of pheophytin after attachment of an electron (these states have about the same energy). State 2 can be compared with that of the Q_A-site to which an electron is bound (it has to lie somewhat below state 1, otherwise there is no preferential direction for hopping; it has to lie much above state 0, otherwise little storage is possible).

Denote the density of occupied states by [0], [1] and [2]. Denote the transition rates between the states by r_{01}, r_{10}, r_{12} and r_{21}, where r_{01} refers to the transition from state 0 to state 1, r_{10} from 1 to 0, and so on. [They have the following typical values: $r_{01} = 10^{-4}$ to 10 Hz (depending on the light intensity), $r_{10} = 10^{9}$ Hz, $r_{12} = 10^{10}$ Hz (the inverse of the attachment time of 100 ps) and $r_{21} < 10^{7}$ Hz.] In dynamic equilibrium:

$$r_{01}[0] + r_{21}[2] = (r_{10} + r_{12})[1]$$

$$\frac{[2]}{[1]} = \frac{r_{10} + r_{12}}{r_{21}} - \frac{r_{01}}{r_{21}}\frac{[0]}{[1]}$$

The storage efficiency is the ratio of the net input of state 2 and the output of state 1:

$$\eta = \frac{r_{12}[1] - r_{21}[2]}{(r_{10} + r_{12})[1]} = \frac{r_{12}}{r_{10} + r_{12}} - (1 - \frac{r_{01}}{r_{10} + r_{12}}\frac{[0]}{[1]})$$

where the term in brackets () is obtained by substitution of the foregoing equation. The term in brackets can be neglected if r_{21} is relatively small, which implies that state 1 is practically only populated from state 0. In that case the storage efficiency becomes $1/(r_{10}/r_{12} + 1)$. [For the above typical values the ratio r_{10}/r_{12} is about 0.1.]

This analysis suggests that the storage efficiency is essentially fixed by only one prosthetic molecule (pheophytin). It further suggests that the structural relation of this molecule to the charge-separator (the special pair) is essential for a low ratio r_{10}/r_{12} (thus for few back-reactions).

5. WHAT IS ESSENTIAL FOR A PHOTOCHEMICAL DEVICE?

In as far natural evolution can be understood it is not teleological: there is no predetermined goal. Evolution rather is the ongoing adaptation of dissipative structures to a changing environment, which is changed by this adaptation itself. If these structures have a goal, it is to persist or to reproduce themselves. There seems to be redundancy, as many structures have no (more a) clear function in coping with the environment.

We may enjoy the richness of these structures, but our evaluation of natural processes has to be functional. If our goal is to make a photochemical device, then there is no point in trying to copy the entire photosynthetic structure of plants. Even if the function of parts is clear, we may not need that function.

5.1 Superfluous

More than 99 percent of the protein structure seems to be just a support for the prosthetic molecules that matter. We can replace it by a piece of glass or some other cheap solid.

The second structure we may not need is at the membrane surface, where reactions take place with Q_BH_2. The synthesis of very elaborated products like fruits or flowers, in which much energy is used to make shape, colour and perfume, has the function of reproduction. If we simply want to convert sunlight into useful chemical energy, these last stages can be replaced by much simpler reactions aimed at exploiting the stabilized charge to make, for instance, hydrogen.

The third structure we may not need is the chlorophyll antenna. Light has to be absorbed, of course, but the natural light-absorbing pigments are unstable. They can be replaced by stable artificial dyes like transition-metal complexes. Nature provides a good example, however, in having a large number of pigments per reaction centre. The principles of the transfer of electronic excitations in artificial dyes are sufficiently well known to design a large and organized array of dyes for the capture of photons. Such an array should be based on coordination- or covalent bonds.

[Photon capture in simpler systems is less efficient. A slab of crystalline silicon, for instance, absorbs photons only if phonons are absorbed as well. As a result of this condition the absorption coefficient is low, so that thick slabs are needed. Hydrogenated amorphous silicon absorbs photons much better, by virtue of the disorder, but that same disorder leads to faster charge recombinations and to some instability. However, the main disadvantage of such simple systems is that photon absorption and charge generation are firmly coupled. There is no intermediate state of excitation which allows for a structural separation of these processes, whereas such a separation is needed if both are to be optimized.]

5.2 Necessary

Which photosynthetic structures of a plant do we need to copy? That is: which functions are really necessary? We need generation, separation and stabilization of charge, and the pertinent structures are in the membrane. We therefore have to find stable alternatives for the special pair, the pheophytin and both quinones which, moreover, have to be charge-coupled.

To start with the first, porphyrins have attracted much interest as they are somewhat similar to the central structure of a special-pair molecule. They have been described in 3.2. If they are excited, they release electrons indeed. But especially in the excited state they are not very stable; the break-down in that state is faster than the (thermal) build-up of the ground state. [The molecule does not seem to survive more than 10^5 excitation-release events, whereas some 10^8 are needed for a useful technology.] The environment of the porphyrin molecules might be used for their stabilization, as the photo-activity appears to be sensitive for the molecular arrangement. But porphyrins are not the only option. Also transition metal complexes can be charged by light (if a suitable electron acceptor is added), in particular ruthenium complexes; they will be mentioned below.

The role of pheophytin may be played by various molecules, which are able to accept charge at fitting energy levels and to transfer the charge to sites where it can be stabilized in a chemical reaction. The difficulty is not to find suitable molecules, but to prevent the back-reaction which (as stated at the end of 4.) may be linked to structure. Structure refers to both geometrical and electrical (field) arrangements. Structure is also important for the catalysis of the chemical reaction. In view of this difficulty it is useful to look at the problem in its simplest form: Consider the conversion of water into oxygen and hydrogen with the help of photons, electron donors [d] and electron acceptors [a]. If the excited state of [d] is denoted by [d^*], the reaction scheme will be:

$$[ph] + [d] \rightarrow [d^*]$$

$$[d^*] + [a] \rightarrow [d^+] + [a^-]$$

$$4[d^+] + 4OH^- \rightarrow O_2 + 4[d] + 2H_2O$$

$$4[a^-] + 4H^+ \rightarrow 4[a] + 2H_2$$

Back-reactions, especially in the second step, should be prevented. It is also required that [d] and [a] are able to dissociate H_2O. One has studied the possibility that [d] is $Ru(bpy)_3^{++}$, a ruthenium bipyridyl complex, and [a] is MV^{++}, a methyl viologen; their redox forms are suitable for the dissociation. In an attempt to prevent back-reactions one has locked both [d] and [a] in the cages of a molecular seeve (zeolite Y). The narrow windows between these cages (being only 0.7 nm in diameter) appear to block the back-reaction, but they make the following steps in the reaction scheme more difficult as well. It is doubtful whether the scheme can be realized with purely geometrical structures. This remark brings us to the next subject.

6. ACADEMIC RESEARCH OF DEVICE-STRUCTURES

So far, the possibility of photochemical conversion by devices is studied only at academies. Results of these studies are discussed at international conferences which are held every even year since 1976. The last conference (IPS-10, see the Literature below) has been evaluated by the president of the first conference. Initially there was the prospect of cheap hydrogen from solar-driven decomposition of water, he said, but after 20 years of research there still is no device which can do it. He added that the failures have helped to better understand how photochemical conversion can be achieved and that useful structures have been found.

The first structure to be mentioned is that of *Grätzel*, who got his idea for it from a study of photosynthetic membranes in plants. It consists of a wafer of porphyrin between a wide-gap semiconductor and an aqueous electrolyte. This device appears to function as a solar cell if the outer surfaces of the wafer are provided with transparent electrodes: light produces an electrical current through an external circuit between the electrodes. The mechanism is not completely understood, but the charge is clearly released by the photo-active porphyrin (not by the semiconductor, which has a gap in excess of the photon energy) and it is separated by the interface of semiconductor and electrolyte, which acts as a p-n junction; less clear is the role of the ion conducting electrolyte. [These 'organic solar cells' have a conversion efficiency of a few percent and they are entering a phase of industrial development.]

Although the mechanism of this device is not well understood, enough is known for an improvement of its efficiency and stability. Grätzel has recently prepared extremely thin wafers, in which the semiconductor is replaced by a film of oxide grains (TiO_2, ZnO, Nb_2O_5, SnO_2 and FeO_3), about 1 nm in size, on a conducting glass support. The grains are sintered together to a network (so that charge percolation is rapid) but not enough to lose roughness (so that the surface of the film is hardly smaller than the sum of grain surfaces). Roughness improves the coupling to the photo-active layer, for which the unstable porphyrin is replaced by a ruthenium bipyridyl complex. The energy levels of bipyridyl ligands appear to fit to the conduction band of the above oxides, with the result that the conversion efficiency is increased above 0.10. A last improvement consists in the use of molten-salt electrolytes to ensure a long-term stability of the output.

The above device is photo-electrical, not photochemical: it lacks the pendant of quinones. We may look once more at the photosynthetic membranes to find other useful structures. It is possible to design and synthesize multi-haem-proteins, as shown recently by *Dutton* and collaborators. Haem is a small molecular group occurring in haemoglobin and (among others) cytochrome. It has the flat structure of porphyrin, with the difference that the central atom is of iron (instead of magnesium) which is bound to a C-pentagon stretching out from the plane. These haem groups can be fitted (by a hydrogen bond in the plane and another in the out-stretching pentagon) between two polypeptide-chains. Only few sites of the (helical) chains appear to be available for a bond. Using empirical rules, however, one has been successful in the synthesis of a short (62 residues) double α-helical peptide which accommodates 2 bis-histidyl haems. This artificial peptide resembles long natural polypeptides, also in their redox properties, and it could be more stable. Can redox centres now be built in at will? If this proves to be feasible, then small charge-separating redox structures can be designed, consisting of double α-helical peptides linked with haems and activated by, for instance, a ruthenium porphyrin.

Also *Lehn*'s supramolocular structures deserve attention. [Jean-Marie Lehn from the Université Louis Pasteur at Strasbourg has received a Nobel Prize for his work on supramolocular chemistry.] It is possible to form very large and highly ordered structures of molecules, provided certain conditions are met by which the entropy is minimized. The formation of such structures from photo-sensitive components is expected to perturb the ground state and the excited state of the individual components, giving rise to novel features. Depending on the arrangement of the components a number of processes may take place: photo-induced transfer of excitations, charge separation by electron or proton transfer, perturbation of optical transitions and polarizabilities, modification of redox potentials in the ground state and the excited state, photo-regulation and switching of physicochemical properties, selective photochemical reactions, etc. The following devices are being investigated: (1) a photo-convertor formed from luminescent lanthanide cryptates using a sequence of excitation-transfers; (2) a photo-switch formed by a metal complex, where a redox component between luminescent and non-luminescent states can be inverted; (3) another photo-switch formed from molecular wires, where the switching results from a non-linearity of the optical absorption and the electronic conductivity; (4) a photo-induced proton pump with long lifetimes (as yet no information on the components and the structure has been published).

7. PROSPECTS OF A CONVERSION TECHNOLOGY

The above leads to two conclusions. Much progress has been made in the research of photo-active charge-separation devices, up to the point of industrial applications. The progress will be accelerated by novel methods in organic- and supramolocular chemistry (or nanometer physics). These methods will probably play a role in the future industry. This is the first conclusion.

The second conclusion is that artificial photochemical conversion is still utopian. Utopia comes from the Greek words ου τοπος which mean: no place (the place does not exist). There is no proof that photochemical conversion technology will be possible, since even Lehn's new photo-induced proton pump has not yet been linked to a proton-catching device which gives the stable energy-rich chemical product we are looking for. The hydrogen-evolving cathode of electrolysers comes to the mind, but this cathode does not seem to attract much interest in the research of photochemical conversion.

At the end it should be pointed out that the present photo-electric cells, in combination with the present electrolysers, are able to convert sunlight in hydrogen with a maximum energy efficiency of about 0.12.

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