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Solar Energy Conversion from Water Photolysis by Biological and Chemical Systems

Invited Review

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ABSTRACT

The production of chemicals and fuels, or energy-rich compounds, from water by sunlight is described as a particularly attractive means for the conversion of solar energy to a valuable renewable resource. The redox properties of photoexcited molecules and the operating mechanism of light-driven systems are first considered. The mechanism of water oxidation carried out by higher plants and green algae—which is actually one of the most important biochemical reactions—as well as that of artificial photosystems, up-to-now designed trying to simulate the natural process with higher efficiency and simplicity, are likewise discussed. A number of biological and chemical light-driven systems are presented as practical ways to solar energy conversion.

Index Entries: Water photolysis; artificial photosynthesis; energy-rich compounds; solar energy conversion; photochemical systems.

Abbreviations: chl, chlorophyll; E_O', standard redox potential; E^{0-0}, 0–0 spectroscopic energy; F, flavin; MV, methyl viologen; MO_2, metal dioxide; P and P*, ground and energized states of a pigment; $Ru(bpy)_3^{n+}$, *tris*(2,2′-bipyridine)ruthenium(n); V^{0-0}, electron potential gap between the zero vibrational levels of two orbitals.

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INTRODUCTION

Within the last two decades, the design of solar energy conversion devices for the production of specific fuels and chemicals has become one of the most attractive lines of research within the framework of renewable energies (*1–8*). The objective is to increase the consumption of solar energy in relation to the consumption of fossil fuels (oil, gas, and carbon).

A profound understanding of the reaction mechanism of biological photoconversion processes—mainly with reference to the relationships between structure and function in the photosynthetic apparatus of green plants—will allow the scientists to discover new molecular systems for the design of photoreactors capable of capturing solar energy in a more simple and economic way. Plant photosynthesis has, of course, the advantage of the many years that complex molecules, anchored in equally complex membranes, have spent in their own evolution with the only objective of undergoing specific reactions for their own subsistence with increasing efficiencies. Photochemical, or artificial, systems can in turn offer the additional possibilities not only of working with higher efficiency and flexibility than the natural systems but also of using their chemistry for the production of fuels or chemicals of particular interest.

When considering new approaches to solar energy conversion, it is first necessary to realize that the electromagnetic radiation reaching the earth from the sun is about 51% infrared, 40% visible, and 9% ultraviolet, and exhibits maximum irradiance within the green region of the spectrum, at about 500 nm (*9*). This is one of the reasons why much more attention has to be paid to photosystems driven by visible light—as is the plant photosynthetic apparatus—in comparison with those driven by ultraviolet radiation, even though the latter has a higher energy content per photon than the former. Living organisms actually use energy sources that are able to break chemical bonds between atoms without altering or damaging their structures. Free energy values of chemical reactions are, in general, in the order of several eV per covalent bond (1 eV $bond^{-1} \approx 100$ kJ $mol^{-1} \approx 25$ kcal mol^{-1}), that is, in the same order as visible photons and thus in the same order as most photochemical reactions. Probably, it is not a simple coincidence that the energy exchanges in chemical reactions, which do keep the world alive, have values quite similar to that of the light that the sun—in fact, our primary energy source—is continuously sending to our planet.

Although the main aim of this review article is that of offering a general survey of water photolysis by chemical and biological systems, we shall also feature a brief overview of the basics of photochemistry—paying special attention to the redox reactions undergone by photoexcited molecules—and present some guidelines for selecting systems to be used for solar energy conversion.

Table 1
Standard Potential Values of Some Redox Pairs of Interest in Solar Energy Conversion

Redox pair	Reduction half-reaction	E'_0, pH 7 (V)[a]
H_2/H^+	$2H^+ + 2e \longrightarrow H_2$	-0.42
H_2O_2/O_2	$O_2 + 2e + 2H^+ \longrightarrow H_2O_2$	+0.30
NH_4^+/N_2	$N_2 + 6e + 8H^+ \longrightarrow 2NH_4^+$	-0.28
NH_4^+/NO_3^-	$NO_3^- + 8e + 10H^+ \longrightarrow NH_4^+ + 3H_2O$	+0.35
$(CH_2O)/CO_2$	$CO_2 + 4e + 4H^+ \longrightarrow (CH_2O) + H_2O$	-0.42
CH_4/CO_2	$CO_2 + 8e + 8H^+ \longrightarrow CH_4 + 2H_2O$	-0.30
H_2O/O_2	$O_2 + 4e + 4H^+ \longrightarrow 2H_2O$	+0.82

[a]Values as reported in ref. 17.

PRODUCTION OF ENERGY-RICH COMPOUNDS

A wide variety of substances have been produced by different processes capable of capturing, converting, and finally storing solar energy in the form of chemical energy. Among the different approaching ways of general interest so far investigated is mainly hydrogen production by reduction of protons (*see* the following discussion); other case studies are the reduction of molecular oxygen to generate hydrogen peroxide (*10,11*), the production of ammonia by reduction of either dinitrogen or nitrate (*12–14*), the fixation of carbon dioxide to form carbohydrates and hydrocarbons (*15*), even the production of electricity (*16*).

Table 1 shows the midpoint redox potentials of the different pairs involved in such reduction reactions of special interest in solar energy conversion. As can be seen in the table, their standard potential values at neutral pH are quite different from one another, varying from redox potentials as negative as those of the hydrogen electrode and the couple carbohydrate/carbon dioxide (E'_0, pH 7, −0.42 V) to values so positive as that of the pair ammonia/nitrate (E'_0, pH 7, +0.35 V) (*17*). In every case, however, the resulting products can be considered to be energy-rich compounds capable of releasing a high amount of energy upon combustion

with oxygen, or disproportionation into water and oxygen, as is the case for hydrogen peroxide. Table 2 presents the corresponding values for standard and specific enthalpies of such energy-releasing reactions, that is, the changes in enthalpy per mol and per g (expressed without the minus sign) of the substances, respectively (*18*). Although the highest standard combustion enthalpy values correspond to carbon-containing products (carbohydrates and hydrocarbons), the maximum specific enthalpy obviously belongs to molecular hydrogen because of its low mol wt. Hydrogen peroxide, in its turn, releases an appreciable amount of energy upon its disproportionation into water and oxygen, actually being used, as a source of energy, to propel rockets. Hydrogen peroxide, however, finds its main applications in industry as a bleaching agent and in pharmacy because of its antiseptic properties (*19*). Similarly, ammonia is not only a powerful source of energy when burned with oxygen but also a useful fertilizer capable of greatly increasing the productivity of crops when added to soil or water.

Considering the aforementioned discussion, reduction reactions are sufficiently representative examples of processes in which oxidized molecules completely devoid of useful chemical potential are being reduced to generate some fuels or chemicals. If such reactions could be driven, in one way or another, by visible light in the presence of an adequate photosensitizer (that is, if the solar energy could be used to promote a reaction yielding an energy-rich compound), one could state, in principle, that such a reaction is a solar energy conversion process in which at least part of the solar energy is being stored in the final products.

Notwithstanding, when selecting a photochemical system to be used for solar energy conversion, it is first necessary to consider the energy levels not only of the final products, but also of the initial substrates, or reactants (Fig. 1). Actually, the redox reactions of electronically photoexcited molecules can be used for photochemical transformation of lower energy reactants into higher energy products, the light energy being stored as chemical energy in the final products. Photoexcited molecules can likewise be used for simple catalytic purposes when the exceptional tendency of excited states to undergo redox reactions (*see* the following discussion) is used to obtain products that would have been obtained with much lower efficiency in the dark by a simple thermal reaction. In consequence, not all the light-driven systems, but only a small proportion of those described in the literature, are really useful for "storing" solar energy in the form of chemical energy (*20,21*).

In this context, the previously cited processes for the production of specific fuels and chemicals can be considered as solar energy conversion processes only when the energy level, or energy content, of the final products is higher than that of the reactants. The so-called "sacrificial" photosystems (*22–24*), in which an electron donor—usually a small organic

Table 2
Thermochemical Properties of Some Energy-rich Compounds

Fuel	Combustion equation	Standard enthalpy[a] ($kJ\ mol^{-1}$)	Specific enthalpy ($kJ\ g^{-1}$)
Hydrogen	$2H_2(g) + O_2(g) \text{ ----> } 2H_2O(l)$	-285.83	142.92
Hydrogen peroxide[b]	$2H_2O_2(l) \text{ ----> } 2H_2O(l) + O_2(g)$	-98.05	2.88
Ammonia	$4NH_3(g) + 5O_2(g) \text{ ----> } 4NO(g) + 6H_2O(l)$	-292.38	17.20
Carbohydrate[c]	$(CH_2O)(s) + O_2(g) \text{ ----> } CO_2(g) + H_2O(l)$	-468.01	15.60
Methane	$CH_4(g) + 2O_2(g) \text{ ----> } CO_2(g) + 2H_2O(l)$	-890.36	55.65

[a]Values calculated from enthalpies of formation listed in ref. 18.
[b]Hydrogen peroxide rather undergoes a disproportionation reaction.
[c]The enthalpy values of each sugar building-unit, (CH_2O), are referred to those of glucose under identical conditions.

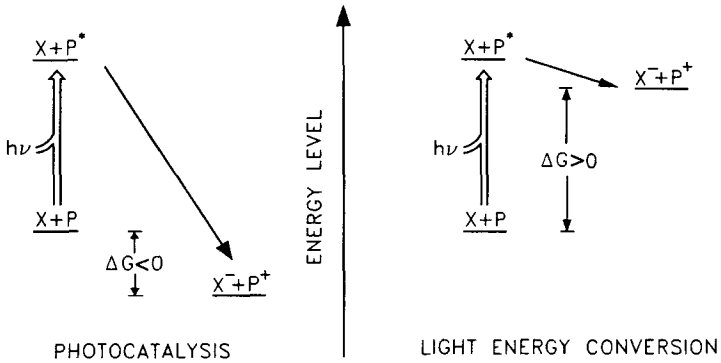

Fig. 1. Schematic drawing of the two types of photoreactions driven by a pigment, P, or light-absorbing compound. Depending on whether the relative energy level of the final product is either lower (left) or higher (right) than the initial substrates, the process is respectively named photocatalysis or light energy conversion. A reaction in which any molecule, X, is reduced by the photoexcited pigment, P*, is presented as a typical example.

molecule (EDTA, ascorbate, dithioerythritol, amino acids, and many others) keeping more chemical energy inside it than the final products themselves—is consumed throughout the photochemical reaction, cannot properly be considered to drive a solar energy conversion process. It is a simple photocatalytic reaction. This is why much more attention has been paid to biological and chemical systems that use water as the electron donor, either by taking advantage of all or part of the plant photosynthetic apparatus or by simulating the natural process (*3,25,26*). As the redox potential value of the couple water/oxygen is quite high (E_O', pH 7, +0.82 V)—it is in fact more positive than any other of the redox pairs of interest listed in Table 1—the light-excited electrons are flowing from a low to a higher energy level when water is used as the electron source (*see* the following discussion). However, not only does the investigation work on such solar energy conversion processes, but also on sacrificial (photocatalytic) systems that are so interesting as to supply valuable information to get a more profound understanding of light-driven reactions.

OPERATING MECHANISM OF LIGHT-DRIVEN REDOX SYSTEMS

The first act in any light reaction is physical rather than chemical by nature and can be represented by the following simple equation:

$$P + \text{light} \longrightarrow P^*$$

where P denotes a pigment (light-absorbing molecule) in its lowest energy level (ground or fundamental state) and P* designates an electronically

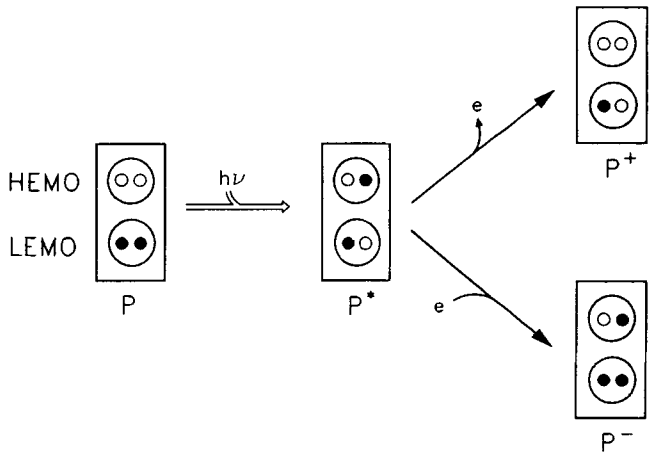

Fig. 2. Redox properties of photoexcited molecules. Upon excitation by a photon, one electron is promoted from a fully occupied low-energy molecular orbital (LEMO) to an empty high-energy molecular orbital (HEMO). The so energized molecule, P*, has *both* lower ionization energy and higher electron affinity than the same molecule in its ground state, so being capable of *either* donating or accepting an electron to become respectively oxidized, P^+, or reduced, P^-, with higher efficiency.

photoexcited state of the same molecule (*27*). The electronic configuration of the resulting energized molecule differs from that of the basal state in that an electron has been promoted from a fully occupied low-energy molecular orbital (LEMO) to another empty high-energy molecular orbital (HEMO), a situation that can be schematized as shown in Fig. 2.

The excitation of an electron to a higher energy orbital greatly modifies the redox properties of the molecules, the photoexcited state actually exhibiting both a decreased ionization potential value, and an increased electron affinity. That is, the energized molecule can donate an electron—particularly, the photoexcited electron—with higher efficiency than the unenergized molecule. It can alternatively accommodate an electron from a donating substrate in a lower energy level—particularly, in the hole left by the photoexcited electron. In other words, a light-excited molecule can indistinctively behave as a better reductant or as a better oxidant than the same molecule in its ground state (*27,28*).

Assuming that both the ground and excited states lie in their lowest vibrational levels—that is, the corresponding vibrational quantum number is 0—the extra energy content of the energized molecule, P*, with respect to the ground sate, P, is the so-called 0–0 spectroscopic energy, $E^{0\text{-}0}$. Equally assuming some thermodynamic simplifications, such as the lack of changes in the entropic content of the photoexcited state with respect to the basal state, the redox potential value, E'_O, of the system can be calculated by means of the following equations, depending on the photoexcited state acts either as an electron donor (that is, it is the reduced form of the corresponding redox pair):

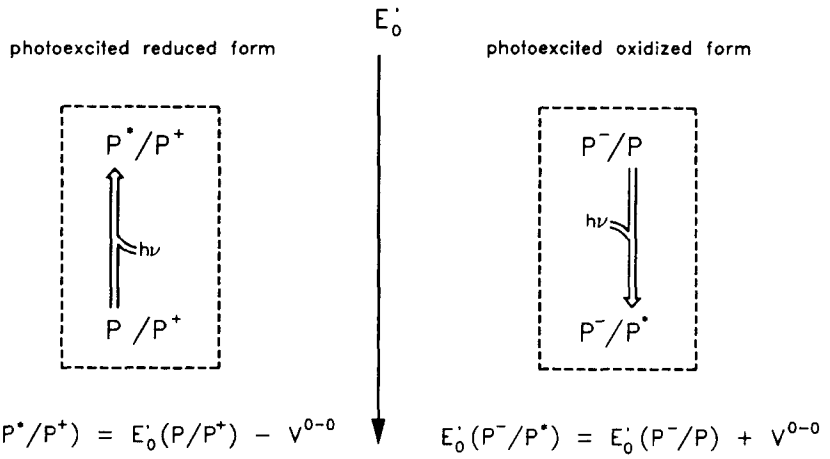

Fig. 3. Light-induced redox potential changes. The standard potential value, E'_O, of redox couples either decreases or increases upon photoexcitation of the reduced (left) or oxidized (right) form, respectively. In other words, when the photoexcited molecule, P*, acts as the reduced form of the couple (P^*/P^+), the redox potential is decreased with respect to that of the basal pair (P/P^+). On the contrary, when the photoexcited species is the oxidized form of the pair (P^-/P^*), the redox potential is increased in comparison with that in the dark (P^-/P). V^{0-0} refers to the electronic potential gap between the low and high energy orbitals between which the electrons are jumping because of excitation by photons. *See text* for details.

$$E'_O\,(P^*/P^+) = E'_O\,(P/P^+) - V^{0-0} \quad (V)$$

or as an electron acceptor (that is, it is the oxidized form of the pair):

$$E'_O\,(P^-/P^*) = E'_O\,(P^-/P) + V^{0-0} \quad (V)$$

where V^{0-0} corresponds to the potential difference expressed in volts (V) between the zero vibrational levels of the photoexcited and ground states (Fig. 3). In consequence, V^{0-0} has the same absolute value than the 0–0 spectroscopic energy, E^{0-0}, expressed in eV. From the two preceding equations, it can be inferred that the midpoint redox potential of the photoexcited pair is more negative, or more reducing, when the energized form is the reduced form, but the redox potential becomes more positive, or more oxidizing, when the oxidized form is the energized one. Photoexcitation of one electron in the reduced or oxidized form of a redox couple thus determines a decrease or increase, respectively, in the redox potential value equal to 60 mV (this is equivalent to a tenfold increase in the concentration of the pertinent reduced or oxidized form) per each 60 meV (ca. 6 kJ mol^{-1}) in the energy content transmitted by the absorbed photon (*29*).

The best known example in biology of a redox pair of energized reduced form-type (Fig. 3) is that of chlorophyll *a* in the photosynthetic reaction centers. Chlorophyll *a* is a light-absorbing compound able to

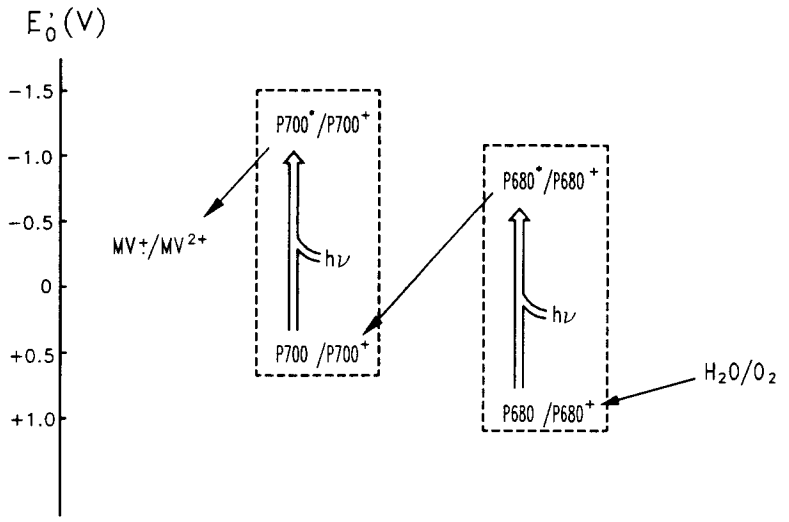

Fig. 4. Water oxidation by the biological photosynthetic apparatus coupled with methyl viologen reduction. At the expenses of sunlight energy, electrons are driven from water to the redox level of the hydrogen electrode, or methyl viologen, in an uphill reaction. Chlorophyll *a* of both photosynthetic reaction centers (P680 in PSII, P700 in PSI) is the photoexcited pigment that transduces solar energy into redox energy by operating at two alternating potentials.

transduce light energy into redox energy by operating at two alternating redox potentials. In fact, chlorophyll *a* exhibits two redox pairs that share the same oxidized form: the high potential, or basal, pair (chl/chl$^+$) in which the reduced form is unenergized and stable; and the low potential, or energized, pair (chl*/chl$^+$) in which the reduced form is photoexcited and unstable. As shown in Fig. 4, the midpoint redox potential value of chlorophyll *a* in photosystem II (PSII), or P680, is shifted from +1.0 V to −0.8 V, approximately, upon photoexcitation to its singlet state by red photons, whereas that of chlorophyll *a* in photosystem I (PSI), or P700, is shifted from ca. +0.5 V in the dark to −1.3 V in the light (*30,31*).

Another biological photosystem of special interest in photochemistry is that of flavins, which appear as prosthetic groups in a wide variety of enzymes and catalize important metabolic redox reactions. In contrast to chlorophyll, flavins belong to the group of energized oxidized form-type redox pairs (Fig. 3), so increasing their redox potential upon energization of the oxidized form (*10,29*). Flavins are likely systems able to transduce light energy into redox energy by operating at two alternating redox potentials and exhibiting two redox pairs that share the same reduced form: the low potential, or basal, pair (F^-/F) in which the oxidized form is unenergized and stable; and the high potential, or energized, pair (F^-/F*) in which the oxidized form is photoexcited and unstable. Actually, the midpoint redox potential of flavins, at pH 7, is shifted from −0.22 V in

the dark to +1.85 V when photoexcited to its triplet state by blue photons (*32,33*). It must be noted that the photochemically reactive species of flavins is their relatively long-lived triplet or metastable state—its lifetime is within the range between 10 and 100 μs in free solutions—which is formed upon loss of part of the excitation energy of the different singlet states by vibrational relaxation (*34,35*).

BIOLOGICAL WATER PHOTOOXIDATION

Light-driven water oxidation as sensitized by chlorophyll *a* in photosystem II, or P680, is one of the most important reactions in biology. In fact, the molecule of water is the primary electron donor for the endergonic reduction of the primordial bioelements carbon, nitrogen, and sulfur, so allowing their assimilation and subsequent incorporation into biomolecules such as proteins, lipids, carbohydrates, or nucleic acids. The driving force for such reactions is that of sunlight, which actually promotes the photolysis of water into hydrogen (electrons and protons) and oxygen; as a consequence, the electrons are driven in an uphill reaction from the redox level of the water/oxygen couple to the redox level of the hydrogen electrode (*29*).

The water molecule has two identical H–O bonds forming an angle of 104.5°, each H–O bond being highly polarized because of the great difference in electronegativity (1.4) between hydrogen and oxygen (*36,37*). The energy required to break each H–O bond of a water molecule is 4.8 eV, which is much higher than it would be if the bond were unpolarized (3.5 eV $bond^{-1}$). Since the energy content of the red light driving the natural photosynthetic process in green plants is much lower—about 2 eV per photon—one red photon would not have enough energy as to break the H–O bond, according to the Stark-Einstein law of the photochemical equivalence principle, by just exciting one electron from the outer shell to an antibonding orbital. Actually, more than one quantum of visible radiation is required to promote water photolysis.

In plant photosynthesis, the photolysis of water appears to proceed by rather following a surrounding strategy—not well known as yet—in which not only redox but acid/base reactions are simultaneously taking place (*31,37,38*). In a general sense, therefore, the biophotolysis of water must be more properly described as a photooxidation of water: The water molecule is not directly broken into hydrogen and oxygen by photons but oxidized in a multistage process throughout in which electrons and protons are sequentially released in a rather dark reaction. This process is catalyzed by a manganese-containing enzyme, which is known as the oxygen-evolving complex (OEC) because oxygen is being formed and evolved along the course of water oxidation:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e$$

To establish the mechanism of water photooxidation to molecular oxygen is a key problem in photosynthesis. In the scheme put forward by Arnon in 1959 (*39*), water was the initial electron donor and $NADP^+$ the final electron acceptor in the chloroplast electron transport chain driven by light-excited chlorophyll. Soon afterwards, in 1960, Hill and Bendall (*40*) proposed the well-known Z-scheme of photosynthesis to postulate the existence of two light reactions, one for oxidizing water, the other for reducing $NADP^+$ (Fig. 4). Many authors have since then tried to elucidate the molecular mechanism of water oxidation, a large number of working hypotheses being reported in the literature (*38,41,42*).

At present it is assumed that water oxidation to molecular oxygen is carried out on the internal surface of the thylakoid membrane on the oxidizing side of photosystem II, where the actual light energy-transducing molecule (P680) appears to exist as a chlorophyll dimer. Photoexcitation of P680 generates its singlet energized state—the quantum efficiency of chlorophyll in its triplet state is rather low, and it is the singlet state that undergoes photochemical reactions. P680* is a strong reductant as the redox potential of the pertinent pair is greatly shifted to much more negative values (Fig. 4). P680* first reduces a pheophytin molecule—the primary electron acceptor of PSII, usually designated Q since it is a quencher of chlorophyll fluorescence—to finally yield reduced ferredoxin or pyridine nucleotides. The resulting $P680^+$ is a strong oxidant that promotes the oxidation of the primary donor to PSII (usually represented as Z) and the concomitant turnover of the water oxidation system. Actually, the cation radical $P680^+$ successively oxidizes manganese ions in the oxygen-evolving complex, the accumulation of four positive holes, or the transfer of four electrons along the photosynthetic transport chain, finally giving rise to the oxidation of two water molecules as well as the concomitant evolution of one oxygen molecule.

According to the classical Kok-Joliot model (the well-known water-oxidizing clock, or cycle), the O_2-evolving complex can cycle through five different oxidation states (S_0, S_1, S_2, S_3, S_4), photoexcitation of P680 thus promoting the advance of the OEC through each S state (*43,44*). When the clock reaches the S_4 state, it has released four electrons and is ready to complete the water-splitting reaction. The clock then removes four electrons from two water molecules, releases O_2, and drops from S_4 back to S_0, making it possible for the cycle to begin again (*30,31,38,45*).

The function of the manganese cluster in OEC, as well as those of Cl^-, Ca^{++} and HCO_3^- ions, are still controversial (*38,46*). Manganese is believed to make up at least part of the charge accumulator, as has been long known, O_2 production does not take place unless there are four Mn atoms in photosystem II for every P680 molecule. Chloride anions appear to organize the PSII proteins into a stable structure, whereas calcium cations probably play a structural or regulatory role. A specific requirement for bicarbonate anions has been described, but their function likewise remains obscure (*47*).

Various models for biological water photooxidation have been proposed, but the mechanism of water-splitting is still not clearly understood (*41*). Water oxidation is believed to occur only after the accumulation of four positive holes (or charge equivalents) in the OEC, that is, after the formation of the S_4 state (*48*). As the structure of the Mn cluster is not well established, the different proposed mechanisms depend on the chosen structural model—binuclear or tetranuclear clusters—for the Mn unit organization (*49–52*). It is generally assumed that the water molecule in the S-cycle is coordinating the Mn cations, forms a peroxo intermediate (Mn-O-O-Mn) in a first two-electron oxidation step, and finally gives rise to O_2 in a second two-electron oxidation step (*48–50*). Recently, Volkov (*42*) has proposed a 2:2 electron mechanism based on thermodynamic and kinetic considerations, which implies the formation of hydrogen peroxide, H_2O_2, as an intermediate.

Elucidation of the mechanism of water photooxidation is a major problem in photosynthesis, but it is indeed of great significance in designing artificial systems for solar energy conversion. Up to now, several biological or semisynthetic systems based on the use of the natural photosynthetic apparatus have been described for the production of energy-rich compounds. In all cases, a redox mediator—ferredoxin, flavodoxin, methyl viologen (*see* Fig. 4)—is used to accept electrons from PSI and subsequently donate them to adequate catalysts—platinum, hydrogenase, and many others—which, in turn, are able to drive the reactions yielding the final products (*53–56*). For instance, a large number of experimental photosystems have been constructed for the production of H_2 using whole cells of blue-green algae, isolated chloroplasts, and thylakoid membranes (*57*). Some compounds, mainly quinones, have exceptionally been reported to accept electrons on the reducing side of PSII (*58*).

Greenbaum (*59*) has recently prepared platinized chloroplasts, which have been reported to be a novel photocatalytic material that is capable of the sustained simultaneous photoevolution of hydrogen and oxygen when irradiated with visible light. Willner et al. (*60*) have constructed a photosynthetic bio-model for CO_2 fixation, which attempts to regenerate NADPH by a photosensitized electron transfer process initiated by synthetic/artificial systems; the regenerated cofactor is then coupled to the enzymatic reduction of CO_2 to organic compounds. The production of electricity from sunlight energy either by (a) thylakoid-based electrochemical cells using artificial mediators for electron transfer from the thylakoid material to the working electrode or by (b) PSII membrane particles deposited on semiconductor electrodes (*61,62*) has likewise been reported.

In the last years we have been working in the construction of several light-driven devices able to produce hydrogen peroxide by reduction of molecular oxygen. Using spinach thylakoids and whole cells of the blue-green alga *Anacystis nidulans*, the endergonic reduction of O_2 to H_2O_2 with electrons from water can be observed. The reaction proceeds by univalent

steps via superoxide radicals and is accelerated by a number of redox mediators, such as quinones, viologens, and flavins (*63*). The H_2O_2-forming activity can be significantly prolonged when the thylakoids or cells are immobilized in inert supports such as agar or alginate (*56,64*).

WATER OXIDATION BY ARTIFICIAL PHOTOSYNTHESIS

Most of the artificial sunlight-converting processes try to mimic with higher efficiency, simplicity, and stability the light-induced charge separation that takes place in the chloroplast of green plants. The main goal in designing a photochemical system for producing energy-rich compounds, in which water acts as the primary electron source, is the light-induced generation of both a strong reductant—capable of reducing either protons, oxygen, nitrate, dinitrogen, or carbon dioxide—and a strong oxidant—capable of promoting water oxidation (*1–7*).

One of the most extensively studied photosensitizers in artificial photosynthesis is the metal complex *tris*(2,2′-bipyridine)ruthenium(II), the so-called $Ru(bpy)_3^{2+}$, which has been shown to undergo facile light-induced electron transfer reactions. It is well established that the lowest excited state of $Ru(bpy)_3^{2+}$ has metal-to-ligand charge transfer (MLCT) orbital character and, formally, triplet multiplicity, with an extra free energy content (0–0 espectroscopic energy) of 2.12 eV (*65,66*). Visible light irradiation thus induces a considerable charge separation in the luminescent state of the complex, which has simultaneously both oxidizing [Ru(III)] and reducing [$(bpy)_3^-$] sites. In fact, it is both a moderately strong oxidant (E'_O, $Ru(bpy)_3^{3+}/{}^*Ru(bpy)_3^{2+}$, +0.84 V) and reductant (E'_O, ${}^*Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$, −0.86 V) (*66–68*). Even though from a thermodynamic point of view the ruthenium complex can both oxidize and reduce water, the most frequent reactions photosensitized by $Ru(bpy)_3^{2+}$ are those in which the photoexcited triplet state of the complex undergoes oxidative quenching. In this case, $Ru(bpy)_3^{2+}$ exhibits two redox pairs that share the same oxidized form—it belongs, like chlorophylls, to the group of energized reduced-form pairs—so decreasing the redox potential of the basal pair upon photoexcitation of the reduced species (Fig. 5). In fact, the midpoint potential value of the ruthenium complex shifts from +1.26 V in the dark to −0.86 V upon photoexcitation to its triplet state by blue photons. The energized state of the ruthenium complex is able to mediate one-electron reduction reactions and generate reducing equivalents, which can be directed toward the formation of several energy-rich compounds (*11,66,69*).

In general, the most thoroughly investigated model system is that containing $Ru(bpy)_3^{2+}$ as the photosensitizer and methyl viologen as an electron relay, the monovalent radical cation of the viologen (MV^+) being

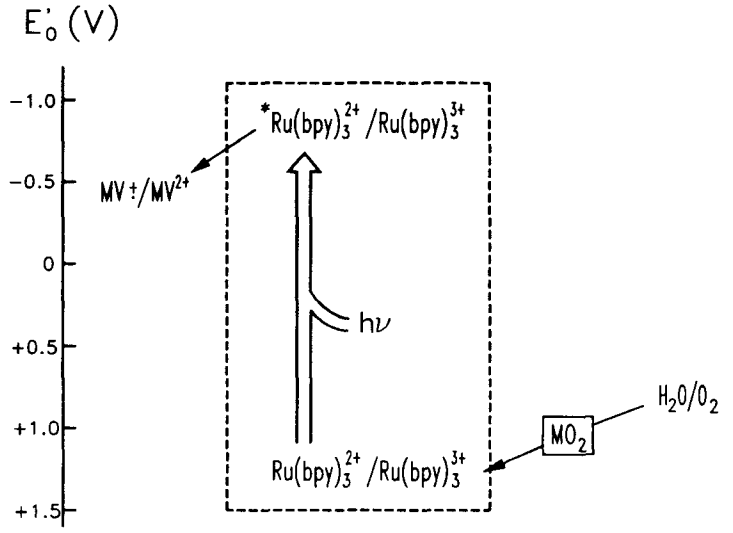

Fig. 5. Artificial water photolysis as photosensitized by *tris*(2,2'-bipyridine)ruthenium(II) and concomitant reduction of methyl viologen. By operating in a way similar to that of chlorophyll *a*, that is, working at two alternating redox potentials, the ruthenium complex can drive the light-induced transport of electrons from water to the redox level of the hydrogen electrode, or methyl viologen. A metal dioxide, MO_2, acts as a redox catalyst to facilitate water oxidation.

formed upon oxidative quenching of the luminescent lowest excited state of the complex (*22,69*). Once the photoexcited ruthenium complex has been oxidized by methyl viologen at low potential (−0.86 V), it has to be re-reduced in the dark at high potential (Fig. 5). Actually, $Ru(bpy)_3^{3+}$ can accept an electron from appropriate electron donors at the redox potential of +1.26 V (*70,71*), so promoting a light-induced electron flow against potential gradient. From a thermodynamic point of view, the oxidized species of the ruthenium complex is an oxidant so strong as to oxidize water (*69,72,73*). From a kinetic point of view, the process of water photooxidation must be found feasible in the presence of appropriate electron carriers and/or electron-hole accumulating catalysts (*74,75*). Notwithstanding, most $Ru(bpy)_3^{2+}$-based photosystems up-to-now utilized requires for a sacrificial electron donor (EDTA, semicarbazide, triethanolamine) that donates electron to the oxidized species of the ruthenium complex (*10,22,66,76–78*).

As discussed earlier, biological water photooxidation involves four consecutive steps with the formation of highly reactive intermediates. Similarly, hole-accumulating catalysts are required when using a single-electron oxidant in artificial water cleavage. A few years ago, Grätzel's group reported the $Ru(bpy)_3^{2+}$-sensitized photochemical oxidation of water to generate molecular hydrogen. Under certain experimental condi-

tions, the reaction was catalyzed by semiconductor particles composed by metal dioxides like TiO_2 or RuO_2, which acted as hole-transferring catalysts (*79–81*). By removing valence electrons, the photoexcited sensitizer created a number of positive holes in the semiconductor particles; such holes were in turn able to promote the water oxidation by subsequent electron transfer and proton dissociation (*82*).

Sustained water cleavage by visible light and simultaneous hydrogen evolution were obtained in solutions containing $Ru(bpy)_3^{2+}$ as the photosensitizer, methyl viologen as the redox mediator to reduce protons, and colloidal TiO_2 loaded with ultrafine deposits of RuO_2 and Pt as a bifunctional catalyst to oxidize water (*81,83–87*). Positive holes in TiO_2 are trapped by the RuO_2-catalyst, which subsequently oxidizes water, whereas the Pt-catalyst reduces water to molecular hydrogen. The system suffered, however, from low efficiency and stability, the metal catalyst being affected by poisoning and photocorrosion reactions.

As an alternative to biological systems, we have also studied artificial model systems for the possible design of long-term practical approaches to the synthesis of H_2O_2 from O_2 reduction (*10,11,88,89*). A photochemical system for H_2O_2 production has recently been studied by coupling $Ru(bpy)_3^{2+}$-sensitized water photooxidation with oxygen reduction, methyl viologen acting as an electron relay connecting the two processes with one another (unpublished results). As shown in Fig. 5, the ruthenium complex reduces the viologen compound, which, in turn, reduces oxygen to H_2O_2. The resulting oxidized form of the metal complex is subsequently reduced with electrons coming from water in a reaction catalyzed by metal dioxides such as TiO_2 or RuO_2. Further research is however required to select optimum conditions impeding side and back reactions so as to increase the final peroxide yield.

Several attempts have also been made to design photoelectrochemical cells that use semiconductor electrodes in place of the thylakoid membranes (*see* earlier discussion). Since the classical works by Fujishima and Honda (*90,91*) describing water photoelectrolysis with TiO_2 photoanodes, significant advances in photoelectrochemical cells have been obtained (*92–94*). A novel two-compartment solar cell, termed the semiconductor septum electrochemical photovoltaic (SC-SEP) cell, has been demonstrated to generate hydrogen from seawater without externally applied voltage and using only visible light. Specifically, the SC-SEP cell consists of a semiconductor septum electrode, an example of which is an *n*-type polycrystalline cadmium selenide (CdSe) deposited on the metal (e.g., nickel foil) separating two compartments filled with electrolytes (*95*).

In the last years, much research is being carried out to find quite more efficient and stable photosensitizers and catalysts (*96–98*). In particular, important efforts are being directed toward the design of metal-derived complexes able to directly photosensitize water oxidation. Comte et al. (*99*) have recently synthetized a new oxobridged Ru dimer with outstanding

stability and activity approaching the turnover frequency of the oxygen-evolving complex in green plants. Grätzel (*100*) has reported the spectral sensitization of wide band oxide semiconductors, such as titanium dioxide. By using charge transfer dyes molecularly engineered to be chemisorbed at the semiconductor/solution interface in conjunction with a novel structured semiconductor surface, important advances in the field of spectral sensitization appear to be achieved. We have recently demonstrated that the presence of small amounts of iron ions (< 0.5%) in TiO_2 matrices facilitates the photoreduction of methyl viologen (*101*).

Plant photosynthesis takes place in a membranous microenvironment in such a way that charge separation between an electron donor-acceptor pair is achieved and further backward reactions are retarded. Several artificial photosystems have been described making use of the properties of surfactant molecules in aqueous solutions. Surfactant agents spontaneously produce molecular assemblies in water, so mimicking the biological photosynthetic environment. Examples of these molecular assemblies are micelles, microemulsions, or vesicles, which dispose of a charged lipid-water interface (*27,102,103*). This interface provides a microscopic barrier that can be used to promote the light-induced electron transfer and charge separation of oxidizing and reducing equivalents and, at the same time, to decrease the backward electron transfer reaction between the two redox equivalents.

Significant attention is likewise being paid to the influence of molecular assemblies on electron transfer and stabilization of charge separated pairs. For example, zeolites, which are microporous aluminosilicates, can be used as templates for molecules involved in electron transfer so as to restrict molecular motions: Covalently linked $Ru(bpy)_3^{2+}$-diquat cations immobilized on zeolites L exhibit photoinduced charge separated states of about 1 μs lifetime, as compared to 5 ns in solution (*104*).

CONCLUSIONS AND PERSPECTIVES

Natural photosynthesis is actually the main way for conversion and storage of solar energy; the key reaction in this process being the photolysis, or photooxidation, of the water molecule by the photosystem II of higher plants and green algae. The initial production rates of biophotolytic systems using either whole cells, chloroplasts, thylakoids, or photosynthetic membranes are rather high, but these systems finally suffer from light inactivation causing low stability. However, the use of immobilization techniques to stabilize the photosynthetic activity and metabolic/genetic manipulations is a rather promising alternative for improving functional stability of biological structures.

On the other hand, artificial photosynthesis is at present in a very rudimentary phase of development. Even though the use of synthetic

catalysts to achieve water cleavage is, with no doubt, a highly promising area of study, intensive research is still required in order to discover new catalytic compounds, more stable against poisoning and corrosion, more efficient in promoting water photolysis, and more effective in impeding side and back reactions. In this context, artificial photosystems based on the photosensitizer immobilization and physical separation of the different reactions will surely have substantial practical impact.

Renewed interest appears to exist in the development of renewable energy sources, that is, in solar energy conversion by either biological, chemical, or semisynthetic procedures. However, both high-quality and applied research will be required, as well as collaborative work of photobiologists, photochemists, and photoelectrochemists, because of the multidisciplinary nature of this field of research.

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