JOURNAL OF SOLID STATE CHEMISTRY 22, 3–8 (1977)

Photochemical Conversion and Storage of Solar Energy*†

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Received March 11, 1977

The possibilities for the photochemical storage of solar energy are examined from the standpoint of maximum efficiency and mechanism. Loss factors are considered for a general endergonic photochemical reaction and it is concluded that a realistic maximum solar energy storage efficiency for any photochemical system is 15–16%. The natural process of photochemical solar energy storage, namely, photosynthesis, is analyzed and it is found that the maximum solar energy storage efficiency of photosynthesis is 9.5 ± 0.8%. Kinetic and thermodynamic limitations on a photochemical energy storage process are identified and it is shown that the desirable production of hydrogen and oxygen from water probably cannot be sensitized with visible light if only one photochemical step is employed. However, by analogy with the mechanism of photosynthesis, two photochemical reactions operating in series permit a full utilization of the photochemically active part of the solar spectrum. A possible scheme is described and analyzed as to its possibilities and potential difficulties. Finally, some practical considerations are presented not only for the photochemical production of hydrogen but also for solid state photovoltaic devices.

Introduction

Solar energy is an immense energy resource as each year the earth receives about 5400 Q[1] of energy. The estimated fossil and uranium fuel reserves available on earth total only about 200 Q (*1*), or about 2 weeks of the total solar input. However, solar energy suffers from two disadvantages–it is intermittent and varies considerably with the seasons, and it is widely distributed and hence the energy density at any one place is not high. Thus energy storage and large areas of collectors are important requirements for the utilization of solar energy. Nature has solved both of these problems and for billions of years has been using and storing solar energy through photosynthesis, the natural process of solar energy storage. It is estimated (*2*) that each year about 5×10^{10} tonnes of carbon are fixed through photosynthesis. This represents a storage of about 2 Q per year or about 0.04% of the world's yearly solar input. Looked at from another aspect, the storage of solar energy via photosynthesis is occurring at a rate over five times the current world rate of human consumption of energy. Unfortunately, with the exception of wood, most of the products of photosynthesis are not in a convenient form for use by man as an energy source, although the prospects for the production of a synthetic natural gas from the anaerobic digestion of biomass look very promising.

Since photosynthesis is the only known efficient method for the photochemical storage of solar energy, it is important to understand the mechanism and efficiency of photosynthesis if we hope to be able to design artificial systems.

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* Part of the Solar Energy Symposium of the 1976 Pacific Conference on Chemistry and Spectroscopy.

† Contribution No. 173 of the Photochemistry Unit, University of Western Ontario.

[1] 1 Q = 10^{18} Btu ~ 10^{21} J or 1 Q is equivalent to the heat of combustion of over 2 miles^3 of bituminous coal.

Printed in Great Britain

ISSN 0022-4596

Maximum Possible Efficiency for the Photochemical Storage of Solar Energy

A general photochemical energy storage reaction can be represented by an endergonic chemical reaction driven uphill by light energy. This process is illustrated for the reaction

$$R \rightarrow P$$

in Fig. 1. With the sun as the light source, there are three basic energy losses which must be incurred:

(1) Light with wavelengths greater than the wavelength λ^* corresponding to the 0–0 transition[2] from R to R^* cannot be absorbed and hence this energy cannot be used to drive photochemistry.

(2) Light with wavelengths less than λ^* may be absorbed but the process of internal conversion will rapidly degrade the energy to the lowest vibronic level of R^* and hence the *excess* energy in each photon will be lost as heat.

(3) The reaction $R^* \rightarrow P$ must be exergonic because if P is to have a reasonable lifetime, then an activation barrier must be built in for the back reaction $P \rightarrow R^*$. Such an activation barrier can be achieved only with the loss of some of the excitation energy of R^* as heat. There also may be thermodynamic limitations on the efficiency of conversion (*3–5*). In photovoltaic devices an activation barrier must be established to prevent electron–hole recombination.

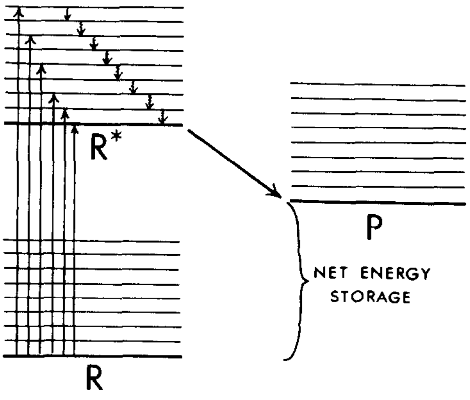

FIG. 1. Energy level diagram representing a general photochemical reaction R → P where the reaction is endothermic.

The solar energy storage efficiency of a photochemical reaction will be defined as

$$\eta = \frac{\text{rate of chemical free energy storage (Wm}^{-2}\text{) in the chemical products}}{\text{solar irradiance (Wm}^{-2}\text{) incident on the reacting system}} \times 100. \quad (1)$$

For the purposes of the calculation η can be expressed as:

$$\eta = 100 \int_{\lambda_{\min}}^{\lambda_*} E_\lambda(\text{rel})\, \chi_\lambda\, \alpha_\lambda\, \phi_\lambda\, \varepsilon_\lambda\, d\lambda. \quad (2)$$

For the wavelength range λ to $\lambda + d\lambda$:

$E_\lambda(\text{rel})$ = fraction of solar irradiance in the wavelength band;
χ_λ = fraction of photon energy in the wavelength band available for photochemistry at the wavelength λ^*;
α_λ = absorption coefficient;
ϕ_λ = quantum yield for the production of products;
ε_λ = ΔG for the overall reaction divided by the energy of one Einstein at the wavelength λ^*;
$\lambda_{\min}$ = lowest wavelength for which the integrand is significantly above zero.

The analysis of the maximum possible efficiency will first be made with the following extreme assumptions:

(1) Every photon of light which is absorbed will contribute toward the production of P from R. That is, the quantum yield for the production of P will be assumed to be 1.0.

(2) The absorption coefficient α_λ will be taken to be 1.0 for $\lambda \leqslant \lambda^*$ and 0.0 for $\lambda > \lambda^*$. This means that all photons with $\lambda \leqslant \lambda^*$ will be absorbed.

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[2] In a solid state device this would correspond to the band gap.

(3) λ^* will be taken as 700 nm since there are very few photochemical reactions with λ^* greater than 700 nm.

(4) The solar spectrum will be taken as the British RD6500 standard daylight spectral distribution curve (*6*).

(5) The energy loss in the reaction $R^* \rightarrow P$ will be taken as about 50 kJ mole^{-1}. That is, the activation barrier for the reaction $P \rightarrow R^*$ will be 50 kJ mole^{-1}. This value corresponds to about a 30% loss of energy in the reaction $R^* \rightarrow P$.

With the above assumptions an analysis was carried out at 10 nm intervals. The calculated energy losses incurred were:

Loss term No. 1	47%
Loss term No. 2	14%
Loss term No. 3	11%

Hence, the maximum possible efficiency under the above assumptions is 28%.

Of course, a real system will incur further losses due to:

(1) Incomplete absorption of sunlight with $\lambda \leqslant \lambda^*$. 0.75 would probably be a reasonable value for the integrated absorption coefficient of a real absorber.

(2) Loss of some photons due to fluorescence, internal conversion to the ground state, side reactions, etc. A real system is unlikely to exhibit a quantum yield of greater than 0.90.

(3) The activation barrier for the reaction $P \rightarrow R^*$ in a real system is likely to be greater than the 50 kJ mole^{-1} assumed above, especially if more than one step is involved. We will assume a value of 70 kJ mole^{-1} or an energy loss of about 40% in the reaction $R^* \rightarrow P$.

When these modified, more realistic, conditions are imposed the energy storage efficiency drops to about 16%. Hence, an efficiency of 15–16% represents a realistic maximum efficiency for a photochemical solar energy storage system. If λ^* is increased to about 1000 nm as is the case for photovoltaic devices such as the silicon solar cell, the maximum efficiency would be about 20%.

Solar Energy Storage Efficiency in Photosynthesis

The overall cheminal reaction of green plant and algal photosynthesis is:

$$\mathrm{CO_2(g,\ 0.0032\ atm) + H_2O(l) \rightarrow \tfrac{1}{6}C_6H_{12}O_6(s) + O_2(g,\ 0.21\ atm)} \qquad (3)$$

for which $\Delta H = 467$ kJ mole^{-1} and $\Delta G = 496$ kJ mole^{-1} at 298 K as calculated from standard enthalpies and free energies of formation corrected to the pressures indicated.

The analysis of the efficiency η was carried out using Eq. (2) again at 10 nm intervals. The same RD6500 standard daylight solar spectral distribution (*6*) was used. λ^* was taken as 700 nm and hence $\chi_\lambda = \lambda/700$ nm. α_λ values for a green leaf were taken from experimental measurements (*7*). ϕ_λ values were taken as experimental values for *Navicula minima* (*8*) up to 640 nm and *Chlorella pyrenoidoisa* (*9*) from 640 to 700 nm. At the "effective" wavelength of 700 nm, $\varepsilon_\lambda = 2.903$. λ_{min} was taken as 360 nm.

With the above assumptions and conditions, the overall gross efficiency of photosynthesis is calculated to be 9.5 ± 0.8%. Thus photosynthesis comes rather close to achieving the realistic maximum efficiency of 15–16% for a photochemical solar energy storage system.

Mechanism of Photosynthesis

It is not possible in this article to explain in full the details of the mechanism of photosynthesis. Several recent books and articles cover the subject well (*10–13*). An analysis of the mechanism reveals the following features for the light-driven reactions:

(1) The photochemical reactions consist exclusively of one-electron transfer reactions from a special chlorophyll species to an acceptor with the transfer taking place across the thylakoid membrane of the chloroplast.

(2) In each photochemical step about 55% of the light energy at 700 nm is converted to chemical energy of the immediate primary products.

(3) Two photochemical reactions operate *in series* to take electrons from water and raise the electron energy sufficiently to reduce $NADP^+$ (nicotinamide adenine dinucleotide phosphate).

(4) The quantum yield for each photochemical electron transfer is close to 1.0 electrons per photon.

(5) Since the production of one oxygen molecule in the reaction of photosynthesis requires that *four* electrons be removed from water and since there are two photochemical electron transfer reactions, a minimum of *eight* photons must be absorbed for each oxygen molecule evolved.

As we shall see later these observations on the mechanism of photosynthesis suggest some possible ways in which an artificial system might function. They also point to certain limitations.

Threshold Wavelength for the Photochemical Production of a Fuel

The photochemical production of a fuel is clearly a desirable way to store solar energy. Most fuels are highly reduced chemical substances (e.g., hydrogen, methane, etc.). The stored chemical energy in the fuel is released by combustion with oxygen. Thus we require a photochemical reduction reaction to provide a fuel. Let us see what the limitations will be on a photochemical reduction.

Since there are no known photochemical processes which can transfer more than one electron at a time, we will assume that the maximum quantum yield for the production of a fuel by a *single* photochemical reduction is $1/n$ where n is the number of electrons transferred per molecule of fuel produced, or n Einsteins of light must be absorbed per mole of fuel produced. From this we can derive the threshold wavelength for the reaction as

$$\lambda_{\max} = nN_0hc\varepsilon/\Delta G, \qquad (4)$$

where ε is the fraction of the photon energy at $\lambda_{\max}$ which is converted to chemical free energy of the fuel, N_0 is Avogadro's number, h is Planck's constant in kilojoules, c is the speed of light in meters per second, ΔG is the Gibbs free energy change in the fuel production reaction in kilojoules per mole of fuel produced.

Photochemical Decomposition of Water into Hydrogen and Oxygen

The photochemical generation of hydrogen and oxygen from water

$$H_2O(l) \xrightarrow[\text{sensitized}]{h\nu} H_2(g) + \tfrac{1}{2}O_2(g) \qquad (5)$$

is a very attractive goal for the photochemical storage of solar energy. Hydrogen is almost an ideal fuel and the starting material is certainly cheap. Water does not absorb at solar wavelengths; hence, the reaction must be sensitized by dyes. Various possible schemes and cycles have been reviewed recently (*14*). ΔG^0 for reaction (5) is 237.2 kJ $mole^{-1}$ and $n = 2$. If we take the maximum value of $\varepsilon \sim 0.70$, a very optimistic value, then from Eq. (4) $\lambda_{\max}$ is calculated to be ~700 nm (see Fig. 2). However, the reaction mechanism may well be rather complex involving several steps and ε is quite

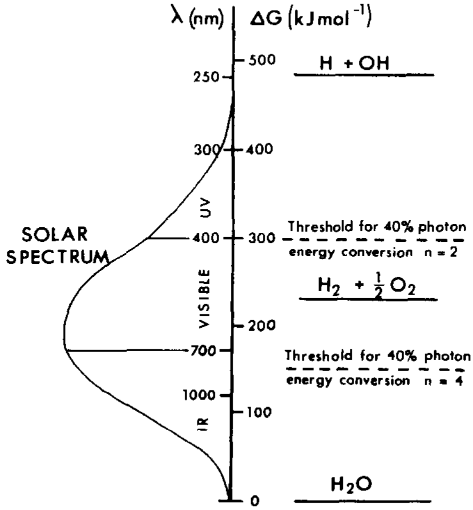

FIG. 2. Energy analysis for the reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ compared to the solar spectrum. The threshold wavelength is determined by Eq. (4)

likely to be much less than 0.70. If ε is as low as 0.40 then λ_{max} becomes ~400 nm and *it would not be possible to sensitize the production of hydrogen from water with visible light* if only *one* photochemical step is employed.

It is useful to draw an analogy between the hydrogen/oxygen production from water (reaction (5)) and the reaction of photosynthesis (reaction (3)). $\mathscr{E}^\circ$ for the former reaction is 1.23 V and for the latter is 1.28 V. In photosynthesis $\varepsilon \leqslant 0.36$. Thus a similar λ_{max} situation applies to the photosynthesis reaction. It is important to recognize that Nature solved this difficulty by using *two* photochemical reactions operating in series. This effectively doubles λ_{max} for the reaction because two photons are employed for every electron transferred. Similarly if we employ two photochemical reactions operating in series to bring about reaction (5), then with ε ~0.40, λ_{max} becomes ~800 nm. This would allow effective use of the solar spectrum and would be expected to yield an energy storage efficiency similar to that of photosynthesis, namely about 10%.

A Possible Scheme

If we accept that it will be necessary to use two photochemical steps to sensitize reaction (5), then it would be sensible to make one step a photochemical reduction and the other a photochemical oxidation. A possible scheme is shown in Fig. 3. *D* is a dye which will be a good electron donor in its excited state and hence a strong photochemical reducing agent. *A* is a dye which is a good electron acceptor in its excited state and hence a strong photochemical oxidizing agent. D^+ and A^- are returned to their photochemically active states by coupling the two cells electrochemically.

There are two problems which must be solved if this scheme is to be successful:

(1) Reverse electron transfer reactions are usually very fast in photochemical electron transfer reactions and hence we must find some method of slowing down the back reaction to permit forward secondary reactions to occur with high efficiency. In photosynthesis a membrane structure is used to inhibit back electron transfer, so some method of employing artificial membranes, vesicles or micelles may have some success.

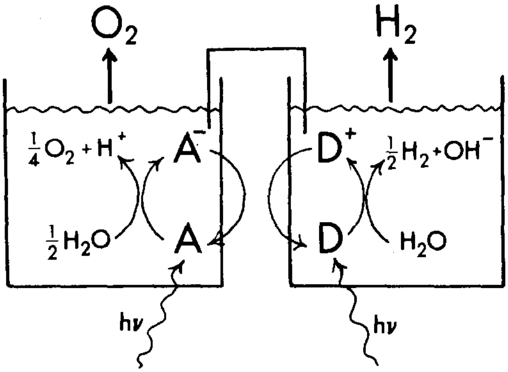

FIG. 3. Scheme for the sensitized decomposition of water using two coupled photochemical systems. *D* and *A* are dyes which in their excited states are, respectively, strong reducing and strong oxidizing agents.

(2) Since photochemical electron transfer reactions transfer only one electron at a time, some method of storage of electrochemical equivalents must be found. Two electrons must be stored to produce one hydrogen molecule and four positive charges must be stored to produce one oxygen molecule. A manganese enzyme is thought to carry out the storage of positive charges in photosynthesis so if the structure of this enzyme can be determined, it may be possible to synthesize an analogous inorganic complex which will achieve this same job *in vitro*. On the reduction side, the enzyme hydrogenase is known to carry out the function of storage of two electrons to produce a hydrogen molecule from two hydrogen ions. Hence, again a knowledge of the structure of the enzyme may permit the synthesis of an artificial analog.

Other Systems

The limitations considered above apply also to the photoelectrolysis of water using semiconductor electrodes (*15*). Illumination of only one electrode corresponds to the single photochemical process with λ_{max} ~400 nm. Indeed the only working systems employ ultraviolet light. However, if both electrodes are illuminated and semiconductors with smaller band gaps are used, then λ_{max} would be ~800 nm.

It is conceivable that other systems for photochemical fuel production can be achieved such as the reduction of CO_2 to methane or methanol. Also we may find it better to produce oxidation products other than oxygen. For example, waste organics in sewage or biological wastes could be photooxidized to serve as the source of electrons for the production of a high grade fuel such as hydrogen.

Conclusions

This article has attempted to analyze the possibilties, limitations, and prospects for the photochemical storage of solar energy. It should be possible to mimic the natural process of photosynthesis but much basic research is needed yet. Nevertheless, the promise of a successful system is very great and should justify a significant research effort to try and establish a working laboratory system. Only then will it be possible to answer the questions of economics and feasibility for a practical system.

Acknowledgment

The author would like to acknowledge the aid of Dr. Mary Archer who made many helpful suggestions.

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