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Solar Fuels

The production of energy-rich compounds by the photochemical conversion and storage of solar energy.

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Most of the current and proposed applications of solar energy are based on the collection and conversion of sunlight as heat to be used directly in space and water heating or to be converted to electricity by means of a Carnot engine. Some applications allow for the direct conversion of sunlight to electricity as in the silicon solar cell; however, additional steps must be taken if energy storage is required. In this era of depleting fossil fuel resources, it would be highly desirable to have an efficient and economical way of directly converting and storing solar energy as a chemical fuel. My objective in this article is to define qualitatively and quantitatively the thermodynamic and kinetic limits on the photochemical conversion and storage of solar energy as it is received on the earth's surface, to evaluate a number of possible reactions with particular emphasis on the production of solar hydrogen from water, and to develop a scheme by which hydrogen fuel might be generated.

General Requirements for a Fuel-Generation Reaction

Although there are many possible endergonic reactions which, in principle, could be used to store chemical energy, it would be most desirable, from a practical standpoint, to generate a fuel that is already in use from fossil fuel sources. Thus for the purposes of this article I will adopt a limited definition of a fuel as any reduced chemical substance, produced as a result of an endergonic photochemical reaction, which on reaction with oxygen will release the stored chemical energy. A general reaction producing a fuel F is hence written as

$$A + B \overset{h\nu}{\rightleftharpoons} F + O_2 \qquad (1)$$

(where $h\nu$ indicates a photochemical process) and where the stoichiometry need not be that given in Eq. 1; the back reaction serves to release the stored energy.

Many investigators have considered the general requirements for a practical solar fuel-generation reaction (*1-3*). In summary, they are:

1) Equation 1 must be endergonic.

2) The process must be cyclic; that is, the exergonic back reaction of $F + O_2$ must lead eventually to the complete regeneration of $A + B$.

3) Side reactions leading to the irreversible degradation of A, B, or any photochemical sensitizers must be almost totally absent.

4) The back reaction must be extremely slow under ambient conditions to permit long-term storage of the fuel but should proceed rapidly under special controlled catalytic conditions or elevated temperatures so as to release the energy when desired.

5) The reaction should be capable of operating over a wide bandwidth of the visible and ultraviolet portions of the solar spectrum with a threshold wavelength well into the red or near-infrared region.

6) The quantum yield for the production of F should be as high as possible.

7) It should be possible to store and transport F easily.

8) The reagents and any container material used should be cheap and nontoxic, and the reaction should be unaffected by oxygen.

At present, the only working system that satisfies nearly all of these requirements is the photosynthesis reaction; however, several possible systems have a potential to satisfy most of the requirements. These systems will be considered in detail in this article.

The Photochemical Reaction

The generation of a fuel F with solar energy used as the driving force requires one or more endergonic photochemical steps. The reagents A and B need not be involved directly as absorbers if a photochemical catalyst is used which will sensitize the reaction. For example, chlorophyll sensitizes the reaction of photosynthesis but is not a direct reagent.

A general representation of an endergonic photochemical step is shown in Fig. 1, where R is the absorber and P is the primary product of the photochemical step. The reaction may involve more than one reactant, but the overall process will be considered to be first order. This point will be expanded on later.

There are three fundamental loss processes that must be incurred in the photochemical step or steps (*4*):

1) Photons having a wavelength λ such that $\lambda \geq \lambda_g$, where λ_g is the wavelength corresponding to the energy E_g, do not have sufficient energy to raise R to R^* and thus cannot contribute to the photochemistry.

2) Photons that are absorbed with $\lambda < \lambda_g$ may raise R to R^*, but the very efficient process of internal conversion will reduce R^* to its lowest vibrational level within a few picoseconds and hence the excess photon energy above E_g will be lost as heat.

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3) The conversion of R^* to P must be an exergonic reaction so that an activation energy E_r^* for the back reaction will be established (see Fig. 1). Otherwise, P would have no stability to allow for storage or subsequent reactions leading to chemical storage.

The solar spectrum for air mass (AM) 1.2 (a bright sunny summer day near noon) (*5, 6*) is shown in Fig. 2. Most photochemical reactions have band-gaps such that λ_g is in the visible or ultraviolet region. Thus at least 52 percent of the solar spectrum is lost in the first loss term. There are, however, some photochemical processes that occur in the infrared such as photoionization in the silicon photocell (λ_g = 1100 nanometers) and the primary photochemical process in certain photosynthetic bacteria, for example, *Rhodopseudomonas viridis* (λ_g = 980 nm). Thus it may be possible to develop efficient infrared sensitizers.

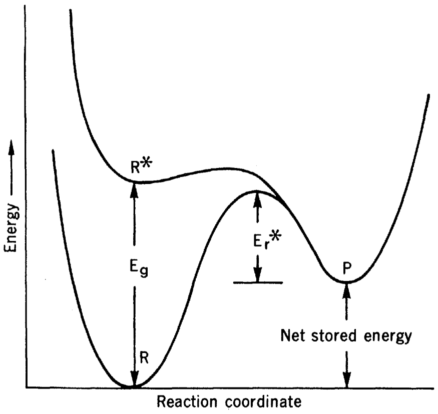

Fig. 1. Energy profile for a general endergonic photochemical reaction $R \rightarrow P$; E_g is the minimum energy gap between the lowest vibrational levels of the excited state R^* and the ground state of R, and E_r^* is the activation energy for the back reaction $P \rightarrow R$.

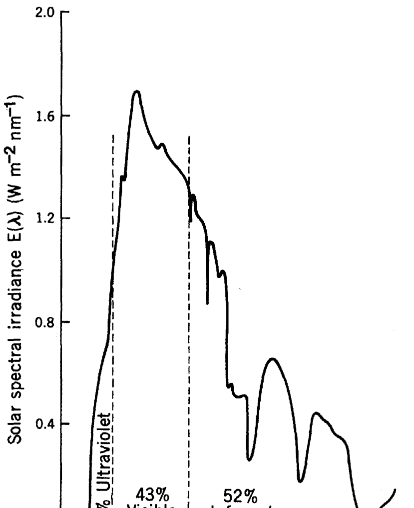

Fig. 2. Solar spectral distribution for AM 1.2 [distribution T/S from (*6*)]. The spectrum is shown only out to 1500 nm; however, the 52 percent for the infrared portion of the spectrum refers to the total integrated irradiance for $\lambda > 700$ nm.

The quantitative evaluation of the first two loss terms can be carried out as follows: if $N_s(\lambda)$ is the incident solar photon flux in the wavelength band from λ to $\lambda + d\lambda$ (in photons per square meter per second per nanometer) and $\alpha(\lambda)$ is the absorption coefficient of the absorber, then the absorbed flux of photons with $\lambda \le \lambda_g$ is given by

$$J_e = \int_0^{\lambda_g} N_s(\lambda)\alpha(\lambda)d\lambda \tag{2}$$

The available solar power E (in watts per square meter) at the band-gap energy is thus

$$E = J_e \cdot \frac{hc}{\lambda_g} \tag{3}$$

where h is Planck's constant, and c is the speed of light. Then the fraction η_E of the incident solar power available to initiate photochemistry is

$$\eta_E = \frac{E}{\int_0^{\infty} E(\lambda)d\lambda} \tag{4}$$

where the denominator in Eq. 4 is the total incident solar power.

If we make the ideal assumption that $\alpha(\lambda) = 1$ for $\lambda \le \lambda_g$ and $\alpha(\lambda) = 0$ for $\lambda > \lambda_g$, then we can compute an ideal maximum value of η_E as a function of λ_g. This is shown as curve E in Fig. 3; η_E has a maximum value of 47 percent at 1110 nm for AM 1.2, but the maximum is very broad in that η_E is > 45 percent between 800 and 1300 nm. It is a common misconception among photochemists that η_E represents the fraction of the solar power that can be converted to chemical energy. In the next section I will attempt to show the fallacy of this view.

Limits on the Conversion of Light Energy to Chemical Energy

Many investigators have treated the problem of thermodynamic limits on the conversion of light to chemical energy (*7, 8*); however, Ross and Hsiao (*9*) have recently published a particularly lucid treatment, based on the original treatment by Ross and Calvin (*8a*), which I will briefly summarize here.

Consider a dilute solution of a dye D in equilibrium in the dark with a black box at temperature T_L as shown in Fig. 4a. The blackbody radiation will cause a very small but finite fraction of the dye molecules to be in the excited state D*. Let x_L be the mole fraction of D* molecules at equilibrium. Since the system is completely at equilibrium, the chemical potentials μ of ground and excited states must be equal, that is,

$$\mu_D{}^e = \mu_{D^*}{}^e = \mu_{D^*}{}^0 + RT \ln x_L \tag{5}$$

Now let us consider the situation in Fig. 4b with an external light beam irradiating the system. Some of the absorbed light will induce D → D* transitions, and hence the mole fraction of D* will increase under steady-state conditions. It is assumed that D* has a sufficient lifetime (greater than a few picoseconds) so that a Boltzmann distribution will be established among the vibrational levels of D*; D* can then be considered as a separate chemical species which has come to vibrational equilibrium at the temperature T_L. Let x_H be the new mole fraction of D*. If the ground state is not significantly depleted (that is, the mole fraction of the ground state is essentially unity with or without the light beam), then

$$\mu_D = \mu_D{}^e$$

However, the chemical poential of D* will increase and now

$$\mu_{D^*} = \mu_{D^*}{}^0 + RT \ln x_H \tag{6}$$

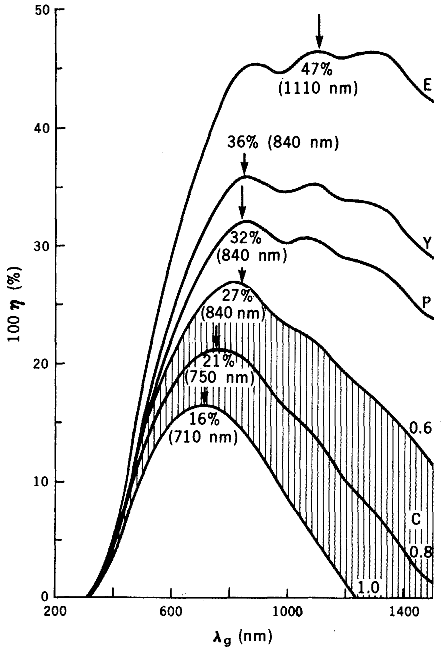

Fig. 3. Plots of the efficiencies η_E, η_Y, η_P and η_C as a function of the wavelength λ_g corresponding to the energy gap. E_g. The distributions have been calculated for AM 1.2 solar radiation [taken from distribution T/S of (*6*)]. Curves E, Y, P, and C are plots of η_E, η_Y, η_P, and η_C, respectively, as defined in Eqs. 4, 10, 13, and 17, respectively; η_C has been calculated for energy losses of 0.6, 0.8, and 1.0 eV, respectively, as indicated on the figure.

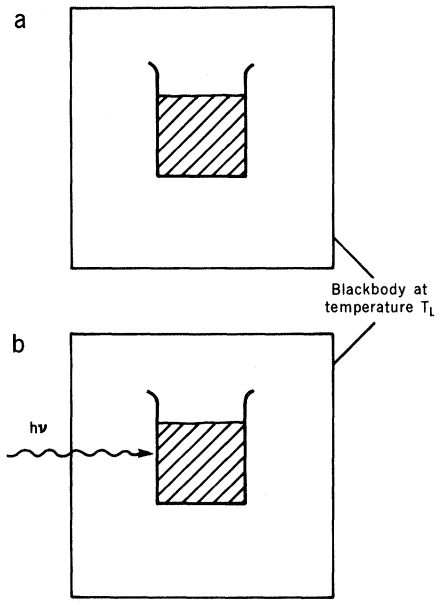

Fig. 4. (a) A dilute solution of a dye in equilibrium with a blackbody at temperature T_L but with no external irradiation. (b) Same system as in (a) but with an external light beam irradiating the dye solution.

Thus, the difference in μ which can be generated by the action of light between ground state and excited states is

$$\mu = \mu_{D*} - \mu_{D*}^{e} = RT \ln (x_H/x_L) \quad (7)$$

Clearly $\mu \rightarrow 0$ as the intensity of the external light source goes to zero ($x_H \rightarrow x_L$). Under conditions where there is no net storage of energy (that is, the quantum yield for storage $\phi_{st} = 0$), μ will have its maximum value, μ_{max}.

Ross and Hsiao (*9*) have derived the following expression for μ_{max}

$$\mu_{max} \doteq \frac{N_0 hc}{\lambda_g} + RT \ln \int_0^{\lambda_g} N_s(\lambda) d\lambda - RT \ln \left[\frac{8\pi n^2 kT}{h\lambda_g^{\,2}}\right] \quad (8)$$

where $N_s(\lambda)$ is the flux of solar photons (in photons per square meter per second per nanometer) in the wavelength band from λ to $\lambda + d\lambda$, N_0 is Avogadro's number, and n is the refractive index of the medium, and k is the Boltzmann constant.

The maximum thermodynamic photochemical power yield possible is then

$$Y = \frac{J_e \cdot \mu_{max}}{N_0} \quad (9)$$

The maximum thermodynamic efficiency is given by

$$\eta_Y = \frac{Y}{\int_0^{\infty} E(\lambda) d\lambda} \quad (10)$$

where η_Y is plotted as curve Y in Fig. 3. It should be noted that Y represents the yield obtainable only under conditions where chemical storage is achieved reversibly, that is, such that energy is drawn into storage infinitesimally slowly or where $\phi_{st} \rightarrow 0$.

Clearly we wish to know what the maximum yield would be under conditions where energy is drawn off into storage at a maximum rate. The rate of energy storage can be defined as

$$P = J_e(1 - \phi_{loss})\mu \quad (11)$$

where ϕ_{loss} represents the total quantum yield of all processes that do not lead to energy storage (for example, fluorescence and nonradiative decay to the ground state). Drawing off energy into storage will reduce the mole fraction of D*, and hence μ will be less than μ_{max}. Equation 11 must be solved for a maximum such that ϕ_{loss} is minimized while keeping μ as high as possible.

Using expressions derived by Ross and Hsiao (*9*) along with their estimate that $\phi_{loss} \approx RT/\mu_{max}$, one can obtain the following equation for the optimal energy storage rate

$$P = \frac{J_e}{N_0}\left[\mu_{max} - RT \ln \left(\frac{\mu_{max}}{RT}\right)\right] \times \left[1 - \frac{RT}{\mu_{max}}\right] \quad (12)$$

where it is assumed that nonradiative losses are insignificant (that is, $\phi_{internal\ conversion} = 0$). Then the maximum fraction of the solar power which can be converted into chemical energy η_P is

$$\eta_P = \times \frac{P}{\int_0^{\infty} E(\lambda) d\lambda} \quad (13)$$

the quantity η_P was calculated for AM 1.2 solar radiation and is plotted as curve P in Fig. 3. It maximizes at 32 percent at 840 nm. Interestingly, ϕ_{loss} varies from 0.01 at 400 nm to 0.04 at 1500 nm and is only 0.022 at the maximum of the curve so that most of the difference between curves Y and P is due to a drop in μ from μ_{max}.

Curve Y is quite general and applies to any conversion of solar power to electricity or stored chemical energy. Ross and Hsiao (*9*) have calculated curves E, Y, and P for AM 0 solar radiation.

Since μ depends on the light intensity, η_P can be increased by concentration of sunlight (for example, at 100 suns, η_P increases from 32 to 36 percent at 840 nm); however, one then has to contend with heat dissipation problems and so the gain may not be too significant since η_P drops rapidly with temperature (for example, at 500 K η_P drops to 24 from 32 percent at 840 nm).

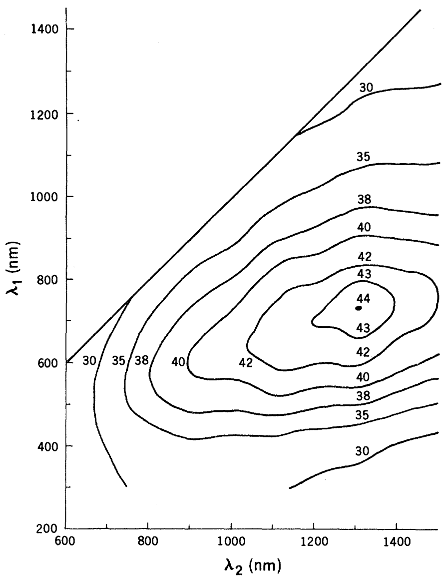

Fig. 5. Contours of η_P (in percentages) as a function of λ_1 and λ_2 for a system sensitized by two absorbers with AM 1.2 solar energy. These efficiencies were calculated with the use of Eqs. 8, 12, and 13 with

$$J_e = \int_0^{\lambda_1} N(\lambda) d\lambda \text{ for } 300 \text{ nm} \leq \lambda \leq \lambda_1$$

and

$$J_e = \int_{\lambda_1}^{\lambda_2} N(\lambda) d\lambda \text{ for } \lambda_1 < \lambda \leq \lambda_2.$$

Another way in which η_P may be increased is to use two separate photochemical sensitizers in two distinct photosystems, each with a different range of spectral sensitivity. Figure 5 shows contours of η_P for two sensitizers with AM 1.2 solar radiation in which sensitizer 1 absorbs all the light with $\lambda \leq \lambda_1$ and sensitizer 2 all the light in the range $\lambda_1 < \lambda \leq \lambda_2$. Although the maximum of 44 percent occurs for $\lambda_1 = 830$ nm and $\lambda_2 = 1320$ nm, there is a wide range of values in which η_P is above 40 percent. For three sensitizers the maximum efficiency is 50 percent for $\lambda_1 = 570$ nm, $\lambda_2 = 820$ nm, and $\lambda_3 = 1330$ nm. Thus the improvement gained in going from two to three sensitizers probably will not be cost-effective when one balances the marginal improvement in efficiency with the added complexity of the system. Ross and Hsiao (*9*) have calculated similar contours for AM 0 solar radiation.

For conversion to electricity the thermodynamic limit may well be approached. For example, a gallium arsenide solar cell has been reported (*10*) with an efficiency (AM 1.4) of 23 percent ($\lambda_g = 920$ nm). However, the requirement of energy storage imposes an additional kinetic requirement which is essentially the third loss factor considered in the beginning of this article (see Fig. 1). Thus, for a consideration of the limits on energy storage, we must develop a kinetic argument.

If the photochemical step is first order (that is, either unimolecular or bimolecular where the two molecules are restricted to react only with each other as in a solid state or on a membrane), then we can apply unimolecular rate theory (*11*) to calculate E_r^* (in electron volts)

$$E_r^* = \frac{-kT}{e} \ln \left[\frac{h}{kT\tau} \right] \tag{14}$$

where e is the charge on the electron and τ is the lifetime of the primary products assuming that the only reaction possible is the back reaction. For example, if $\tau = 1$ second, then $E_r^* = 0.8$ electron volt; for $\tau = 1$ millisecond, then $E_r^* = 0.6$ eV.

The creation of this activation barrier must be done at the expense of the excitation energy, and the loss is constant and independent of λ_g. Thus we can define a chemical yield C (which, of course, must be less than P)

$$C = E \cdot \eta_{\text{chem}} \tag{15}$$

and

$$\eta_{\text{chem}} = \frac{\Delta G}{E_g} \tag{16}$$

where ΔG is the net free energy storage in the photochemical step. Then

$$\eta_C = \frac{C}{\int_0^{\infty} E(\lambda) d\lambda} = \eta_E \cdot \eta_{\text{chem}} \tag{17}$$

The quantity η_C is plotted as curve C in Fig. 3, assuming that $E_{R^*} - E_p = 0.8$ eV. The maximum yield is 21 percent at 750 nm. Plots are also shown in Fig. 3 for $E_{R_*} - E_p = 0.6$ eV which maximizes at 27 percent for $\lambda_g = 840$ nm and $E_{R_*} - E_P = 1.0$ eV which maximizes at 16 percent for $\gamma_g = 710$ nm.

One may argue that the loss could be smaller if τ were made shorter; however, secondary reactions necessary to stabilize the reaction products must be exergonic, which will thus incur additional losses.

As before, the coupling of two photosystems in series can improve the yield. For example, with $E_{R^*} - E_p = 0.8$ eV, η_C is 29 percent for $\lambda_1 = 600$ nm and $\lambda_2 = 850$ nm.

If the photochemical step is second order as for the bimolecular reaction of two components in solution, then the factor $E_{R^*} - E_P$ can be quite small because of the short lifetime of the collision complex. However, in this case the back reaction will be virtually diffusion-controlled and no net storage will occur. Anything which will slow down the back reaction must either involve exergonic secondary reactions or conversion of the process to first order (for example, by confining the reactants to a surface or a membrane). Hence, it is unlikely that one can avoid a loss of perhaps 0.6 to 1.0 eV in any photochemical endergonic step.

In photosynthesis, the energy loss in the primary photochemical step is about 0.8 eV for photosystems I and II of green plant and algal photosynthesis and also for bacterial photosynthesis (*12*). Also $\lambda_g \simeq 700$ nm for green plant and algal photosynthesis, a value near optimum on curve C of Fig. 3.

An Estimate of Chemical Storage Efficiency

Curves P and C (Fig. 3) represent ideal limits of conversion efficiencies; however, there are other loss factors to be considered as indicated in the following general expression for the energy storage efficiency

$$\eta_{\text{storage}} = \eta_{\text{abs}} \eta_E \eta_{\text{chem}} \eta_{\phi} \eta_{\text{coll}} \tag{18}$$

where η_{abs} is the fraction of incident photons with $\lambda \leq \lambda_g$ which are absorbed; η_{ϕ} is the quantum yield for the photochemical step or steps; and η_{coll} is the fraction of product which can be collected and stored.

It is unlikely that η_{abs} will be greater than ~ 0.75 for most absorbers, and η_{ϕ} and η_{coll} are unlikely to be greater than 0.9 each. Thus, if we take all of the factors together with the maximum value of $\eta_E \eta_{\text{chem}} = 0.21$ from Fig. 3, then we find that the net yield of product in a photochemical energy storage reaction is unlikely to be greater than 12 to 13 percent. This figure should not be discouraging because photosynthesis, which must be considered a very useful process, has a net efficiency of ~ 6 percent under ideal conditions and 1 to 3 percent under actual field conditions (*12*).

A potentially more serious problem than that of low efficiency is the requirement that the photochemical absorber operate without any significant side reactions. For example, if the quantum yield for the side reactions were 1 percent, then after only 100 cycles the concentration of the absorber would have decreased to ~ 37 percent of its original concentration. In photosynthesis, each chlorophyll molecule processes at least 10^5 photons in its lifetime in a leaf. This means that the quantum yield for reactions leading to the degradation of chlorophyll must be less than 10^{-5}.

Some Possible Fuel-Generation Reactions

The thermodynamic and kinetic limitations developed above apply in general to any photochemical energy storage reaction. However, at this point, I shall consider only fuel-generation reactions that have the potential to satisfy most of the practical requirements listed at the beginning of this article. One of the important requirements is that the reactants be cheap and readily available. Naturally, constituents of the atmosphere and liquid water fill this requirement admirably. Table 1 lists most of the endergonic fuel-generation reactions that use nitrogen, carbon dioxide, and water as reactants, including the photosynthesis reaction. It is significant that the potential difference $\Delta \mathscr{E}^{\circ}$, which is the potential stored per electron transferred, is between 1.06 and 1.48 volts for all of these reactions. Thus the energy requirements for the photochemistry are about the same for each of these reactions if we assume that the reactions must be sensitized by one-electron photochemical charge transfer reactions.

The quantity $\lambda_{\max}$ in the last column of Table 1 is the threshold wavelength for the photochemical reaction calculated from

$$\lambda_{\max} = \frac{n N_0 h c \eta_{\text{chem}}}{\Delta G} \tag{19}$$

where n is the number of photons that must be absorbed to carry out the overall reaction and ΔG is the free energy change in the overall reaction. In computing $\lambda_{\max}$, I have assumed that only one electron can be transferred in each photochemical step and hence n is the same as the number of electrons transferred (column 4 in Table 1). Also, if we accept that ~ 0.8 eV must be lost in each photochemical step, then η_{chem} will be given by

$$\eta_{\text{chem}} = \frac{\Delta G}{\Delta G + 0.8\, n e N_0} \tag{20}$$

We immediately see that the last reaction in Table 1, the photosynthesis reaction, is in trouble because $\lambda_{\max}$ is known to be 700 nm. The implication is that the photosynthesis reaction cannot be operated at 700 nm with one photochemical system (that is, one electron transferred per photon absorbed) (*12*). Indeed, in order to be able to use the longer-wavelength photons, photosynthesis has used two photosystems operating in series so that eight photons are used to drive the reaction instead of four. Now $\lambda_{\max}$ is 872 nm (column 7 of Table 1), which leaves plenty of scope for an absorber at 700 nm.

Although λ_{max} in column 6 of Table 1 represents the maximum threshold for the photochemistry where only one photosystem is employed, the true λ_{max} is almost certain to be considerably less than the values in Table 1 because of subsequent secondary reactions which must be exergonic and hence will lose more energy. For example, in photosynthesis $\eta_{chem} = 0.35$ (*12*). If we calculate λ_{max} from Eq. 19 using this value for η_{chem}, then the λ_{max} values for all of the reactions in Table 1 become less than 425 nm (for reactions using one photosystem) and most are well into the ultraviolet. Thus we must conclude that, if we wish to have an efficient energy storage reaction which will utilize the abundant photons in the visible region of the solar spectrum, it is likely that more success will be achieved if attention is given to photochemical processes employing two coupled reactions so that two photons are used for every electron transferred in the ultimate reaction (*4*). Values of λ_{max} for two photosystems are given in column 7 of Table 1.

The Water Decomposition Reaction

Of all the photochemical energy storage reactions proposed, the production of hydrogen and oxygen from water is certainly the most attractive:

$$H_2O \rightarrow H_2 + 1/2\ O_2$$

Hydrogen is an almost ideal fuel, and the starting material is certainly cheap.

Water is transparent to solar radiation in the visible and ultraviolet and does not begin to absorb until below 200 nm. Thus the direct photolysis of water with solar radiation is not possible and hence the reaction must be sensitized by oxidation-reduction catalysts in cyclic reactions. Several investigators have considered the general problem of the photolytic decomposition of water (*1-3*, *13*). Recently, Balzani *et al.* (*2*) have considered various possible cycles involving transition metal complexes as catalysts; they classify them into four categories depending on the type of intermediates formed. A modification of their figure 1 is shown in Fig. 6 in which the threshold wavelengths have been calculated with Eqs. 19 and 20, that is, assuming that at least 0.8 eV must be lost in each photochemical step, and a fifth cycle has been added in which two photons are used, one in each of two photochemical reactions which each have the same λ_{max}, to transfer each electron.

Several systems corresponding to cycles C1 and C2 have been described (*14*). Recently, a promising C3 cycle was reported by Mann *et al.* (*15*). However, as is evident from Fig. 6, cycles C1, C2, and C3 are restricted to the ultraviolet. Only cycles C4 ($\lambda_{max} = 611$ nm) and C5 ($\lambda_{max} = 877$ nm) have threshold wavelengths in the visible and near-infrared region. A very interesting C4 cycle involving water splitting at 400 to 500 nm on a monolayer of a surface-active ruthenium complex was described by Sprintschnik *et al.* (*16*); however, there has been considerable difficulty in repeating this experiment (*17*).

Cycle C5, which involves two photochemical systems, should have a somewhat better efficiency than cycle C4 because of a better match to the solar spectrum (see curves C in Fig. 3) especially if additional energy losses are necessary to drive secondary reactions. For example, if the equivalent of 1.0 eV must be lost in each photochemical step, then the efficiency η_C would be 13 percent for cycle C4 ($\lambda_{max} = 557$ nm) and 16 percent for cycle C5 ($\lambda_{max} = 768$ nm). Of course, if λ_{max} for one photosystem is chosen to be to the blue of that of the second photosystem, then an even greater efficiency gain can be obtained, as was noted earlier. Almgren (*8*) has also pointed out the desirability of a C5 cycle.

I have proposed a two-photosystem scheme corresponding to cycle C5 (*4*). A modified version of that scheme is shown in Fig. 7. The right-hand compartment contains an aqueous solution of a dye D which is a strong donor (reducing agent) in the excited state D*; D* transfers an electron to a charge-storage catalyst M. The cycle is repeated again with another photon so that M ultimately accepts two electrons. In the M^{2-} state the catalyst is capable of reducing two H^+ ions to form a molecule of H_2 without the necessity of forming H atoms.

The left-hand compartment contains an aqueous solution of a dye A which is a strong acceptor (oxidizing agent) in the excited state A*; A* accepts electrons from the charge-storage catalyst N one at a time until four electrons have been removed. In the state N^{4+} the catalyst is capable of oxidizing two water molecules to produce one molecule of O_2.

For every four electrons cycled in the system, four H^+ ions are produced on the left and consumed on the right. Thus there must be a membrane connecting the two compartments which is permeable to protons. It must also allow transfer of electrons from A^- to D^+ so as to return the dyes to their photoactive states.

In the thylakoid membrane of photosynthesis, a pool of plastoquinone molecules serves the function of transferring electrons and protons across the membrane. Perhaps a similar ploy could be

Table 1. Some endergonic fuel-generation reactions starting with N_2, CO_2, and H_2O.

Reaction	$\Delta H°$ (kJ/ mole)*	$\Delta G°$ (kj/ mole)	n†	$\Delta\mathcal{E}°$ (V)	λ_{max} (nm)‡ One photo-system	λ_{max} (nm)‡ Two photo-systems
$H_2O(\ell) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$	286	237	2	1.23	611	877
$CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2(g)$	283	257	2	1.33	581	845
$CO_2(g) + H_2O(\ell) \rightarrow HCOOH(\ell) + \frac{1}{2} O_2(g)$	270	286	2	1.48	543	804
$CO_2(g) + H_2O(\ell) \rightarrow HCHO(g) + O_2(g)$	563	522	4	1.35	576	840
$CO_2(g) + 2\ H_2O(\ell) \rightarrow CH_3OH(\ell) + \frac{3}{2} O_2(g)$	727	703	6	1.21	616	881
$CO_2(g) + 2\ H_2O(\ell) \rightarrow CH_4(g) + 2\ O_2(g)$	890	818	8	1.06	667	932
$N_2(g) + 3\ H_2O(\ell) \rightarrow 2\ NH_3(g) + \frac{3}{2} O_2(g)$	765	678	6	1.17	629	895
$CO_2(g) + H_2O(\ell) \rightarrow \frac{1}{6} C_6H_{12}O_6(s) + O_2(g)$	467	480	4	1.24	607	872

*$\Delta H°$ and $\Delta G°$ are the standard enthalpy and standard Gibbs free energy, respectively. All thermodynamic data have been obtained from (*29*) except data for $C_6H_{12}O_6(s)$, which were obtained from (*30*). †n is the number of electrons which should be transferred in an electrochemical reaction for the reaction as written. ‡λ_{max} is calculated from Eq. 19, assuming that η_{chem} is given by Eq. 20 and n doubled for two photosystems.

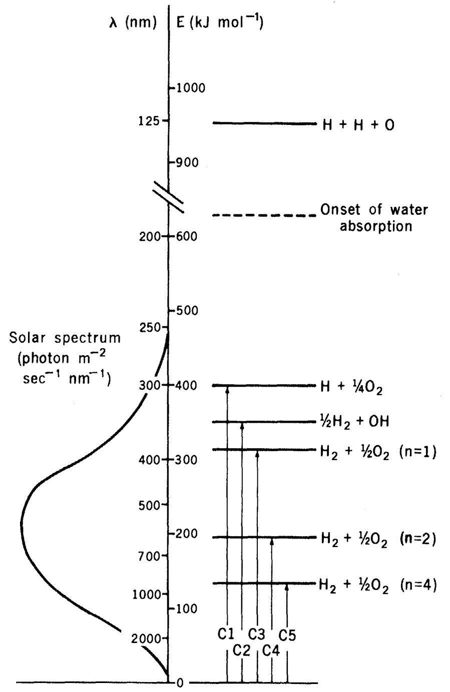

Fig. 6. Energies of the various possible intermediate states relative to the energy of the liquid water compared with the solar spectrum (AM 0). Threshold wavelength and energies have been calculated with the use of Eqs. 19 and 20, assuming a loss of 0.8 eV in each photochemical step. In cycles C3, C4, and C5, *n* refers to the number of photons that must be absorbed to drive the reaction as written [this diagram is a modification of figure 1 in (*2*)].

used in an artificial system with a quinone-impregnated membrane.

An essential feature of the scheme in Fig. 7 is the need for charge-storage catalysts. Hydrogenase, which catalyzes the reduction of H^+ ions to H_2 (*18*), is an example of an electron charge-storage catalyst, whereas in photosynthesis a manganese-containing enzyme is thought to perform the function of storing four positive charges to enable O_2 to be produced directly from water. Calvin (*19*) has proposed a binuclear manganese complex as an N-type catalyst, and Dzhabiev *et al.* (*20*) have implicated dimeric complexes in the kinetics of oxidation of water by Mn(IV). If we can understand the structure and the mechanistic details of the natural enzymes, then perhaps it may be possible to synthesize artificial catalysts.

As yet, no one has assembled a complete working system according to the scheme in Fig. 7. However, in my research group, we have been concentrating on developing partial reactions in order to study each photosystem in turn. We have found that a solution containing EDTA (ethylenediaminetetraacetic acid), the dye proflavine, methyl viologen, and the enzyme hydrogenase, when illuminated with blue light, does evolve H_2 with a yield of ~ 0.2 percent (*21*). In this case EDTA is being oxidized instead of water; however, the reaction does demonstrate the feasibility of the reduction half reaction. Recently, a similar photochemical reducing system has been described by Lehn and Sauvage (*22*) in which H_2 is produced from triethanolamine based on the use of ruthenium and rhodium complexes and a colloidal platinum catalyst. We are also studying the cation dye *N*-methylphenazinium, which is a fairly good photochemical oxidizing agent (*23*); however, as yet, we have not found a suitable O_2-evolving charge-storage catalyst.

The limitations and considerations that have been developed here for the photochemical decomposition of water by solar energy apply also to the photoelectrolysis of water, which has attracted much attention (*3, 24*) since the original experiments by Fujishima and Honda (*25*). The analog to a single photochemical system (for example, cycle C4) is a cell in which only one electrode is illuminated. Indeed, the only cells that work, unassisted by an external potential, are those that require ultraviolet illumination. The electrochemical analog to two photochemical systems is a cell in which both electrodes participate in the photochemistry. The requirement for two photosensitive electrodes was pointed out by Manassen *et al.* (*26*). Nozik (*27*) has proposed such a cell and has had some limited success. Recently, Fong *et al.* (*28*) described a photogalvanic water-splitting system in which chlorophyll, a dihydrate, is used with a λ_{max} of 740 nm. This system contains only one photosensitive electrode and thus corresponds to a C4 cycle. This system requires further investigation as the reported λ_{max} probably exceeds that determined by the second law of thermodynamics, unless the process at the electrode is biphotonic.

Conclusions

Within the kinetic and thermodynamic limitations on the conversion of light energy to chemical energy, I have shown that a reasonable goal for solar energy storage efficiency in a fuel-generation reaction would be ~ 10 to 13 percent but probably not much higher than 13 percent. A consideration of various possible fuel-generation reactions indicates that the most efficient energy storage process would be one in which two photosystems operate in series in one-electron oxidation-reduction reactions much as photosynthesis functions, although the simpler single photosystem may operate with lower efficiency at shorter wavelengths. Finally, the very promising reaction of decomposing water to H_2 and O_2 is analyzed and a detailed two photosystem scheme is presented by which the reaction might be sensitized with the best energy storage efficiency.

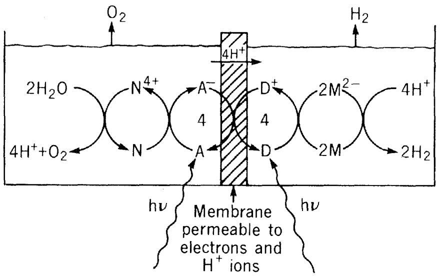

Fig. 7. A scheme for the sensitized photolysis of water based on the use of two photochemical reactions coupled in series. Symbols are explained in the text.

Clearly, much more basic and mission-oriented research will be necessary to establish if a workable fuel-generation system can be developed. Such a process would have a decided advantage over the solar generation of electricity in that conversion and storage are carried out in the same process. However, unless comparable efficiency and economics can be maintained, it will be more advantageous to use solar electricity to electrolyze water to generate the H_2 fuel. No one can say at this point which system will be more economical, and indeed we may find that each has its own special area of application. The challenge now is to chemists, physicists, and biologists to develop systems that at least work in the laboratory before economic evaluations can be made. Hopefully, this article will help to provide some guidelines and objectives for the research that must be done.

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31. This article was written while I was on leave as a visiting professor in the Chemistry Institute, Aarhus University, Aarhus, Denmark. I am very grateful to Dr. J. A. Pedersen, Prof. L. T. Muus, and their colleagues for inviting me and for providing the environment and opportunity for me to develop these ideas. I am also grateful to Prof. R. T. Ross for letting me see a preprint of his paper and to Prof. A. Yu. Borisov and M. S. Chan for their helpful comments. Publication 182 of the Photochemistry Unit, Chemistry Department, University of Western Ontario.

Gene Dosage Compensation and the Evolution of Sex Chromosomes

In diploid organisms compensation evolved gradually and led to heteromorphic sex chromosomes.

John C. Lucchesi

Summary. Dosage compensation is a mechanism by means of which the activity of X-linked or Z-linked genes is made equal in the two sexes of organisms with an XX compared to XY or ZZ compared to ZW basis of sex determination. In mammals, compensation is achieved by the inactivation of one X chromosome in somatic cells of females. In *Drosophila*, compensation does not involve inactivation. The two X chromosomes in females as well as the single X in males are regulated, and individual genes are thought to respond independently to the regulatory mechanism. It is proposed that in both groups of organisms the evolution of heteromorphic sex chromosomes was gradual and occurred as the direct result of the evolution of dosage compensation rather than the reverse.

In diploid, sexually reproducing organisms, the genetic information responsible for initiating the various manifestations of sexual differentiation is often restricted to one pair of homologous chromosomes, that is, the sex chromosomes. In many instances, evolution has led to a visible structural modification of one of these homologs while the other remained unchanged. The sex that carries the heteromorphic pair of chromosomes (XY or ZW) is termed heterogametic; the opposite sex, with two unchanged homomorphic chromosomes (XX or ZZ) is said to be homogametic.

Inherent to such a system for sex determination is an inequality in the dosage of genes present on the X or Z chromosomes, in males and females. Yet, many of these genes mediate basic functions, not related to sex differentiation. The phenotypic product of such genes is usually found to be equivalent in the two sexes, indicating that a compensatory mechanism is operative, presumably for the purpose of preventing differential selection between the sexes. This manifestation, termed "dosage compensation" by H. J. Muller *et al.* (*1*), has been studied in the fruit fly *Drosophila* and in mammals. In the mammals, compensation is achieved by the inactivation of one X chromosome in somatic cells of females. The molecular basis for this phenomenon is not known, nor are the circumstances of its appearance in the class Mammalia understood, although the evolution of compensation in the group has been the subject of speculation (*2*). In *Drosophila*, compensation does not involve chromosome inactivation. Both X chromosomes in females as well as the single X in males appear to be regulated and individual genes are thought to respond independently to the regulatory mechanism. Different species within this genus can be arranged in a series that may represent a recapitulation of actual evolutionary steps in the history of the regulatory phenomenon of dosage compensation.

The main purpose of this article is to develop the thesis that the evolution of heteromorphic sex chromosomes is the direct consequence of the evolution of dosage compensation, and not the reverse. In a primitive diploid organism with a simple, two-allele mating-type system of sex determination, dosage compensation was probable; its occurrence led to sex chromosome heteromorphism. The evolution of these two phenomena was gradual, beginning at

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