

## Photosynthesis as a Model for Photochemical Hydrogen Generation

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Introduction

Using solar radiation as an energy source has been considered for years, and a large number of attempts have been made to harness this seemingly "free" and clean energy directly. Most of the successful techniques rely on the heating effect of long wavelengths or on direct photovoltaic production of an electric current. Attempts at conversion of solar radiation to a chemically stored form of energy have been largely unsuccessful for one or a number of the following reasons: 1) the energy of a single photon of most of the light which reaches the earth's surface is insufficient to bring about a reasonably endothermic reaction; 2) the stored reaction products tend to recombine too readily before they should; 3) the reaction products do not combine readily enough at the desired time; 4) the reactants or reaction products are highly corrosive, toxic, expensive or otherwise difficult to work with; 5) since only a weakly endothermic photochemical reaction can be brought about, a large volume of reaction products must be stored for use during dark periods.

We have recently begun a feasibility study on a closed-cycle photochemical process for splitting water into hydrogen and oxygen. The novelty of the proposed method lies in the fact that the energy of two photon captures is added together in the cycle just as plants add photon energies during photosynthesis. In this way, a highly endothermic reaction, such as the photolysis of water, can be brought about by photons of relatively low energy and the five problems just mentioned can be largely eliminated. Hydrogen is an especially interesting reaction product, as many recent articles have pointed out, because it can be burned to produce heat, used in a fuel cell to produce electricity directly, or used as a chemical feedstock for coal liquefaction, etc.

Energetics of Photolysis and the Solar Spectrum

At 25°C, the free energy change for the conversion of liquid water to oxygen and hydrogen is 56.7 kcal/mole (1.23 electron volts). However, from the relationship  $E = hc/\lambda$ , one can calculate that only photons of a wavelength less than about 504 nm will have sufficient energy to do this and only about 15% of the incident solar energy at the earth's surface satisfies this criterion. (See Figure 1). The differential curve, which shows absorption bands for H<sub>2</sub>O, O<sub>2</sub>, etc., is taken from Levine *et al.* (1). An integrated curve also is shown. Even a 100% efficient conversion process would fail to be of much interest. If two equally energetic photons could funnel their energies into one reaction, though, the wavelength limit would be doubled and about 64% of the incident radiation could be utilized. A three-photon process in which the energy requirement is equally divided would result in a wavelength limit of 1512 nm, and about 84% of the incident radiation would be suitable.

The efficiency of such conversion processes as well as the fraction of the spectrum which can be utilized must, of course, also be

considered. To do this we can construct from Figure 1 a second plot (Figure 2) which decomposes the energy flux as a function of wavelength into photon flux vs. wavelength relationships, both differential and integral. We will next assume that the amount of energy which can be captured from any given photon is no more than that of the least energetic photon in whatever photon population we are considering. Such an assumption is quite realistic and parallels what we would expect to obtain in a photochemical excitation process. (The manufacturers of solar cells face a similar dilemma. To capture a larger fraction of the solar spectrum, they must decrease the band gap and thus the output voltage of the cell.) By multiplying the integral photon flux at a given wavelength by this minimum photon energy and comparing with integral energies found from Fig. 1, we can find a conversion efficiency and also an efficiency based on the total solar energy flux. For the single photon process, these efficiencies are 90% of the photons with sufficient energy, but only about 10% relative to the whole spectrum. For a two-photon process the efficiencies are 67% for the population (up to 1008 nm) and 37% for the entire spectrum. For three photons, the population efficiency (for wavelengths to 1512 nm) has dropped to 52% because so little energy is extracted from each photon, that the spectrum efficiency increases only to 38%. As an alternate to drawing each of the two or three photons from the same population, we can divide the total population into two (or more) sub-populations, a short wavelength high energy band and a long wavelength low energy band. Since we have already found that two-photon processes can use a reasonably large fraction of the spectrum, we will henceforth limit ourselves to such schemes. We also will assume that the low wavelength limit is set low enough to capture all of the high energy photons. The efficiency of a two-photon process depends on two factors: the upper wavelength cutoff point for the entire population,  $\lambda_u$ , and the wavelength,  $\lambda_c$ , at which the change from one sub-population to another takes place. The overall efficiency can be limited by too few photons in the high energy band, too few in the low energy band, or insufficient photon energy in the low energy band to make up a total of 56.7 kcal/mole. Using the data in Figures 1 and 2, the influence of  $\lambda_u$  and  $\lambda_c$  on efficiency has been calculated and is shown in Figure 3. Efficiency is a rather strong function of  $\lambda_c$  which determines the number of photons in each band. For wavelengths below 1008 nm, the peak efficiency corresponds exactly to the efficiency obtained by drawing photons from the same population because each photon has at least half of the required energy. However, it is now possible to use photons beyond 1008 nm by dividing the energy unequally. An interesting result which emerges is that a new upper wavelength limit of 1280 nm exists. Beyond this point the photon energies are insufficient even though the total number of photons is increased. At this wavelength and the optimum  $\lambda_c$  of 830 nm the efficiency is 59% of the whole spectrum and 75% of the photon population absorbed, a considerable improvement over the two-photon efficiencies obtained from a single population division. In closing this section we should point out that we have completely neglected fluorescence, competing reactions, etc. which produce non-unitary quantum yields. Actual efficiencies may be considerably lower than those which we have given here.

### The Photosynthetic Cycle

Having decided that a two-photon process can efficiently capture a significant fraction of the solar radiation, particularly if wavelengths up to 1280 nm can be used and different populations are chosen

for each of the two photons, we now consider how to couple their energy. The cycle is very similar to that involved in photosynthesis, so a brief description of nature's scheme as it is presently understood, will be given first (see Figure 4) (2, 3, 4).

Chlorophyll a 670 is a pigment which when photochemically excited forms a strong oxidant (chl a<sup>+670</sup>) and a weak reductant (reduced plastoquinone). The strong oxidant regenerates the original chl a 670 by an unknown series of reactions (collectively called the Hill Reaction) which ultimately extract an electron from water in the presence of Mn<sup>++</sup> and Cl<sup>-</sup>, liberating oxygen gas and hydrogen ions. The plastoquinone regenerates itself by contributing its electron to a chain of cytochrome compounds. As the electron falls toward a more oxidized state, part of its energy is trapped by converting ADP (adenosine diphosphate) to ATP (adenosine triphosphate) an energy source molecule used in cellular reactions. The electron eventually winds up in a compound called plastocyanin. This entire scheme of photon trapping and electron transport reactions is referred to a photosystem II.

The second series of reactions is called photosystem I. A pigment P700 is excited by the second photon, contributing its electron to an unknown compound X and thereby creating a very strong reductant. The weak oxidant, P700<sup>+</sup> returns to its original state by extracting the electron from plastocyanin. The compound X contributes its excess electron to a slightly less strong reductant, ferredoxin. The reducing energy of ferredoxin is used to create a second type of energy storage and transport molecule, NADPH, from NADP. This compound then supplies the energy to create carbohydrates from carbon dioxide and carry out other endothermic cellular reactions.

#### The Proposed Photolytic Cycle

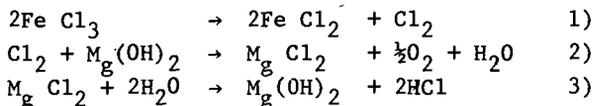
The cycle shown in Figure 5 is quite similar in principle to photosynthesis. Specific dyes are shown, but these are for convenience only and their choice was dictated primarily by what has already been described in the literature. Corresponding to photosystem II is a scheme based on the dye methylene blue. Excited by a photon, it extracts an electron from Fe<sup>++</sup> forming the colorless leucomethylene blue and Fe<sup>+++</sup>. (Actually the reaction occurs in two steps and 2 electrons are transported.) This reaction is well documented in the literature (5). We then postulate that a carrier molecule, such as one or more cytochromes, would extract the electron and carry it to a second system containing a dye such as acridine.

Upon photon excitation, the acridine is converted to an acridan. Unlike the methylene blue system, there is little or no tendency for the reaction to spontaneously reverse itself. Leucomethylene blue plus Fe<sup>+++</sup> tend to react and regenerate the ferrous ion plus original dye. Although to our knowledge cytochromes have not been tried as electron donors for acridine, a wide variety of compounds including allylthiourea, isopropyl alcohol, ethanol, toluene, ethylene diamine tetraacetic acid, and ascorbate are effective (6, 7), so the carrier and donor molecules probably will not be too critical.

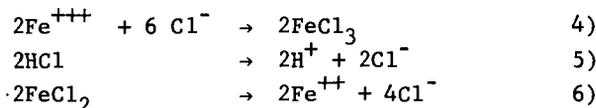
The reduced acridan molecule has a redox potential more negative than that of the hydrogen electrode. It is therefore thermodynamically capable of producing hydrogen gas given a source of protons. We postulate that it will be quite easy to use the energy of the reduced acridan to reduce one of the viologens (methyl viologen,

benzyl viologen, etc.) which is slightly less negative in redox potential than the acridan. It is known that reduced viologen molecules plus protons will regenerate the oxidized viologen, liberating hydrogen gas, in the presence of the enzyme hydrogenase (8).

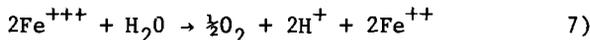
The scheme as shown is incomplete because the electron has been obtained by the conversion of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$  and the proton source has not been shown. Obviously the Hill Reaction would be the ideal answer to this problem, but since it is unknown, we will borrow a few reactions from a proposed thermochemical hydrogen cycle to illustrate how the problem could be handled with known reactions (9):



The temperatures at which these reactions proceed are 300°C, 50 to 90°C, and 350°C respectively. Now we add three simple reactions representing crystallization and dissolution of a gas and solid:



The net result of all six reactions is therefore



Our cycle is therefore closed, the ferric ion returned to ferrous ion, oxygen liberated, and the hydrogen ions needed for hydrogen production are supplied. Such an additional set of reactions could be supplied with low grade heat from photons not used in the primary photochemical reactions.

An important consideration in successfully carrying out all of the foregoing reactions is obviously separation of the various steps. Ferric ion, a strong oxidant, certainly would react very vigorously and rapidly with the acridan or viologen, strong reductants. Fortunately, coupling the dyes and even the hydrogenase enzyme to a solid surface presents little difficulty, so the circulation of fluids over beds of solid material can be carried out readily. This is one simple expedient to separate the reactants, but of course there are others too.

In summary, an examination of the mechanisms involved in photosynthesis, of previous work on photosensitive synthetic dyes, and of some pertinent theory suggest that it should be possible to split water into hydrogen and oxygen with moderate efficiency using a significant fraction of the photons in sunlight. Considerable experimental work is needed to verify the possibility of coupling certain steps in the suggested sequence and to determine the ease with which individual reactions could be segregated to prevent undesirable energy "short-circuiting" reactions.

Acknowledgment

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References

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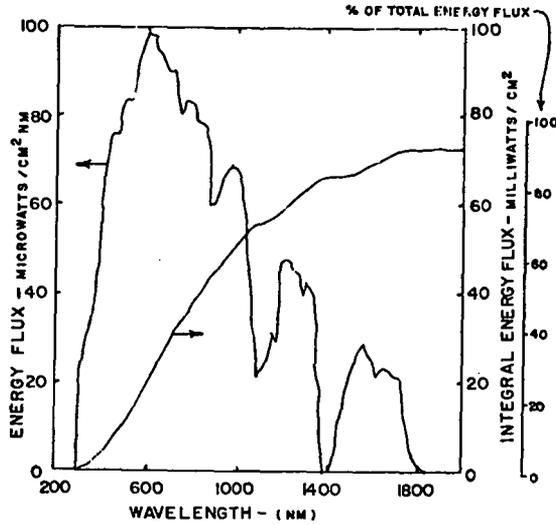


Figure 1. Solar Energy Flux at the Earth's surface (1) between 200 and 2000 nm and the integrated flux curve. About 10 percent of the total radiation has a wavelength greater than 2000 nm and is not shown.

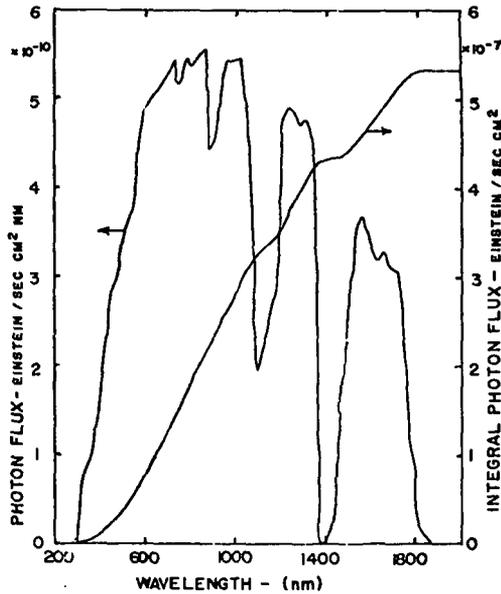


Figure 2. Photon Flux at the Earth's surface, differential and integral. This data was derived from Fig.1 using  $E = h\nu$ .

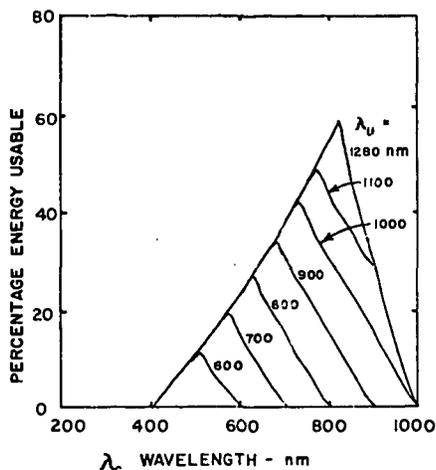


Figure 3. Percentage of the total Solar Flux which can be used in a two-photon process in which each photon is drawn from a different population. The upper cutoff wavelength ( $\lambda_u$ ) is a parameter and the wavelength at which the change ( $\lambda_c$ ) is the independent variable.

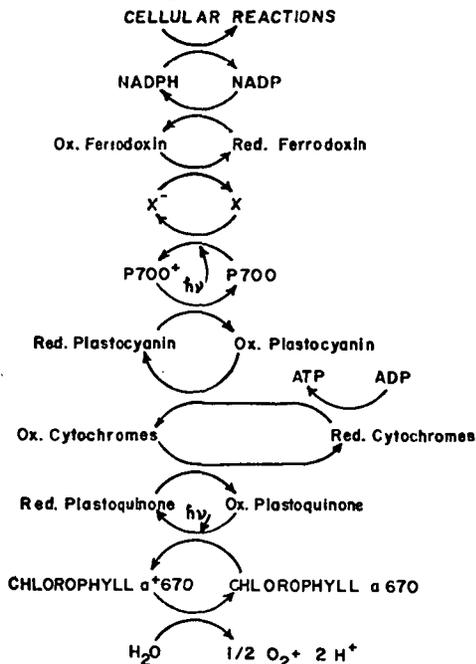


Figure 4. The coupled reactions of photosynthesis as presently understood.

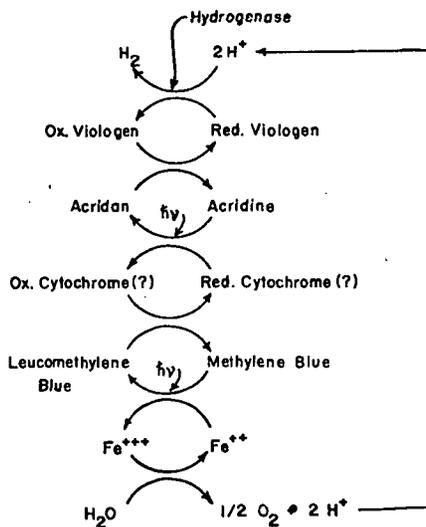


Figure 5.

The proposed photochemical cycle to split water. The ferric to ferrous conversion with attendant release of oxygen is discussed in the text.