ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 102 (1996) 3–6

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Introduction

Photochemistry under the sun XVIIth International Conference on Photochemistry. Imperial College Meeting

George Porter

In photochemistry, one source of photons dominates all others in practical importance: the sun. However, apart from agriculture, solar photochemistry is known to industry more for its destructive than its synthetic power. The most outstanding photochemical problems in organic materials, natural or synthetic, are the fading of pigments, the yellowing of fibres and the phototendering of all organic materials in sunlight. In the atmosphere, all the major problems, e.g. photochemical smog and the depletion of stratospheric ozone, are photochemical in origin and the photomedical effects of sunshine, such as skin cancer, spoil what pleasure we used to obtain from a healthy-looking suntan.

All this would be a disappointment to the early photochemists who had great hopes. I will quote three of them.

First, Michael Faraday. In his only book, *Chemical Manipulation*, he tells us how to design a laboratory as follows: "The solar rays have been found to be highly influential in causing chemical change: they effect combinations and decompositions in a manner unobtainable by any other agent, and are now frequently resorted to, not merely in the preparation of peculiar substances, as phosgene gas, chloride of carbon etc., but also in the processes of analysis. It would be well, therefore, in the construction of a laboratory to provide what is possible for the direct admission of solar light, so that chemists would more frequently try the chemical powers of this peculiar agent, at present but little known."

Second, Giacomo Ciamician, the pioneer of organic photochemistry and known particularly for his work on the photoenolization of benzophenone in isopropanol solutions, wrote in 1812: "On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry."

Third, more cynical, but more realistic, was Jonathan Swift, recording Gulliver's visit to the Lagado Academy (probably modelled on The Royal Society!). "I met a man who had been eight years upon a project for extracting sunbeams out of cucumbers, which were to be put into vials hermetically sealed, and let out to warm the air in inclement summers. He told me, says Gulliver, 'he did not doubt in eight years more, he should be able to supply the Governor's gardens with sunshine at a reasonable rate'; but he complained that his stock was low and entreated me to give him something as an encouragement to ingenuity, especially since this had been a very dear season for cucumbers."

Like all of us today, he had funding problems!

However, Swift's King of Brobddingnag gave it as his opinion that "he who made two ears of corn or two blades of grass grow where only one grew before would deserve better of mankind and do a more essential service for the country than a whole race of politicians put together."

Indeed, solar photochemistry is by far the most important of all chemical processes; without it there would be little chemistry of interest on earth and we would not be here to see it anyway.

Life and its evolution, which began more than 3 billion years ago, have been powered by the sun, with the green plants acting as the light harvesters for most of this time. The photosynthesis of organic materials, carried out by the higher plants, provides all our food, most of our fuel, many of our bulk materials and chemicals such as oils and pharmaceutical products.

One of the first of all technologies was agriculture, where man has manipulated nature to his own advantage for over 5000 years. It is by far the largest industry of mankind. However, the technology has hardly begun. Today, all the powers of the physical and biological sciences, including genetic engineering, are being applied to transforming the plant world, and the potential for development can hardly be exaggerated, especially when the fossilized products of past photosynthesis, such as oil, begin to be depleted.

The first purpose must be to improve the efficiency with which plants collect and store power from the sun. Let us look at what may be photochemically possible within the laws of thermodynamics and what we know of the primary

PII S1010-6030(96)04390-0

processes of photosynthesis. Only if natural photosynthesis can compete economically in some particular product, as it most obviously can with food and has, in the past, with fuels, will it be preferred to non-biological methods of energy production and storage, including other methods of solar energy conversion, such as photovoltaic cells or windmills.

Can photosynthesis provide the future power needs of mankind?

1. Power for the world

The quantities of solar power available on earth are far greater than mankind uses.

1.1. Comparison of world energy needs with the solar energy resource

The world consumes each year from commercial sources 8 billion tons of oil equivalent or 9.5 TW for distribution to 5.3 billion people, i.e. 1.8 kW per person. The average solar power at the earth's surface is 2 MW per hectare or 26 × 1012 kW, i.e. 5000 kW per person.

It is worth noting that the value of 1.8 kW per person is a world average and conceals huge differences between countries. The 1.2 billion people in the developed countries consume twice as much energy as the 4.1 billion people in the developing countries. The power per capita in the USA is 10 kW and in Europe is 5 kW; the average in the rest of the world is 1 kW. Some 2 billion people in the world use non-commercial fuels, principally wood and dung, as their principal source of energy.

These numbers imply, at first glance, that there is over 2000 times more solar energy at the earth's surface than the total consumed by all mankind. However, much of this energy is low grade and unavailable for conversion to work or free energy. In addition, unfortunately, photosynthesis, which is the main process used to collect this solar energy, is not very efficient. The energy stored by agricultural products, such as sugar cane or coppice wood, averaged over the year, is typically somewhat less than 1% of the energy from the sun falling on the same area of land, as shown in Table 1 [1].

The sources of inefficiency are manifold. Those imposed by thermodynamics and the limitations of using polychromatic light may be summarized as shown in Table 2. The major loss of 62% (4) due to the large wavelength spread of solar radiation and the fact that the green leaf has only one threshold, can in principle be reduced by the use of multiple traps with different thresholds, in a sandwich configuration, as has been performed with some silicon photovoltaic cells. A three-component system could bring the overall efficiency above 40%. The threshold of green plants at 700 nm is not optimal, and theoretical efficiencies of single-threshold absorbers are optimal (37%) at a threshold of 1100 nm as in silicon. Bacteriochlorophyll has a threshold at 870 nm in bacterial photosynthesis, which should give a theoretical efficiency between that of green plants and silicon, but bacteria are not capable of complete photosynthesis involving water splitting and the elimination of oxygen.

Table 2
Theoretical efficiencies of solar energy storage as work or free energy or chemical potential

Losses due to	Efficiency
1. Entropy of 6000 K radiation	0.95
2. Entropy of scattered radiation	0.82
3. Non-equilibrium at finite power	0.94
4. Polychromatic source	0.38
5. Transfer to store	0.95
Total at 700 nm threshold	0.27

The second largest loss of 18% (2) can be greatly reduced by the use of concentrators. However, although these could in theory improve the efficiency of the plant itself, they occupy an increased area and nothing is gained unless the concentrators are cheaper than the plants covering the same area, which is unlikely.

Therefore the theoretical maximum thermodynamic efficiency of converting solar energy into work using chlorophyll, with a threshold absorption at 700 nm, without multiple absorbers and concentrating mirrors, is 27%. This is far greater than that achieved in agricultural practice.

However, there are other greater losses in the photosynthetic process itself. These include inefficiencies in the chemical and biophysical processes following absorption of a photon, further to those already accounted for in calculating the theoretical maximum. One is the use of eight photons, which results from the need for a four-electron transfer for each dioxygen and two photons per transfer, one each for the two steps of photosystem 1 (PS1) and photosystem 2 (PS2). The excess energy is available for inefficiencies in energy transfer (probably negligible) and electron transfer where losses are inevitable to prevent back reactions.

$$CO_2 + H_2O = CH_2O + O_2 \quad \Delta G = 500 \text{ kJ mol}^{-1}$$

Table 1
Energy stored by agricultural products

Crop	Tons (dry) hectare per year	Kilowatt per hectare (GJ per year × 0.1)	Solar efficiency (%)
Best potato yield	22	18.7	1.25
Coppice wood	21	10	0.67
Rape seed	7	3	0.2
Oil only		1.5	0.1

Table 3
Causes of reduction in efficiency

Causes of loss	Efficiency reduction
Thermodynamic	0.27
Eight-quantum requirement	0.35
Irradiation saturation	0.3
Respiration, photoinhibition, reflection, cover, etc.	0.4
Overall efficiency	1%

Table 4
Land available worldwide

World land available	Billion hectares
Cultivated	1.4
Cultivatable	3.0
Forest	4.4
Desert	1.7
Rocky, arid	2.6
Total	13

The quantum yield (linear region) is 8–9. Light of 680 nm gives 176 kJ einstein^{-1}. The minimum quanta is 500/176 = 2.84. With eight quanta, the efficiency is reduced by 2.84/8 = 0.355; 27% reduced by 0.355 is 9.6%.

(Another way of looking at this is that water splitting by electrolysis requires a potential of 1.23 eV; a 680 nm light quantum is equivalent to 1.86 eV, so that 0.66 of its energy would be used, bringing the efficiency of 27% down to 17.8%. For four electrons and four photons this is 500/4 = 125 kJ = 1.3 eV. However, it seems that this is too close a fit, and the next step after one photon is two photons leading to half 17.8% or 8.91% efficiency.)

Even this is reduced further by the fact that these values refer to optimum conditions where all the radiation is used. This is usually not the case, because the concentration of carbon dioxide can be the limiting factor, which reduces the quantum yield and the efficiency by a further factor of 0.3 owing to radiation saturation. The linear (with solar intensity) region only operates at very low intensities, and saturation typically occurs at one-fifth of the peak solar intensity. Other factors, such as plant respiration, which is the reverse of photosynthesis, reduce the efficiency further to about 1% overall (see Table 3).

1.2. *Availability of land for world power*

The land which is available worldwide, divided broadly into its present uses is shown in Table 4.

Using only the cultivated and cultivatable land, the world yields obtainable, at the attainable efficiency of 1%, a poor efficiency of 0.2% and a possible future efficiency of 5% are shown in Table 5.

The 11% of cultivatable land needed at 1% efficiency is less than one-third of that used for food production.

These values provide an immense incentive to improve the efficiency of photosynthesis, natural or mimetic. Oils derived from rape and sunflower seed are esters of glycerol and fatty acids. To be used as fuels, e.g. in a diesel engine, it is preferable to hydrolyse them and to use only the hydrocarbon moiety; this is already performed in modest quantities.

An improvement by a factor of two to three could make the production of diesel fuels photosynthetically competitive with those derived from mineral oils, a great challenge to photochemistry and photosynthesis research.

1.3. *Recent advances in the photochemistry of photosynthesis*

The two primary processes of plant photosynthesis are light harvesting and electron and proton transfer across the membrane to bring about the oxidation of water and the reduction of carbon dioxide. The principal recent advances in understanding these processes are given below.

1. The isolation of pigment–protein complexes (light-harvesting units and reaction centres) from photosynthetic bacteria and plants and their structural determination by image-enhanced electron microscopy, X-ray crystallography and electron crystallography. Notable examples are the determination of the three-dimensional structure of the reaction centre of the purple bacterium *Rhodopseudomonas viridis* by X-ray diffraction to 2.3 Å by Michel and Deisenhofer [2] and the determination of the structure of the light-harvesting complex of PS2 of green plants by electron diffraction to 3.4 Å resolution by Kühlbrandt et al. [3].
2. The theory of energy transfer, first given in its resonance (coulombic energy) transfer form by Theodore Förster and augmented by Dexter to include exchange interactions, which is still satisfactory for most purposes. The theory of electron transfer, developed notably by Marcus and also based on the Fermi golden rule, is also in good accord with observation.
3. The measurement of the rates of these elementary processes fully time resolved down to events of a few tens of femtoseconds duration (see, for example, Durrant et al. [4]).

Table 5
World yields obtainable at different efficiencies

	Efficiency 5%	Efficiency 1%	Efficiency 0.2%
Solar power (kW per hectare)	100	20	4
Area for 10 TW (million hectares)	100	500	2500
Percentage of land available	2.2	11	55

Also of great promise is the sequencing of the amino acids of the proteins and nucleic acids of the nuclei in these complexes, and the identification of many of the genes with their functions. At a microbiological level, methods of gene transfer via recombinant DNA techniques into the nuclei of plants, which has lagged somewhat behind recombinant DNA techniques in bacteria, are now being routinely applied. Many of these techniques are now within the capabilities of third year undergraduates. These include the use of tumifaciens vectors and the later shot-gun techniques which hold the promise of a wide variety of transgenic species. One example is the introduction of genetic material from the Californian Bay laurel tree to oilseed rape. This produces lauric acid, a key material for soaps and detergents. It is currently imported from Southeast Asia where it is extracted from coconut or palm kernel oil.

It will probably be at least half a century before wood or other primitive sources of biomass can overtake the fossil fuels, dwindling and increasingly expensive as they must become. The time for the economic use of renewable oil fuels may be sooner. Changes in energy sources can occur on a huge scale in quite short times. The change from 90% wood to 90% coal took less than 100 years and that from coal to 80% oil less time still.

Research will not be undertaken commercially for financial reward, even in advanced and farsighted countries such as Japan, unless there is a reasonable probability of a payback in less than 10 years. However, factors other than economics may enter the equation, e.g. conservation, inability of some countries to pay for imports and government subsidies, such as "seed corn", to start indigenous industries.

Much of this may seem to lie some distance in the future. However, it is big business and can happen very quickly. A successful product can be cloned and can be spread rapidly over huge areas. There are no scale factors slowing development as there are in most manufacturing industries.

The photochemist, like the chemist, has hitherto used the methods of in vitro organic chemistry (following Ciamician) to synthesize the natural products made by photosynthesis, with the objective of obtaining them more cheaply and making modified structures. In the future, we shall see more attention being given to the natural products themselves, produced in greater yield and in more useful modifications within the genetically engineered plant. One of the prerequisites of this approach will be a better understanding of the primary photochemical processes which occur during plant photosynthesis.

We may now be approaching the second green revolution, when it will become possible for us to design photosynthesis, and indeed evolution itself, to make the products we desire, efficiently, economically and with the minimum need for energy or further processing.

References

[1] G. Porter, *J. Chem. Soc., Faraday Trans. 2, 79* (1983) 473.

[2] H. Michel and J. Deisenhofer, *Biochemistry, 27* (1988) 1.

[3] W. Kühlbrandt, D.N. Wang and Y. Fujiyoshi, *Nature, 367* (1994) 614.

[4] J.R. Durrant, G. Hastings, D.M. Joseph, J. Barber, G. Porter and D.R. Klug, *Proc. Natl. Acad. Sci. USA, 89* (1992) 11 632.