

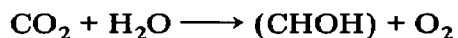
ARTIFICIAL PHOTOSYNTHESIS

ANTHONY HARRIMAN

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)

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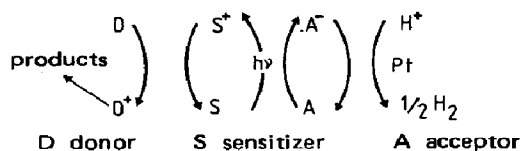
Sunlight and photochemistry have long been synonymous and it was only the advent of flash photolysis, especially laser photolysis, that persuaded photochemists to seek alternative light sources. Now, it is somewhat sad that our self-imposed energy crisis has forced us to reconsider ways to use sunlight to drive photochemical reactions. Storing sunlight as a chemical fuel, derived from readily available reagents, is a well-established idea and green plants have done so successfully for billions of years. Indeed, it is towards green plants that we must look as we attempt to construct our own solar energy storage devices. Green plant photosynthesis can be expressed as



where eight photons of red light are used to drive two separate photosystems, one resulting in the reduction of CO_2 to carbohydrate and the other oxidizing water to oxygen. Although carbohydrate is a suitable fuel for plants, it lacks the versatility and storage capacity for our purposes and it would be better to replace this half of the process with the photogeneration of hydrogen from water. This half-reaction represents the simplest natural photosynthetic process and, since primordial times, primitive bacteria have used near-IR light to reduce water in the presence of inorganic or organic wastes. Thus, if we mimic and adapt the natural photosynthetic processes there would be no energy shortage on the planet.

By the early 1970s the difficulties of photodissociating water had been well documented [1 - 3]. The only known photosystems capable of forming hydrogen or oxygen from water involved UV irradiation of metal cations [4] such as $\text{Ce}^{3+}|\text{Ce}^{4+}$. The great problem of the period was how to couple together the one photon-one electron chemistry of simple photo-induced redox reactions with the multielectronic dissociation of water. The required breakthrough came in the mid 1970s and, like all such events, a great deluge of ideas appeared together. Whilst most of us were convinced that some type of binuclear metal complex was required as photosensitizer, Shilov *et al.* [5], Lehn and Sauvage [6] and Whitten and coworkers [7] produced somewhat more appropriate ideas. Perhaps the most significant discovery of the 1970s came from Shilov's laboratory where it was found that colloidal platinum catalysts could be used to store many electrons for finite times. Thus, ultrafine dispersions of noble metal catalysts were

used to trap electrons from one-electron-reduced radicals in aqueous solution and so to couple together the photochemistry and the water reduction:



Although hydrogen formation occurred at the expense of consuming some added electron donor (*e.g.* an amine), the system gave the first example of hydrogen photoproduction with visible light. The work of Lehn and coworkers came a little time later and was somewhat similar but it had the great advantage that it could be demonstrated before a live and sceptical audience.

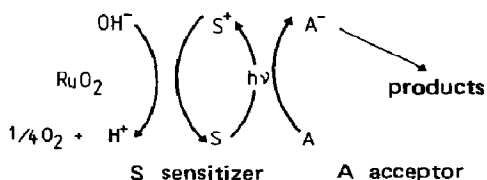
The work of Whitten and coworkers became classic, not because it turned out to be irreproducible but because it generated such intense interest world wide. The idea that monomolecular assemblies of surfactant ruthenium complexes could photodissociate water into hydrogen and oxygen caused enormous debate and their paper was perhaps the most publicized and discussed article in photochemistry in the 1970s. It initiated innumerable research programmes and, even today, it still provokes argument.

The work of Shilov and Lehn was repeated in many laboratories and, very quickly, modified and improved versions began to appear. The basic concepts of the above scheme are common to all such systems, only the names of the reagents have changed. Quantum efficiencies and longevities have improved drastically and the solar energy collection efficiency has been increased to above 50% [8]. Although all these hydrogen evolving photosystems involve destruction of a donor it is now possible to use genuine waste materials, such as H₂S or ethanol [9], and we are very close to mimicking bacterial photosynthesis.

Production of the fuel, *e.g.* hydrogen, is only part of a solar energy storage device. Although it is sufficient for primitive bacteria to survive on waste material, mankind's energy needs are somewhat greater and it is necessary that we extend these simple systems by replacing the waste donor with a replenishable reagent such as H₂O, CO₂ or nitrogen. Although far from easy, the photo-oxidation of water to oxygen is the simplest of these alternatives and much attention has been focused on this reaction. When our own work on artificial photosynthesis began, we realized that the oxidation step would be the problem since it involves a four-electron process and the product is a powerful inhibitor of photochemistry. It is commonly believed that the natural photosynthetic oxygen evolving mechanism employs a manganese complex as oxidant and we began by looking at possible manganese complexes as *in vitro* oxygen evolving catalysts. At the time, we were looking for compounds capable of undergoing a four-electron change and it seemed that only a binuclear complex could be suitable. As

it turned out, the most effective manganese compound for oxygen evolution, at least *in vitro*, is the simplest manganese compound MnO_2 .

The work on photochemical oxygen production has been a great struggle. The most significant advance was made by Kiwi and Grätzel [10] who found that noble metal oxides, *e.g.* RuO_2 , were able to catalyse the oxidation of water by strong one-electron oxidants such as tris(2,2'-bipyridyl)ruthenium(III) ($(\text{bipy})_3\text{Ru}^{3+}$). This finding was quickly confirmed by others and an oxygen evolving photosystem was constructed based on similar principles to the Shilov hydrogen evolving photosystem:



Unlike the Shilov cycle, the choice of photosensitizer is crucial for efficient oxygen evolution and only $(\text{bipy})_3\text{Ru}^{2+}$ functions well, for which we have obtained quantum efficiencies for oxygen production as high as 70%. These photosystems rely on the destruction of the electron acceptor (usually persulphate). Also, we must question the validity of using $(\text{bipy})_3\text{Ru}^{2+}$ in a solar energy storage device. Attempts to replace it with more applicable photosensitizers have resulted in failure or controversy and only very recently have we been able to use metalloporphyrins as photosensitizers in such systems [11].

Accepting the limitations of the oxygen half-reaction, we must try to couple together hydrogen and oxygen evolving photosystems and, hopefully, to remove the need for sacrificial redox agents. This has not been achieved to date, although claims to the contrary exist. Simply adding colloidal platinum and RuO_2 catalysts to a photoredox system such as $(\text{bipy})_3\text{Ru}^{2+}$ -methyl viologen does *not* result in the generation of hydrogen and/or oxygen [12]. More ingenuity is required to overcome the problems of catalyst selectivity. This is the big problem of the moment and it is rather alarming to consider that the same problem has dominated photogalvanic cells for decades and it remains unsolved today.

Much research has centred on the intricate sequence of photoinduced electron transfer processes that are involved in natural photosynthesis. Here, a metalloporphyrin drives a photoredox reaction with unit quantum efficiency and still produces highly energetic species that are spatially remote. Attempting to mimic such processes is a great challenge but real progress has been made. From the early days of Rehm and Weller [13] the subject has developed into a fine blend of synthetic chemistry and precise photophysical evaluation. Now, electron donors and acceptors are being attached to a single chromophore and modest spatial separation of the photoinduced charges can be obtained. Orientation and distance effects are being studied and real developments can be expected soon.

So, where are we now, how much progress has been achieved and what must be done in the future? We are somewhat further advanced than when the *Journal of Photochemistry* started. This is certainly true for hydrogen and oxygen generation and our understanding of electron transfer reactions has improved enormously. However, we are nowhere near constructing a practical solar energy storage device based on artificial photosynthesis and patience is still required from funding authorities. Genuine progress has been made, mostly in fundamental aspects, but much of it is hidden beneath the huge pile of literature that has accumulated. Out of the 1000 or so papers describing sacrificial hydrogen photoproduction perhaps only a dozen are worth reading twice. This torrent of publications has abated now, partly because fewer researchers are engaged in the subject and partly because the work has become difficult again. Until the next breakthrough, we can expect a fairly quiet time and, in fact, the real urgency of the mid and late 1970s has been replaced with a calm rationalization. This has allowed more thorough and involved studies to be performed and one of the real pleasures of working in the subject has been the multidisciplinary approach that facilitates many different experimental techniques.

Much remains to be done in the future. We must learn not to speculate, to be modest in our claims and, above all, to obtain reproducibility of our results. These are the most important goals of the near future. We need to return to the natural analogues; perhaps the joys of producing hydrogen and oxygen in model systems have led us to believe that we can devise our own systems without recourse to learning from nature. We will surely pay dearly for such arrogance. The biggest problems to face us at present are how to couple together two separate photosystems and how to immobilize the systems without losing the efficiency or flexibility of the homogeneous ones. These problems are severe but solvable well before the *Journal of Photochemistry* reaches Volume 50.

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