

## PURE AND APPLIED PHOTOCHEMISTRY

George Porter

The Royal Institution, 21 Albemarle Street, London W1X 4BS

The basic theory and limitations of in vitro photosynthesis are understood and seem, to the author, to hold out a promise of success in the foreseeable future considerably greater than, for example, that of nuclear fusion. This optimistic view is supported by the abundantly successful process of photosynthesis in vivo.

The special theme which has been chosen for this 26th International Congress of Pure and Applied Chemistry is "Chemistry and the Welfare of Mankind". It is generally recognised that the sciences, wisely applied, can contribute greatly to man's welfare by alleviating suffering and the miseries of hard labour. In this way applied chemistry contributes to man's material welfare. But man has spiritual needs as well and what is less widely accepted is that pure chemistry and all the fundamental sciences are not mere adjuncts of technology but have a deeper purpose. They attempt to fill one of man's greatest needs which is to understand his world and himself and his purpose. Applied chemistry has undoubtedly increased our health and our wealth. By improving his understanding, pure chemistry can perhaps contribute something to that other essential for the welfare of man ... his happiness.

The branch of chemistry which interests me particularly is photochemistry. It is a science with many attractions and, until a few years ago, these attractions were mainly scientific and philosophical. Whilst the ordinary chemist worked in the comparative gloom of his laboratory, bringing about his reactions in boiling acids and other unnatural ways, the photochemist looked to the sun. Ever since the first morning of creation, life has been not merely a chemical process but a photochemical one. Photochemical reactions created organic molecules from the constituents of the primitive atmosphere, the more sophisticated processes of photosynthesis made it possible for simple cells to become autotrophic, and these processes maintain life today. To understand them more fully would give us great satisfaction; it would perhaps make us a little happier for that reason alone, even if the knowledge in itself were to contribute nothing to our material welfare.

The fundamental knowledge of photochemistry gained in this way can however, like all knowledge, be used and the rapid advances in basic understanding of excited molecules which have taken place over the last few decades now promise an equally rapid phase of applications to new products and new processes. And, as we have come to realise that the fossil store of photosynthesised fuels will be exhausted in a few decades, the possibility of applying our knowledge of photochemistry to man's welfare has entered a new dimension of magnitude and urgency. The greatest material need of man is food and his second greatest need, in technological society of today, is energy. All of the former and most of the latter are provided for us by photochemical and photobiological reactions. The understanding of these processes and their application is the greatest of all challenges to the photochemist ... pure or applied.

In this lecture I would like, first, to review the new attitudes to photochemistry which have appeared since 1950 and the advances in theory and experiment which have accompanied them. Then, after a brief reference to some of the more important recent applications of photochemistry, I will discuss the possibility of applying what we know of photosynthesis to practical purposes.

## PHYSICS AND CHEMISTRY OF THE EXCITED STATE

The photochemists of the last century used light much as they used heat, as a means of adding energy to a chemical substance so as to bring about reaction. If they found new products they were satisfied and did not enquire too much about how it all happened. During the first half of the present century physical chemists became increasingly interested in photochemistry as a means of preparing free radicals and atoms and

elucidating the kinetics of their reactions. They had some notable successes, such as the discovery of chain reactions in the photochemical combination of hydrogen and chlorine, but their main concern was with the dark reactions of the chemically reactive but physically stable intermediates.

Over the last thirty years photochemistry has become recognised as a distinct and separate part of chemistry which deals with a distinct and separate species ... the electronically excited state. Since every molecule has several excited states but only one ground state, photochemistry is concerned with more species than the whole of conventional chemistry.

Direct study of the kinetic behaviour of the excited state and detailed investigation of its structure requires direct observation of this state by time-resolved spectroscopy, but many of its physical chemical properties may be derived very simply from conventional steady state spectroscopic measurements and much of recent progress is attributable to this marriage of spectroscopy and photochemistry. Important examples are:

#### Ionisation potential and electron affinity

These are derived from a simple thermodynamic cycle involving only the spectroscopically determined energy of the excited state above that of the ground state and a knowledge of the electron affinity and ionisation potential in the ground state. In the excited state, the ionisation potential is less than the ground state and the electron affinity is greater by an amount equal to the energy of the excited state above the ground state. This accounts for the increased ease of electron transfer and chemical reactivity usually found in the excited state.

#### Dipole moment

An estimate of the difference in dipole moment between two electronic states may be obtained from the dependence of the energy of the transition, measured spectroscopically, on the dielectric constant of the solvent and by application of Onsager's expression for the solvation energy of a dipole (1). The bathochromic shift commonly observed in polar solvents implies a higher dipole moment in the excited state, whilst the converse effect occurs in  $n-\pi$  transitions and is one of the principal criteria characterising  $n-\pi$  states.

#### Acidity constant

Protonic equilibria are often established within the lifetime of the excited state and the change in pK between excited and ground state may be derived from the spectra in acidic and basic solutions using the Förster thermodynamic cycle (2). Triplet state pK determinations are usually made by direct titration in flash photolysis experiments (3). The pK in the excited singlet may differ from the ground state by as much as 6 pK units whilst that of the triplet is usually intermediate in value.

Several new photochemical phenomena have been discovered, in the first place, from simple steady state spectroscopic observations. One of the most far reaching is the discovery of excimers (4), dimers which are stable in the electronically excited state but not in the ground state, and exciplexes which are similar species in which the association is between two different molecules. A new emission spectrum, attributable to the excimer or exciplex, appears at high concentrations and the thermodynamics of the excited state equilibria are readily derived from studies of the spectrum as a function of concentration.

Kinetic data can also be obtained from steady state spectroscopic studies provided some absolute rate, such as that of fluorescence, is known from independent measurements. Important as these steady state techniques have been, the introduction of direct time-resolved spectroscopy has now transformed experimental studies of the excited state.

#### Flash photolysis and kinetic spectroscopy

The introduction of flash photolysis, using electrical discharge lamps of a few microseconds duration made possible the direct observation not only of intermediates such as free radicals but also of the excited state itself. Only triplet states, whose lifetimes, even in fluid solvents and gases, usually exceed one microsecond, were accessible to these classical methods. The excited singlet, with lifetimes typically in the nanosecond region, became accessible first in emission, using repetitive spark methods with the later addition of single photon counting and, later, in absorption with the advent of the Q switched solid state laser. Over the last few years the use of mode-locked lasers has extended the time resolution of these methods into the picosecond region.

A wide variety of ingenious arrangements have been used but the two approaches which will probably be most useful in the picosecond region over the next few years are (a) a mode-locked solid state laser from which a single pulse is selected, and amplified if necessary, and a detection system consisting of a streak camera, image intensifier, vidicon tube and optical multichannel analyser. The advantage of this system is that a single shot is sufficient, so that the irreproducibility from one shot or one sample to another is

eliminated. It is more suitable for emission than absorption work and the high intensity necessary for single shot work is already known to cause, in certain cases, non-linear effects, which are usually an unwanted complication (5). (b) A continuous-wave mode-locked dye laser, usually pumped by an argon-ion or other laser, is used to produce some  $10^4$  pulses/s (by acoustooptical cavity dumper). The beam is split, part being used for excitation and the other part for monitoring, and the signal is averaged over many pulses. This method has several advantages; low pulse intensity, increased precision by signal averaging, tuneable wavelength and the possibility of obtaining sub-picosecond time resolution (6).

There are very few molecular processes which are too fast to be resolved by these methods and indeed the techniques are approaching the uncertainty time limit of chemistry. On the other hand, the extension of flash techniques into the picosecond region has greatly multiplied the number of fundamental primary processes which can be studied. The wide variety of these sub-nanosecond molecular events is indicated in Fig. 1.

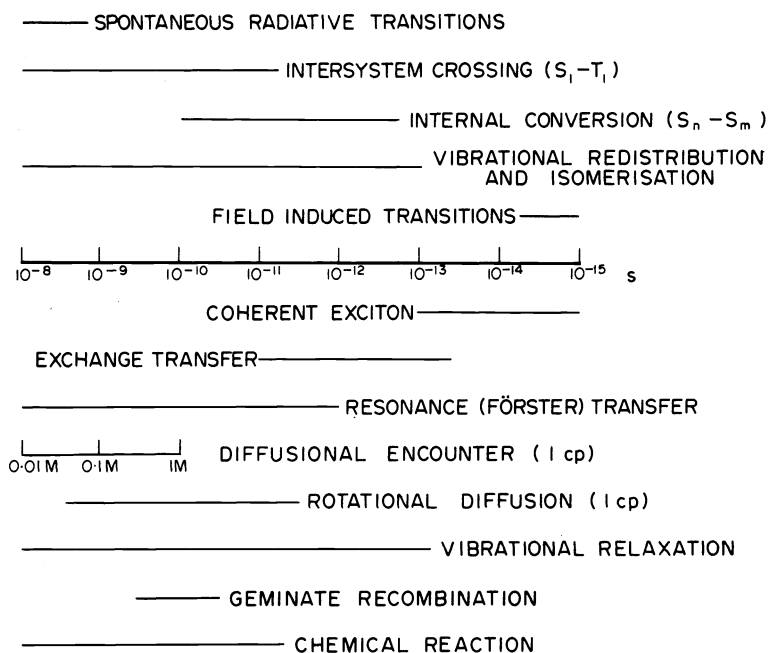


Fig. 1. Time range of molecular events in the sub-nanosecond region

#### Molecular photophysics

The main impact of these very fast techniques has so far been in studies of the rapid physical processes which immediately follow light absorption. The reasons for this are twofold; first, an understanding of the physical transitions and energy states involved must precede a proper understanding of the chemical processes and, second, physical processes usually precede chemical processes in time and indeed there are few chemical processes in the sub-nanosecond range.

All discussions of photophysics and photochemistry begin with the Jablonski diagram, a modern form of which is shown in Fig. 2. It is the chart on which the photochemist plots the course of molecular change and navigates among the islands of excited states, each with their own contours of rotational and vibrational energy levels. Picosecond experiments are throwing much light on rotational diffusion, intramolecular and intermolecular vibrational relaxation. Of even greater importance are intermolecular and intramolecular electronic energy transfers and it is in this area that there have been the most significant theoretical advances.

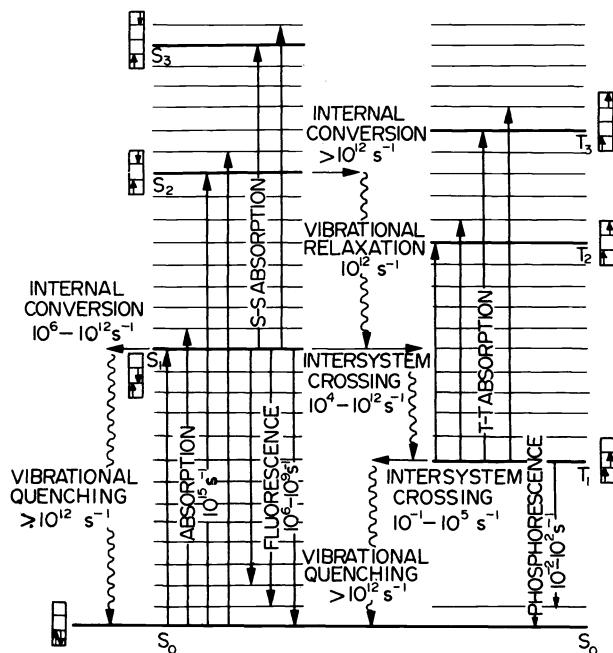


Fig. 2. Jablonski diagram showing molecular energy levels and transitions between them

Intermolecular energy transfer has been rather well understood for some years since Förster, following Perrin, described it in terms of a resonance between the transition dipole of donor and acceptor molecules and a transfer of energy similar to that between two coupled pendulums (7). Förster's theory has been fully confirmed experimentally and has been extended to stronger coupling involving multipoles or exchange energies.

Even more fundamental to photochemistry is the radiationless intramolecular crossing from one electronic "stationary" level to another, known as internal conversion (no spin change) or intersystem crossing (spin change). The final result of such a crossing is that the molecule appears in a lower energy level and there was some early misunderstanding as to when the energy was lost. I recall a discussion on this problem which took place in Hakone in 1962, in which the view was strongly advanced that crossing could only occur in the presence of collisional perturbation. It is now understood that the rate determining process, at least in large molecules, is intramolecular transfer between isoenergetic levels and this occurs even in the isolated molecule in the gas phase. The isoenergetic process is no longer a mystery and is quite analogous to an intermolecular energy transfer with the two coupled oscillators now within the same molecule. The Fermi "golden rule" provides a starting point for the theory of both intermolecular and intramolecular processes (8).

#### Chemistry of the excited state

This is a subject as vast and at least as varied as chemistry itself and there are, as yet, few unifying generalisations. One, which introduces quite new ideas, is the principle of conservation of orbital symmetry, proposed by Woodward and Hoffmann (9) and applicable to concerted reactions. In such a reaction, the change must occur so that the orbital symmetry is conserved throughout the change and, although applicable quite generally to thermal reactions as well, it is of particular interest in photochemistry since the orbital symmetry of ground and upper electronic states is generally different and, therefore, reactions in the ground state are predicted, and found, to lead to different products from those of reactions which occur in the excited state.

The fact that the excited state is a new species, with its own structure and chemistry is nowhere better illustrated than in the photochemistry of compounds which have two excited electronic states, close together in energy but with different properties. Such cases are quite common, particularly in molecules which have an  $n-\pi$  and a low lying  $\pi-\pi$  state. To give a specific example, *p* amino benzophenone has  $n-\pi$  and  $\pi-\pi$  levels of similar energy and the order of these can be reversed by changing the solvent owing to the different sense of the dipole moment change in the two states. Like most carbonyl compounds, the excited triplet state abstracts hydrogen from most solvents to form a ketyl radical but, whilst *p*-aminobenzophenone abstracts from paraffin hydrocarbons it is almost inert in

alcohols. The explanation of this remarkable observation is that the  $n-\pi$  state abstracts hydrogen because the electronic transition has made the oxygen of the carbonyl group more electrophilic whilst this is not the case in the  $\pi-\pi$  state. The  $n-\pi$  state is the lower of the two in paraffins whilst the  $\pi-\pi$  state is lower in alcohols (10). This is an excellent illustration of how the electron distribution, rather than the energy, determines the chemistry of excited states.

#### APPLIED PHOTOCHEMISTRY

The applications of photochemical methods to the heavy chemicals industry have been disappointing and limited mainly to halogenation reactions and the nitrosyl chloride method for the manufacture of polyamides. Of far greater importance to the polymer and fibre industry is the adverse effect of photochemical reactions in the phototendering of these materials as well as the fading of the dyes incorporated with them. These reactions occur even in hydrocarbon polymers such as polyethylene and, in this case as in many others, are often to be attributed to small amounts of carbonyl substituents which initiate hydrogen abstraction reactions and further oxidation. Although broadly understood, these reactions are still one of the most serious problems of the polymer industry.

Photochemical polymerisation is becoming of large scale importance in the UV curing of lacquers, so providing an alternative to the thermal processes with all their attendant problems of solvent disposal and pollution. On a smaller but, at present, even more important scale, photoresist methods have supplemented the conventional photographic process (still the most spectacular application of photochemistry in the service of man) and are the basis of many of the miracles of the modern large scale integrated circuit.

As a preparative process, the separation of isotopes by specific photochemical reactions provides one of the unique applications of photochemistry especially with the help of lasers, which provide not only the monochromatic radiation but the high intensity necessary if two quantum processes are to be practicable.

There are many properties of excited states which are only just beginning to be applied. Optical brighteners and photochromic materials have been used for some time and the wide possibilities of fluorescence probes for identification are becoming appreciated. With the newer facilities of the laser, fibre optics, microcircuit light sources and liquid crystal shutters, a new technology of photonics is appearing in which all the properties of the excited state are potentially applicable.

#### Photochemistry and the environment

Photochemical processes have recently appeared on the environmental scene in several ways. Smog formation, such as that which has come to be identified with Los Angeles, is associated with the pollutants  $O_3$  and  $NO_2$  which damage materials such as rubber and vegetation and irritate eyes and respiratory tract. There is a diurnal variation in their concentration which clearly associates their formation with sunlight and this has been shown to be a photochemical reaction between oxygen and the NO and hydrocarbons from automobile exhaust gases. An interesting aspect of the reaction is that it probably involves singlet oxygen, at least in part, formed by energy transfer from a triplet carbonyl derivative of the hydrocarbons.

So complex are the reactions occurring in our atmosphere today that any attempt to understand the early history of the atmosphere may seem hopeless. Nevertheless the origin of life is inextricably linked with the origin of the atmosphere and both are attracting the attention of many scientists among whom photochemists are very prominent. When mixtures of gases of composition resembling the primitive atmosphere before it became oxidising are irradiated with ultra-violet light, most of the basic materials without which life could hardly have arisen, amino acids, nucleic acids, sugars and porphyrins, as well as polymers of these compounds, have been identified in the photochemical products (11).

As we have come to realise the importance of photochemistry in creating our atmosphere and the degree to which man is adding new substances to it, there has been increasing concern about the influence of atmospheric photochemistry on the stationary state composition of the atmosphere. Today, all oxygen in the atmosphere passes through the photochemical cycle of photosynthesis in the short period of two thousand years. Our life depends, for protection from UV radiation, on an ozone layer whose equivalent thickness at NTP is only  $\frac{1}{2}$  mm. The temperature of the earth is very sensitive to infra-red absorption by  $CO_2$ . These compounds are maintained in a quite delicate balance in rather small amounts, by photochemical reactions. Changes in the rate of fuel combustion and even the type of agriculture, affect the  $CO_2$  concentration, and gases such as NO from aircraft as well as chlorine oxides which may enter the stratosphere as a result of the extensive use of visible-light-stable aerosols such as the chlorofluorocarbons, are known to catalyse the photodecomposition of ozone. Although present indications are that the ozone layer is rather well able to resist such insults and restore itself, there is a need to monitor any changes carefully and continually if we are to have early warning of deterioration or catastrophe.

## PURE AND APPLIED PHOTOSYNTHESIS

Of the many ways which have been proposed for the collection and storage of solar energy the only large scale process available at present is that of photosynthesis. Nature has learned to cope with the problems of the intermittency of solar energy by storing that energy as a chemical fuel and by devising a cyclic process which returns the waste products to the atmosphere. For this reason the use of the natural photosynthetic process itself is still a serious contender as a practical means of solar energy utilisation. But the living plant is not ideal for man's energy purposes other than food; it is labour intensive in its collection and requires large quantities of water and fertiliser. The attractions of carrying out a purely photochemical process which is able to replace natural gas by hydrogen and liquid fossil fuels by, for example, methanol, need no elaboration.

There are, therefore, two incentives for studying the primary processes of photosynthesis: the desire to understand one of nature's most elegant and effective mechanisms and the desire to emulate and improve upon it for practical purposes.

Let us select from the whole complex scheme of plant photosynthesis the one which seems most promising for the purpose of solar energy utilisation. This is the splitting of water into oxygen and a fuel which, on combination with the oxygen of the atmosphere, releases energy. If that fuel could be hydrogen it would fill an immediate need in the existing system of distribution.

Detailed progress in understanding photosynthesis has recently been made in the study of pigment-protein complexes from photosynthetic bacteria. But these bacteria effect what is essentially photosystem I and are not able to decompose water. We are, therefore, from the practical point of view, more interested in photosystem II of the green plants and algae, and this is a system where our ignorance of the primary processes is greatest.

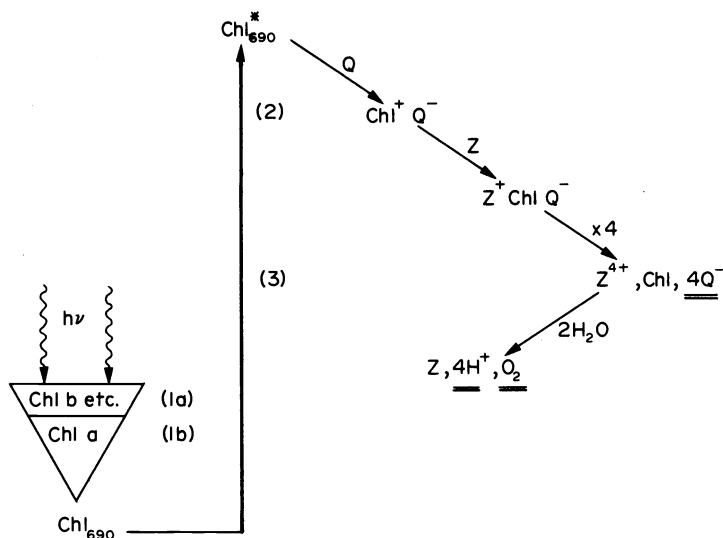


Fig. 3. Model for photosystem II

The principal steps which must be reproduced if we are to construct an *in vitro* model of photosystem II, capable of liberating  $\text{O}_2$  from water, are shown in Fig. 3 and consist of the following:

1. A light harvesting unit composed of about 300 pigment molecules which absorb sunlight and channel the energy efficiently to one trap where photochemical reaction can take place.
2. Electron transfer from a donor to an acceptor.
3. Oxidation of water by the donor.

Let us look at these processes in turn, enquiring how they occur *in vivo* and whether they can be reproduced *in vitro*. It will be wise to learn all we can from the natural photosynthetic process but not necessarily to imitate exactly; it may be that there are alternative ways which are easier to achieve in the laboratory or on the industrial scale. We recall how man's long-standing desire to fly was only achieved when he gave up attempts

to model the birds. The green plant was not designed to supply chemical fuels such as hydrogen or other chemical fuels for man and is probably far more elaborate than a system designed optimally for this purpose. Nevertheless, the natural photosynthetic process is the only successful one we know, and is of fundamental interest because of the elegant photophysical and photochemical principles which it employs.

#### Light harvesting in the photosynthetic unit

The photosynthetic unit contains some 300 pigment molecules including chlorophyll-a, chlorophyll-b, carotenes and xanthophylls and, in the red algae particularly, phycobilisomes containing phycoerythrin, phycocyanine and allophycocyanine. The molecule with the lowest excited singlet level is chlorophyll-a and there is good evidence that energy transfer among the pigment molecules results in efficient transfer of the excitation to chlorophyll-a (process 1a) and then among chlorophyll-a molecules to the trap (process 1b).

Recently, picosecond flash methods have made it possible to observe these rapid energy transfer processes directly and a good illustration is afforded by a recent result from our laboratory (12) showing energy transfer between four pigments of the red alga Porphyridium cruentum illustrated in Fig. 4. The sequence of singlet excitation energies, highest first, is phycoerythrin (PE), phycocyanine (PC), allophycocyanine (APC) and chlorophyll-a (CHL). The laser pulse at 530 nm excites mainly the phycoerythrin and the fluorescence of the four pigments is monitored respectively at 576 nm, 640 nm, 661 nm and 685 nm. The sequence of grow-in and decay of the four fluorescences is seen to follow the predicted energy transfer sequence very clearly.

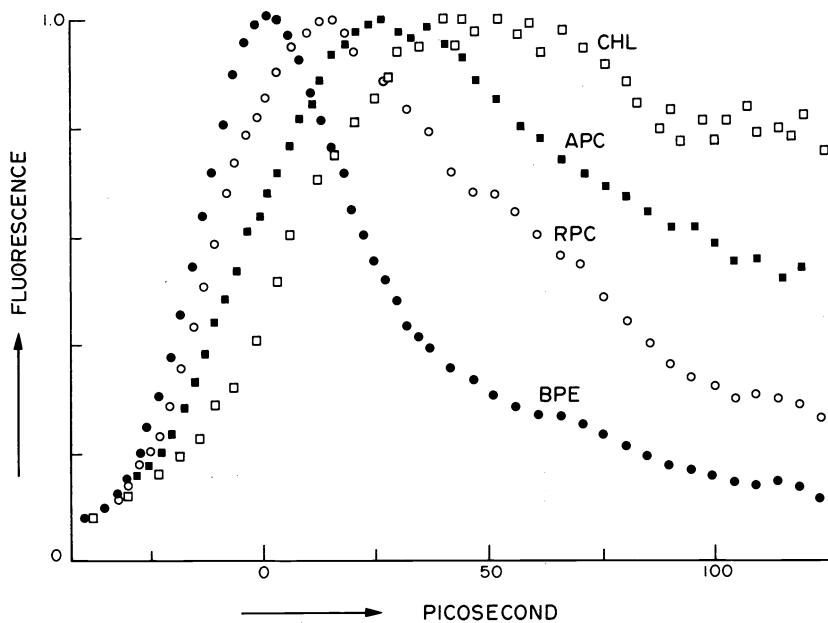


Fig. 4. Energy transfer in Porphyridium cruentum. Fluorescence of BPE (phycoerythrin) at 576 nm decays by transfer in 70 ps to RPC (phycocyanine) which fluoresces at 640 nm. This transfers in 90 ps to APC (allophycocyanine) which fluoresces at 661 nm. Finally, this transfers in 120 ps to chlorophyll-a (CHL) which fluoresces at 685 nm and decays in 180 ps by transfer to the trap

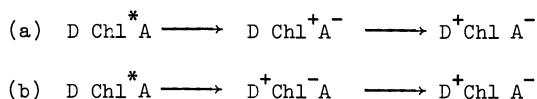
Transfer of this kind is easily reproduced in the laboratory and is well understood in terms of Förster's theory of resonance energy transfer between the coupled electronic oscillators of the donor and acceptor. Efficient energy transfer from chlorophyll-b to chlorophyll-a, (50% efficient at 70 Å) has been observed, under a variety of conditions including monolayers (13) and lipid multilayers (14).

When one attempts to reproduce, *in vitro*, the light harvesting antenna in which some hundred identical molecules transfer energy to a trap of slightly lower energy (16), difficulties appear. As the concentration of the chlorophyll antenna molecules is increased to the point where efficient energy transfer takes place between them, the energy is dissipated by an alternative route known as concentration quenching. The mechanism of

concentration quenching in this case was by no means clear at first, since it occurs in rigid media under a wide variety of conditions (13,14,15) and there are no spectral changes corresponding to aggregation or dimer formation. Beddard and I (16) have proposed that concentration quenching in chlorophyll occurs by successive energy transfer (Förster type) and trapping. The trap is merely a pair of molecules in the random distribution which are close enough to interact when one of them is electronically excited and this interaction results in quenching by incipient or complete excimer formation. Monte Carlo calculations showed that the average separation for 50% quenching between chlorophyll-a molecules is 10 Å. An efficient light harvesting antenna of chlorophyll-a must therefore have no molecules separated by less than 10 Å but all of them close enough for efficient transfer. This is not attainable in a random array and one concludes that the chloroplast (in which the average concentration of chlorophyll is about  $10^{-11}$ M) must have these molecules held apart from each other. The arrangement in the chloroplast is not known but a recent structure determination on a bacteriochlorophyll-protein complex (17) has shown that the average nearest neighbour separation is 12 Å, almost ideally designed for energy transfer. Attempts to prepare in vitro arrangements which have these properties have so far been unsuccessful.

#### Electron transfer involving chlorophyll

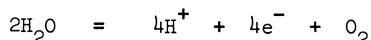
The nature of the trap of photosystem II and the excited species P690 is not known for certain but it is very probably a chlorophyll monomer in a special environment or a chlorophyll dimer. It could, in principle, mediate in the electron transfer between donor D and acceptor A in one of two ways:



Primary electron-transfer processes with excited chlorophyll (both singlet and triplet) both as donor and acceptor have been carried out in vitro but process (a) above, with singlet chlorophyll as donor occurs much more readily. In the chloroplast, quinones (plastoquinone) are either the primary acceptor or are closely linked with it in the transport chain and, therefore, transfer to such a quinone from singlet chlorophyll is a probable model of this stage of the photosynthetic process. Electron transfers to a variety of quinones have been observed under a variety of conditions, including fluid solvents (18) and lipids (19). In the latter, although diffusion is inhibited, the transfer occurs over an average separation between chlorophyll and quinone, of 20 Å.

#### Oxidation of water

Almost nothing is known about this process in vivo except that manganese seems to be involved. In order to liberate one molecule of oxygen, four electrons must be transferred from water:



and there is strong evidence, from successive flash experiments, that four successive electron transfers must occur before molecular oxygen is eliminated.

Hitherto, attempts to liberate oxygen from water using visible light have not been successful (with the possible exception of some experiments using semiconductor electrodes) and this is not surprising since there was no apparent means of effecting four electron transfers successively within a single complex. However, manganese, which is used by the chloroplast in this reaction, is well known (20) to form binuclear complexes, which may be bridged by oxygen, and to be readily converted between the oxidation states  $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$ . This immediately suggests that such a binuclear complex in the lowest oxidation state,  $\text{Mn}^{\text{II}}-\text{Mn}^{\text{II}}$ , may donate four electrons to become  $\text{Mn}^{\text{IV}}-\text{Mn}^{\text{IV}}$  which might then be capable of oxidising water and eliminating molecular oxygen.

Attempts in our laboratory were at first aimed at reacting excited chlorophyll-a (singlet) with quinone, as already described in the preceding section, and then reacting the  $\text{Chl}^+$  with various manganese complexes. This was not successful because, as separate experiments showed, manganese complexes are efficient quenchers of singlet chlorophyll without there being any resultant electron transfer. It was not possible to arrange the concentrations of the three separate components of this reaction so as to bring about a measurable amount of water decomposition. Recently, this difficulty has been overcome (21) by combining the photosensitiser and the manganese as a complex and reacting this with quinone. We have not yet used chlorophylls for this purpose but have used instead the related complexes of manganese with tetrapyrrolylporphyrin, and phthalocyanine, solubilised by substitution of sulphonate groups. The reaction of these complexes with quinones, on excitation with visible light, is readily observed in flash photolysis experiments by the successive oxidation of  $\text{Mn}^{\text{II}}-\text{Mn}^{\text{III}}-\text{Mn}^{\text{IV}}$  (resting form  $\text{Mn}^{\text{III}}$ ) and the reduction of



quinone to semiquinone. Quantum yields (based on a four electron transfer) are about 5% and preliminary measurements using an oxygen-sensitive electrode indicate that an equivalent amount of oxygen is liberated.

Hydroquinones react spontaneously with air, liberating energy and are therefore low grade fuels. In principle they may be converted to quinone and hydrogen, and the hydrogen used as a transportable fuel. In such a system, the quinone and the manganese complex are recycled and the only overall reaction is the decomposition of water into hydrogen and oxygen. Complexes such as those of phthalocyanine are strong absorbers throughout the visible region.

Although a number of problems remain to be solved, this simple photochemical reaction, occurring in homogeneous solution, appears promising and (if it can be made to work with an overall energy efficiency of say 10%) it has advantages over most other systems so far proposed for solar energy collection. Any collecting device for solar energy, working in a desert region with an insolation of  $250\text{W m}^{-2}$  and with an efficiency of 10%, must cost less than  $20\$ \text{m}^{-2}$  if it is to be competitive with alternative forms of power production at present day prices. This rules out, on economic grounds, photovoltaic devices of the type known at present and it is difficult to see how any electrode system can be constructed within this economic constraint. On the other hand, it should not be difficult to produce transparent containers for a homogeneous photochemical reaction which are economical within this limit.

The greatest contribution the photochemist could make to the welfare of mankind would be to provide an efficient means for the collection and storage of solar energy in vitro before our wells of fossil fuels run dry.

#### REFERENCES

1. L. Onsager, J. Am. Chem. Soc. **58**, 1486-1493 (1936).
2. T. Förster, Z. Electrochem. **54**, 42-46 (1950).
3. G. Jackson and G. Porter, Proc. Roy. Soc. **260**, 13-30 (1961).
4. T. Förster and K. Kasper, Z. Electrochem. **59**, 976-980 (1955).
5. G. Porter, J.A. Synowiec and C.J. Tredwell, Biochim. Biophys. Acta **459**, 329-336 (1977).
6. E.P. Ippen, C.V. Shank and A. Bergman, Chem. Phys. Letters **38**, 611-614 (1976).
7. T. Förster, Ann. Physik. **6(2)**, 55-75 (1948).
8. K.F. Freed and J. Jortner, J. Chem. Phys. **52**, 6272-6291 (1970).
9. R. Hoffmann and R.B. Woodward, Accounts of Chem. Research **1**, 17-22 (1968).
10. G. Porter and P. Suppan, Trans. Faraday Soc. **62**, 3375-3383 (1966).
11. C. Ponnampuruma, The Origins of Life, Thames and Hudson (1972).
12. G. Porter, C.J. Tredwell, G.F.W. Searle and J. Barber, Biochim. Biophys. Acta. In press
13. S.M. de B. Costa, et al., Proc. Roy. Soc. **A326**, 503-519 (1972).
14. A.R. Kelly and G. Porter, Proc. Roy. Soc. **A315**, 149-161 (1970).
15. G.S. Beddard, S.E. Carlin and G. Porter, Chem. Phys. Letters **43**, 27-32 (1976).
16. G.S. Beddard and G. Porter, Nature **260**, 366-367 (1976).
17. R.E. Fenner and R.W. Matthews, Nature **258**, 573-577 (1975).
18. J.M. Kelly and G. Porter, Proc. Roy. Soc. **A319**, 319-329 (1970).
19. G.S. Beddard, G. Porter and G.M. Weese, Proc. Roy. Soc. **A342**, 317-325 (1975).
20. A. Yamamoto, L.K. Phillips and M. Calvin, Inorg. Chem. **7**, 847-852 (1968).
21. A. Harriman and G. Porter, Nature. In course of publication.