Photosensitised Reduction of Water to Hydrogen using Water-soluble Zinc Porphyrins

By Anthony Harriman,* George Porter and Marie-Claude Richoux

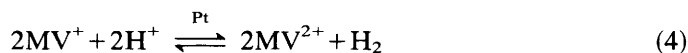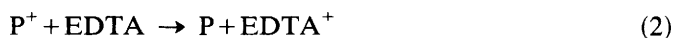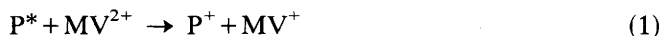Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS

We have confirmed an earlier report by Kalanasundaram and Gratzel that a positively charged, water-soluble zinc porphyrin photosensitises the reduction of water to H_2 with high efficiency. Using MV^{2+} as electron relay and EDTA as sacrificial electron donor, the quantum yield for production of $\frac{1}{2}H_2$ is *ca.* 0.6. The reaction mechanism involves reduction of MV^{2+} by triplet porphyrin and the porphyrin π-radical cation so produced is reduced by EDTA. The concentrations of reactants have been optimised for production of H_2 and to limit destruction of the porphyrin. Under optimised conditions the turnover with respect to the porphyrin can reach 6000.

In addition, some consideration has been given to ways of improving ϕ_{H_2} and of increasing the fraction of sunlight that can be harvested. In this respect, Cd porphyrins may possess suitable properties.

Finally, we note that the porphyrin π-radical cation may possess the thermodynamic capacity to oxidise water to O_2, but this is very much borderline.

Over the past decade or so there has been considerable interest in systems capable of the photodissociation of water upon excitation with visible light since this provides a means of storing sunlight in the form of a chemical fuel.[1] Progress in this field had been fairly slow until the discovery, a few years ago, that redox catalysts could be used to promote formation of both hydrogen[2-4] and oxygen[5-7] from water. Now that the principle of these systems has been established, it is possible to optimise the two separate cycles (*i.e.* H_2 and O_2 formation steps) and to link the two units together so that the overall photodissociation of water may be realised.[8] Of the two cycles, the H_2-producing unit is by far the best characterised and, at the present time, the most suitable system appears to consist of a chromophore (P), methyl viologen (MV^{2+}) as electron relay, a sacrificial electron donor (such as EDTA, H_2S or cysteine) and a colloidal Pt catalyst. The principal reaction scheme may be written

$$P^* + MV^{2+} \rightarrow P^+ + MV^+ \tag{1}$$

$$P^+ + EDTA \rightarrow P + EDTA^+ \tag{2}$$

$$EDTA^+ \rightarrow products \tag{3}$$

$$2MV^+ + 2H^+ \underset{}{\overset{Pt}{\rightleftharpoons}} 2MV^{2+} + H_2 \tag{4}$$

although other variations are possible. Overall, the system produces H_2 at the expense of consuming the sacrificial electron donor. Obviously, once the system has been optimised for production of H_2 it will be necessary to replace this sacrificial donor with a redox couple that is common to a corresponding system for production of O_2 from water or the system must be designed so that the ultimate electron donor is water:

$$4P^+ + 2H_2O \rightarrow 4P + 4H^+ + O_2. \tag{5}$$
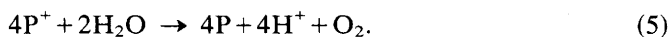
Much work has been directed towards producing efficient catalysts, either colloidal Pt[9] or biological enzymes such as hydrogenase.[10] Also, some work has been directed towards understanding the functions of the sacrificial electron donor.[11] Furthermore, it is known that the solution pH is critical and most studies have used the ruthenium complex ($bipy_3Ru^{2+}$) as chromophore. For there to be useful storage of solar energy, the chromophore, apart from being cheap and stable, must absorb an appreciable fraction of the solar spectrum and must give a high quantum yield for production of H_2. Nature makes extensive use of metalloporphyrins as chromophores in the photosynthetic process and such compounds could be useful in artificial systems since they absorb strongly in the visible region and are known to participate in photoredox reactions.[12] In fact, very recently Kalyanasundaram and Gratzel[13] reported that "in the presence of a colloidal Pt catalyst, a water soluble, cationic zinc porphyrin sensitised photoreduction of water to H_2 with remarkable efficiency". In this communication we confirm this finding whilst providing a more quantitative estimate of the H_2-producing efficiency and we note that this system is close to the optimum for a three-component H_2-producing unit.

EXPERIMENTAL

EDTA (B.D.H.) and MV^{2+} (Sigma) were used as received whilst the Pt–PVA catalyst was prepared according to a literature method[9] and the final concentration of Pt determined by atomic absorption. *meso*-Tetra(4-pyridyl) porphine (TPyP) was prepared and purified as before[14] and zinc(II) was inserted by stirring the free base porphyrin (0.5 g) with zinc acetate (3 g) in glacial acetic acid (80 cm³) for 5 h at 80 °C. After removal of the acetic acid, the dried product was chromatographed on a talc column using benzene + methanol as eluent. Methylation was achieved by stirring ZnTPyP (0.5 g) in dried CH_3I (50 cm³) at room temperature for 3 days. The compound, after successive reprecipitations from NaI solution, gave a satisfactory elemental analysis.

All solutions were prepared using water (A.R. grade) redistilled from permanganate. The solutions were buffered to pH = 5.0 using potassium hydrogen phthalate and the ionic strength was maintained at 0.05 by addition of NaCl. For flash photolysis experiments the solutions were outgassed by the freeze–pump–thaw method whilst all other measurements were made with N_2-purged solutions.

Absorption spectra were recorded with a Perkin-Elmer 200 spectrophotometer and luminescence spectra were recorded with a Perkin-Elmer MPF 4 spectrofluorimeter. The fluorescence properties were measured at room temperature using the optically dilute method.[15] Fluorescence quantum yields were estimated relative to Rhoadmine 6G in ethylene glycol and the spectra were fully corrected for the spectral responses of the instrument. The fluorescence lifetimes were measured by single-photon counting. All phosphorescence spectra were recorded at 77 K in a water/glycerol glass.

Triplet lifetimes were measured by conventional flash photolysis (pulse duration of 10 μs, maximum energy 200 J). The photolysis lamps were filtered through $K_2Cr_2O_7$ solution to remove light of $\lambda < 500$ nm. Triplet-quenching rate constants were determined by measuring the triplet lifetime in the presence of at least five different concentrations of quencher and have a reproducibility of ±15%.

A 200 W Xe arc was used for steady-state irradiation experiments. The excitation light was passed through a cold-water finger and a 500 nm cut-off filter and focussed onto a sample cell (solution volume 20 cm³) thermostatted at 20 °C. For quantum-yield measurements, a Bausch and Lomb monochromator was used to isolate a narrow region (550 ± 30 nm). The sample solution was continuously stirred throughout the irradiation period and the concentration of H_2 was determined by gas chromatography using the conditions recommended by Valenty.[16]

ABBREVIATIONS

EDTA ≡ ethylenediaminetetraacetic acid disodium salt

TPP ≡ 5,10,15,20-tetraphenylporphine

OEP ≡ octaethylporphine

TBP ≡ tetrabenzporphine

Pc ≡ phthalocyanine

Nc ≡ naphthocyanine

ZnTPyP R =

ZnTMPyP^{4+} R = — CH$_3$

ZnTSPP^{4-} R = — SO$_3^-$
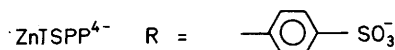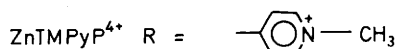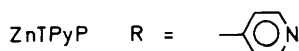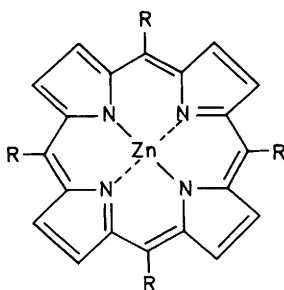
RESULTS AND DISCUSSION

REDOX REACTIONS

The ground-state absorption spectrum, together with fluorescence and phosphorescence spectra, of ZnTMPyP^{4+} in aqueous solution is shown in fig. 1. Using these spectral data the energy levels of the excited singlet and triplet states were located at 198 and 152 kJ mol^{-1}, respectively. The fluorescence quantum yield was found to be 0.025 whilst actinometric ns flash photolysis gave an estimate of the quantum yield for triplet-state formation (ϕ_T) of 0.90 ± 0.10. Thus, internal conversion from the first excited singlet state to the ground state is negligible since the sum of the fluorescence and triplet yields is unity, within experimental limits. The efficient intersystem-crossing process (k_{isc}) results in a short singlet-state lifetime (τ_s) (table 1) and this limits the utility of the singlet state. Thus, the addition of high concentrations of MV^{2+} and EDTA had no effect on either the ground-state absorption spectrum or the fluorescence yield. From these studies, we have estimated that the bimolecular rate constants for quenching the excited singlet state by these quenchers must be $<3 \times 10^7$ dm^3 mol^{-1} s^{-1}. This means that at concentrations of EDTA or MV^{2+} <0.5 mol dm^{-3} there will be no singlet-state reaction so that any observed photochemistry can be attributed to the triplet manifold.
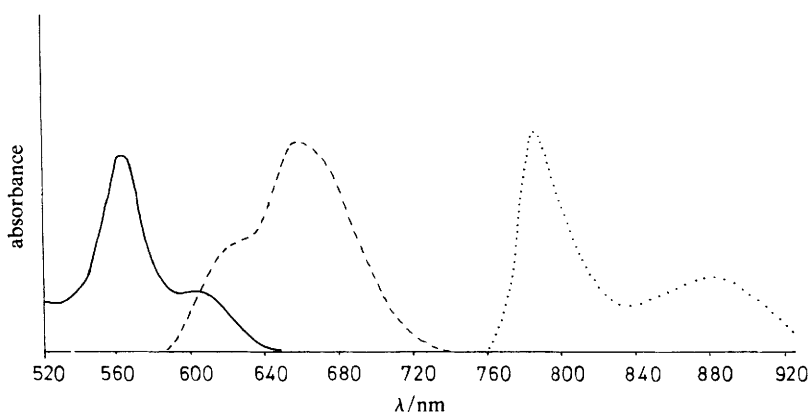
FIG. 1.—Absorption (———), fluorescence (----) and phosphorescence ($\cdots\cdots$) spectra of ZnTMPyP^{4+} in aqueous solution.

TABLE 1.—PHOTOPHYSICAL PROPERTIES OF ZnTMPyP^{4+} IN AQUEOUS SOLUTION (pH 5.0, $u = 0.05$)

ϕ_F	τ_S/ns	k_{isc}/s^{-1}	ϕ_T	τ_T/μs	E_T/kJ mol^{-1}
0.025	1.4	6.4×10^8	0.9	655	152

In fact, the triplet state has a long lifetime (τ_T) which enables bimolecular reactions to proceed even at low concentrations of quencher. The triplet state was quenched by both EDTA and MV^{2+}; the quenching rate constants are collected in table 2. These values appear to be in poor agreement with those reported previously[13] but this discrepancy may be due to differences in the ionic strength (u) of the medium. We have carried out all our experiments at a constant u value of 0.05 but the previous study did not use an ionic strength mediator and so comparison of the two sets of rate constants is difficult. Classical kinetic theory relates the observed rate of electron transfer between ions A and B of charge Z to the ionic strength of the medium by the equation

$$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{u} \qquad (6)$$

where k_0 refers to electron transfer at zero u. For reaction between triplet ZnTMPyP^{4+} and MV^{2+}, the product $Z_A Z_B$ is $+8$ so that the rate of reaction should show a sharp increase with increased u. In contrast, the rate of reaction between triplet ZnTMPyP^{4+} and EDTA at pH5 should decrease with increased u since

TABLE 2.—TRIPLET-QUENCHING RATE CONSTANTS FOR REACTION OF ZnTMPyP^{4+} WITH EDTA AND MV^{2+}

quencher	k/10^5 dm^3 mol^{-1} s^{-1}
EDTA	1.7 ± 0.3
MV^{2+}	180 ± 20

EDTA is present in ionised form. Thus, since we have used a much higher u value than that of Kalyanasundaram and Gratzel, we would expect our rate constants to be higher for quenching by MV^{2+} and lower for quenching by EDTA, as observed, but it is not possible to be more quantitative.

The quenching efficiencies are low, even allowing for electrostatic repulsion between $ZnTMPyP^{4+}$ and MV^{2+}. In fact, recent work[17] has shown that the positive charge on $MnTMPyP^{4+}$ resides mainly at the pyridyl N atoms and is not delocalised over the pyrrole rings where the redox reaction probably takes place. This is in contrast to sulphonic acid groups which show extensive charge delocalisation over the whole porphyrin molecule.[17] Instead, as suggested by Kalyanasundaram and Gratzel, the low quenching rate constants are probably a reflection of the modest thermodynamic driving forces involved in the reactions.

When MV^{2+} is present in high concentration, flash spectroscopy shows the formation of radical-ion products consistent with the reaction

$$*ZnTMPyP^{4+} + MV^{2+} \rightarrow ZnTMPyP^{5+} + MV^+. \tag{7}$$

The reduced viologen has characteristic absorption maxima at 395 and 605 nm[18] whilst the porphyrin π-radical cation has strong absorption in the 600–800 nm region.[19] The radical ions are reasonably long-lived ($t_{\frac{1}{2}} \approx 300\ \mu s$) and decay via a second-order kinetic process. This can be attributed to diffusional recombination

$$ZnTMPyP^{5+} + MV^+ \rightarrow ZnTMPyP^{4+} + MV^{2+} \tag{8}$$

since the two species decay with an identical rate constant of $(3.7 \pm 0.4) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$. Despite this efficient recombination process, the observed rate constant is extremely high for reaction between two positively charged species and the yield of separated ion products is high. Using ns flash photolysis and with an initial concentration of MV^{2+} of $8 \times 10^{-3}\ mol\ dm^{-3}$, the quantum yield for production of $ZnTMPyP^{5+}$ was estimated to be (0.75 ± 0.08). This value is very high and means that practically all of the triplet state can be converted into redox products under these conditions. In fact, the quantum yield for formation of redox products (ϕ_{PROD}) can be considered as the product of three probabilities

$$\phi_{PROD} = \phi_T \phi_Q \phi_S \tag{9}$$

where ϕ_T is the quantum yield for formation of the triplet state and ϕ_Q is the probability of quenching the triplet state by a particular concentration of quencher:

$$\phi_Q = k_7(MV^{2+})/k_7(MV^{2+}) + (\tau_T^{-1}). \tag{10}$$

Under the conditions employed, $\phi_T = (0.9 \pm 0.1)$ and $\phi_Q = 1.0$ so that the probability of the quenching act leading to the formation of separated ion products (ϕ_S) must be ca. 0.8. This is surprisingly high for a photoredox reaction and must reflect some degree of electrostatic repulsion between the products within the solvent cage. This would help to overcome geminate recombination. In this respect, note that ϕ_{PROD} for reaction between $ZnTSPP^{4-}$ and MV^{2+} is <0.1 under similar conditions.

A further complication observed with $ZnTSPP^{4-}$ is that there is extensive ground-state complexation with MV^{2+}. This results in static quenching and does not yield photoredox products. A similar effect was reported recently[20] for reaction between sulphonated phthalocyanines and MV^{2+}.

At high concentrations ($0.3\ mol\ dm^{-3}$) of EDTA, flash spectroscopy shows the formation of a long-lived intermediate that can be attributed to $ZnTMPyP^{3+}$

$$ZnTMPyP^{4+} + EDTA \xrightarrow{h\nu} ZnTMPyP^{3+} + EDTA^+. \tag{11}$$

The transient decayed predominantly by second-order kinetics, presumably due to disproportionation

$$2\,ZnTMPyP^{3+} \rightleftharpoons ZnTMPyP^{4+} + ZnTMPyP^{2+} \tag{12}$$
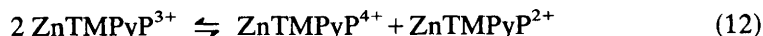
although at longer times decay was no longer simple second-order but contained contributions from competitive processes. This reaction sequence was not reversible and resulted in extensive bleaching of the chromophore.

Since the triplet-quenching rate constants exhibited by MV^{2+} and EDTA are quite dissimilar it is possible to control the reactant concentrations so that the photochemistry occurs exclusively *via* reaction between triplet $ZnTMPyP^{4+}$ and MV^{2+}. The redox products produced by this process are sufficiently long-lived for EDTA to intercept reverse electron-transfer and so stabilise the MV^+. Thus, the overall scheme may be written:

$$*ZnTMPyP^{4+} + MV^{2+} \rightarrow ZnTMPyP^{5+} + MV^+ \tag{13}$$

$$ZnTMPyP^{5+} + EDTA \rightarrow ZnTMPyP^{4+} + EDTA^+ \tag{14}$$

$$EDTA^+ \rightarrow products. \tag{15}$$

Using a constant concentration of MV^{2+} (5×10^{-3} mol dm^{-3}), the concentration of EDTA was varied ($1 - 20 \times 10^{-3}$ mol dm^{-3}) and the lifetime of $ZnTMPyP^{5+}$ and MV^+ measured. By this method, the rate constant for reaction (14) was determined to be $(2.7 \pm 0.6) \times 10^6$ dm^3 mol^{-1} s^{-1} [21] and it was found that with concentrations of EDTA $> 10^{-2}$ mol dm^{-3} most, if not all, of the initially produced MV^+ was stable towards reverse electron-transfer with $ZnTMPyP^{5+}$. Although these rate constants were measured by flash photolysis techniques, they should hold for steady-state irradiation experiments.

PRODUCTION OF HYDROGEN

Using the above rate constants it is possible to obtain a reaction mixture in which the concentration of each reactant has been selected in order to achieve the optimum steady-state yield of MV^+. Thus, irradiation of an outgassed solution containing $ZnTMPyP^{4+}$ (2×10^{-5} mol dm^{-3}), MV^{2+} (8×10^{-3} mol dm^{-3}) and EDTA (15×10^{-3} mol dm^{-3}) in water at pH 5.0 resulted in the formation of MV^+ as a permanent product (fig. 2). Under such conditions, the quantum yield for production of MV^+, determined using light of $\lambda = (550 \pm 30)$ nm, was (0.75 ± 0.10). This value is in excellent agreement with that predicted on the basis of the flash photolysis experiments.

Now, it is well known that MV^+ is able to reduce water to H_2 in the presence of a catalyst, such as colloidal Pt, or an enzyme, such as hydrogenase

$$2\,MV^+ + 2H^+ \rightleftharpoons 2MV^{2+} + H_2 \tag{16}$$

and, as such, it should be possible to use the above photoredox system to photosensitise the reduction of water to H_2. Previous work[13] has shown that this situation is realised and, using a colloidal Pt–PVA catalyst,[9] we have confirmed this finding. Under the above experimental conditions and using a Pt concentration of *ca.* 10^{-5} mol dm^{-3}, the quantum yield for production of H_2 (ϕ_{H_2}) was measured (fig. 3) and found to be approximately 0.30 under optimum conditions. This optimum value decreases with longer irradiation times, probably due to competitive absorption of light by unreacted MV^+. This shows that the limiting step in our system is not the photoproduction of MV^+ but the effectiveness of the catalyst in promoting reaction
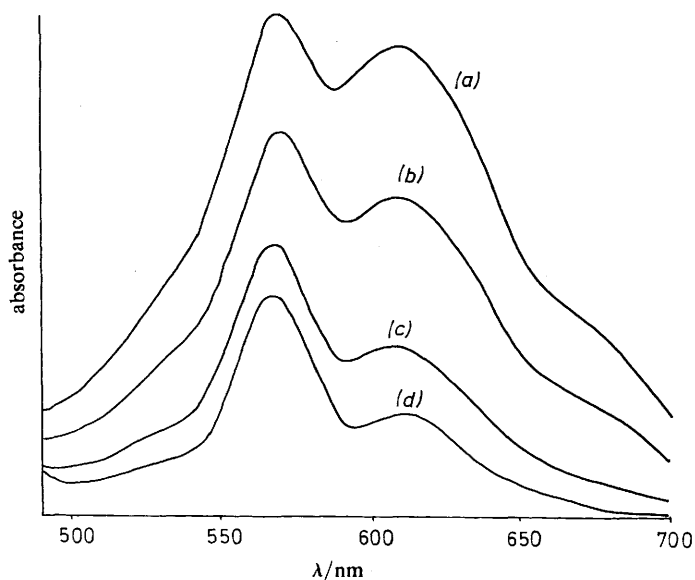
FIG. 2.—Absorption spectral changes following irradiation of an outgassed solution of $ZnTMPyP^{4+}$ $(2 \times 10^{-5}$ mol dm^{-3}), MV^{2+} $(8 \times 10^{-3}$ mol dm^{-3}) and EDTA $(15 \times 10^{-3}$ mol dm^{-3}) in water at pH5. Irradiation times: (a) 0, (b) 10, (c) 35 and (d) 90 s.

between MV^{+} and H_2O. Note that the concentration of H_2 was estimated after allowing the solution to stand in the dark so that all the MV^{+} had decayed. Identical experiments performed without the Pt–PVA catalyst or without EDTA gave no detectable yield of H_2. Experiments carried out without MV^{2+} did give H_2 but in quite low yield ($\phi_{H_2} = 0.02$).

Under optimised conditions the efficiency of proton reduction *via* MV^{+} is *ca.* 80%. This efficiency is determined, at least to a high degree, by the history of the
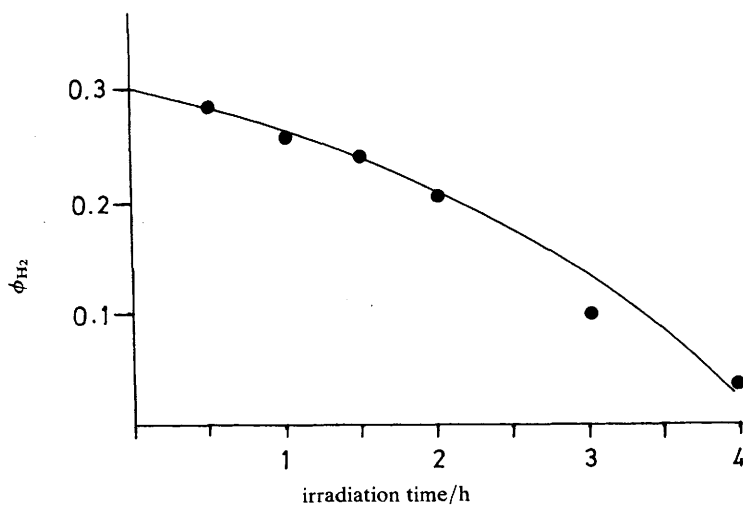

FIG. 3.—Quantum yield for production of H_2 as a function of irradiation time.

catalyst. Using different batches of Pt–PVA, not only was the lifetime of MV$^+$ affected but also the conversion efficiency appeared to change. In qualitative terms, it seems that a smaller particle size helps to preserve the stoichiometry of reaction (16) but we are not in a position to provide quantitative confirmation of this proposal.

SIDE REACTIONS

Prolonged irradiation of ZnTMPyP^{4+} in aqueous solution at pH 5 results in a small bleaching effect but the quantum yield for loss of the chromophore is $<10^{-5}$. Similarly, as shown in fig. 4, prolonged irradiation of ZnTMPyP^{4+} in the presence of
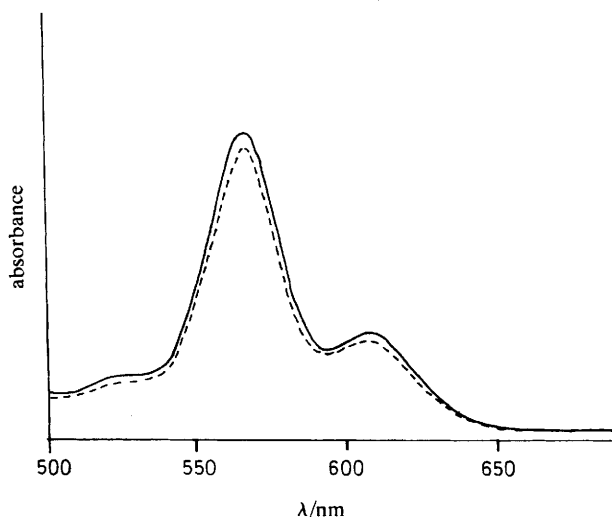

FIG. 4.—Absorption spectral changes following prolonged irradiation of an outgassed solution of ZnTMPyP^{4+} (2×10^{-5} mol dm^{-3}) containing MV^{2+} (8×10^{-3} mol dm^{-3}).

MV^{2+} (8×10^{-3} mol dm^{-3}) does not lead to destruction of the chromophore and the mixture is quite photostable. This confirms the reversibility of the electron-transfer steps [reactions (7) and (8)]. However, irradiation of ZnTMPyP^{4+} in the presence of EDTA (15×10^{-3} mol dm^{-3}) results in irreversible reduction of the porphyrin (fig. 5). This photoreduction process, which is similar to that reported for other zinc porphyrins,[22] is efficient and leads to formation of dihydro, tetrahydro and hexa-hydro zinc porphyrins. All the products are photoactive and some steps are reversible and affected by oxygen so that quantum-yield measurements are irre-producible. This irreversible loss of the porphyrin is only partially inhibited by the presence of a Pt–PVA catalyst.

The occurrence of this photoreduction process means that, in order to achieve a high turnover with respect to the chromophore, it is essential that the overall reaction proceeds through an oxidative cycle in which the primary photochemical step involves electron transfer from triplet ZnTMPyP^{4+} to MV^{2+}. The concentration of EDTA must be kept sufficiently low to prevent involvement of EDTA in the primary photoreaction but, at the same time, it must be sufficiently high to ensure rapid reaction between ZnTMPyP^{5+} and EDTA.
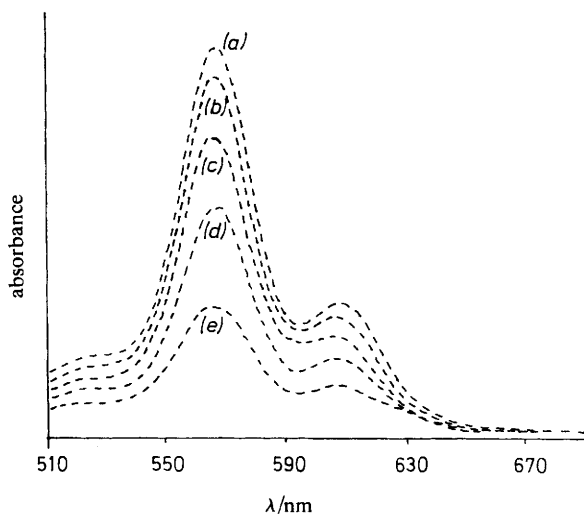
FIG. 5.—Absorption spectral changes following irradiation of an outgassed solution of ZnTMPyP^{4+} (2×10^{-5} mol dm^{-3}) containing EDTA (15×10^{-3} mol dm^{-3}). Irradiation times: (a) 0, (b) 7, (c) 21, (d) 43 and (e) 95 min.

When the optimum concentrations of reactants are employed, high turnovers with respect to the chromophore can be achieved. Fig. 6 shows the absorption spectrum of the chromophore after prolonged irradiation in the presence of the optimum amounts of MV^{2+} (8×10^{-3} mol dm^{-3}) and EDTA (10×10^{-3} mol dm^{-3}) and with an excess of EDTA (50×10^{-3} mol dm^{-3}). For both systems, the quantity of H$_2$ produced was fifty times the initial concentration of chromophore but in the presence of excess EDTA *ca.* 50% of the chromophore had been converted into a reduced zinc porphyrin (probably the chlorin). With the optimised concentrations there is virtually no loss of chromophore and, in an exhaustive irradiation, it was possible to obtain a very high turnover with respect to the chromophore and also a moderate turnover with respect to MV^{2+} and Pt. In this experiment, irradiation was
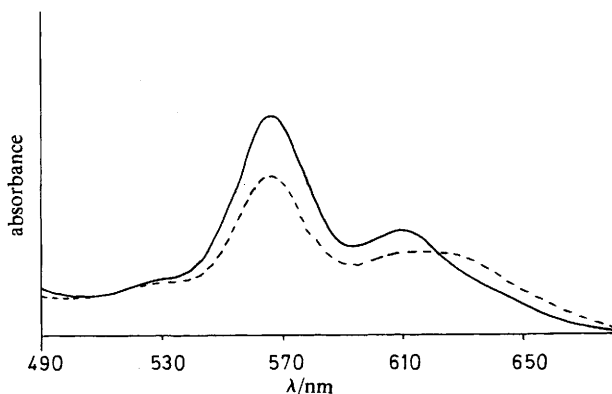

FIG. 6.—Absorption spectral changes after aeration of an irradiated outgassed solution of ZnTMPyP^{4+} (2×10^{-5} mol dm^{-3}) containing optimum amounts of MV^{2+} (8×10^{-3} mol dm^{-3}) and EDTA (10×10^{-3} mol dm^{-3}) (————) and in the presence of excess EDTA (50×10^{-3} mol dm^{-3}) (— — — —).

intermittent and, during the dark periods, the evolved H_2 was removed by purging with N_2 and fresh aliquots of EDTA were added to maintain the optimum concentration (10×10^{-3} mol dm^{-3}). In addition, the solution contained an unusually high concentration of buffer in an attempt to retain the original pH. At the end of the experiment, the total concentration of evolved H_2 was *ca.* 3×10^{-2} mol dm^{-3} which corresponds to a turnover with respect to ZnTMPyP^{4+}, MV^{2+} and Pt of 6000, 7 and 200, respectively. Although high, the turnover for the chromophore compares unfavourably with that of the natural photosynthetic process (*ca.* 10^5).

OPTIMISATION

In order to optimise this system for storage of solar energy, it is necessary to improve the reaction efficiency in two directions: to increase ϕ_{H_2} up to the maximum of 0.5 and to increase the fraction of solar energy absorbed by the chromophore.

First, let us consider ways of increasing ϕ_{H_2}. For the system as described, ϕ_{H_2} is limited by ϕ_T, ϕ_S and the efficiency with which MV$^+$ reacts with water to produce H_2. This latter step can be improved by using more efficient catalysts and, in our opinion, it should be possible to achieve the stoichiometry of reaction (16) in the near future. The application of redox catalysts to solar energy storage systems is still in its infancy and more efficient catalysts should become available as research progresses. As such, we are optimistic on this point. However, the observed ϕ_S value is very high for a photoredox reaction in fluid solution and, without introducing some degree of heterogeneity into the system,[23] it may not be possible to improve upon this value. To increase ϕ_T it will be necessary to replace zinc with a heavier metal ion, but the replacement ion must not shorten τ_T to an unworkable degree (say <1 μs). Thus, the metal ion must be diamagnetic and a few possible metalloporphyrins are listed in table 3. Here, we provide a rather limited selection of τ_T and ϕ_T values for some

TABLE 3.—TRIPLET QUANTUM YIELDS AND LIFETIMES OF SOME METAL *meso*-TETRAPHENYLPORPHINES MEASURED IN ORGANIC SOLVENTS AT ROOM TEMPERATURE

compound	ϕ_T	τ_T
MgTPP	0.80	—
H_2TPP	0.82	1.5 ms
ZnTPP	0.88	1.2 ms
CdTPP	1.00	~0.3 ms
PdTPP	1.00	430 μs
Cr^{III}TPP	1.00	250 ns
CuTPP	1.00	90 ns

metal *meso*-tetraphenylporphyrins, measured in organic solvents. From the data, perhaps CdTPP and PdTPP may be suitable chromophores if they possess photoredox properties similar to those of ZnTPP.

In order to push the absorption spectrum further into the near i.r. it will be necessary to change the porphyrin skeleton. Although many variations on the basic porphyrin ring are possible, detailed photophysical studies have been attempted only with the more common structural units. In table 4 we have compiled some relevant data for a few zinc porphyrins. The structural unit affects both ϕ_T and the triplet energy (E_T) so that some compromise in overall properties must be made. The

TABLE 4.—PHOTOPHYSICAL DATA FOR SOME ZINC PORPHYRINS MEASURED IN ORGANIC SOLVENTS AT ROOM TEMPERATURE

compound	ϕ_T	τ_T/ms	E_T/kJ mol^{-1}	E_S/kJ mol^{-1}
ZnOEP	0.90	—	170	207
ZnTPP	0.88	1.2	153	198
ZnTBP	0.77	0.52	147	188
ZnPc	0.68	0.18	109	178
ZnNc	~0.50	0.17	~100	153

limiting value of E_T is reached by obtaining the lowest triplet energy conducive with the compound retaining the ability to photoreduce MV^{2+}. That is, the redox potential of the triplet excited state (E_T°) must be less than that of MV^{2+} ($E^\circ = -0.44$ V). Normally, E_T° is obtained from the ground-state redox potential by the relationship

$$E_T^\circ = E^\circ - E_T \qquad (17)$$

and it is this relationship that imposes the limitations on E_T. Thus, we note that for ZnTPP E_T° is *ca.* -0.6 V, hence the triplet possesses the thermodynamic capacity to reduce MV^{2+}, but the triplet state of zinc phthalocyanine does not possess this ability.[20] Unfortunately, for all porphyrins there is a large $E_S - E_T$ value (3000–5000 cm^{-1}) so that there is a problem in absorbing a large fraction of the solar spectrum and still retaining a reasonably high E_T. Of the compounds listed in table 4, ZnTBP represents the most suitable chromophore as regards absorption characteristics but there is only a marginal improvement over ZnTPP. The actual E_S and E_T values depend upon the central metal ion but we note that whilst CdTBP absorbs at longer wavelength than ZnTBP, PdTBP has $E_S = 195$ kJ mol^{-1} and $E_T = 155$ kJ mol^{-1}, absorption characteristics very similar to ZnTPP. Therefore, at the present time ZnTPP appears to be a suitable chromophore for three-component H_2-producing systems although it may be possible to increase ϕ_{H_2} by using a positively charged, water-soluble CdTBP.

CONCLUSION

The results reported in this paper have confirmed the findings of Kalyanasundaram and Gratzel[13] that ZnTMPyP^{4+} photosensitises the reduction of water to H_2 with high efficiency. In fact, the quantum yield for production of H_2, under our conditions, reached a maximum value of 0.3. This can be improved by the use of a more effective colloidal Pt catalyst and a further improvement may be achieved by replacing Zn with Cd. However, at the present time it is difficult to see how to increase the fraction of solar energy absorbed by the chromophore without attempting to use sensitisers. Replacing the basic TPP skeleton with more elaborate structural units, such as TBP, gives a marginal improvement but at the cost of rendering the synthesis difficult and expensive whilst the commercially available Pc derivatives are not suitable chromophores for such systems.[20] Currently, we are investigating the possibility of using chlorins rather than porphyrins. However, we note that the problem could be overcome if it were possible to use the singlet excited state as the primary electron donor since we could use Pc derivatives. So far, this has not been realised except by green plants.

One of the most important points raised by the original paper[13] was that the $ZnTMPyP^{4+}/MV^{2+}$ system had the necessary thermodynamic capability to photodissociate water into H_2 and O_2. Thus, the redox potential of the $ZnTMPyP^{5+/4+}$ couple was measured at $+1.20$ V which is sufficient to oxidise water to O_2, especially if a RuO_2 catalyst is used to mediate electron transfer.[7] We have not attempted to measure this redox potential but we feel that it is a little too high. The triplet energy of $ZnTMPyP^{4+}$, as measured by phosphorescence, is 1.58 eV and since the triplet state is capable of the reduction of MV^{2+} then E_T° must be < -0.45 eV. A reasonable estimate would place E_T° between -0.5 and -0.7 eV. This suggests that E° for the $ZnTMPyP^{5+/4+}$ couple lies in the range $+0.9$ to $+1.1$ eV but this may still be sufficient for oxidation of water to O_2.[7]

[1] A. Harriman and J. Barber, *Topics in Photosynthesis*, ed. J. Barber (Elsevier, New York, 1979), vol. 3, chap. 8.
[2] B. V. Koryakin, T. S. Dzhabiev and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, 1977, **233**, 620.
[3] J. M. Lehn and J. P. Sauvage, *Nuov. J. Chim.*, 1977, **1**, 449.
[4] K. Kalyanasundaram, J. Kiwi and M. Gratzel, *Helv. Chim. Acta*, 1978, **61**, 2720.
[5] J. Kiwi and M. Gratzel, *Nature (London)*, 1979, **281**, 657.
[6] J. M. Lehn, J. P. Sauvage and R. Zeissel, *Nuov. J. Chim.*, 1979, **3**, 423.
[7] K. Kalyanasundaram, O. Micic, E. Pramauro and M. Gratzel, *Helv. Chim. Acta*, 1979, **62**, 2432.
[8] K. Kalyanasundaram and M. Gratzel, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 701.
[9] J. Kiwi, *Isr. J. Chem.*, 1979, **18**, 369.
[10] M. W. W. Adams, K. K. Rao and D. O. Hall, *Photobiochem. Photobiophys.*, 1979, **1**, 33.
[11] M. Kirch, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345.
[12] A. Harriman, G. Porter and N. Searle, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1515.
[13] K. Kalyanasundaram and M. Gratzel, *Helv. Chim. Acta*, 1980, **63**, 478.
[14] A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1543.
[15] A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1978.
[16] S. J. Valenty, *Anal. Chem.*, 1978, **50**, 669.
[17] I. A. Duncan, A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1415.
[18] J. A. Farrington, M. Ebert and E. J. Land, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 665.
[19] A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, 1970, **92**, 2982.
[20] A. Harriman and M. C. Richoux, *J. Photochem.*, 1980, **14**, 253; *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1618.
[21] B. N. Bandyopadhay and A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 663.
[22] *Porphyrins and Metalloporphyrins*, ed. K. M. Smith (Elsevier, New York, 1975).
[23] P. A. Brugger, P. P. Infelta, A. M. Braun and M. Gratzel, *J. Am. Chem. Soc.*, 1980, **102**, 2461.