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Influence of Electrostatic Forces upon the Efficiency of Charge Separation for the Zinc Porphyrin/Methyl Viologen System

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The bimolecular rate constant for quenching the triplet excited state of a metalloporphyrin by methyl viologen depends upon the electronic charge on the porphyrin ring. The rate constant increases with increased electrostatic attraction between the reactants and this is due to efficient formation of an encounter complex and a high thermodynamic driving force for formation of an ion-pair. However, dissociation of the ion-pair to separate ion products is favoured by strong electrostatic repulsion between the products due to electrostatic factors. In addition the yield of redox products depends upon the amount of electronic energy that must be dissipated in the form of heat, and the rate of internal conversion of the ion-pair decreases significantly with increased energy.

The photochemistry of porphyrins has been studied intensively during the last decade, partly because of the possibility of using such compounds as photosensitisers for transformation of solar energy into a storable form of energy. In particular, the photosensitised dissociation of water into H_2 and O_2 has attracted considerable attention, and previous work has established that zinc porphyrins can function as efficient sensitisers[1-3] for the photochemical production of hydrogen in aqueous solution. Indeed, three separate laboratories have found that positively charged water-soluble zinc porphyrins are particularly effective photosensitisers when methyl viologen (MV^{2+}) is used as electron relay,[4-6] whilst negatively charged compounds are very much less promising.[7,8]

The overall reaction mechanism for the former system involved electron transfer from the triplet excited state of the Zn porphyrin ($^*ZnTMPyP^{4+}$) to MV^{2+}, followed by the reduction of the oxidised form of the porphyrin by an irreversible redox couple such as EDTA:

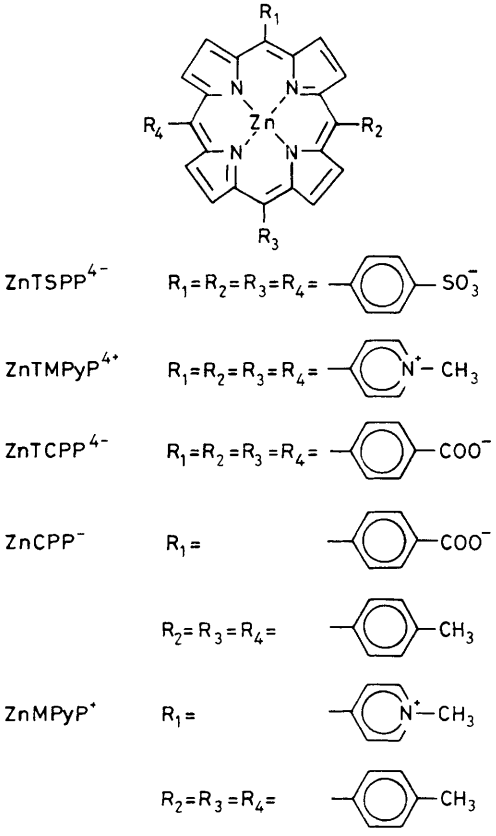
$$\begin{gathered}{}^*ZnP+MV^{2+} \rightarrow ZnP^{+}+MV^{+}\\ ZnP^{+}+EDTA \rightarrow ZnP+EDTA^{+}\\ EDTA^{+} \rightarrow \text{products}\\ MV^{+}+H_2O \rightarrow MV^{2+}+\tfrac{1}{2}H_2+OH^{-}.\end{gathered}$$

The high quantum yield for H_2 production obtained with $ZnTMPyP^{4+}$ ($\phi_{\frac{1}{2}H_2} = 0.60$) was attributed to the strong electrostatic repulsion between the primary redox products (ZnP^{+} and MV^{+}), which favoured dissociation of the ion-pair into redox ion products. Similar proposals have been made for other systems,[9,10] but there has not been a systematic study made to confirm or refute this hypothesis. In this paper we report the results of a study aimed at evaluating the importance of electrostatic factors in determining $\phi_{\frac{1}{2}H_2}$ for the zinc porphyrin sensitised reduction of H_2O to H_2

using EDTA as sacrificial donor, and in so doing we attempt to optimise the reaction for production of H_2.

Unfortunately, the study was complicated by some synthetic problems, since symmetrically substituted porphyrins with four identical groups (either *N*-methyl, carboxylic or sulphoxylic) are prepared readily, but it is very difficult to separate and purify the compounds having only two or three charges. Consequently, we have been able to study only zinc porphyrins possessing four identical charges or a single positive or negative charge. Abbreviations for the various porphyrins mentioned are shown below.

ABBREVIATIONS



EXPERIMENTAL

EDTA (B.D.H.) and methyl viologen (Sigma) were used as received. $ZnTCPP^{4-}$ and $ZnTSPP^{4-}$ were prepared from the metal-free compounds and a large excess of Zn acetate by stirring in aqueous solution at 343 K overnight. The excess of Zn acetate was removed on an ion-exchange column. $ZnTMPyP^{4+}$ was prepared from meso-tetra(4-pyridyl)porphine (TPyP) as described before.[5] $ZnCPP^-$ was prepared as indicated by Anton and Loach[11] by mixed condensation. 4-Carboxybenzaldehyde (1.0 g) and 4-tolualdehyde (4.0 g) were heated in propionic acid (170 cm^3) until the solvent began to reflux. Pyrrole (2.7 g) was added and the mixture refluxed for 30 min. After cooling overnight the solid material was filtered and washed with methanol and hot water and chromatographed on alumina. After elution of TPP the required compound passed down the column and was collected. The solvent was removed under reduced pressure and the solid dried at 373 K under vacuum. Samples of the above product were analysed by electrophoresis in aqueous medium (pH 7.0, NaCl 1 mol dm^{-3}), and it was found that the isolated product was a mixture of which the predominant component possessed a single negative charge but that there was also a significant quantity (*ca.* 20%) of the dicarboxy compound. Zinc was inserted as for $ZnTCPP^{4-}$.

$ZnMPyP^+$ was prepared by the method of Little *et al.*[12] Pyridyl tritolylporphyrin was prepared by refluxing for 1 h 1.5 g of pyridinecarboxyaldehyde with 5.06 g of 4-tolualdehyde in 187.5 cm^3 of propionic acid containing pyrrole (3.78 g). After cooling overnight the solid was filtered and washed with methanol and left to dry at 100 °C for 1 day. This compound was dissolved in chloroform and chromatographed on alumina to remove TTP. The residue was redissolved in chloroform and refluxed with a saturated solution of zinc acetate in methanol until the absorption band situated at 650 nm disappeared (*ca.* 2 h). After cooling, the solvent was removed under reduced pressure and the residue stirred with water (60 cm^3) at 373 K 1 h. Undissolved solid was removed and washed with warm water (100 cm^3). The solid was dried for 3 days at *ca.* 373 K, then rechromatographed on alumina with $CHCl_3$ as eluent. Three fractions were collected. The first fraction contained the required product, the second fraction was a zinc chlorin and the third fraction contained an unidentified product. After evaporation of the solvent methylation was achieved by stirring the compound with a large excess of methyl iodide at room temperature for 3 days. The final product was isolated by filtration and dried under vacuum. It was sparingly soluble in water but dissolved in ethanol and this solvent was used for all studies with this compound.

Solutions for steady-state irradiation experiments contained a zinc porphyrin at a concentration such that the optical density at the irradiation wavelength ($\lambda = 565 \pm 5$ nm) was 0.5 for a 1 cm pathlength. The solutions were prepared from triply distilled water, buffered to pH 6.9 with 0.01 mol dm^{-3} phosphate, and contained MV^{2+} (10 mmol dm^{-3}) and EDTA (10 mmol dm^{-3}). Irradiations were performed with an Applied Photophysics model U.V.30 quantum-yield reactor equipped with a high-radiance monochromator. The solutions were purged thoroughly with N_2 prior to irradiation and the light intensity was calibrated with a standard thermopile. The concentration of reduced MV^+ was monitored by absorption spectroscopy and the concentration of evolved H_2 was measured by gas chromatography.

Absorption spectra were recorded with a Perkin Elmer model Hitachi 200 spectrophotometer and all luminescence measurements were made with a Perkin Elmer MPF4 spectrofluorimeter. Fluorescence quantum yields were measured by the optically dilute method, as described previously, using ZnTPP as standard. Phosphorescence spectra and lifetimes were recorded in frozen glasses (glycerol/water, 1/3) at 77 K, as described in a previous paper.[13] Room-temperature flash-photolysis studies were made with conventional microsecond equipment using $KCrO_4$ filter to remove excitation light of $\lambda < 470$ nm. Triplet quenching rate constants were determined by measuring the triplet lifetime of the Zn porphyrin in the presence of a known concentration of quencher; at least four different concentrations were used for each study and the observed rate constants had a reproducibility of ±20%. All solutions for luminescence and flash-photolysis studies were outgassed by the freeze–pump–thaw method.

RESULTS AND DISCUSSION

SPECTROSCOPIC PROPERTIES

As reported previously[5] the zinc porphyrins are good candidates for use in solar-energy storage devices since they are capable of harvesting a reasonable fraction of the solar spectrum (*ca.* 30%). All the zinc porphyrins studied here absorb strongly in the visible region between 500 and 650 nm with two main Q bands, one at *ca.* 560 nm and the other at *ca.* 600 nm as shown in fig. 1. The Soret band is found between 420 and 430 nm. Although the absorption spectra of $ZnTMPyP^{4+}$, $ZnCPP^-$, $ZnTCPP^{4-}$ and $ZnTSPP^{4-}$ are similar we notice a shift of the absorption peaks to the red as the porphyrin becomes more positively charged. Because of the low solubility of the compound in water, we were obliged to study $ZnMPyP^+$ in ethanol solution instead of water, but it is well-known that $\pi \rightarrow \pi^*$ transitions are shifted to the red when polar solvents are used, so that we would expect an absorption shift of *ca.* 4 nm to the red if the compound were dissolved in water.

The fluorescence emission maxima of the five zinc porphyrins depend also on the nature of the water solubilising groups, and the spectra are represented in fig. 2. From these fluorescence maxima we have calculated that the singlet energies are 195 ± 2 kJ mol^{-1}. The phosphorescence emission measured at 77 K did not seem to be affected by the nature of the water-solubilising group in such a consistent manner. However, the accuracy of the phosphorescence emission measurements is not so high as for the fluorescence measurements, due to the need to use wide bandwidths so that minor variations in the emission maxima may be lost. However, the triplet energies have been calculated to be 156 ± 2 kJ mol^{-1}. Therefore, the type of substituent used to induce solubility in water appears to have very little effect upon the energy of the excited states of Zn porphyrins.

QUENCHING

Previously, we reported that the lifetime of the excited singlet state of $ZnTMPyP^{4+}$ determined in outgassed aqueous solution was very short ($\tau_S = 1.4$ ns), so that intermolecular reaction involving the excited singlet manifold was unlikely except at very high concentration of quencher.[5]

As shown in table 1 the other water-soluble zinc porphyrins also have very short singlet lifetimes, and concentrations of MV^{2+} and EDTA as high as 0.05 mol dm^{-3} exhibited no quenching effect upon the observed lifetime of lowest-energy excited singlet state of the metalloporphyrins. With the negatively charged porphyrins, some static quenching occurred at high concentration of MV^{2+} ($\geqslant 5 \times$ mmol dm^{-3}) so that, under such conditions, it was possible to observe a decrease of the fluorescence intensity of the porphyrins. This static quenching most probably reflects some degree of ion-pair formation as described for reaction between negatively charged zinc phthalocyanines and MV^{2+}.[7,8] In contrast to the singlet excited states, the triplet excited states of all the zinc porphyrins were long lived and the triplet lifetimes (τ_T) are collected in table 1. Addition of MV^{2+} resulted in a decrease in the triplet lifetimes as monitored by conventional flash photolysis, and the observed bimolecular quenching rate constants [$k(MV^{2+})$] are given in table 1.

The magnitude of these quenching rate constants is dependent upon the nature of the water-solubilising groups; there is a thousand-fold increase in $k(MV^{2+})$ upon changing from a positively charged periphery group to a negatively charged one. Since the general properties of the triplet excited state of the zinc porphyrins are not affected by the type of water-solubilising groups used, nor is there any spectral evidence to suggest static quenching at the low concentrations of MV^{2+} used for these studies, the differences observed for $k(MV^{2+})$ must be attributed to differences in the efficiency of the quenching mechanism. This quenching mechanism is believed to be predominantly electron transfer.

The scheme given below gives a simple representation of intermolecular electron transfer from the triplet excited state of a zinc porphyrin (*P) to MV^{2+}. The scheme is a general one and involves formation of an encounter complex within which there is virtually no binding energy between the reactants. The formation of such an encounter complex will be a diffusion-controlled process (k_{DIFF}) and, since the complex will be a very weak one, it will be reversible (k_{DISS}). Once formed, the complex

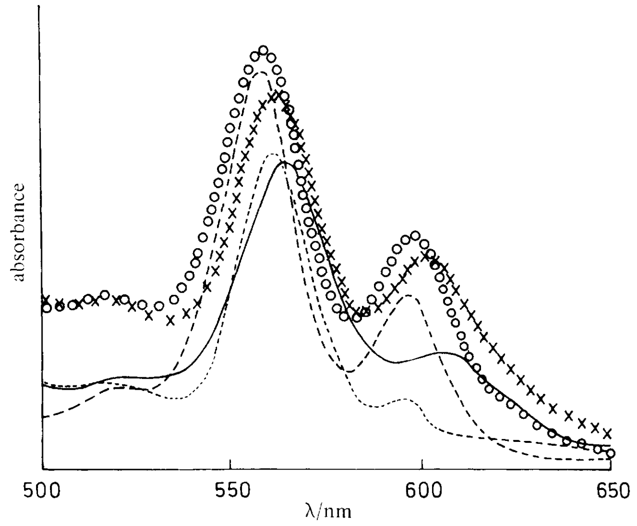


FIG. 1.—Absorption spectra: (——) ZnTMPyP^{4+}, (– – – –) ZnTSPP^{4-}, (○○○○) ZnTCPP^{4-}, (× × × ×) ZnCPP^{-}, (. . . .) ZnMPyP^{+}.

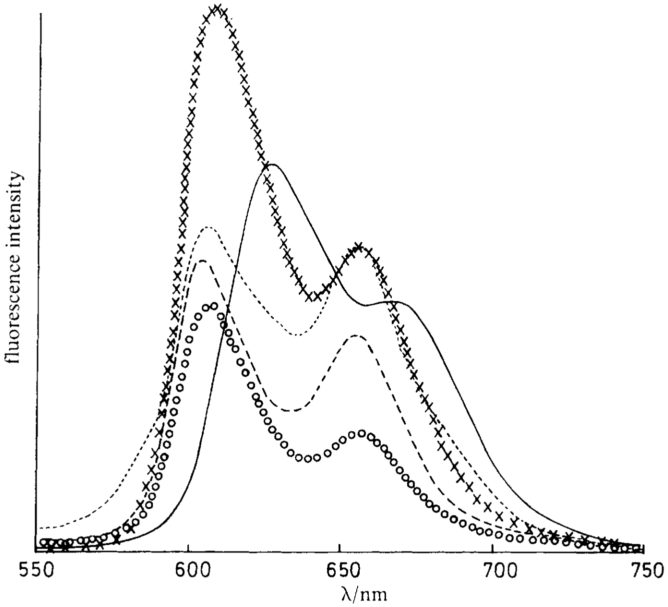


FIG. 2.—Fluorescence spectra: (——) ZnTMPyP^{4+}, (– – – –) ZnTSPP^{4-}, (○○○○) ZnTCPP^{4-}, (× × × ×) ZnCPP^{-}, (. . . .) ZnMPyP^{+}.

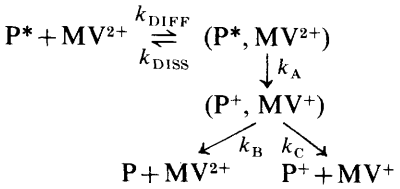
may undergo an electron-transfer process to form an ion-pair (k_A) wherein the redox products are caged by the solvent. The ion-pair may decay either to reform the ground-state reactants (k_B) or to form separated ion products (k_C). An important feature of this scheme is that formation of the ion-pair (k_A) is considered as an irreversible process. It could be argued that this step should be reversible, but in order to evaluate

TABLE 1.—PHOTOPHYSICAL PROPERTIES OF SOME ZINC PORPHYRINS AND THE BIMOLECULAR RATE CONSTANTS FOR QUENCHING THE TRIPLET EXCITED STATE WITH MV^{2+}; OBSERVED [$k(MV^{2+})$] AND CALCULATED FOR ZERO IONIC STRENGTH [$k(MV^{2+})^{\circ}$]

compound	E_S /kJ mol^{-1}	E_T /kJ mol^{-1}	τ_T(300 K) /μs	τ_T(77 K) /ms	τ_S(300 K) /ns	$k(MV^{2+})$ /dm^3 mol^{-1} s^{-1}	$k(MV^{2+})^{\circ}$ /dm^3 mol^{-1} s^{-1}
ZnTMPyP^{4+}	190	157	655	3.3	1.4	1.80×10^{7}	2.7×10^{5}
ZnMPyP^{+}[a]	197	154	570	2.5	—	2.14×10^{7}	2.1×10^{7}
ZnCPP^{-}	196	158	1470	—	—	1.04×10^{9}	3.0×10^{9}
ZnTCPP^{4-}	197	154	1300	1.4	1.6	1.3×10^{10}[b]	2.7×10^{10}
ZnTSPP^{4-}	198	156	1500	2.5	1.7	1.4×10^{10}[b]	2.9×10^{10}

[a] In ethanol solution; [b] ref. (4).

the individual rate constants involved in the overall scheme we have assumed that k_A is very much greater than the reverse step.



SCHEME

The rate of formation of the encounter complex (k_{DIFF}) can be calculated from the Debye expression for diffusional encounter between two ions of charges z_A and z_B[14]

$$k_{DIFF} = 4\pi r_{AB} D_{AB} N_A \, \delta/(\exp\delta - 1)$$

where

$$\delta = z_A z_B e^2/\varepsilon k T r_{AB}$$

and $r_{AB} = 1.0$ nm, $D_{AB} = 10^{-5}$ cm^2 s^{-1}. N_A is Avogadro's constant.

Now, as we have shown previously,[15] the standard free-energy change ($\Delta G^{\ominus}$) associated with the formation of a very weakly bound complex between charged ions can be calculated from the expression

$$\Delta G^{\ominus} = z_A z_B e^2/r_{AB}\varepsilon$$

where ε is the permittivity of the solvent. This free-energy change can be used to calculate the equilibrium constant for formation of the encounter complex (K)

$$K = k_{DIFF}/k_{DISS}$$

so that k_{DISS} can be obtained (table 2). However, note that the reactant molecules are not spheres, as assumed in the above model, and specific solvation terms are far from negligible. In fact, we might expect to find significant differences in the overall structure of the encounter complex (and the ion-pair) as the local charges on the porphyrin periphery are changed, and consequently all rate constants that have been derived from this treatment are subject to considerable error. Hopefully, the derived values will still reflect the overall trends inherent in the 'true system'.

With the exception of ZnMPyP$^+$, which was studied in ethanol solutions, there is

TABLE 2.—RATE CONSTANTS DESCRIBING FORMATION AND DECAY OF THE ENCOUNTER COMPLEX

compound	k_{DIFF} /dm^3 mol^{-1} s^{-1}	k_{DISS}/s^{-1}	P	k_{A}/s^{-1}
ZnTMPyP^{4+}	1.3×10^8	2.95×10^{10}	2.08×10^{-3}	6.1×10^7
ZnMPyP$^{+\,a}$	2.6×10^9	2.08×10^{11}	3.1×10^{-3}	1.7×10^8
ZnCPP$^-$	1.0×10^{10}	2.06×10^9	—	—
ZnTCPP^{4-}	3.0×10^{10}	1.3×10^8	0.90	11.7×10^8
ZnTSPP^{4-}	3.0×10^{10}	1.3×10^8	0.97	4.2×10^9

[a] In ethanol.

a steady decrease in k_{DISS} as the degree of electrostatic attraction between the reactants is increased. Thus, k_{DISS} for ZnTMPyP^{4+} is some hundred times greater than that found for ZnTSPP^{4-} or ZnTCPP^{4-}.

Now, the bimolecular triplet quenching rate constants [k(MV^{2+})] can be expressed in the form

$$k(\mathrm{MV}^{2+}) = \frac{k_{\mathrm{DIFF}} k_{\mathrm{A}}}{k_{\mathrm{A}} + k_{\mathrm{DISS}}}$$

so that k_{A} can be evaluated. However, the measured k(MV^{2+}) values are strongly dependent upon the ionic strength (μ) of the medium, and the calculated k_{DIFF} and k_{DISS} values refer to zero ionic strength. Consequently, the measured k(MV^{2+}) values have been corrected to zero ionic strength using the relationship

$$\log k(\mathrm{MV}^{2+}) = \log k(\mathrm{MV}^{2+})^{\circ} + 1.02\, z_{\mathrm{A}} z_{\mathrm{B}} \sqrt{\mu}$$

and the calculated values k(MV^{2+})$^{\circ}$ are given in table 1. The use of these values, together with the calculated k_{DIFF} and k_{DISS} values, allows calculation of k_{A}, and the derived values are given in table 2.

The derived k_{A} values refer to the rate of electron transfer from the triplet excited state of the zinc porphyrins to MV^{2+}. The probability of electron transfer (P) can be expressed in the form

$$P = \frac{k_{\mathrm{A}}}{k_{\mathrm{A}} + k_{\mathrm{DISS}}} = \frac{k(\mathrm{MV}^{2+})^{\circ}}{k_{\mathrm{DIFF}}}$$

and it can be seen from table 2 that the nature of the water-solubilising groups has a marked effect upon P.

In fact, P varies from 0.2% for ZnTMPyP^{4+} to 90% for ZnTSPP^{4-}, and inspection of the data provided in table 2 shows that this variation is due to the differences in k_{DISS}. The derived k_{A} values, although different for each metalloporphyrin, fall within a fairly narrow range, but the k_{DISS} values vary over a much wider range and this variation can be attributed to electrostatic factors. Where there is strong electrostatic attraction between the reactants, k_{DISS} is low and the probability of quenching is high. Thus the electrostatic factors that determine the stability of the encounter complex are of extreme importance in controlling the overall triplet quenching efficiency.

Since k_{A} refers to the rate of electron transfer, there should be a correlation between the derived k_{A} values and the overall standard free-energy change associated with the electron-transfer step ($\Delta G^{\ominus}_{\mathrm{ET}}$). This latter term can be calculated from the relevant redox potentials

$$\mathrm{P}^+ + \mathrm{e}^- \rightarrow \mathrm{P}^* \quad E^{\ominus}(\mathrm{P}^+/\mathrm{P}^*)$$

$$\mathrm{MV}^{2+} + \mathrm{e}^- \rightarrow \mathrm{MV}^+ \quad E^{\ominus}(\mathrm{MV}^{2+}/\mathrm{MV}^+)$$

and the redox potential of the triplet excited state of the zinc porphyrin [$E^{\ominus}(P^+/P^*)$] can be obtained by subtracting the triplet energy from the ground-state redox potential

$$E^{\ominus}(P^+/P^*) = E^{\ominus}(P^+/P) - E_T.$$

Ground-state redox potentials have been measured for some of the zinc porphyrins used in this study, but data are not available for the singly charged compounds. In general, positively charged substituents have little effect upon the redox potentials but negatively charged substituents lower $E^{\ominus}(P^+/P)$ by *ca.* 60 mV per substituent. Using these approximations, we have estimated $E^{\ominus}(P^+/P^*)$ values for $ZnCPP^-$ and $ZnMPyP^+$ (table 3).

Using the above redox potentials, we have calculated $\Delta G^{\ominus}_{\mathrm{ET}}$ for the process

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

and we have included a correction to account for any changes in electrostatic forces associated with the electron-transfer step. The data (table 3) are most interesting in that they show that as the overall standard free-energy changes become more negative, the rate of electron transfer becomes faster, which infers that the high probability for electron-transfer quenching (P) observed with the highly negatively charged zinc porphyrins is due to the high thermodynamic driving force available for the reaction. In contrast, with $ZnTMPyP^{4+}$ the overall $\Delta G^{\ominus}_{\mathrm{ET}}$ is positive, so that electron transfer should be prohibited on thermodynamic grounds. That electron transfer does take place for this compound, albeit at very slow rate, shows the limitation of such calculations.

TABLE 3.—REDOX POTENTIALS FOR THE TRIPLET STATES, STANDARD FREE ENERGY CHANGES FOR FORMATION OF THE ION-PAIR AND CALCULATED RATE CONSTANTS FOR IONIC SEPARATION AND RECOMBINATION OF THE ION-PAIR

compound	$E^{\ominus}(P^+/P^*)$/eV	$\Delta G^{\ominus}_{\mathrm{ET}}$/eV	k_{-C}/dm^3 mol^{-1} s^{-1}	k_C/s^{-1}
$ZnTMPyP^{4+}$	−0.44	0.12	6.4×10^8	1.9×10^{10}
$ZnMPyP^+$	−0.52	−0.04	2.6×10^9	1.0×10^{10}
$ZnCPP^-$	−0.62	−0.17	5.5×10^9	5.5×10^9
$ZnTSPP^{4-}$	−0.75	−0.35	1.3×10^{10}	1.7×10^7
$ZnTCPP^{4-}$	−0.82	−0.42	1.3×10^{10}	1.7×10^7

The ion-pair formed by the electron-transfer process (k_A) can dissociate to ground-state reactants (k_B), which may be a spin-forbidden step, or to separated ion products (k_C), and the partition between these two decay routes controls the yield of redox products. Once formed, the redox products will recombine *via* a diffusion-controlled reverse electron-transfer step k_{-C}.

$$P^+ + MV^+ \underset{k_C}{\overset{k_{-C}}{\rightleftharpoons}} (P^+, MV^+) \xrightarrow{k_B} (P, MV^{2+}).$$

The procedure outlined above for calculation of k_{DIFF} and k_{DISS} can be used to estimate k_{-C} and k_C since k_{-C} is diffusion-controlled, and the equilibrium constant (K) for formation of an ion-pair from the separated ion products can be expressed in the form

$$K = k_{-C}/k_C.$$

The derived values are collected in table 3, and again it can be seen that the nature of the water-solubilising groups has some effect upon the magnitude of k_C. As expected, strong electrostatic repulsion between the reactants within the ion-pair leads to a higher rate of dissociation. Now, the yield of redox products depends upon the partition fraction of the ion-pair

$$\phi_S = \frac{k_C}{k_B + k_C}$$

and, as we have shown previously,[5] ϕ_S can be related to the quantum yield for formation of separated products (ϕ_{ions})

$$\phi_{ions} = \phi_T \times \phi_Q \times \phi_S.$$

In this expression, ϕ_T refers to the quantum yield for formation of the triplet excited state of the zinc porphyrin (assumed to be 0.90 for all the porphyrins studied here) and ϕ_Q refers to the probability of quenching the triplet excited state of the porphyrin at a given concentration of quencher:

$$\phi_Q = \frac{k(MV^{2+})[MV^{2+}]}{k(MV^{2+})[MV^{2+}] + \tau_T^{-1}}.$$

The ϕ_{ions} values were measured by flash-photolysis techniques and are collected in table 4, together with the derived ϕ_S terms. These ϕ_S terms, together with the calculated k_C values, allow estimation of k_B (table 4).

TABLE 4.—EFFICIENCY OF CHARGE SEPARATION AND RATES OF NON-RADIATIVE DECAY FOR THE ION-PAIR

compound	$\phi_{ions} = \phi_{MV^+}$	ϕ_S	k_B/s^{-1}	$\Delta G_B^\ominus/eV$
$ZnTMPyP^{4+}$	0.75	0.83	1.34×10^9	−1.58
$ZnMPyP^+$	0.10	0.11	6.59×10^{10}	−1.55
$ZnCPP^-$	0.037	0.04	1.58×10^{11}	−1.48
$ZnTSPP^{4-}$	< 0.01	< 0.01	$> 2.67 \times 10^{11}$	−1.41
$ZnTCPP^{4-}$	< 0.01	< 0.01	$> 2.67 \times 10^{11}$	−1.34

The nature of the water-solubilising group has a marked effect upon the magnitude of ϕ_S. In fact, ϕ_S varies from 0.83 for $ZnTMPyP^{4+}$ to < 0.01 for $ZnTSPP^{4-}$ and $ZnTCPP^{4-}$. Thus, the use of a highly positively charged zinc porphyrin appears to favour formation of redox ions from the photoreduction of MV^{2+}.

Deactivation of the ion-pair to ground-state reactants (k_B) is a type of non-radiative decay and, as such, the rate of the process should depend inversely upon the energy gap separating the initial and final states. The energy gap refers to the amount of electronic energy that must be converted to vibrational degrees of freedom and can be calculated from the redox potentials of the reactants. Thus, the standard free-energy change associated with decay of the ion-pair to ground-state reactants ($\Delta G_B^\ominus$) was calculated from the $E^\ominus$ values for the processes

$$P^+ + e^- \rightarrow P$$
$$MV^+ \rightarrow MV^{2+} + e^-$$

and was corrected for any change in the electrostatic forces during the electron-transfer step. The calculated values are given in table 4, and it is seen that in all cases this process is highly exothermic. In fact, the calculated $\Delta G_B^\ominus$ values show that there is a substantial amount of electronic energy that must be dissipated in the form of heat, and if the system is subject to the Franck–Condon principle then this dissipation step may be relatively slow. It appears that quite small increases in $\Delta G_B^{\ominus}$ result in substantial decreases in k_B. Thus, the rate of deactivation of the ion-pair to ground-state reactants is restricted by the ability of the reactants to dissipate large amounts of vibrational energy. The zinc porphyrins are large planar molecules that are not readily amenable to geometry changes, so that the majority of the excess energy must be removed *via* the MV^{2+} molecule.

Overall, the above work has highlighted that a combination of electrostatic factors and free-energy driving forces can lead to favourable conditions for formation of separated ion products. With $ZnTMPyP^{4+}$ and MV^{2+}, the strong electrostatic repulsion between the reactants results in an unstable encounter complex but assists dissociation of the ion-pair, whilst the high redox potential for oxidation of ground-state $ZnTMPyP^{4+}$ ensures that there is virtually no thermodynamic driving force for formation of the ion-pair; however, once it is formed, the ion-pair cannot easily dissipate its large amount of electronic energy into vibrational degrees of freedom. When added together these factors favour poor triplet quenching rate

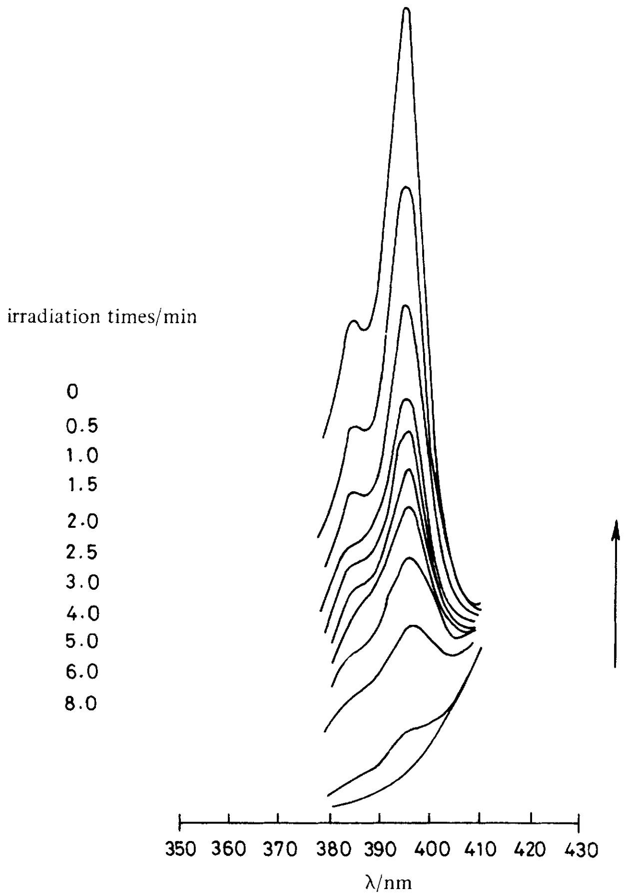


FIG. 3.—Absorption spectral profile showing the appearance of MV^{+} as a function of the irradiation time for the $ZnTMPyP^{4+}$ system.

constants but high yields of redox products. With highly negatively charged metalloporphyrins such as $ZnTSPP^{4-}$ and $ZnTCPP^{4-}$ the converse is true, and although these systems give high triplet quenching rate constants, the yields of redox products are very low.

PHOTOGENERATION OF HYDROGEN

Previously it was demonstrated that a weak reductant such as EDTA could intercept reverse electron transfer between P^+ and MV^+ by reducing P^+. Since the oxidised form of EDTA undergoes irreversible decomposition, this has the effect of stabilising MV^+. As such, irradiation of $ZnTMPyP^{4+}$ in aqueous solution at pH 6.9 containing MV^{2+} (10^{-2} mol dm^{-3}) and EDTA (10^{-2} mol dm^{-3}) resulted in a build-up in the concentration of MV^+, as shown in fig. 3. For this system, the rate of appearance of MV^+ was very fast, as shown by fig. 4, confirming the high efficiency for formation of redox products expected from a highly positively charged chromophore. In identical experiments both $ZnMPyP^+$ and $ZnCPP^-$ gave rise to formation of MV^+, although at much slower rates than found for $ZnTMPyP^{4+}$ (fig. 5). In contrast, irradiation of the highly negatively charged chromophores, $ZnTSPP^{4-}$ and $ZnTCPP^{4-}$, did not lead to reduction of MV^{2+}. Thus, the yields of MV^+ obtained from steady-state irradiations in the presence of EDTA as a sacrificial electron donor follow the order expected on the basis of the calculations outlined earlier.

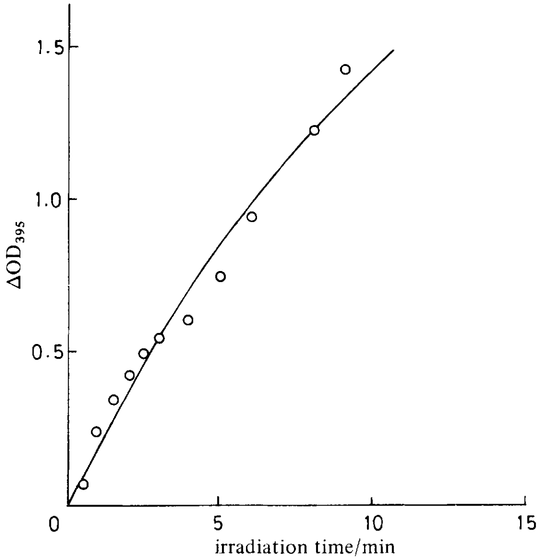


FIG. 4.—Rate of formation of MV^+ as a function of the irradiation time for the $ZnTMPyP^{4+}$ system. OD($ZnTMPyP^{4+}$, 1 cm) = 0.5.

Quantum yields for the formation of MV^+ ϕ_{MV^+} from the above systems were measured for irradiation at 567 ± 2 nm and are collected in table 4. The observed ϕ_{MV^+} values range from 0.75 for $ZnTMPyP^{4+}$ to < 0.01 for $ZnTSPP^{4-}$ and $ZnTCPP^{4-}$, and provide further substantiation for the hypothesis that strongly positively charged chromophores favour the photoreduction of MV^{2+} to MV^+.

It is well-established that colloidal dispersions of noble metals such as Pt or Pd are able to catalyse the exchange reaction between MV^+ and H_2O. Consequently,

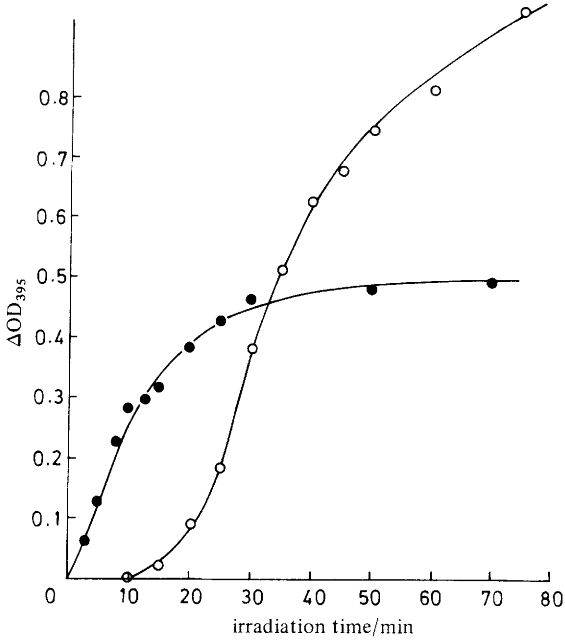


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FIG. 5.—Rate of formation of MV^+ as a function of the irradiation time for $ZnMPyP^+$ (—●—) and $ZnCPP^-$ (—○—). OD($ZnMPyP^+$, 1 cm) = 0.05, OD($ZnCPP^-$, 1 cm) = 0.5.

irradiation of the above systems in the presence of colloidal Pt allowed the reduction equivalence stored on MV^+ to be converted into H_2

$$2\,MV^+ + 2\,H_2O \xrightarrow{Pt} H_2 + 2\,MV^{2+} + OH^-.$$

With $ZnTmPyP^{4+}$ the quantum efficiency for formation of H_2, $\phi_{\frac{1}{2}H_2}$, was 0.60 at pH 5 and for short irradiation periods, so that almost all of the reduced MV^+ could be used for hydrogen production. Hydrogen was also obtained with $ZnMPyP^+$ and $ZnCPP^-$ chromophores, but no H_2 could be observed, under our conditions, with $ZnTCPP^{4-}$ and $ZnTSPP^{4-}$ as chromophore.

CONCLUSIONS

The above work has shown that the nature of the water-solubilising groups can have a drastic effect upon the efficiency of the metalloporphyrin photosensitised reduction of water to H_2. Using MV^{2+} as electron relay, optimum results were obtained with a highly positively charged metalloporphyrin, and the effects of the water-solubilising groups can be explained in terms of electrostatic factors and ground-state redox potentials. In fact, the high redox potential reported for $ZnTMPyP^{5+}/ZnTMPyP^{4+}$ couple suggests that the oxidised form should be capable of the oxidation of water to oxygen, in the presence of a suitable catalyst. Thus, with the $ZnTMPyP^{4+}/MV^{2+}$ system it may be possible to achieve complete cleavage of water into H_2 and O_2. Obviously, as regards a practical solar-energy storage device, it is not desirable to produce a mixture of hydrogen and oxygen since such mixtures are explosive and expensive to separate; instead, the gaseous products must be produced at remote sites so that the hydrogen can be collected. Before this can be achieved, however, it is necessary to use the oxidised form of $ZnTMPyP^{4+}$ to liberate O_2 from water and the feasibility of this process will be outlined in a later paper.

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