LUMINESCENCE OF PORPHYRINS AND METALLOPORPHYRINS VIII: LUMINESCENCE AND HYDROGEN PHOTOGENERATION FROM PORPHYRIN CONJUGATE DIACIDS

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Summary

Porphyrin conjugate diacids are formed by addition of two extra protons to the pyrrole nitrogen atoms of the porphyrin ring and the compounds derived from tetraphenylporphine absorb strongly at wavelengths above 600 nm. The absorption and fluorescence properties depend on inductive effects of any substituents on the phenyl rings. No phosphorescence was detected although the diacids show relatively long-lived triplet states at room temperature. The diacids photosensitize the dissociation of formic acid into hydrogen and CO_2 although the rates of hydrogen formation are slow.

1. Introduction

There have been innumerable reports describing luminescence [1] and photochemical [2] properties of porphyrins and metalloporphyrins in recent years and such compounds have found particular use in model systems for the storage of solar energy [3]. The photophysical properties of paramagnetic [1], diamagnetic [1] and non-metal [4] porphyrins have been described in some detail and there have been several theoretical models proposed [5 - 7] to account for their structure and luminescence behaviour. Rather surprisingly, little attention [8 - 10] has been given to the porphyrin conjugate diacids, as formed by adding two extra protons to the central nitrogen atoms:

$$H_2P + 2H^+ \rightleftharpoons H_4P^{2+} \tag{1}$$

Normally, diamagnetic metalloporphyrins have D_{4h} symmetry with near degeneracy of the a_{1u} and a_{2u} orbitals so that two strong absorption transitions (Q bands) are prominent in the visible region. This near degeneracy collapses for the metal-free porphyrins which show D_{2h} symmetry and a more complicated absorption profile in the visible region. On addition of two further protons to the pyrrole nitrogen atoms, the D_{4h} symmetry is restored and the absorption spectrum simplifies although the presence of these extra protons causes the porphyrin ring to become non-planar [11].

For the conjugate diacids derived from *meso*-tetraphenylporphyrins the Q absorption bands occur in the near-IR region [10] and the compounds are capable of collecting a large fraction of the solar spectrum (about 50%). Thus, they could be attractive photosensitizers and we have considered this point in respect of the photodissociation of formic acid. This reaction could become an important part of a solar energy storage device based on the intermediate storage of hydrogen via the photoreduction of CO_2:

$$CO_2 + H_2O \xrightarrow{h\nu} HCOOH + \tfrac{1}{2}O_2 \tag{2}$$

$$HCOOH \xrightarrow{h\nu} H_2 + CO_2 \tag{3}$$

2. Experimental details

The conjugate diacids of tetraphenylporphyrin (H_4TPP^{2+}), the sodium salt of *meso*-tetrakis(4-sulphonatophenyl)porphyrin (H_4TSPP^{2-}), the chloride salt of *meso*-tetrakis(N,N,N-trimethyl-4-aminophenyl)porphyrin (H_4TAPP^{6+}) and the chloride salt of *meso*-tetrakis(N-methyl-4-pyridyl)porphyrin (H_4TMPyP^{6+})
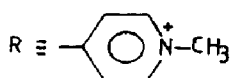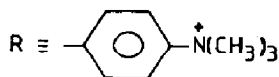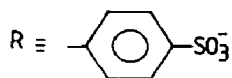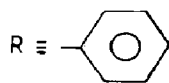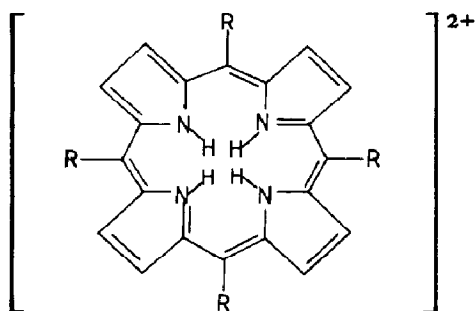
were prepared by dissolving the corresponding metal-free porphyrins [12] in dilute HCl solution (1 mol dm^{-3}). Formation of the diacids requires the stepwise addition of two protons to the central nitrogen atoms of the

porphyrin ring and the nature of the water-solubilizing groups on the porphyrin affect the pK values for both proton additions:

$$H_2P + H^+ \overset{pK_3}{\rightleftharpoons} H_3P^+ \qquad (4)$$

$$H_3P^+ + H^+ \overset{pK_4}{\rightleftharpoons} H_4P^{2+} \qquad (5)$$

For H_2TSPP^{4-} and H_2TAPP^{4+}, pK_4 occurs within 0.2 pH units of pK_3 and the pK_3 values are given in Table 1. For H_2TMPyP^{4+}, pK_3 occurs at about 1.6 whilst pK_4 has been located at about 0.6 [14]. In HCl solution (1 mol dm^{-3}) all three porphyrins exist in the form of the conjugate diacids although at this pH it must be expected that the sulphonic acid groups on H_4TSPP^{2-} will also be protonated [16]. Thus, the abbreviation used for this diacid does not truly represent the overall electronic charge on the molecule. The absorption spectra of the diacids in HCl solution (1 mol dm^{-3}) were in good agreement with values reported in the literature [15, 17]: H_4TSPP^{2-}, λ = 648 nm (log ϵ = 4.64), λ = 589 nm (log ϵ = 3.96), λ = 435 nm (log ϵ = 5.61); H_4TAPP^{6+}, λ = 643 nm (log ϵ = 4.47), λ = 591 nm (log ϵ = 3.69), λ = 436 nm (log ϵ = 5.51); H_4TMPyP^{6+}, λ = 640 nm (log ϵ = 4.28), λ = 589 nm (log ϵ = 4.12), λ = 444 nm (log ϵ = 5.50).

Absorption spectra were recorded with a Perkin–Elmer 554 spectrophotometer and luminescence spectra were recorded with a Perkin–Elmer MPF 4 spectrofluorometer. Fluorescence quantum yields were measured by the optically dilute method [18] using $ZnTMPyP^{4+}$ (ϕ_F = 0.02) as standard. The fluorescence spectra were corrected using the methods recommended by Argauer and White [19]. Excited singlet state lifetimes were measured by the time-correlated single-photon counting technique. Flash photolysis studies were performed with conventional equipment using outgassed solutions of the diacids in 1 N HCl.

Steady state irradiations were made with an Applied Photophysics 950 W xenon arc lamp filtered to remove IR light and light of λ < 620 nm. Evolved hydrogen was measured by gas chromatography and CO_2 was detected with lime water. The solutions (25 cm^3) were saturated with

TABLE 1

Photophysical properties of the conjugate diacids in 1 N HCl solution

Diacid	pK_3 [a]	f_Q	$f_{Q(0,0)}/$ $f_{Q(0,1)}$	k_F ($\times 10^7$ s^{-1})	ϕ_F	τ_S (ns)	k_Q ($\times 10^8$ s^{-1})	τ_T (μs)
H_4TSPP^{2-}	4.9	0.218	4.83	3.1	0.103	3.46	2.6	282
H_4TAPP^{6+}	3.6	0.202	3.74	3.5	0.071	2.00	5.2	268
H_4TPP^{2+}	4[b]	0.228	2.43	3.4	0.095	—	—	—
H_4TMPyP^{6+}	1.4	0.145	1.42	1.9	0.016	0.86	11.4	90

[a] From refs. 13 - 15.
[b] C_6H_6–HCl.

nitrogen and sealed into Pyrex cells of total volume 35 cm^3. Aliquots of the vapour phase (100 μl injections) were sampled by gas chromatography after various irradiation times.

3. Results and discussion

The absorption spectra of the various conjugate diacids are qualitatively similar; that of H_4TAPP^{6+} is shown in Fig. 1. These spectra can be described in terms of two fairly intense transitions in the near-IR region (Q(0,0) and Q(0,1)) and a strong transition around 440 nm (B(0,0)). The total oscillator strengths f_Q for the Q transitions are not too dissimilar for the various compounds but the location of the Q(0,0) transition and the relative strengths of the Q(0,0) and Q(0,1) transitions do depend on the nature of the periphery group. These values are collected in Table 1 and it is seen that, relative to the unsubstituted tetraphenylporphyrin H_4TPP^{2+}, H_4TSPP^{2-} and H_4TAPP^{6+} exhibit modest red shifts whilst H_4TMPyP^{6+} shows a slight blue shift. The ratio of oscillator strengths for the Q transitions also depends on the type of substituent and that of H_4TSPP^{2-} is much higher than those found for the positively charged compounds.

According to the four-orbital model, as developed by Gouterman [5], the a_{1u} and a_{2u} orbitals of H_4TPP^{2+} will be degenerate. The inductive effect of substituents added to the 4 position of the phenyl rings is normally more pronounced on the a_{2u} orbital and electron-donating substituents will raise the energy of this orbital by increasing its electron density. This leads to a decrease in the energy of the first absorption transition and an increase in its oscillator strength due to partial removal of the degeneracy. Thus, the observed absorption spectral changes can be understood in terms of the substituent inductive effect on the a_{2u} orbital. The same effect will influence the redox potential of the porphyrin and the dissociation constant of the diacid (the pK_3 values are given in Table 1). That a single effect is responsible
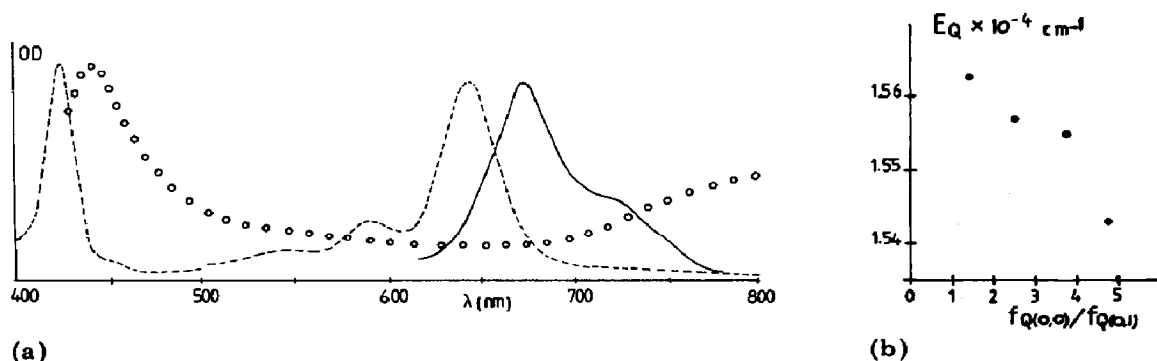

(a)   (b)

Fig. 1. (a) Absorption (— — —), fluorescence (———) and triplet–triplet absorption (○ ○ ○) spectra of H_4TAPP^{6+} in 1 N HCl; (b) plot of the energy E_Q of the first Q transition *vs.* the ratio $f_{Q(0,0)}/f_{Q(0,1)}$ of oscillator strengths for the two Q bands for the various diacids in 1 N HCl.

for influencing both the position and the intensity of the Q(0,0) transition is shown by Fig. 1(b).

For H_4TSPP^{2-}, dimerization and aggregation were evident, even at low concentrations (about 10^{-5} mol dm^{-3}) in 1 N HCl. The dimer, which does not fluoresce ($\phi_F < 10^{-3}$), shows a large red shift in absorption ($\lambda = 707$ nm (log $\epsilon = 4.75$), $\lambda = 668$ nm (log $\epsilon = 4.31$), $\lambda = 489$ nm (log $\epsilon = 4.21$)) which corresponds to an exciton coupling energy [20] of about 2200 cm^{-1}. This corresponds to a porphyrin face-to-face separation distance of about 3.2 Å. The other diacids appeared to be in the form of monomers since linear Beer's law plots were observed, at least up to 3×10^{-4} mol dm^{-3}. For the positively charged diacids, we would expect to observe an anion dependence of the absorption spectra since ion pairing should occur at high concentrations of electrolyte. Such effects have been recorded [8] for H_4TPP^{2+} whilst Table 2 gives absorption and fluorescence data for H_4TAPP^{6+} obtained in different acids (1 mol dm^{-3}). The haloacids give red shifts in the absorption spectra and low fluorescence quantum yields relative to $HClO_4$ solution. The relative fluorescence quantum yields are readily understood in terms of the heavy-atom effect but the slight dependence of the absorption spectrum on the type of anion used suggests that ion pairing occurs. On the basis of the observed fluorescence quantum yields, ion pairing might occur also with SO_4^{2-} and NO_3^- ions but absorption spectroscopy does not support this idea.

All the conjugate diacids showed moderately strong fluorescence and the corrected fluorescence spectrum observed for H_4TAPP^{6+} is given in Fig. 1. In all cases, the corrected fluorescence spectrum showed good mirror symmetry with the absorption transitions in the Q region although, relative to metalloporphyrins, quite large Stokes' shifts were found (about 600 cm^{-1}). This suggests that the singlet excited state is even more distorted from planarity than is the ground state. The fluorescence excitation spectra correlated well with the absorption spectra throughout the entire visible region. The fluorescence quantum yields ϕ_F and excited singlet state lifetimes τ_S, measured in dilute air-equilibrated 1 N HCl solution, are given in Table 1

TABLE 2

Absorption and fluorescence properties of H_4TAPP^{6+} in different acids (1 mol dm^{-3})

Acid	λ_{abs}(max) (nm)	λ_{fluo}(max) (nm)	ϕ_F [a]
$HClO_4$	640	663	0.125
H_2SO_4	639	664	0.103
HNO_3	639	664	0.098
HCl	643	669	0.071
HBr	643	668	0.010
HI	645	—	<0.0005

[a]±5%.

together with the calculated rate constant k_F for fluorescence. Clearly, k_F is related to the absorption spectral profile and, whilst raising the electron density on the a_{2u} orbital by electron-donating substituents (*e.g.* SO_3H) results in a substantial increase in $f_{Q(0,0)}$, the overall f_Q value is not significantly affected by the substituent. Thus, the various diacids show quite similar k_F values although that of H_4TMPyP^{6+} is lower than the others. The calculated k_F values are in good agreement with those determined from the measured fluorescence properties (*i.e.* $k_F = \phi_F/\tau_S$).

As shown in Table 1, H_4TSPP^{2-} and H_4TPP^{2+} show reasonably long excited singlet state lifetimes and quite high fluorescence yields whereas H_4TMPyP^{6+} shows a short τ_S and a low ϕ_F. Similar effects have been noted previously for the corresponding metal-free and zinc(II) porphyrins [21]. The measured lifetimes can be expressed in the form

$$\tau_S = \frac{1}{k_F + k_Q} \tag{6}$$

where k_Q is the combined rate constant for all non-radiative decay routes from the excited singlet state. The value of k_Q is seen to increase quite markedly along the series $H_4TSPP^{2-} \approx H_4TPP^{2+} < H_4TAPP^{6+} < H_4TMPyP^{6+}$ so that the observed decreases in ϕ_F and τ_S can be attributed to corresponding increases in the non-radiative processes (Table 1).

These non-radiative processes include contributions from internal conversion, quenching by chloride ions, oxygen and other impurities and intersystem crossing. No low temperature phosphorescence could be detected in 1 N HCl–glycerol (2:1) snows at 80 K and we estimate that, in all cases, $\phi_P < 10^{-3}$. The metal-free porphyrins also show very little phosphorescence. That the triplet manifold is populated on excitation to the singlet state was confirmed by room temperature flash photolysis studies using outgassed 1 N HCl. The excited triplet state absorbs strongly in the near-IR and visible regions (Fig. 1) and the triplet lifetimes τ_T are collected in Table 1. These lifetimes are long and approach those of the corresponding zinc porphyrins. In all cases, the triplet decay function correlated to a single-exponential component although repeated flashing of the samples resulted in bleaching of the chromophore. The measured triplet lifetime of H_4TMPyP^{6+} is clearly much shorter than those of the other diacids and, for this compound, a second long-lived transient was observed in the flash photolysis records. This effect is exemplified by Fig. 2 which shows the absorbance changes, measured at 470 nm, after flash excitation ($\lambda_{ex} > 550$ nm) of the various diacids. Only H_4TMPyP^{6+} shows a prominent second transient. This species, which had a lifetime approaching 1 s, was not identified but, on the basis of its absorption spectrum, it could be either the π radical anion or the phlorin. Presumably, it arises from reaction between the triplet state and some oxidizable impurity. This impurity is unlikely to be Cl^- ions since the redox potential of the $Cl_2^{-}|Cl^-$ couple is 2.3 V whilst the half-wave potential for one-electron reduction of H_4TMPyP^{6+} in 1 N HCl is 0.18 V [17] and a crude estimate of the dication triplet energy (based on H_2TMPyP^{4+}) is about 1.5 eV. Thus,
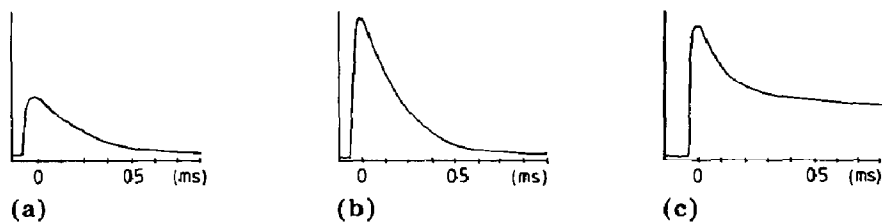
Fig. 2. Oscilloscope traces recorded at 470 nm after flash excitation of (a) H_4TSPP^{2-}, (b) H_4TAPP^{6+} and (c) H_4TMPyP^{6+} in 1 N HCl solution.

reaction between triplet dication and Cl^- ions is improbable ($\Delta G° = +58$ kJ mol^{-1}) and the corresponding singlet state reaction ($\Delta G° = +19$ kJ mol^{-1}) is also unlikely to occur. It is possible that the photoreaction involves a biphotonic process or oxidation of ground state H_4TMPyP^{6+} by triplet dication but such possibilities were not pursued.

Except for the absence of phosphorescence, the photophysical properties of the conjugate diacids resemble those of diamagnetic metalloporphyrins, such as the zinc(II) complexes. This suggests that the diacids could be useful photosensitizers, especially where strongly acidic conditions are required. In fact, if the diacid could be photoreduced by the addition of two electrons then the two extra protons on the pyrrole nitrogen atoms might be converted into hydrogen without the need of a noble metal catalyst:

$$H_4P^{2+} + 2e \longrightarrow H_2P + H_2 \tag{7}$$

Steady state irradiation of outgassed solutions of the various diacids resulted in only a bleaching of the Q absorption bands and no clear product absorptions could be detected. No hydrogen was evolved during these photoreactions and the presence of colloidal platinum had no effect. However, when an electron donor, such as ascorbate or formic acid, was present irradiation ($\lambda > 620$ nm) resulted in formation of a phlorin-type product. These products were identified by their characteristic absorption spectra; that recorded for photoreduction of H_4TMPyP^{6+} with formic acid is given in Fig. 3 and it compares well with that obtained by electrochemical reduction of H_4TMPyP^{6+} in 1 N HCl solution [17]. From these electrochemical studies [17] and by comparison of the observed absorption spectra with spectra of phlorins formed from diamagnetic metalloporphyrins [22], it was concluded that the diacid phlorins were present in the monoprotonated forms (e.g. H_5P^+). The phlorins were stable in the absence of oxygen but aeration of the solutions caused re-formation of the diacids with very little loss of chromophore. The phlorins did not evolve hydrogen on standing or on irradiation with visible light but, on addition of colloidal platinum, hydrogen formation was observed with H_4TAPP^{6+} and H_4TSPP^{2-} systems. The phlorin observed with H_4TMPyP^{6+} was unaffected by the presence of colloidal platinum (at least over several hours standing):

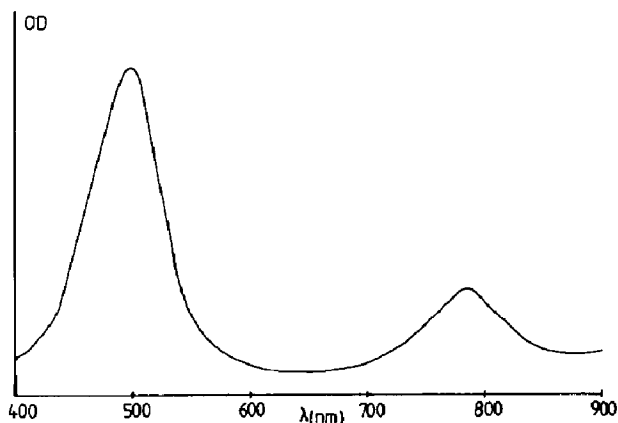$$H_4P^{2+} + HCOOH \xrightarrow{h\nu} H_5P^+ + CO_2 + H^+ \tag{8}$$
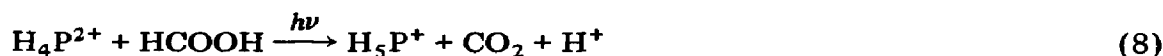
Fig. 3. Absorption spectrum of the product observed after irradiation of H_4TMPyP^{4+} in 1 N $HClO_4$ solution containing formic acid (0.5 mol dm^{-3}).

$$H_5P^+ + H^+ \underset{Pt}{\overset{Pt}{\rightleftharpoons}} H_4P^{2+} + H_2 \qquad (9)$$

Figure 4 shows typical hydrogen-evolving profiles for irradiation ($\lambda > 620$ nm) of the conjugate diacids in 1 N HCl containing formic acid (0.5 mol dm^{-3}) and colloidal platinum (about 5×10^{-5} mol dm^{-3}). Although no hydrogen was observed with H_4TMPyP^{6+}, quite efficient hydrogen generation was found with H_4TSPP^{2-}. During the latter photoreaction, CO_2 was evolved, as detected with lime water, so that the overall reaction scheme can be written

$$H_4TSPP^{2-} + HCOOH \overset{h\nu}{\longrightarrow} H_5TSPP^{3-} + CO_2 + H^+ \qquad (10)$$
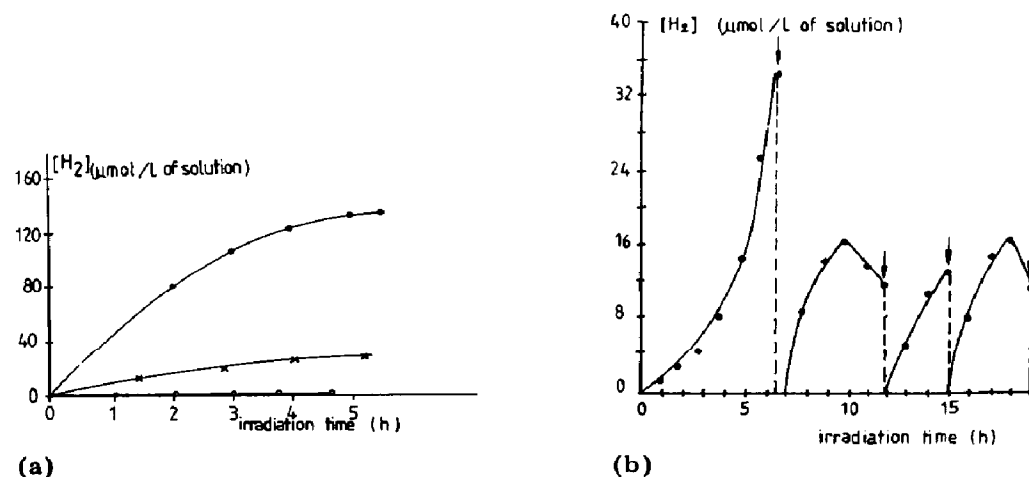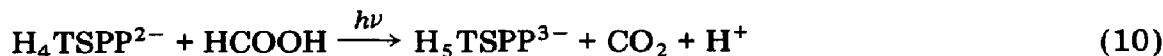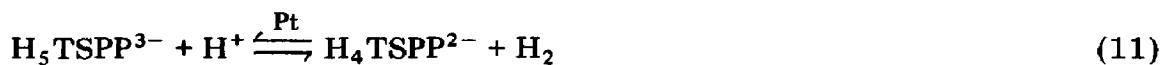

(a)

(b)

Fig. 4. (a) Yield of hydrogen as a function of irradiation time for photolysis of the various diacids in 1 N $HClO_4$ solution containing formic acid (0.5 mol dm^{-3}): —●—, H_4TSPP^{2-}; —×—, H_4TAPP^{6+}; —○—, H_4TMPyP^{6+}. (b) Effect of purging the solution with nitrogen to remove the evolved hydrogen for H_4TSPP^{2-}.

$$H_5TSPP^{3-} + H^+ \underset{Pt}{\overset{Pt}{\rightleftharpoons}} H_4TSPP^{2-} + H_2 \tag{11}$$

The overall reaction corresponds to the photodissociation of formic acid:

$$HCOOH \longrightarrow H_2 + CO_2 \qquad \Delta G^\circ = -38.5 \text{ kJ mol}^{-1} \tag{12}$$
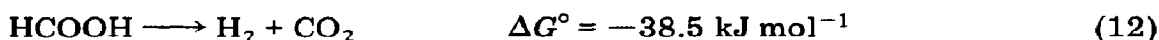
This reaction is thermodynamically downhill and the same products can be obtained by stirring formic acid with platinum or palladium adsorbed onto charcoal [23] at moderate temperatures (about 60 °C). Thus, the photo-reaction is of limited practical importance although formic acid has great potential as a "hydrogen carrier" in solar energy storage devices.

Both singlet and triplet excited states of the diacids were quenched by formic acid in 1 N $HClO_4$ solution. For H_4TAPP^{6+}, the singlet quenching rate constant was found to be 2.3×10^8 dm^3 mol^{-1} s^{-1}, by fluorescence spectroscopy, whilst the triplet quenching rate constant was 3×10^5 dm^3 mol^{-1} s^{-1}, as measured by flash photolysis. Under the conditions of the steady state irradiations ($[HCOOH] = 0.5$ mol dm^{-3}), the predominate reaction involves the triplet excited state of the diacids. Thus, the first step in the overall process can be written as

$$^*H_4P^{2+} + HCOOH \longrightarrow H_4P^{\cdot} + \dot{C}OOH + H^+ \tag{13}$$
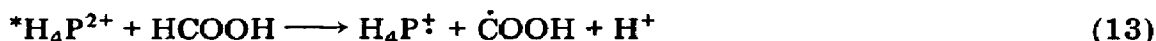
The formate radical has a pK transition at 1.4

$$\dot{C}OOH \overset{}{\rightleftharpoons} CO_2^{\cdot -} + H^+ \tag{14}$$

and in 1 N acid the protonated form will predominate. This species is a strong reducing agent ($E_{1/2} = -0.97$ V) [24] and it should be able to reduce both ground state and reduced diacids:

$$H_4P^{2+} + \dot{C}OOH \longrightarrow H_4P^{\cdot} + H^+ + CO_2 \tag{15}$$

$$H_4P^{\cdot} + \dot{C}OOH \longrightarrow H_5P^+ + CO_2 \tag{16}$$
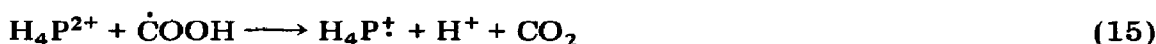
In addition, π radical anions tend to disproportionate rapidly in solution [22]

$$2H_4P^{\cdot} \underset{H^+}{\overset{H^+}{\rightleftharpoons}} H_4P^{2+} + H_5P^+ \tag{17}$$

so that the overall consequence is a one-photon–two-electron reduction of the diacid to the phlorin.

As shown by Fig. 4, hydrogen evolution ceased after about 5 h irradiation although there was virtually no loss of the chromophore at this stage. Removing the evolved hydrogen by flushing with nitrogen restored the hydrogen-evolving capacity, as shown by Fig. 4(b). By repeated flushing with nitrogen it was possible to convert a reasonable percentage (15%) of the formic acid into hydrogen and CO_2 at 15 °C (no hydrogen is formed in the absence of light at this temperature). This reaction, which took several days to accomplish, corresponds to a turnover number with respect to H_4TSPP^{2-} of about 5000 and even then the chromophore had not been destroyed. Thus, the diacid shows remarkable stability under such conditions.

These findings suggest that the limiting yields of hydrogen, as shown by Fig. 4, are set by thermodynamic barriers:

$$H_5P^+ + H^+ \xrightleftharpoons{Pt} H_4P^{2+} + H_2 \tag{18}$$

Although the reduction potentials of the diacids other than H_4TMPyP^{6+} are not known they probably decrease in the order

$$H_4TMPyP^{6+} > H_4TAPP^{6+} > H_4TSPP^{2-} \tag{19}$$
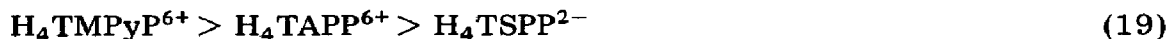
in line with those of the metal-free porphyrins [25]. This is the relative order of the observed rates of hydrogen formation.

Acknowledgments

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