Pulsed Irradiation of Water-soluble Porphyrins

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Nanosecond laser flash photolysis and pulse radiolysis have been used to characterise the excited states and radicals of *meso*-tetraphenylporphyrin tetrasulphonic acid as the tetrasodium salt (Na₄TPPS) and of *meso*-tetra-*N*-methylpyridylporphyrin as the tetra-*p*-toluenesulphonate (TMPyrP). After 347 nm irradiation, aqueous Na₄TPPS forms triplet states ($\phi_T = 0.76$) and photoionises monophotonically ($\Phi_I = 0.029$), while TMPyrP forms only triplets ($\Phi_T = 0.92$) and does not photoionise. The difference and corrected spectra of the triplet states and the semi-oxidised and semi-reduced radicals of these molecules have been obtained.

It has been known for over 70 years that porphyrins such as haematoporphyrin cause photodynamic activity in man.¹ In recent years² it has been established that certain porphyrins, including haematoporphyrin, are useful in the phototherapy of malignant tumours. In such treatment the tumour accumulates porphyrin and subsequent irradiation of the tumour can lead to marked regression. Currently the most used porphyrin is the so-called haematoporphyrin derivative containing, among other constituents, haematoporphyrin mono- and di-acetates.³ Several other porphyrin derivative for this important therapeutic use. These include Na₄TPPS and TMPyrP, which are the subject of the present paper. We have attempted to generate and to characterise the excited state and radical species of such porphyrins; clearly a complete understanding of the phototherapeutic process must depend on a thorough understanding of the role of such species.

EXPERIMENTAL

meso-Tetraphenylporphyrin tetrasulphonic acid [5,10,15,20-tetra(*p*-hydroxysulphonylphenyl)porphyrin] was prepared as its tetrasodium salt (25% yield) by the direct sulphonation of *meso*-tetraphenylporphyrin⁵ and was recrystallised from water + ethanol. *meso*-Tetra(*N*-methyl-4-pyridyl)porphyrin tetra-*p*-toluenesulphonate was obtained by the alkylation of *meso*-tetra(4pyridyl)porphyrin with methyl-*p*-toluenesulphonate (reflux in dimethylformamide overnight).⁶ The product crystallised on cooling: it was removed by filtration, washed with acetone and dried *in vacuo* (36%). These two porphyrins are both soluble in water because of the peripheral charged substituents: in one case the substituents are negatively charged, in the other they are positively charged.

The porphyrin radical ions were studied by pulse radiolysis using a 9-12 MeV Vickers linear accelerator, as previously described by Keene,⁷ with 1 cm or 2.5 cm quartz cells.

One-electron oxidations were carried out on aqueous 1×10^{-4} mol dm⁻³ porphyrin solutions containing 5×10^{-2} mol dm⁻³ NaN₃ or KCNS in 10^{-2} mol dm⁻³ phosphate buffer, pH 7.0. At this pH the porphyrins exist as the free base (H₂P). Pulse radiolysis of aqueous NaN₃ or KSCN generates, respectively, N₃ and (SCN)₂⁻ radicals *via* electron transfer from the primary OH radical:

$$N_3^- \text{ (or } 2 \text{ SCN}^-) + OH^- \rightarrow OH^- + N_3^- \text{ [or } (\text{SCN})_2^{--}\text{]}.$$
(1)

From earlier studies,⁸ it might be expected that N_3' or $(SCN)_2^{-1}$ would oxidise porphyrins according to: H P+N⁺ [or (SCN)⁻¹] \rightarrow H P⁺⁺ + N⁻ (or 2 SCN⁻) (2)

$$H_2P + N_3^{-1} [or (SCN)_2^{-1}] \rightarrow H_2P^{++} + N_3^{-1} (or 2 SCN^{-1}).$$
 (2)

Since OH[•] itself tends to form adducts with organic solutes, it is not an ideal oxidant. The solutions were saturated with N₂O to remove hydrated electrons (e_{ao}^{-}) by:

$$e_{a0}^{-} + N_2 O \rightarrow N_2 + OH^{-} + OH^{-}.$$
 (3)

Under such conditions $G(OH^{-})$ is currently believed to be 6.1.⁹ The concentration of radical cations produced was determined using air-saturated aqueous KSCN as the dosimeter $G[(SCN)_2^{--}] = 2.9$, $\varepsilon_{(SCN)_2^{--}}$ taken to be 7100 dm³ mol⁻¹ cm⁻¹ at 500 nm.¹⁰ The difference extinction coefficient of the porphyrin radical cation ($\Delta \varepsilon_{H_2P}^{-+}$) can be found from the expression:

$$\Delta \varepsilon_{\mathbf{H}_{2}\mathbf{P}^{'+}} = \varepsilon_{(\mathrm{SCN})_{2}} - \frac{2.9}{6.1} \frac{\Delta \mathrm{OD}_{\mathbf{H}_{2}\mathbf{P}^{'+}}}{\mathrm{OD}_{(\mathrm{SCN})_{2}^{'-}}}$$

where $\Delta OD_{H_2P^{++}}$ is the observed difference (radical – ground state) optical density and $OD_{(SCN)a^{-}}$ denotes the thiocyanate radical optical density obtained in air-saturated solution. The corrected extinction coefficient ($\varepsilon_{H_2P^{++}}$) is obtained by adding on the appropriate ground-state extinction (ε_G). Due to possible errors in the *G* value estimates used, the extinctions obtained are considered to be correct to $\pm 15\%$.

One-electron reduced porphyrin radicals were generated in 10^{-3} mol dm⁻³ phosphate buffer (pH 7.0) and in 10^{-1} mol dm⁻³ NaOH containing 10^{-4} mol dm⁻³ porphyrin and 10^{-1} mol dm⁻³ propan-2-ol. Radicals of similar porphyrins have been shown previously to have a pK value around 9.7.¹¹ Thus, at neutral pH, the radical H₄P⁻ is observed, while in 10^{-1} mol dm⁻³ NaOH the radical H₂P⁻⁻ is observed.

The porphyrin may be reduced directly by primary e_{aq}^{-} as in:

$$H_2P + e_{aq}^- \to H_2P^{-}.$$
 (4)

The interfering primary radicals OH[•] and H[•] are removed by adding propan-2-ol, as in:

$$(CH_3)_2 CHOH + OH^{-} \text{ (or } H^{-}) \rightarrow (CH_3)_2 COH + H_2O \text{ (or } H_2).$$
(5)

The propan-2-ol radical produced also reduces porphyrins by:

$$H_2P + (CH_3)_2COH \rightarrow H_2P^{-} + (CH_3)_2CO + H^+.$$
 (6)

Since this reaction takes place 10 times more slowly than does reaction (4), e_{aq}^{-} was removed by saturating with N₂O so that e_{aq}^{-} was ultimately replaced by an equivalent amount of (CH₃)₂COH. This simplified the growth kinetics of the porphyrin radical.

In 10^{-1} mol dm⁻³ NaOH, the propan-2-ol radical is deprotonated¹² to the anion (CH₃)₂CO⁻, which reacts with H₂P or various deprotonated forms of H₂P as in:

$$H_2P + (CH_3)_2CO^- \to H_2P^{--} + (CH_3)_2CO.$$
 (7)

The concentration of porphyrin radicals produced was estimated by monitoring the e_{aq}^{-} absorption at 700 nm ($\varepsilon = 18500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹³ in N₂-saturated solution containing no porphyrin.

The difference extinction coefficients ($\Delta \varepsilon$) of the radicals were obtained in N₂O saturated solutions using the expression:

$$\Delta \varepsilon_{\mathbf{H}_{2}\mathbf{P}} \cdot -_{(\text{or } \mathbf{H}_{3}\mathbf{P}^{\cdot})} = \frac{OD_{\mathbf{H}_{2}\mathbf{P}^{\cdot}} -_{(\text{or } \mathbf{H}_{3}\mathbf{P}^{\cdot})} \varepsilon_{\mathbf{a}_{q}} G(\mathbf{e}_{\mathbf{a}_{q}})}{OD_{\mathbf{e}^{-}(\mathbf{H}_{3}\mathbf{O}^{\cdot})} G(OH^{\cdot}) + G(H^{\cdot})}$$

where $G(OH^{-}) = 6.1$ in N₂O-saturated solution, $G(H^{-}) = 0.6$ in N₂O-saturated solution and $G(e_{aq}^{-}) = 2.7$ in N₂-saturated solution. $\Delta \varepsilon$ was corrected for ground-state absorption by adding on the appropriate ground-state extinction coefficient (ε_{G}) to give $\varepsilon_{H_{2}P^{-}(or H_{3}P^{+})}$. The extinctions in alkali may be slightly in error since the yield of OH⁻ under such conditions could be higher since OH⁻ will scavenge H⁺ from the spurs, thus enhancing the yield of e_{aq}^{-} reacting with H₂O.

Laser flash photolysis was carried out on aqueous $(5-10) \times 10^{-6}$ mol dm⁻³ porphyrin solutions in 10^{-2} mol dm⁻³ phosphate buffer, pH 7.4, using the 347 nm line of the frequency-doubled ruby laser previously described by McVie *et al.*¹⁴ Triplet-state extinction coefficients ($\varepsilon_{\rm T}$) were measured by the complete conversion method described earlier for protoporphyrin.¹⁵ For Na₄TPPS, the technique had to be modified to allow for interfering photoionisation, in the presence of which the observed difference optical density in argon-saturated solution consists of both triplet-state and the semi-oxidised radical absorption. Since the semi-oxidised radical forms by:

$$H_2 P \xrightarrow{n} H_2 P^{+} + e_{aq}^{-}$$
(8)

the concentration of H_2P^{+} and hence its ΔOD can be deduced by monitoring e_{aq}^- . When all the ground-state molecules have been converted to triplet or H_2P^{+} , the triplet concentration and ΔOD are readily derived so that $\Delta \varepsilon_T$ is given by the expression:

$$\Delta \varepsilon_{\rm T} = \frac{\Delta OD_{\rm observed} - ([e_{\rm aq}]\Delta \varepsilon_{\rm H_2P} + l)}{([\text{ground state}] - [e_{\rm aq}]) l}$$
$$[e_{\rm aq}^{-}] = [\Delta OD_{e_{\rm aq}}(720 \text{ nm})/\Delta \varepsilon_{e_{\rm aq}}(720 \text{ nm})]l$$

where

and *l* is the path length of material excited by the laser beam.
$$\Delta OD_{observed}$$
 is the maximum ΔOD observed in argon-saturated solution at complete conversion of the ground state to triplet or $H_{o}P^{+}$. ε_{T} was obtained by adding on ε_{G} .

Quantum yields of triplet formation (Φ_T) and of photoionisation (Φ_I) were obtained by the comparative technique¹⁶ using anthracene in cyclohexane ($\varepsilon_T = 64700 \text{ dm}^3 \text{ mol cm}^{-1}$ at 414 nm,¹⁷ $\Phi_T = 0.71$) as actinometer. This technique compares the concentration of porphyrin transient with the concentration of anthracene triplets formed by the same number of photons. At laser intensities low enough to ensure < 10% depopulation of the ground state,¹⁸ the quantum yield of porphyrin transient is given by:

$$\Phi_{\rm T} \text{ (or } \Phi_{\rm I}) = \frac{\Phi_{\rm T}^{\rm anth} \Delta \varepsilon_{\rm T}^{\rm anth} \Delta OD_{\rm X}}{\Delta \varepsilon_{\rm X} \Delta OD_{\rm T}^{\rm anth}}$$

where anth denotes anthracene and X denotes porphyrin triplet, porphyrin radical cation or e_{aq}^{-} .

The second-order rates for triplet quenching by oxygen $k_q^{O_2}$, were calculated from the equation:

$$k_{\rm q}^{\rm O_2} = \frac{k_2 - k_1}{[{\rm O}_2]}$$

where k_2 is the first-order rate constant for triplet decay in air-saturated solution, k_1 is the first-order rate constant for triplet decay in argon-saturated solution and $[O_2]$ is the oxygen concentration in air-saturated water = 2.65×10^{-4} mol dm⁻³ at 25 °C.¹⁹

The O_2 , N_2 , argon and N_2O gases used in these experiments were all high purity from the British Oxygen Company.

RESULTS

PULSE RADIOLYSIS OF Na₄TPPS

The semi-oxidised radical (H_2P^{+}) difference and corrected spectra in the 440-900 nm region shown in fig. 1 were generated with N₃ as oxidant $(k = 5 \times 10^9 \text{ dm}^9 \text{ mol}^{-1} \text{ s}^{-1})$. Using KSCN dosimetry the corrected extinction coefficient (ϵ) was found to be 25 150



FIG. 1.—Semi-oxidised radical (H_2P^{+}) of Na₄TPPS in water at pH 7.4. (a) Laser flash photolysis of O₂-saturated 10⁻⁵ mol dm⁻³ solutions: (\bigcirc) difference spectrum ($\varepsilon_{H_1P^{+}} - \varepsilon_G$); (\Box) corrected for ground-state absorption ($\varepsilon_{H_1P^{+}}$). (b) Pulse radiolysis of N₂O-saturated 10⁻⁴ mol dm⁻³ solutions containing 10⁻² mol dm⁻³ NaN₃: (\diamondsuit) difference spectrum ($\varepsilon_{H_2P^{+}} - \varepsilon_G$); (\bigtriangleup) corrected spectrum ($\varepsilon_{H_2P^{+}}$).

dm³ mol⁻¹ cm⁻¹ at 450 nm. The spectrum derived from OH[•] oxidation differed slightly from the ones above, probably indicating the presence of OH[•]-H₂P adducts. No transient attributable to H₂P^{•+} was observed when $(SCN)_2^{--}$ was used as the oxidant.

In argon-saturated solution the initial fast growth of the semi-reduced radical H_3P' , presumably generated by reaction (4), corresponds to a second-order quenching of e_{aq}^- by H_2P of 8.9×10^9 dm³ mol⁻¹ s⁻¹. This was followed by a slower growth, probably resulting from reaction (6), the corresponding rate constant being at least one order of magnitude less than that for reaction (4).

The growth kinetics of H_3P^{\cdot} were much simpler in N_2O -saturated solution, where only reaction (6) is observed. By assuming that the rate of decay of $(CH_3)_2COH$ in the absence of Na_4TPPS is negligible, the second-order rate constant was estimated as 2×10^9 dm³ mol⁻¹ s⁻¹ for this reaction. H_3P^{\cdot} decayed by mixed-order kinetics with a first half-life of 7 ms to a relatively stable product. Using e_{aq}^- as dosimeter, ε for H_3P^{\cdot} was found to be 45380 dm³ mol⁻¹ cm⁻¹ at 460 nm. This value was used to obtain the difference and corrected spectra given in fig. 2.

The semi-reduced radical at high pH (H_2P^{-}) was generated in N_2O -saturated 10^{-1} mol dm⁻³ NaOH by reaction (7). The second-order rate constant for growth of this

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radical corresponded to a value of 1×10^9 dm³ mol⁻¹ s⁻¹ for reaction (7). H₂P⁻⁻ decayed with a first half-life of 640 μ s to a permanent product absorbing in the visible region. The value for $\varepsilon_{H_2P^{--}}$ of 22000 dm³ mol⁻¹ cm⁻¹ at 460 nm was used to derive the difference and corrected spectra shown in fig. 3.

PULSE RADIOLYSIS OF TMPyrP

No semi-oxidised radical absorption was observed for this molecule with N_3° as the oxidant. Because of the results described previously for Na_4 TPPS, experiments using OH[•] or (SCN)₂⁻ as oxidants were not attempted.



FIG. 2.—Semi-reduced radical (H₃P[•]) of Na₄TPPS in water at pH 7.0. Pulse radiolysis of N₂O-saturated 10^{-4} mol dm⁻³ solutions containing 10^{-1} mol dm⁻³ propan-2-ol: (O) difference spectrum (ε_{H_3P} ⁻- ε_G); (D) corrected for ground-state absorption (ε_{H_3P} [•]).



FIG. 3.—Semi-reduced radical (H₂P⁻⁻) of Na₄TPPS in 10⁻¹ mol dm⁻³ NaOH solution. Pulse radiolysis of N₂O-saturated 10⁻⁴ mol dm⁻³ solutions containing 10⁻¹ mol dm⁻³ propan-2-ol: (\bigcirc) difference spectrum $(\varepsilon_{H,P} - -\varepsilon_G)$; (\Box) corrected for ground-state absorption $(\varepsilon_{H,P} -)$.

The semi-reduced radical was studied using 7×10^{-5} mol dm⁻³ TMPyrP with 10^{-1} mol dm⁻³ propan-2-ol. In N₂O-saturated solutions the major process detected corresponded to a growth $(t_1 \approx 2 \,\mu s)$ to a permanent product. This is interpreted in terms of reaction (6), with a corresponding second-order rate constant of 5×10^9 dm³ mol⁻¹ s⁻¹. However, these observations were complicated by slower growth kinetics



FIG. 4.—Semi-reduced radical (H₃P[•]) of TMPyrP in water at pH 7.0. Pulse radiolysis of N₂O saturated 3.5×10^{-5} mol dm⁻³ solutions containing 10^{-1} mol dm⁻³ propan-2-ol: (O) difference spectrum ($\epsilon_{H,P} - \epsilon_G$); (\Box) corrected for ground-state absorption (ε_{H_*P} ·).

at certain values of λ (such as 500, 525, 575 and 600 nm). These may arise from the small yields of radicals other than (CH₃)₂COH in the system²⁰ reacting with this porphyrin. Thus, in order to obtain the spectrum of H_3P with least contamination from the slow growing product(s) the difference spectrum given in fig. 4 was measured soon after the pulse (2 μ s). The difference extinction ($\varepsilon_{H_1P_2}$) was determined at 480 nm where the slowly growing transient appeared not to absorb.

The ground-state absorption spectrum of TMPyrP in 10⁻¹ mol dm⁻³ NaOH indicated that the porphyrin was a mixture of HP- and P2-. The semi-reduced radical grew in with an apparent second-order rate constant of 6.3×10^9 dm³ mol⁻¹ s⁻¹ [reaction (7)]. The radical decayed $(t_{\frac{1}{2}} = 55 \ \mu s)$ to a relatively stable product. The apparent semi-reduced radical extinction coefficient was 42 300 dm³ mol⁻¹ cm⁻¹ at 480 nm and fig. 5 gives the difference and corrected spectra.



FIG. 5.—Semi-reduced radical (H_2P^{-}) of TMPyrP in 10^{-1} mol dm⁻³ NaOH. Pulse radiolysis of N₂O-saturated 7 × 10⁻⁵ mol dm⁻³ solutions containing 10^{-1} mol dm⁻³ propan-2-ol: (\bigcirc) difference spectrum $(\varepsilon_{H_2P}^{-} - \varepsilon_G)$; (\Box) corrected for ground-state absorption $(\varepsilon_{H_2P}^{-})$.

LASER FLASH PHOTOLYSIS OF Na_4TPPS

Following 347 nm excitation of argon-saturated Na₄TPPS solutions $[(0.5-10) \times 10^{-5} \text{ mol dm}^{-3}]$ a short-lived $(t_1 = 2.0 \ \mu\text{s})^{\dagger}$ species (A) was observed superimposed on a much longer-lived $(t_1 = 400 \ \mu\text{s})^{\dagger}$ species (B). The absorption of (A) increased linearly with laser intensity implying that it was formed by a monophotonic process. The short-lived, broad absorption spectrum peaking at 720 nm was quenched by N₂O suggesting that it was due to e_{aq}^{-3} .

Only part of (B), presumably the triplet, was efficiently quenched by O_2 $(k_{q^2}^{O_2} = 1.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$, to leave a residual absorption decaying by first-order kinetics $(k = 2.7 \times 10^3 \text{ s}^{-1})$. The difference spectrum of this residual absorption measured in O_2 -saturated solution 20 μ s after the laser pulse closely resembled that of the semi-oxidised radical generated by pulse radiolysis. Because much lower porphyrin concentrations could be used in laser flash photolysis, it was possible to obtain the H_2P^{+} difference and corrected spectra in the Soret region and these are shown in fig. 1.

The modified complete conversion technique described earlier gave a value for $\varepsilon_{\rm T}$ of 44250 dm³ mol⁻¹ cm⁻¹ at 440 nm. The ΔOD of triplet used in the $\Phi_{\rm T}$ calculation was measured by subtracting the small H_2P^{+} absorption observable in O_2 -saturated solution together with a contribution from the H_3P absorption formed in argonsaturated solution from the overall ΔOD observed in argon-saturated solution. Using the $\Delta \varepsilon_{\rm T}$ derived from the $\varepsilon_{\rm T}$ given above, $\Phi_{\rm T}$ was found to be 0.76 (±0.08). The quantum yield of $e_{\rm aq}^-$ formation monitored at 720 nm in argon-saturated solution was



FIG. 6.—Triplet-triplet spectrum of Na₄TPPS in water, pH 7.4. Laser flash photolysis of argon-saturated 10⁻⁵ mol dm⁻³ solutions: (O) difference spectrum ($\varepsilon_{\rm T} - \varepsilon_{\rm G}$); (D) corrected for ground-state absorption $(\varepsilon_{\rm T}).$



FIG. 7.—Triplet-triplet spectrum of TMPyrP in water, pH 7.4. Laser flash photolysis of argon-saturated 10^{-5} mol dm⁻³ solutions: (O) difference spectrum ($\varepsilon_T - \varepsilon_G$); (D) corrected for ground-state absorption $(\varepsilon_{\rm T}).$

0.023 (\pm 0.005). This value corresponds well with the semi-oxidised radical yield of 0.029 (\pm 0.005) observed in O₂ saturated solution. The full triplet-triplet difference and corrected spectra are shown in fig. 6.

LASER FLASH PHOTOLYSIS OF TMPyrP

Excitation of TMPyrP with 347 nm radiation at pH 7.4 in argon- or N₂O-saturated solution produced only one strong, long-lived ($t_1 = 120 \,\mu s$) transient. This species was quenched by O₂ with a diffusion-controlled second-order rate constant of 1.5×10^9 dm³ mol⁻¹ s⁻¹, implying that it was the triplet. Straightforward application of the complete conversion and the comparative methods yielded, respectively, $\varepsilon_T = 28\,600$ dm³ mol⁻¹ cm⁻¹ at 450 nm and $\Phi_T = 0.92 (\pm 0.06)$. The difference and corrected triplet spectra are given in fig. 7.

DISCUSSION

The very efficient formation of long-lived triplet states by Na₄TPPS ($\Phi_T = 0.76$; $t_{\frac{1}{2}} = 280 \ \mu s$) and TMPyrP ($\Phi_T = 0.92$; $t_{\frac{1}{2}} = 120 \ \mu s$) suggests that both of these compounds are good photosensitisers. While Na₄TPPS does have a lower Φ_T than TMPyrP, it also photoionises monophotonically ($\Phi_I = 0.029$) yielding the very reactive e_{aq}^- . Subsequent reactions of e_{aq}^- may occur, *e.g.* with O₂ to form the superoxide (O₂⁻) radical. We have observed that uro- and cupro-porphyrins also photoionise in aqueous solution.²¹

The fact that TMPyrP is not oxidised by N_3° emphasises the reluctance of this molecule to ionise. This difference in behaviour is not surprising when the polycationic nature of TMPyrP is compared with the polyanionic nature of Na₄TPPS. This implies that the different *meso*-substituents strongly influence the reduction potential of the porphyrin macrocycle. Thus in TMPyrP, electron density may to some extent be drawn away from the porphyrin ring towards the electron deficient *N*-methylpyridyl part, while for Na₄TPPS, the reverse is the case. This is not inconsistent with the reported reduction potentials of these porphyrins.²²

While we have not studied the fluorescence of these porphyrins in detail, that of TMPyrP is clearly much lower than that of Na₄TPPS. This may reflect either aggregation in aqueous solution for TMPyrP or a more rapid intersystem crossing from S₁ to T₁ which is consistent with the higher value of Φ_T obtained for this molecule.

The radical and triplet spectra are similar in the region up to 650 nm. Where measurements have been extended to longer wavelengths the semi-oxidised and semi-reduced radicals appear to have another absorption band at *ca*. 700 nm. The rate constants for reaction of TMPyrP and Na₄TPPS with e_{aq}^- , (CH₃)₂COH and (CH₃)₂CO⁻, along with the spectra of the semi-reduced radicals produced, compare well with information reported for other porphyrins.^{11, 23}

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