Resonance Stabilisation of Zinc Porphyrin π -Radical Cations

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> Pulse radiolytic oxidation of zinc tetrakis(hydroxyphenyl)porphyrins in neutral solution results in formation of the π -radical cations which decay via disproportionation over a few ms. In alkaline solution, the hydroxy groups are dissociated and for the ortho and meta isomers the rate of disproportionation is reduced relative to neutral solution due to Coulombic repulsion between the ions. In contrast, the para isomer shows a very long-lived π -radical cation ($t_{1/2} \approx 5$ s) in alkaline solution. This arises from resonance stabilisation associated with the ability of the substituent to push charge onto the porphyrin ring. The ortho isomer does not exhibit this effect owing to steric hindrance.

Recently, we reported upon the formation and stability of zinc(II) porphyrin π -radical cations in aqueous solution.¹⁻⁶ It was noted that the nature of the water-solubilising group attached to the porphyrin periphery had a pronounced influence on the stability of the π -radical cations. For zinc meso-tetrakis(4-sulphonatophenyl)porphine, the π radical cation³ had a half-life of ca. 6 s at pH 7 and the unsubstituted zinc tetraphenylporphine π -radical cation had a similar half-life in aqueous propan-2-ol.⁴ In marked contrast, it was found⁴⁻⁶ that the ortho, meta and para isomers of zinc tetrakis(Nmethylpyridyl)porphine gave short-lived π -radical cations. Typical lifetimes in neutral aqueous solution ranged from 200 μ s for the para isomer to 20 ms for the meta isomer. For these positively charged compounds, decay of the π -radical cations involved disproportionation to form a π -dication,⁶ which reacted with water to form isoporphyrin⁷ and meso-dihydroxyporphyrins.⁸ A further complication with the latter compounds concerns the tendency of the π -radical cations to complex with anions present in the solution.⁴ These drastic differences in reactivity of the π -radical cations are presumably connected with the ability of the water-solubilising group to donate electronic charge into the porphyrin ring. The negative charge associated with the sulphonate groups is not in conjugation with the porphyrin ring and it tends to be localised at the substituent site. The positive charge on the ortho and para N-methylpyridinium groups can be pushed onto the porphyrin ring and this seems to destabilise the π -radical cations.⁶ On top of this effect, there is the inductive effect of the substituent which affects both redox potential⁹ and reactivity¹⁰ of the porphyrin.

In order to evaluate such hypotheses in more detail, we have studied the one-electron oxidation of the isomeric zinc tetrakis(hydroxyphenyl)porphyrins [ZnT(HOP)P]. In neutral solution, the hydroxy groups are undissociated and the compounds are insoluble

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in water. At pH 12, deprotonation of hydroxyl groups renders the compounds watersoluble and, for the *para* isomer, the resultant negative charge can be pushed onto the porphyrin ring *via* charge resonance.

Experimental

The various ZnT(HOP)P compounds were prepared as before¹¹ and purified by extensive chromatography on silica gel. Water was purified in a Millipore Milli-Q system. All other materials were of the highest available commercial purity and were used as received except for colloidal RuO₂·2H₂O which was prepared as before.³

The general conditions of the pulse radiolysis experiments have been given before.^{4,6} The radiation source was a Febetron 705 accelerator which delivers single 50 ns pulses of 2 MeV electrons. The typical doses used were 560 rad/pulse. The optical detection system consisted of a 300 W Varian xenon lamp, a 2 cm path length sample cell, a Bausch and Lomb monochromator and a photomultiplier. The signals were analysed with a Tektronix 7612 recorder and processed with a PDP 11/34 computer. Cutoff filters were used to minimise photolysis of the solution by the analysing beam and all measurements were made at room temperature. Dosimetry was performed with a conventional thiocyanate oxidation procedure.^{4,6}

For reactions in neutral solution, the porphyrin (*ca.* $10^{-4} \text{ mol dm}^{-3}$) was dissolved in propan-2-ol (125 cm³) containing CCl₄ (5 cm³) and diluted with water (120 cm³) containing phosphate buffer (2×10⁻³ mol dm⁻³) at pH 7. Under these conditions, radiolysis of water results in formation of CCl₃O₂ radicals with G = 6.¹²

$$\begin{array}{r} H_2O & \rightarrow H' + OH' + e_{aq}^- + H_3O^+ + H_2 + H_2O_2 \\ e_{aq}^- + CCl_4 \rightarrow CCl_3^- + Cl^- \\ H' + CH_3CHOHCH_3 \rightarrow H_2 + CH_3\dot{C}OHCH_3 \\ OH' + CH_3CHOHCH_3 \rightarrow H_2O + CH_3\dot{C}OHCH_3 \\ CCl_4 + CH_3\dot{C}OHCH_3 \rightarrow CCl_3^- + HCl + CH_3COCH_3 \\ CCl_3^- + O_2 \rightarrow CCl_3O_2^- \end{array}$$

The same system can be made basic by addition of KOH $(10^{-2} \text{ mol dm}^{-3})$. However, most experiments under basic conditions were performed with N₂O-saturated aqueous solution at pH 12 (KOH) containing the porphyrin (*ca.* $10^{-4} \text{ mol dm}^{-3}$) and KBr $(10^{-2} \text{ mol dm}^{-3})$. Here, radiolysis of water forms Br₂⁻ radicals with G = 6 [ref. (13)]

$$e_{Aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + OH^-$$

 $OH^- + Br^- \rightarrow OH^- + Br^-$
 $Br^+ + Br^- \rightleftharpoons Br_2^-$

although the H^{\cdot} atoms (G = 0.6) may react with the porphyrin.

Steady-state radiolysis experiments were performed with identical solutions to the above using a $\text{Co}^{60} \gamma$ -cell delivering *ca*. 10 krad min⁻¹. The course of reaction was followed by adsorption spectroscopy.

Cyclic voltammetry was performed with a Rank E611 potentiostat driven by a purpose-built triangle-wave generator. A glassy carbon working electrode was used in conjunction with a Pt counter-electrode and a saturated calomel reference. The porphyrin was dissolved in either CH₂Cl₂ containing tetra-*N*-butylammonium chloride $(0.1 \text{ mol dm}^{-3})$ or aqueous KOH $(10^{-2} \text{ mol dm}^{-3})$ containing Na₂SO₄ $(0.1 \text{ mol dm}^{-3})$. The solutions (*ca.* $10^{-3} \text{ mol dm}^{-3}$) were saturated with N₂ prior to the experiment.

Results and Discussion

Previous work⁴ has shown that CCl_3O_2 radicals oxidise zinc porphyrins in neutral solution:

$$ZnT(HOP)P + CCl_{3}O_{2}^{-} \rightarrow ZnT(HOP)P + + CCl_{3}O_{2}^{-}.$$
 (1)

The resultant porphyrin π -radical cations absorb strongly in the near-i.r. region (600-750 nm).¹⁻⁶ By measuring the pseudo-first-order rate constant for appearance of the π -radical cation at 680 nm as a function of the total porphyrin concentration, bimolecular rate constants (k_1) for reaction (1) were determined (table 1). These derived values are all ca. 1.5×10^9 dm³ mol⁻¹ s⁻¹, showing that oxidation is efficient and essentially complete within 100 μ s of the pulse [fig. 1(*a*)]. The site of the hydroxy substituent has no real effect upon the efficiency of the oxidation process, although the absorption spectra of the π^2 -radical cations do show some small variance amongst the isomers (fig. 2).

As shown by fig. 1(b)-(d), the π -radical cations decay over *ca*. 4 ms. In each case, this decay process can be fitted to second-order kinetics and, by comparison with other metalloporphyrins,^{4,6} it most probably corresponds to disproportionation:

$$2 \operatorname{ZnT}(\operatorname{HOP})P^{+} \rightarrow \operatorname{ZnT}(\operatorname{HOP})P + \operatorname{ZnT}(\operatorname{HOP})P^{2+}.$$
 (2)

The second-order nature of reaction (2) was confirmed by varying the radiation dose so that the half-life of the π -radical cation could be related to its initial concentration. From the measured molar extinction coefficients of the π -radical cations at various wavelengths, bimolecular rate constants for reaction (2) (2k₂) were calculated (table 1). The derived values all lie in the range $(2.0 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ showing that the site of substitution has no effect upon the reactivity of the π -radical cation.

The porphyrin π -dications formed by reaction (2) are strong electrophiles and they react with water to form isoporphyrins⁷ and *meso*-dihydroxyporphyrins.⁸ Often, these products are unstable with respect to ring opening,^{6,8} and steady-state γ -irradiation of the various ZnT(HOP)P compounds in aerated aqueous propan-2-ol containing CCl₄ resulted in overall destruction of the porphyrin chromophore. Thus, the radiation chemistry of these compounds can be summarised by the following scheme:



In CH₂Cl₂ solution, the ZnT(HOP)P isomers exhibited a reversible oxidative wave in the cyclic voltammetry studies corresponding to formation of the π -radical cations. Half-wave potentials of 0.62, 0.73 and 0.75 V vs. SCE, respectively, were derived for the para, meta and ortho isomers. For all three compounds, the difference in half-wave potential between removal of the first and second electrons was 0.32 ± 0.04 V. Thus, in CH₂Cl₂ solution all the isomers should be stable with respect to disproportionation, whilst the para isomer should be the more easily oxidised. In fact, the half-wave potential for CCl₃O₂ (as calculated by comparison of the rate constants for oxidation of well characterised redox couples) is 1.52 V vs. SCE, so that the thermodynamic driving force for oxidation of ZnT(HOP)P is sufficiently large for the rate constant to be diffusioncontrolled in all three cases.

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compound	isomer	pН	k_1	k_3	$2k_2 \text{ or } 2k_4$
ZnT(HOP)P	ortho	7	116		22
	meta	7	147	_	21
	para	7	165		18
(HO)ZnT(OP)P ⁵⁻	ortho	12	_	110	5.4
	meta	12		140	6.7
	meta	13		_	6.3
	meta	14	_	_	8.0
	para	12	130	105	ь

Table 1. Rate constants^a for the formation and subsequent disproportionation of
the zinc porphyrin π -radical cations

^a Units, $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^b No decay, or decay too slow to be measured.



Fig. 1. Kinetic traces showing (a) formation and (b-d) decay of the zinc porphyrin π -radical cations in neutral solution as monitored at 680 nm; ZnT(HOP)P (ca. 10⁻⁴ mol dm⁻³) in aerated propan-2-ol-CCl₄-H₂O (pH 7) 125:5:120. Trace (e) was obtained after addition of KOH $(10^{-2} \text{ mol dm}^{-3})$ to the solution used to obtain (d).



Fig. 2. Absorption spectra of the various ZnT(HOP)P compounds in neutral (____) and alkaline (pH 12) (---) solution and of the π -radical cations measured at pH 7 (o_____) and pH12 (•_____). Solution conditions as given for fig. 1. (a) ortho, (b) meta, (c) para.

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The pulse radiolysis experiments were repeated for the para isomer in the presence of KOH $(10^{-2} \text{ mol dm}^{-3})$. Under such conditions, the bimolecular rate constant for oxidation of the porphyrin by CCl₃O₂ was found to be $(1.3 \pm 0.2) \times 10^9$ dm³ mol⁻¹ s⁻¹, similar to that found in neutral solution. However, the π -radical cation was much more stable than found at pH 7 and it did not decay over 400 ms [fig. 1(e)]. Thus, there is a remarkable decrease in the reactivity of this π -radical cation in alkaline relative to neutral solutions.

In basic solutions (pH \ge 12), the hydroxy substituents are deprotonated:¹⁴



so that the porphyrin attains an overall negative charge of $-4[ZnT(OP)P^{4-}]$. In addition, the colour of the solution changes from red to green and absorption spectra (fig. 2) show that the central zinc ion is complexed with an hydroxide ion.¹⁵ This complexation is characterised by a red shift in the porphyrin Q-bands and a change in the relative ratio of the oscillator strengths of the two Q-bands. The effect is especially pronounced for the para isomer, which exhibits a substantial absorption spectral change upon raising the pH to 12 (fig. 2).



O refers to the porphyrin ring

For the ortho and para isomers, complexation is essentially complete at pH 12, but the meta isomer is only fully complexed at pH 14. (Note, under basic conditions the porphyrins are photo-oxidised rapidly in aerated solution. For this reason, the CCl_3O_2 oxidation process should be used with caution.)

In alkaline aqueous solution at pH 12, the porphyrins are oxidised to the corresponding π -radical cations by Br₂⁻ and, again, the derived bimolecular rate constants (k_3) show that the reaction is efficient. Considering the Coulombic repulsion between the reactants, the k_3 values lie close to the diffusion-controlled rate limit (table 1). The absorption spectra of the oxidation products (fig. 2) were in keeping with their assignment as porphyrin π -radical cations and there was no spectral evidence to suggest that the oxidising equivalent resided on the substituent rather than being delocalised over the entire porphyrin molecule.

$$(HO)ZnT(OP)P^{s-} + Br_2^{-} \rightarrow (HO)ZnT(OP)P^{*-} + 2Br^{-}$$
(3)

(Because of the charge of the substituents, the oxidation products are not strictly π -radical cations, but this nomenclature is used to emphasise that the porphyrin ring has been oxidised.) In neutral solution, the various isomeric π -radical cations show similar absorption spectra, characterised by a fairly broad band centred at *ca*. 650-690 nm. For all isomers there is a weak shoulder at *ca*. 760 nm (fig. 2). In basic solution, absorption spectra recorded for the *ortho* and *meta* π -radical cations are similar to those found in neutral solution, but the molar extinction coefficients are lower. This is not the case for the *para* isomer since its absorption spectrum depends markedly upon pH. Increasing the pH to 12 causes a substantial bathochromic shift ($\lambda_{max} \approx 760$ nm) and a pronounced increase in molar extinction coefficient. Thus, the *para* isomer exhibits quite different absorption spectra in neutral and basic solutions for both the ground state and the π -radical cation.

The π -radical cations derived from the *ortho* and *meta* isomers decay over a few ms [fig. 3(a) and (b)] via second-order kinetics:

$$2(HO)ZnT(OP)P^{4-} \rightarrow (HO)ZnT(OP)P^{5-} + (HO)ZnT(OP)P^{3-}.$$
 (4)

The derived bimolecular rate constants for this disproportionation process $(2k_4)$ are collected in table 1 and, again, they show no dependence upon the position of attachment of the hydroxy substituent. The rate constants are about four times slower than found in neutral solution, presumably owing to the increased Coulombic repulsion in basic solution. For the *meta* isomer, the disproportionation rate constant did not change significantly when the pH was raised to 14. This suggests that axial ligation does not influence the reactivity of the π -radical cation to any real extent in this case.^{4,6} However, the $2k_4$ values are close to the diffusion-controlled limit so too much emphasis should not be placed on this point.

In basic solution, the π -radical cation derived from the *para* isomer decays very slowly [fig. 3(c)]. Its half-life is ca. 5 s at pH 12 and, presumably, it is set by reduction with impurities and radiolytic products (e.g. H₂O₂). This finding confirms the experiments performed in H₂O-CCl₄-KOH-propan-2-ol and shows the drastic increase in stability of the π -radical cation when the *p*-hydroxy substituent is deprotonated.

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Fig. 3. Kinetic traces showing decay of the π -radical cations in alkaline solution as monitored at 680 nm; ZnT(HOP)P (10⁻⁴ mol dm⁻³) in N₂O-saturated aqueous solution containing KBr $(10^{-2} \text{ mol dm}^{-3})$ at pH 12. (a) Ortho, (b) meta, (c) para.

At pH 12 (Na₂SO₄ 0.1 mol dm⁻³), cyclic voltammetry recorded for oxidation of the various compounds were not fully reversible. Approximate half-wave potentials derived for the three isomers gave $E_{1/2}$ values of 0.32, 0.66 and 0.42 V vs. SCE, respectively, for the para, meta and ortho isomers. These values again indicate that the para isomer is the more easily oxidised and, in fact, this compound has the lowest oxidation potential found for any water-soluble zinc porphyrin. Oxidation by $Br_2^- (E_{1/2} = 1.45 \text{ V vs. SCE})^{16}$ is thermodynamically favourable for all three isomers, and in view of the calculated ΔG° values (-76 to -109 kJ mol⁻¹) it is not too surprising that k_3 is close to the diffusion-controlled limit.

Overall, these results can be interpreted in terms of resonance stabilisation of the porphyrin π -radical cations. Thus, for the para isomer in basic solution, structures of the following type can be expected:



Here, the substituent increases electron density on the porphyrin ring and this effect seems to stabilise the π -radical cation against disproportionation. The meta isomer is unable to adopt such resonance structures since the negative charge on the substituent can only be delocalised around the phenyl ring. In principle, the ortho isomer should be able to push electron density onto the porphyrin ring via charge resonance, but steric



hindrance between the substituent and prophyrin ring prevents the required geometry being adopted.¹¹ Consequently, only the para isomer can effectively stabilise the π -radical cation by resonance hybridisation and such a simple effect leads to at least a 2000-fold increase in the half-life of the π -radical cation. In fact, at pH 12 the π -radical cation derived from zinc tetrakis(4-sulphonatophenyl)porphine has a half-life³ of only 6 ms so that the *para* hydroxyphenylporphyrin represents a genuine improvement on stability of the π -radical cation.

The low $E_{1/2}$ found for the *para* isomer (*cf.* ZnTSPP⁴⁻ where $E_{1/2} = 0.66$ V vs. SCE)³ suggests that this compound is unlikely to oxidise water to O₂ even in the presence of a good O₂-evolving catalyst. The thermodynamic driving force for O₂ evolution can be expressed in the form

$$\Delta G^{\circ} = -4F(0.32 - 0.99 + 0.059 \text{ pH}) \text{ kJ mol}^{-1}$$

so that water oxidation becomes allowed only at pH>11. Even then, some overpotential (*ca.* 100 mV) is required for efficient O₂ liberation on the surface of the catalyst and we might expect to observe water oxidation only at pH>13. The pulse radiolysis studies showed that the rate of decay of $p(HO)ZnT(OP)P^{4-}$ was unaffected by the presence of colloidal RuO₂·2H₂O at pH 12. Consequently, the bimolecular rate constant for any interaction between the π -radical cation and the catalyst particle must be less than $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In conclusion, the presence of a dissociated hydroxy group at the *para* position of the *meso* phenyls leads to a tremendous increase in the lifetime of the porphyrin π -radical cation. However, this effect is accompanied by a reduction in the half-wave potential for oxidation of the porphyrin such that the π -radical cation has no real capability for water oxidation. Taking these two effects into account suggests that the optimum zinc porphyrin for water oxidation is ZnTSPP⁴⁻ which has a fairly long-lived π -radical cation and a modest $E_{1/2}$. Raising the $E_{1/2}$ value results in a drastic decrease in the stability of the π -radical cation (as demonstrated by the *N*-methylpyridinium porphyrins).^{4,6} Increasing the stability of the π -radical cation reduces $E_{1/2}$ as shown by the present study. Fine tuning of the system might be attempted by replacing Zn^{II} with other cations, but the real benefits could be minor. Perhaps water oxidation can be realised with high-valence metalloporphyrins rather than porphyrin π -radical cations and we will report on such studies in a later paper.

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