On the One and Two-Electron Oxidations of Water-Soluble Zinc Porphyrins in Aqueous Media

Michael Neumann-Spallart and K. Kalyanasundaram*

Institut de Chimie Physique, Ecole Polytechnique Fedérative de Lausanne, Ecublens, CH-1015 Lausanne

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The one and two-electron oxidations of water soluble ionic zinc porphyrins (Zinc-tetra-methylpyridylporphyrin, ZnTMPyP, Zinc-tetra-p-sulphato-phenyl-porphyrin, ZnTPPS, and Zinc-tetra-p-carboxy-phenylporphyrin, ZnTPPC) leading to the porphyrin γ-cations and γ-dications have been investigated in water by electrochemical (cyclic voltammetry and controlled potential electrolysis) and chemical methods. The half-wave potentials for the oxidation are shown to be markedly dependent on the charge on the γ-substituents. While the one-electron oxidations for all these porphyrins are reversible, the dication formation leads to labile isoporphyrins as intermediates.

Introduction

Photodecomposition of water via photoredox reactions of the type

\[ \text{D + A } \xrightarrow{h\nu} \text{ D}^+ + \text{ A}^- \] (1)

\[ 2\text{ A}^- + 2\text{ H}_2\text{O } \xrightarrow{\text{Redox cat.}} 2\text{ A} + \text{ H}_2 + 2\text{ OH}^- \] (2)

\[ 4\text{ D}^+ + 2\text{ H}_2\text{O } \xrightarrow{\text{Redox cat.}} 4\text{ D} + \text{ O}_2 + 4\text{ H}^+ \] (3)

is receiving scrutiny [1–5] all over the world. Partial success has been achieved with photosensitizers such as Ru(bpy)_2^2+ [2], acridine dyes [3] and porphyrins [4].

Porphyrins are attractive as photosensitizers [4, 6, 10] due to their high light absorption in the visible region, long lifetime for their excited states and the ease with which they undergo photoredox reactions. Though the electrochemical studies of porphyrin redox chemistry have been rather extensive [6], they have almost exclusively been performed in non-aqueous aprotic media. Since we were interested in exploring the utility of porphyrins as photoredox sensitizers in water, we decided to investigate the one and two-electron oxidations directly in water. Earlier, we have demonstrated [4a] that water-soluble zinc porphyrins serve very well as photosensitizers for H2-evolution from water via reactions (1) and (2). Towards further exploration of their utility in reaction (3), herein, we describe our studies on one and two-electron oxidation of these porphyrins in water. Data are presented on the half-wave potentials, their spectra and electrochemical reversibility for one and two-electron oxidations of one cationic (ZnTMPyP) and two anionic (ZnTPPS and ZnTPPC) porphyrin systems.

Experimental

Zn Porphyrins ZnTMPyP(Cl−), ZnTPPS(Na+), ZnTPPC(Na+) were synthesized from free base porphyrins (Strem) according to procedure described earlier [4a]. While solutions of ZnTMPyP in water are stable on exposure to room light, the anionic porphyrins slowly decompose. Hence, the solutions of these porphyrins are preferably stored and handled in the dark.

Cyclic voltammetry (CV) and controlled potential electrolysis (CPE) studies were carried out using a Tacussel PRT 30-0.1 potentiostat.

For CPE measurements, a three compartment cell was used. 1 M Na2SO4 served as the support electrolyte. A cylindrical Pt-gauze electrode (3 x 1 cm) served as the working electrode. The coulometric cell constant was ~0.01 s⁻¹.

Results and Discussion

A. Cyclic voltammetry

All the three Zn porphyrins used in this study are highly charged, with ZnTMPyP having 4(+) charges and ZnTPPS, ZnTPPC both having 4(−) charges. Fig. 1 presents typical cyclic voltammograms for the first one-electron oxidation of the three porphyrins in water. Data on the half-wave potentials, anodic–cathodic peak separation and electrochemical reversibility for the first and second electron...
The values measured for the anionic porphyrins are within the range 0.75–0.85 V measured earlier [7] for similar Zn-porphyrins. The shift in $E_{1/2}$, with respect to the neutral Zn-porphyrin ZnTPP, is understandable in terms of the ionic charges carried by the water soluble derivatives. The anionic porphyrins are easier to oxidize and cationic porphyrins difficult to oxidize. For the introduction of four charges, the shifts in potentials are about 180–200 mV.

The first oxidation of the cationic derivative ZnTMPyP appears as a quasi-reversible system. It has a 60 mV peak separation at slow scan rates and it increases with increasing scan rates.

Assuming a value of $D = 1.0 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ and using the tabulated values of $\psi$ for various values of $AE$ of Nicholson [8], the heterogeneous $e^-$ transfer rate constant $k_0$ was computed to be $2.3 \times 10^{-3} \text{cm s}^{-1}$. This value is somewhat lower than those measured by Kadish et al. [9] for one-electron oxidation of metalloporphyrins. In distinct contrast to the ZnTMPyP derivative, the anionic Zn porphyrins ZnTPPS and ZnTPPC exhibit a rather large peak separation (115–150 mV) and for scan rates of 20 mV/V/s it is independent of the sweep rate. In the concentration range employed for the CV studies ($2-10 \times 10^{-4} \text{M}$) one would expect extensive aggregation phenomena. However, recent studies [9] have shown that, for all the three Zn-porphyrins under study, no evidence for aggregation was observed.

### Table I. Cyclic voltammetry data on Zn-porphyrin oxidation.

<table>
<thead>
<tr>
<th>Porphyrin/Medium</th>
<th>Charge</th>
<th>Electrode</th>
<th>$E_{1/2}(1)$, V</th>
<th>$\Delta E$ (mV)</th>
<th>rev./irrev.</th>
<th>$E_{1/2}(2)$, V</th>
<th>$\Delta E$ (mV)</th>
<th>rev./irrev.</th>
<th>$E_{1/2}(1)$-$E_{1/2}(2)$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPPS/H$_2$O</td>
<td>–4</td>
<td>Pt</td>
<td>0.87</td>
<td>130</td>
<td>reversible</td>
<td>1.14</td>
<td>100→200</td>
<td>reversible</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CP</td>
<td>0.87</td>
<td>80</td>
<td>reversible</td>
<td>1.14</td>
<td>80→140</td>
<td>reversible</td>
<td></td>
</tr>
<tr>
<td>ZnTPPC/H$_2$O</td>
<td>–4</td>
<td>Pt</td>
<td>0.80</td>
<td>150</td>
<td>reversible</td>
<td>$\geq 1.42$</td>
<td>$\geq 1.40$</td>
<td>irreversible</td>
<td>$&gt;0.60$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CP</td>
<td>0.80</td>
<td>130</td>
<td>reversible</td>
<td>$\geq 1.34$</td>
<td>$\geq 1.34$</td>
<td>part. rev.</td>
<td>$&gt;0.16$</td>
</tr>
<tr>
<td>ZnTMPyP/H$_2$O</td>
<td>+4</td>
<td>Pt</td>
<td>1.18</td>
<td>150</td>
<td>reversible</td>
<td>$\geq 1.34$</td>
<td>$\geq 1.34$</td>
<td>part. rev.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CP</td>
<td>1.18</td>
<td>60→100</td>
<td>reversible</td>
<td>$\geq 1.34$</td>
<td>$\geq 1.34$</td>
<td>part. rev.</td>
<td></td>
</tr>
<tr>
<td>ZnTPPC/CH$_2$Cl$_2$</td>
<td>0</td>
<td>Pt</td>
<td>1.03</td>
<td>75</td>
<td>reversible</td>
<td>1.34</td>
<td>1.34</td>
<td>reversible</td>
<td>0.31</td>
</tr>
<tr>
<td>Zn MosoP/γ-ButCN</td>
<td>–2</td>
<td>Pt</td>
<td>0.74</td>
<td>75</td>
<td>reversible</td>
<td>1.21</td>
<td>1.21</td>
<td>reversible</td>
<td>0.47</td>
</tr>
<tr>
<td>Zn Haemato/γ-ButCN</td>
<td>–2</td>
<td>Pt</td>
<td>0.77</td>
<td>75</td>
<td>reversible</td>
<td>1.21</td>
<td>1.21</td>
<td>reversible</td>
<td>0.44</td>
</tr>
<tr>
<td>Zn deutero/γ-ButCN</td>
<td>–2</td>
<td>Pt</td>
<td>0.84</td>
<td>75</td>
<td>reversible</td>
<td>1.28</td>
<td>1.28</td>
<td>reversible</td>
<td>0.44</td>
</tr>
<tr>
<td>Zn Copro/γ-ButCN</td>
<td>–4</td>
<td>Pt</td>
<td>0.81</td>
<td>75</td>
<td>reversible</td>
<td>1.29</td>
<td>1.29</td>
<td>reversible</td>
<td>0.48</td>
</tr>
</tbody>
</table>

* All $E_{1/2}$ values are with respect to NHE;
+ range of $\Delta E$ values reported are for scan rates 10–200 mV s$^{-1}$,
Fig. 2. Cyclic voltammetry of anionic Zn porphyrins in 0.1 M Na₂SO₄/H₂O with a carbon paste electrode (0.56 cm²). Scan rates for ZnTPPS and ZnTPPC are 100 mV/s.

Fig. 2 presents cyclic voltammograms covering a wider scan range, beyond the first oxidation. While the second oxidation wave appears reversible for the sulfonated ZnTPPS derivative (at least on fast scan rates), the second electron oxidation is totally irreversible for the carboxy derivative ZnTPPC. Extensive loss of the porphyrin due to this irreversibility is observed after a few scans. The characterisation of the second electron oxidation in aqueous media is also made difficult due to high background at elevated potentials. So except for the case of ZnTPPS, the $E_{1/2}$ (2) values quoted in Table I, are lower bounds, as estimated from the onset of the cathodic waves. For ZnTPPS and ZnTMPyP, $|E_{1/2}(2) - E_{1/2}(1)|$ are in the range of 250 ± 50 mV, as has been observed for most metalloporphyrins.

The oxidation of metalloporphyrins such as Zn or Mg have been characterized [10] as porphyrin ligand oxidations leading to $II$-cation and $II$-dication, the latter being good electrophiles react in nucleophilic solvents such as water or methanol, with the solvent yielding meso-substituted isoporphyrins. Such reactions would account for the irreversibility of the second oxidation waves in aqueous media. As will be shown later, spectral examination of the oxidation products obtained by CPE at potentials beyond $E_{1/2}(1)$ do show good similarity to the spectra of isoporphyrins.

B. Chemical Oxidations

Towards spectral characterisation of the one and two-electron oxidation products, the oxidation of Zn porphyrins in water was also examined with a wide range of chemical oxidants. Oxidants employed were Fe³⁺, Br₂/H₂O, Cl₂/H₂O, PbO₂ and S₂O₈²⁻. The distinctive feature of these porphyrins is their good solubility in water (> 1 x 10⁻³ M) over a wide pH range and strong absorptions in the visible region, ZnTMPyP: $ε_{432} = 1.8 x 10^6$ and $ε_{569} = 1.6 x 10^4$; ZnTPPS: $ε_{420} = 2.22 x 10^5$ and $ε_{585} = 0.72 x 10^4$; ZnTPPC: $ε_{420} = 1.6 x 10^5$ and $ε_{554} = 1.15 x 10^4$. As has been noted earlier [11], we have observed these porphyrins to demetallate to give the diacid form of the metal free porphyrin under very acidic conditions ZnTMPyP pH < 1.0; ZnTPPS pH < 3.0 and ZnTPPC pH < 1.0. In the case of the Na salt of ZnTPPC, the carboxyl group being a weak acid, at pH < 6.0, there is slow conversion of the ZnTPPC salt to the free acid (-COOH) of the ZnTPPC and the free acid due to its limited solubility slowly (over a few hours) comes out of solution.

The behaviour of the two anionic porphyrins ZnTPPS and ZnTPPC towards various oxidants was quite similar. Oxidation with reagents such as Fe³⁺, PbO₂ and Cl₂-water (at very low concentration, at stoichiometric levels) all yield the green monocation radical of the porphyrins. Spectral features of the ZnTPPS⁺ cation obtained via Cl₂-water oxidation is shown as insert in Fig. 3. The $II$-cation radical of the soluble derivatives shows striking similarity to that derived from ZnTPP, viz. ZnTPP⁺, with a broad absorption rising below 700 nm [6a]. The estimated extinction coefficients for the absorption maxima in nm and at isobestic points are as follows:

ZnTPPS⁺: 680 ($ε = 2700$) 538 ($ε₁ = 3100$) 568 ($ε₁ = 3100$) 596 ($ε₁ = 3120$),
ZnTPPC⁺: 680 ($ε = 3060$) 602 ($ε₁ = 4500$) 568 ($ε₁ = 6500$) 580 ($ε₁ = 4400$) 534 ($ε₁ = 4150$).

Oxidation of the two anionic porphyrins either with Br₂-water or Cl₂-water (high concentration) gave, however, a stable orange-yellow product. The Br₂-oxidation product has maxima at 830 nm ($ε = 5200$), 750 nm, 460 nm ($ε = 15.600$), 406 and at 346 nm, while the Cl₂-oxidation product has maxima at 860 nm ($ε = 5200$), 780 nm sh, 592 nm, and 550 nm. Since these products are stable (as compared to isoporphyrins) we attribute them to halogenated derivatives of the porphyrins. Oxidation with Cl₂ in DMF, however, gave the isoporphyrin, as treat-
ment of this product with KI yielded the ZnTPPS back. As mentioned earlier, “isoporphyrins” are meso-substituted products arising from the attack of the solvent on the dications and these are characterized [10 b] by strong absorptions in the near IR region (maxima around 850 nm).

Oxidation of ZnTMPyP in H$_2$O with K$_2$S$_2$O$_8$ yields the monocation (partial oxidation only). Attempts to achieve complete oxidation with excess S$_2$O$_8^{2-}$ lead to slow demetallation. Oxidation with PbO$_2$ yielded an isoporphyrin derivative (absorption maxima at 840, 760 and 438 nm). The isoporphyrin so derived is unstable and slowly reverts back to the porphyrin with a half-life of about 100 min. Oxidation with Br$_2$ or Cl$_2$-water yielded the halogenated derivative.

In the light of half-wave potentials listed in Table I, efficient formation of the monocation (instead of dications or isoporphyrins) with strong oxidants such as Cl$_2$-water or PbO$_2$ is rather surprising. With both the oxidants, the relative yields of the monocation decrease in the order ZnTPPS > ZnTPPC > ZnTMPyP. The yields of the isoporphyrins are in the reverse order. The porphyrin dications can undergo two types of reactions

\[
\begin{align*}
ZnP^{2+} + \text{ZnP} & \rightarrow 2 ZnP^{+} \\
ZnP^{2+} + \text{solvent} & \rightarrow \text{isoporphyrins}
\end{align*}
\]

Presumably reaction (4) is more efficient for anionic porphyrins such as ZnTPPS while reaction (5) is dominant with porphyrins such as ZnTMPyP. CV data obtained for ZnTPPS at high scan rates are in accord with this scheme. The relative intensity of the wave corresponding to dication reduction increases significantly at 0.5–100 V s$^{-1}$.

C. Controlled Potential Electrolysis Studies

Controlled potential electrolysis of ZnTPPS and ZnTPPC in water at 0.89 V and 0.79 V respectively yields clearly the one-electron oxidation product. The estimated extinction coefficients for the 77-monocation absorption maxima are in good agreement with values derived from chemical oxidation studies. The electrochemically generated 77-cation of ZnTPPS, for example, is shown in Fig. 3. Oxidations at potentials higher than this value (even by 50 mV) however yielded increasing amounts of isoporphyrins along with the 77-cations. It may be recalled that isoporphyrins are meso-substituted porphyrins derived from attack of solvents (H$_2$O) on the 77-dications. In the light of \( E = E_{1/2}(2) - E_{1/2}(1) = 0.27 \text{ V} \), this is rather surprising. Presumably, the oxidation waves for the second electron-oxidations are much broader and extend into the first oxidation waves. The electrochemically generated 77-monocations can be reduced back (quantitatively to > 95\%) at 0.54 V.
Since we were interested in the reaction of II-cations with water, we also examined the thermal dark reduction of these II-cations in the absence of any external additives. It was observed that both the II-monocations and isoporphyrins slowly revert back to the porphyrin (the latter via deprotonation to the meso-hydroxy substituted porphyrin?) in the dark. At pH 6.36, the decay of the ZnTPPS monocation absorption (monitored at $\lambda = 680$ nm) follow roughly pseudo first order conditions with a lifetime of about 23 min. For the ZnTPPC monocation, the half-life is about 30 min at pH 6.5. To test the possibility that this thermal reduction of the II-cation is a reaction with water (or hydroxyl radicals—a reaction whose rate is pH dependent) we examined the lifetimes of II-cations generated electrochemically at lower pH values. Indeed oxidation with lowering of pH to 3.0 increases the II-cation lifetimes to over one hour. More detailed studies on the nature of this reaction of porphyrin II-cation radicals with water are under way.

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