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The rate of aerial oxidation of the title porphyrin (**1**) in dichloromethane (DCM), acidified with trifluoroacetic acid (TFA), was found to be first-order in **1** and second-order in TFA at low TFA concentrations, and second-order in both **1** and TFA at higher TFA concentrations. At the lower TFA concentrations, aerial oxidation gives the two-electron oxidised product **2**, while at the higher TFA concentrations, a porphyrin pi-cation radical **3** is formed. These results are rationalised by a kinetic scheme requiring, (i), preequilibrium involving transient formation of a porphyrin tetracation **4**, (ii), two-electron oxidation of **4** to a diprotonated oxidised porphyrin **5**, (iii) reaction of **5** with solvent water and (iv), conproportionation of **5** with **1** to generate **3**.

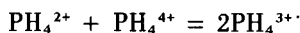
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Introduction.

Recently, we and others have reported the facile aerial oxidation of **1** [2]. The reaction produces reduced oxygen species [2] and has potential application *e.g.*, in fuel cells [3], in the treatment of waste waters [4], and in the generation of novel conducting materials [5].

In solutions acidified with TFA [6], a long-lived radical is generated with an esr spectrum rationalised as a dimer [7a,b] of the porphyrin pi-cation radical **3**. A preliminary uv/visible spectroscopic examination of this reaction [6a], indicated that the aerial oxidation was sensitive to the added concentration of TFA. Thus, at low TFA concentrations, the uv/visible spectrum was initially that of the unoxidised porphyrin dication **1** [8], changing over time to that of the two-electron oxidised species **2** [2a,6a]. At higher TFA concentrations, the uv/visible spectrum closely resembled that of meso-substituted metalloporphyrin pi-cation radicals [9], suggesting that in acidified solutions, direct one-electron oxidation does not take place.

We proposed [6a] that, on addition of acid, two-electron aerial oxidation takes place first, and that at higher TFA concentrations, the diprotonated two-electron oxidised product **5** undergoes a conproportionation reaction with the porphyrin dication **1** to yield the porphyrin pi-cation radical **3**:



In order for the potential applications of this reaction to be realised, we require more detailed knowledge of the aerial oxidation kinetics of porphyrin **1**, which this paper reports. We show that the rate of loss of porphyrin dication **1** is second-order in [TFA], and that at low [TFA], the rate of loss of **1** is first-order, while at higher [TFA], the rate of loss of **1** is second-order.

EXPERIMENTAL

Porphyrin **1** was synthesised and separated by a literature method [1a]. DCM and TFA were used as supplied (Aldrich). The

uv/visible spectroscopy was performed on a Cecil CE 5500 UV Spectrophotometer on a stock solution of **1** ($8 \times 10^{-6} M$) in DCM. Some (3 cm^3) of this solution was pipetted into a uv/visible cuvette. An aliquot of neat TFA was then added using an Eppendorf 4710 Varipipette, the cuvette shaken and immediately placed in the spectrophotometer cell compartment.

The decay of the porphyrin dication **1** B band (at 460 nm) was monitored over 200 seconds, the numerical value of the absorbance being recorded every 20 seconds. This was repeated at the particular TFA concentration using a fresh aliquot of the stock solution, and the mean taken of the absorbances recorded at 20 second intervals. Decay curves were similarly obtained by addi-

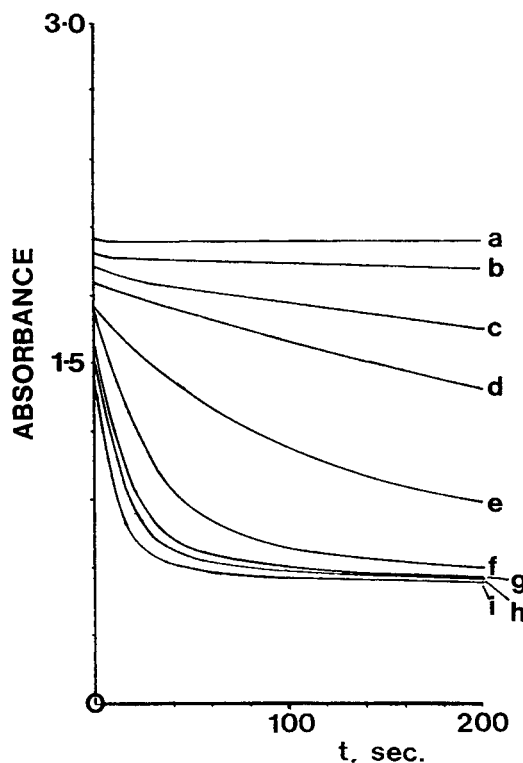


Figure 1. Decay of porphyrin dication (**1**) ($8 \times 10^{-6} M$) B band, over 200 seconds at different [TFA] in the cuvette; a, 0.04 M; b, 0.11 M; c, 0.21 M; d, 0.32 M; e, 0.42 M; f, 0.52 M; g, 0.62 M; h, 0.72 M; i, 0.81 M.

tion of decreasing amounts of TFA to fresh aliquots of the stock solutions. The temperature of the cell compartment was 25°.

Results.

Figure 1 shows the B band decay curves. The greater the concentrations of added TFA, the sharper the decline of the B band absorbance. The gradual change in the shape of these curves - i through to b - suggests a change in the mechanism of the aerial oxidation. This is inferred from uv/visible identification of the final products of aerial oxidation [6]. Thus, after 5 minutes, the porphyrin solutions with the higher concentrations of added TFA (*i.e.*, $>0.4M$ in the cuvette, curves i to f) gave a final uv/visible spectrum corresponding to a porphyrin pi-cation radical [9]. However, porphyrin solutions with lower concentrations of added TFA (*i.e.*, $<0.4M$ in the cuvette, curves e to b) gave a final uv/visible spectrum after 15 minutes, of the oxidised compound **2** [2a-6a].

At the porphyrin concentrations used, Beer's Law holds so that the absorbance of the B band is proportional to the concentration of **1**. For curves i to e, plots of the inverse of

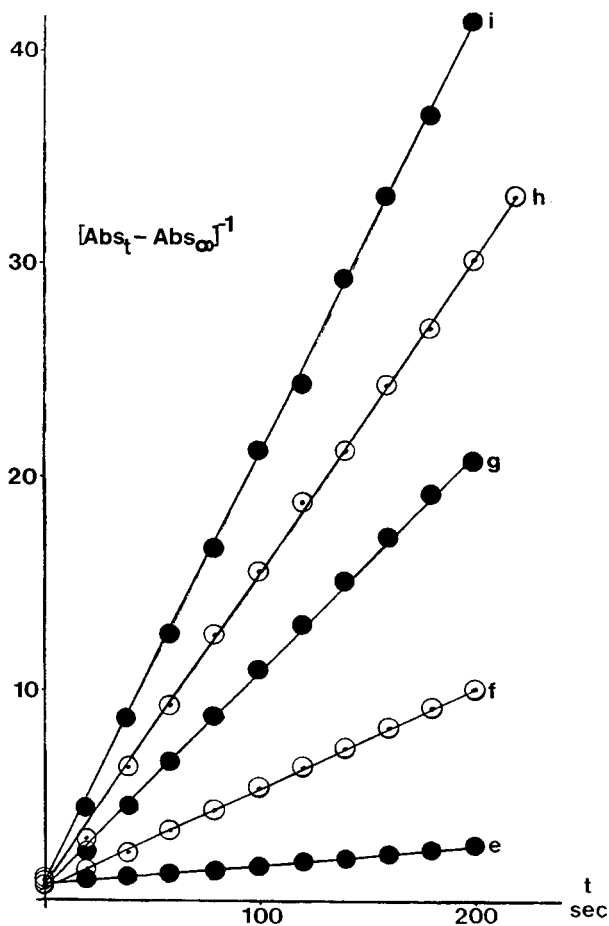


Figure 2. Second-order dependence of decay of B band absorbance on [TFA] for curves e to i inclusive in Figure 1: Abs_t is the absorbance at time t , Abs_∞ at time infinity.

the absorbance (proportional to $[PH_4^{2+}]^{-1}$) against time gave straight lines (Figure 2), behaviour showing that the decay of **1** is second-order with respect to **1**. Also, the positive slopes of the straight lines shown in Figure 2 decrease with decreasing TFA concentrations. When the slopes of these lines were plotted against $[TFA]^2$ (Figure 3), a straight line was obtained showing that the decay of **1** is second-order in TFA as well as **1**, *i.e.*:

$$d/dt[PH_4^{2+}] \cong [PH_4^{2+}][TFA]^2$$

The slope of this line gives a second-order rate constant for the decay of (**1**), $k = 0.41 \pm 0.01 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

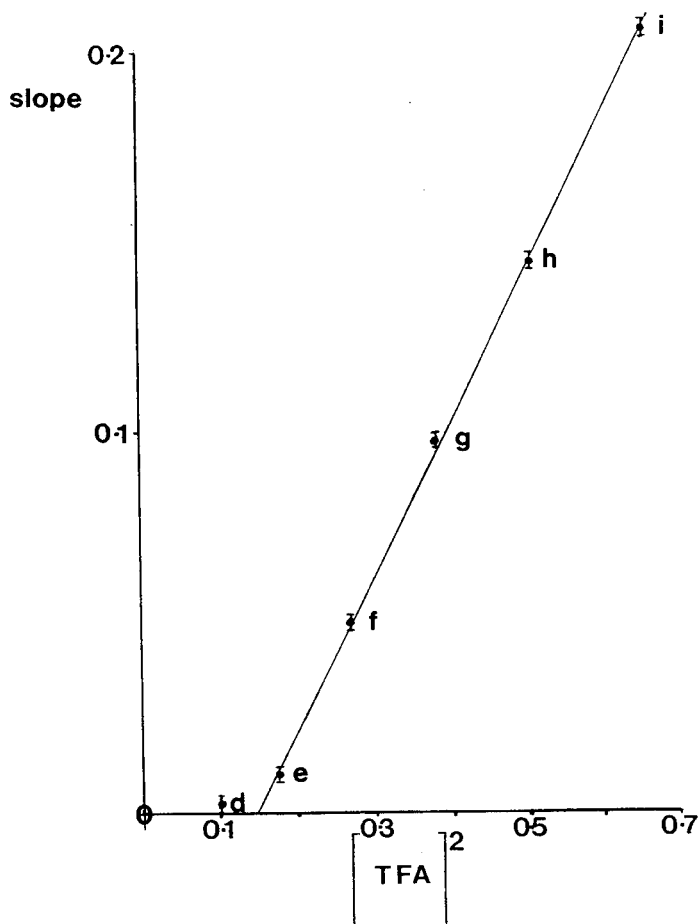


Figure 3. Linear dependence of slopes in Figure 2 on $[TFA]^2$. This gives a rate-constant for second-order decay of dication (**1**), $k = 0.41 \pm 0.01 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

For curves e to b in Figure 1, plots of \log_e (absorbance of **1** against time gave straight lines of negative slopes (Figure 4), behaviour which shows that, at the TFA concentrations represented by curves e to b ($0.42M > [TFA] > 0.04M$), the decay of **1** is now first-order with respect to **1**. Once again, the slopes of the lines in Figure 1 were plotted against $[TFA]^2$ and a straight line obtained (Figure 5), indicating that decay of **1** is still second-order in TFA, *i.e.*:

$$d/dt[\text{PH}_4^{2+}] \cong [\text{PH}_4^{2+}][\text{TFA}]^2$$

The slope of this line gives a first-order rate constant for the decay of **1** at these lower TFA concentrations of $k = 0.027 \pm 0.004 \text{ s}^{-1}$ and a half-life for the decay under these conditions of $t_{1/2} = 25.7 \pm 4 \text{ s}$.

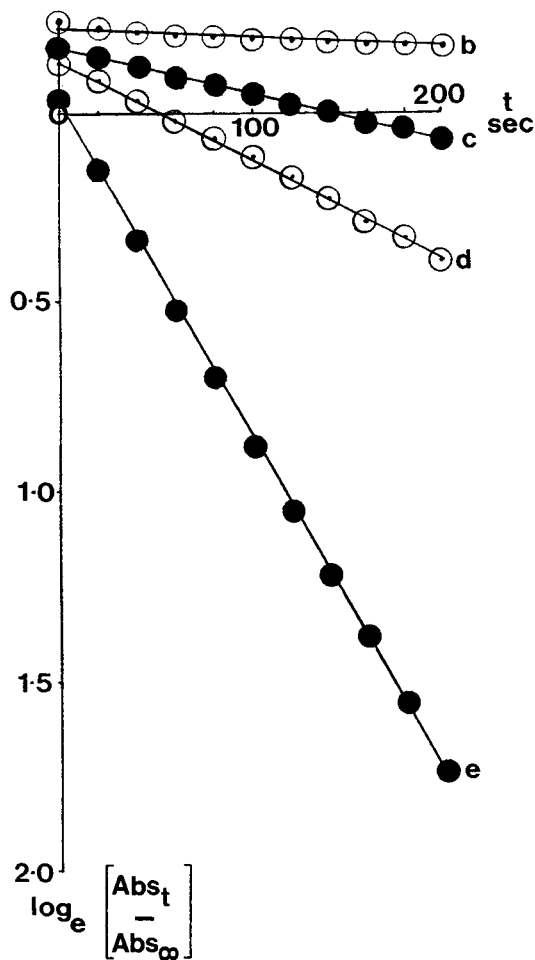


Figure 4. First-order dependence of decay of B band absorbance on [TFA] for curves b to e inclusive in Figure 1.

Curve a (*i.e.*, at $[\text{TFA}] = 0.04 \text{ M}$) shows that at this acid concentration, there is little decay in the absorbance of the B band of **1**. Significantly, very little immediate oxidation of PH_4^{2+} (*i.e.*, the dication **1**) occurs at or below this TFA concentration.

Discussion.

It is known that electrochemical reduction of oxygen in pyridine or DCM produces long-lived $\text{O}_2^{\cdot -}$ [10a]. However, in the presence of proton donors (HA), the mechanism alters to a two-electron reduction to peroxide [10]. This is because further reduction of oxygen occurs at the same potential, *i.e.*, acid addition lowers oxygen's redox potential, and the protonated intermediate, HO_2^{\cdot} , has a higher electron affinity than oxygen.

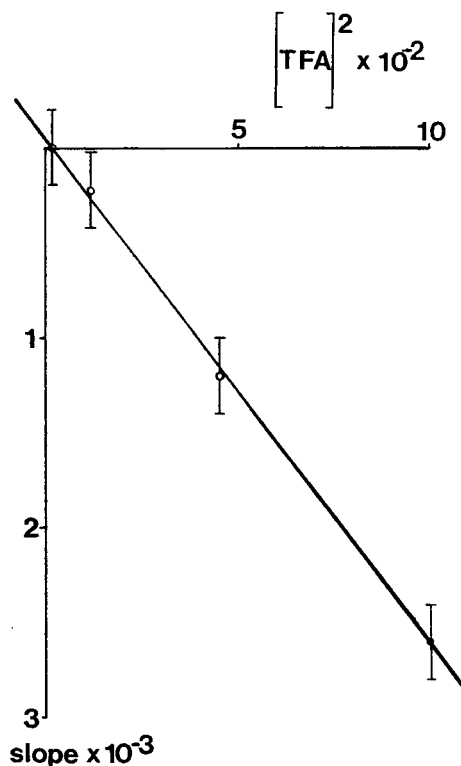


Figure 5. Linear dependence of slopes in Figure 4 on $[\text{TFA}]^2$. This gives a rate-constant for first-order decay of dication **1**, $k = 0.027 \pm 0.004 \text{ s}^{-1}$, and a half-life for dication **1** under these conditions of $t_{1/2} = 25.7 \pm 4 \text{ s}$.

Halogenated hydrocarbons dissolve large volumes of oxygen, a property described by the Ostwald Coefficient (ratio of the volume of gas absorbed to the volume of liquid), which for oxygen in DCM is 0.257 [11].

In the uv/visible cuvette, the DCM volume was 3 ml. Consequently, on saturation with oxygen, the amount of oxygen in the cuvette is approximately 3.5×10^{-5} moles. The amount of TFA added varies between 1.3×10^{-4} moles (0.04 M) and 2.6×10^{-3} moles (0.81 M), while the amount of porphyrin is 2.4×10^{-8} moles. Therefore, $[\text{TFA}] > [\text{O}_2] \gg [\text{PH}_4^{2+}]$. Also the water content is likely to vary between 10^{-5} and 10^{-4} moles [12] so that, under the conditions of the experiment, **1** is the minority constituent of the mixture in the uv/visible cuvette.

We observe that below the minimum concentration of TFA (*i.e.*, $< 0.04 \text{ M}$), very little aerial oxidation occurs, but the porphyrin is in the form of the dication **1**. Porphyrins are well known to rapidly diprotonate in acid solutions [13]. That aerial oxidation takes place when the TFA concentration reaches a certain level suggests a further reaction with TFA. Recent work on the protonation behaviour of porphyrins in acid solutions [14] suggests that after dication formation, porphyrins can protonate further to form tetracations, whose uv/visible spectra are little changed from the dications:

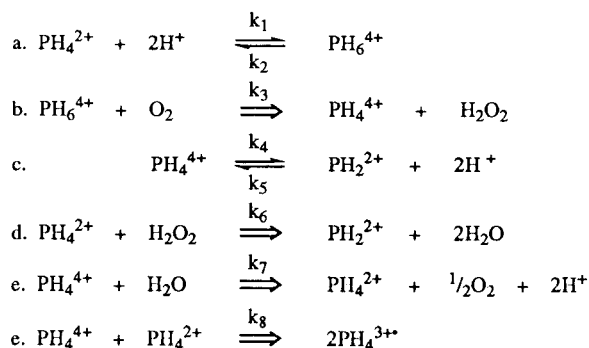
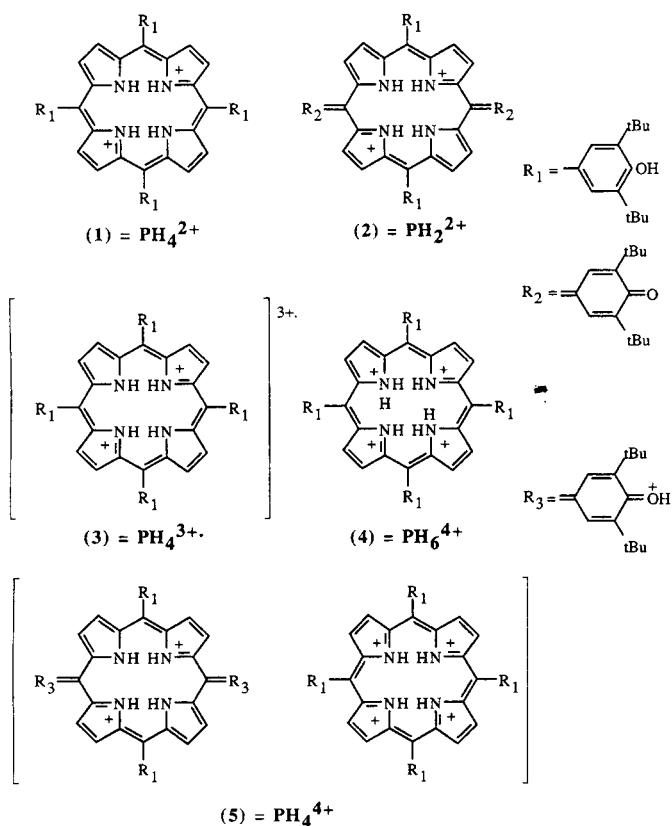


We propose that it is the tetracation **4**, formed in a pre-equilibrium, that undergoes aerial oxidation.

In mesotetraaryl-substituted porphyrins, the aryl groups are almost perpendicular to the plane of the macrocycle. Dication formation leads to molecular distortions such that aryl substituents become more coplanar with the mean porphyrin plane [15]. If electron-donating substituents are suitably positioned on the aryl substituents (*e.g.*, -OH para to the porphyrin meso-carbons), then dicationic positive charge on the macrocycle can be stabilised by delocalisation over the meso-substituents [16].

Porphyrin **1** is unusual in that its meso-substituents so

Scheme



lower the redox potential [17] of the dication, that aerial oxidation takes place to produce **2**, a highly distorted macrocycle with coplanar meso-substituents [18]. In neutral solutions, the oxidised porphyrin **2** is a stable compound [2] but in acidified solutions, we have found that **2** oxidises **1** in a comproportionation reaction to produce the pi-cation radical **3**, PH_4^{3+} [6,7]. We have also found that in acidified solutions, **2** is reduced by traces of water in the solvent [7a].

The reason for the oxidising power of acidified **2** lies in its extended quinonoid structure. Extended quinones protonate non-aqueous acid solutions to yield highly oxidising quinone conjugate acids [19]. Protonation of **2** leads to its conjugate acid **5**, a tautomer of which is the extended protonated quinone shown in the scheme. In the light of this discussion therefore, we propose the following sequence of reactions which we show reconciles the kinetic data obtained from uv/visible spectroscopy:

If $\text{A} = \text{PH}_4^{2+}$; $\text{B} = \text{PH}_6^{4+}$; $\text{C} = \text{PH}_4^{4+}$; $\text{D} = \text{PH}_2^{2+}$ and $\text{E} = \text{PH}_4^{3+}$, then:

$$\begin{array}{l} 1. \quad \frac{d}{dt} [\text{A}] = - k_1[\text{A}][\text{H}^+]^2 + k_2[\text{B}] \\ \quad \quad \quad - k_6[\text{A}][\text{H}_2\text{O}_2] + k_7[\text{C}][\text{H}_2\text{O}] \\ \quad \quad \quad - k_8[\text{A}][\text{C}]. \\ 2. \quad \frac{d}{dt} [\text{B}] = k_1[\text{A}][\text{H}^+]^2 - k_2[\text{B}] \\ \quad \quad \quad - k_3[\text{B}] = 0 \end{array}$$

(the concentration of A in solution is such that $[\text{O}_2] \gg [\text{A}]$, so that $k_6[\text{O}_2] \gg k_3$). Therefore

$$[\text{B}] = \frac{k_1[\text{A}][\text{H}^+]^2}{k_2 + k_3}$$

Substituting for [B] in equation 1 (and letting $k_p = k_1/k_2 + k_3$), we get:

$$3. \quad \frac{d}{dt} [\text{A}] = - k_p k_3 [\text{A}][\text{H}^+]^2 - k_4[\text{A}][\text{H}_2\text{O}_2] + k_7[\text{C}][\text{H}_2\text{O}] - k_8[\text{A}][\text{C}].$$

At very low $[\text{H}^+]$, the amount of C and hydrogen peroxide produced is small because the pre-equilibrium in a. will be over towards the left-hand side of the reaction. Consequently, there will be little of B to be oxidised and so to a good approximation:

4. $\frac{d}{dt} [\text{A}] = - k_p k_3 [\text{A}][\text{H}^+]^2$; *i.e. the loss of A is first-order in [A] and second-order in $[\text{H}^+]$* , as observed. At higher $[\text{H}^+]$, the concentrations of B, C, D, and E become significant. If we assume steady-state concentrations of C and D, then:

$$5. \quad \frac{d}{dt} [\text{D}] = k_4[\text{C}] - k_5[\text{D}][\text{H}^+]^2 + k_6[\text{A}][\text{H}_2\text{O}_2] = 0,$$

so that $k_5[\text{D}][\text{H}^+]^2 = k_4[\text{C}] + k_6[\text{A}][\text{H}_2\text{O}_2]$. Also

$$6. \quad \frac{d}{dt} [\text{C}] = k_p k_3 [\text{A}][\text{H}^+]^2 - k_4[\text{C}] + k_5[\text{D}][\text{H}^+]^2 - k_7[\text{C}][\text{H}_2\text{O}] - k_8[\text{A}][\text{C}] = 0,$$

so that

$$7. \quad [C] = \frac{k_p k_3 [A][H^+]^2 + k_d [A][H_2O_2]}{k_7 [H_2O] + k_8 [A]}$$

Substituting for [C] in equation 3, we get

$$8. \quad d/dt [A] = - \frac{2k_p k_3 k_8 [A]^2 [H^+]^2 - 2k_6 k_8 [A]^2 [H_2O_2]}{k_7 [H_2O] + k_8 [A]}$$

Now, $[H_2O_2] \ll [H^+]$ and we have shown previously [7a] that $k_7 [H_2O] \gg k_8 [A]$. Therefore, to a good approximation

$$9. \quad d/dt [A] = - \frac{2k_p k_3 k_8 [A]^2 [H^+]^2}{k_7 [H_2O]}$$

i.e., at higher $[H^+]$, the rate of loss of A is second-order in both [A] and $[H^+]$, as observed.

This kinetic investigation and analysis supports our belief in a conproportionation mechanism for the production of long-lived radicals by the aerial oxidation of **1** in acidic media [6]. Further work is in progress to characterise radicals produced *via* a similar mechanism from other phenolic porphyrins. We envisage that such compounds could ultimately provide a range of readily-accessible redox-active materials for application in electrocatalysis and molecular electronics.

Acknowledgements.

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