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FACILE AERIAL OXIDATION OF A PORPHYRIN. PART 8[1]. DECAY OF RADICAL FORMED DURING THE AERIAL OXIDATION OF MESO-TETRAKIS(3,5-DI-t-BUTYL-4-HYDROXYPHENYL)PORPHYRIN.

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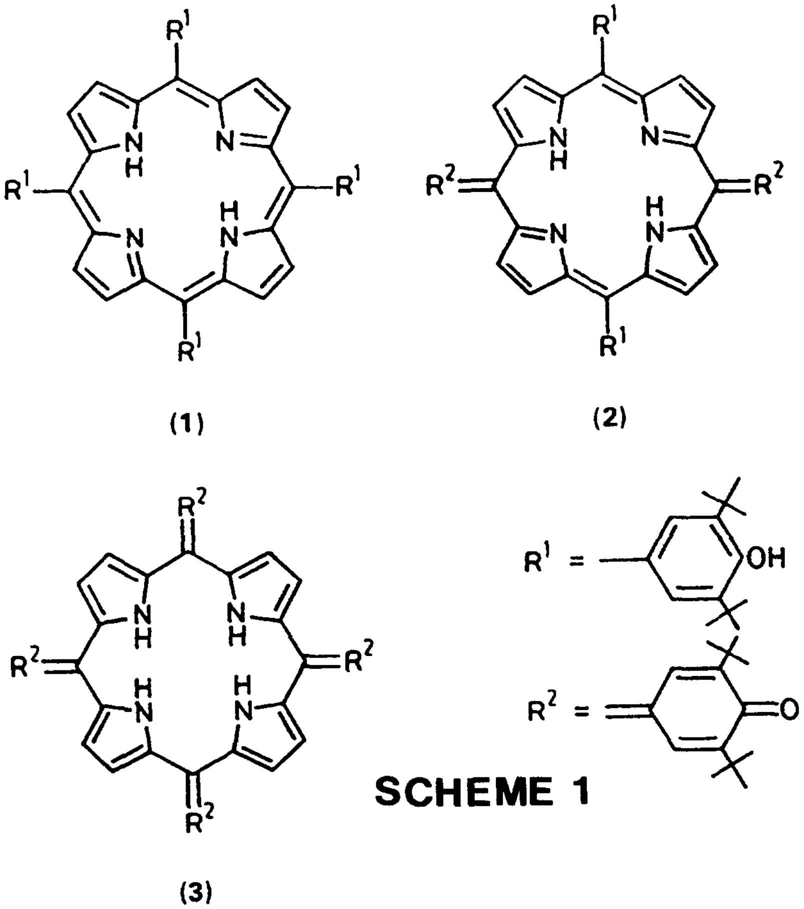
Abstract: The title porphyrin (**1**) undergoes stepwise aerial oxidation via a radical that decays with pseudo-first order kinetics.

Recently, we and others have studied the facile two-electron aerial oxidation of (**1**) in basified dichloromethane.[2] ^{1}H-n.m.r. suggests that the final oxidation product in solution is the porphodimethene (**2**),[2a] while x-ray crystallography shows that, in the solid state, it exists as the tautomeric tetraquinomethide xanthoporphyrinogen (**3**)[3].



SCHEME 1

Aerial oxidation proceeds initially via an intermediate with a strong triplet e.s.r. spectrum (e.g., see Figure inset), that clearly suggests a phenoxy radical with unpaired electron density localised on a meso-substituent.[2e]

We have also observed e.s.r. spectra for some metal complexes of (1) under similar conditions.[2d] The Sn(IV) complex, in particular, was unusual because it gave a weak triplet e.s.r. spectrum in **neutral** DCM. The decay of this radical via second-order kinetics was rationalised in terms of phenoxy-radical dimerisation, followed by heterolytic disproportionation into the starting Sn(IV) porphyrin and the two-electron oxidised product.[2d] We expected a similar second-order decay for the radical derived from the metal-free porphyrin (1). Instead, it decays with first-order kinetics. This paper reports our findings.

Experimental

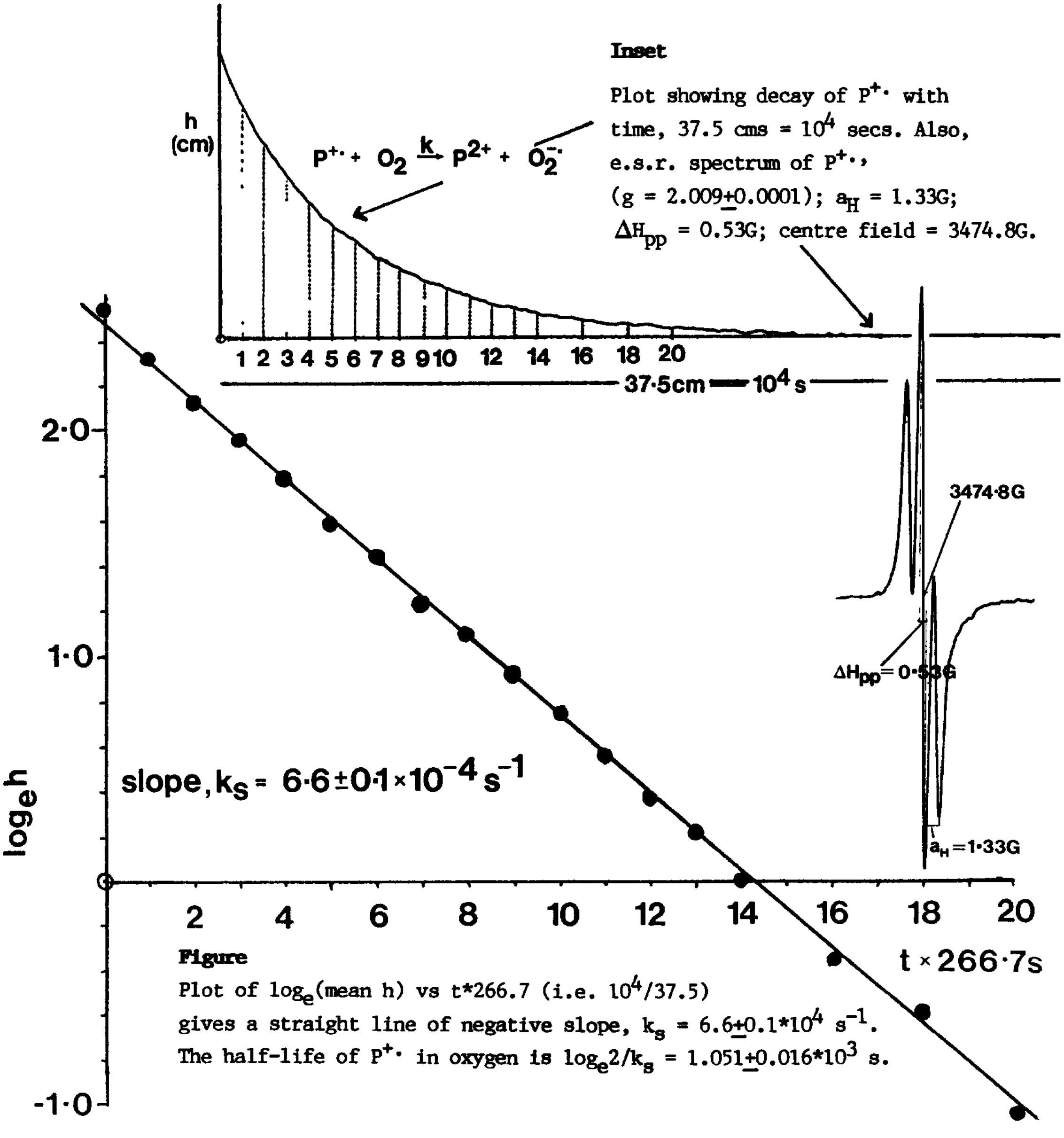
Porphyrin (1) was synthesised as reported earlier.[2a] Oxygen was bubbled through a solution of (1) ($1.33{*}10^{-3}$M) in DCM (freshly distilled from phosphorus pentoxide) for 30 min. To 1 ml of this solution was added the base tetra-n-butylammonium hydroxide in methanol (1M; 0.2 ml). The mixture rapidly changed colour from red, through green, to deep blue, signifying the formation of the radical.[2d,e] This solution was transferred to a flat e.s.r. cell that was carefully positioned within the cavity, maintained at 20°C, of a Bruker ER 200D e.s.r. spectrometer.

The usual triplet e.s.r. spectrum of the radical of (1)[2e] was observed (see Figure inset $g = 2.009 \pm 0.0001$; $a_H = 1.33$G; $\Delta H_{pp} = 0.53$G) with a centre field at 3474.8G. The instrument was then locked onto the middle peak of the triplet, and the decay of the triplet observed over a scantime of 10^4 seconds. This procedure was repeated twice.

Results and Discussion

The colour changes reported on addition of base to DCM solutions of (1) have been observed previously.[2a] The green colour, which persists on outgassing of oxygen from the solution prior to basification, is typical of meso-tetra-4-hydroxyaryl porphyrins in base, and corresponds to formation of the tetraphenoxide.[2f] In the case of (1), this is immediately followed, in the presence of oxygen, by oxidation to the radical and further colour change. In terms of the time for the radical to decay, therefore, these changes do not correspond to kinetically limiting steps.

The decay of the radical is shown in the inset to the Figure. The peak height h was measured at fixed time intervals for each of the three decay curves, and a plot of $\log_e$(mean h) against time (t) gave a straight line of negative slope (Figure), characteristic of a first-order decay process. The slope of this line gave a calculated decay constant, **$k = 6.6 \pm 0.1 * 10^{-4}\ s^{-1}$** (contrasting with a second-order decay constant for the triplet spectrum of the neutral Sn(IV) complex[2d] of $k = 0.98*10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$).



Inset

Plot showing decay of $P^{+\cdot}$ with time, 37.5 cms = 10^4 secs. Also, e.s.r. spectrum of $P^{+\cdot}$, ($g = 2.009 \pm 0.0001$); $a_H = 1.33G$; $\Delta H_{pp} = 0.53G$; centre field = 3474.8G.

Figure

Plot of $\log_e$(mean h) vs t*266.7 (i.e. $10^4/37.5$) gives a straight line of negative slope, $k_s = 6.6 \pm 0.1*10^4\ s^{-1}$. The half-life of $P^{+\cdot}$ in oxygen is $\log_e 2/k_s = 1.051 \pm 0.016*10^3$ s.

As the second oxidation produces the e.s.r.-silent compound (2) or (3), the implication is that the decay is pseudo-first order, and that the oxidising agent (i.e. oxygen) remains at constant concentration with repect to the the radical, $P^{+\cdot}$ e.g.,

$$P + O_2 \xrightarrow{\text{fast}} P^{+\cdot} + O_2^{-\cdot}$$
$$P^{+\cdot} + O_2 \xrightarrow[k]{\text{slow}} P^{2+} + O_2^{-\cdot}$$

If k represents the rate of disappearance of of $P^{+\cdot}$, then:-

$$\frac{-d[P^{+\cdot}]}{dt} = k[P^{+\cdot}][O_2]$$

and if $[O_2]$ remains constant, then:-

$$k[O_2] = k_s\text{, the pseudo first-order rate constant.}$$

so that, $$\frac{-d[P^{+\cdot}]}{dt} = k_s[P^{+\cdot}]$$

In the usual way, cross multiplication and integration give:-

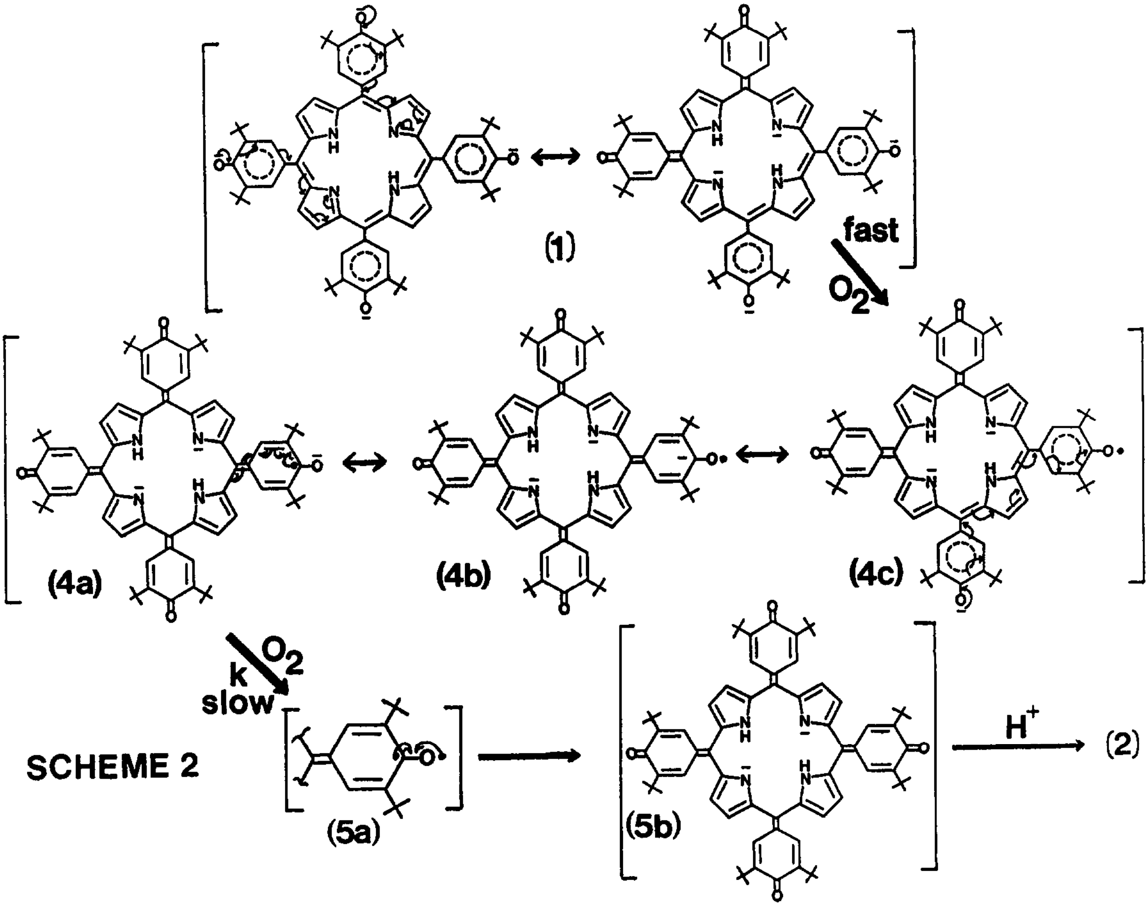
$$\log_e[P^{+\cdot}] = -k_st + \log_e[P^{+\cdot}]_o$$

the last term giving the concentration of the radical at t=0.

As $[P^{+\cdot}]$ is proportional to h, the relative intensity of the radical triplet peak at time t, as read from the decay curve (Figure inset), then a plot of $\log_e h$ against t gives a straight line of slope $-k_s$, the rate constant for pseudo first-order decay of $P^{+\cdot}$. From this it is possible to calculate the half-life, $t_{\frac{1}{2}}$, for $P^{+\cdot}$ in the presence of oxygen as $\mathbf{t_{\frac{1}{2}} = \log_e 2/k_s = 1.051 \pm 0.016 * 10^3}$ seconds.

Halogenated hydrocarbons are known to absorb large quantities of oxygen and DCM at 20°C has an Ostwald Coefficient (i.e., the volume of gas absorbed to the volume of liquid) for oxygen at saturation of 0.257.[4] Assuming the DCM was saturated with oxygen, this gives an oxygen molarity in DCM at 20°C of $1.15*10^{-2}$M, approximately a ten-fold excess in solution over the porphyrin concentration. In addition, oxygen in the head space (2 ml) over the flat cell would equilibrate with the porphyrin solution. Consequently, over the time span of the decay of the radical, **the total oxygen concentration will remain virtually constant**, leading to a pseudo-first order decay.

A plausible reason for the slow decay of $P^{+\bullet}$ is shown in Scheme 2. Here, the flexibility of the macrocycle allows negative charge from the rest of the molecule to captodatively[5] stabilise the phenoxy radical (**4a-c**), after which the second aerial oxidation takes place (**5a-b**), generating (**2**).



SCHEME 2

In the case of the Sn(IV) complex of (**1**),[2d] it is well known that the central cation greatly increases the electrophilicity of the macrocycle[6] and severely reduces its flexibility.[2c,7] The former would increase the acidity of the phenolic protons such that, even under neutral conditions, aerial oxidation would lead to the generation of a small amount of phenoxy radical. The reduced flexibility of the macrocycle would then ensure that the unpaired electron would be isolated on a meso-substituent. The radical could then survive long enough to decay with a 2nd order mechanism via peroxy dimer formation and heterolytic cleavage.

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