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Facile Aerial Oxidation of a Porphyrin. Part 13.[1]

GENERATION OF π-CATION RADICALS via ACID ADDITION TO MESOTETRAKIS(3,5-DI-t-BU-4-HYDROXYPHENYL)PORPHYRIN AND ITS TWO-ELECTRON OXIDATION PRODUCT.

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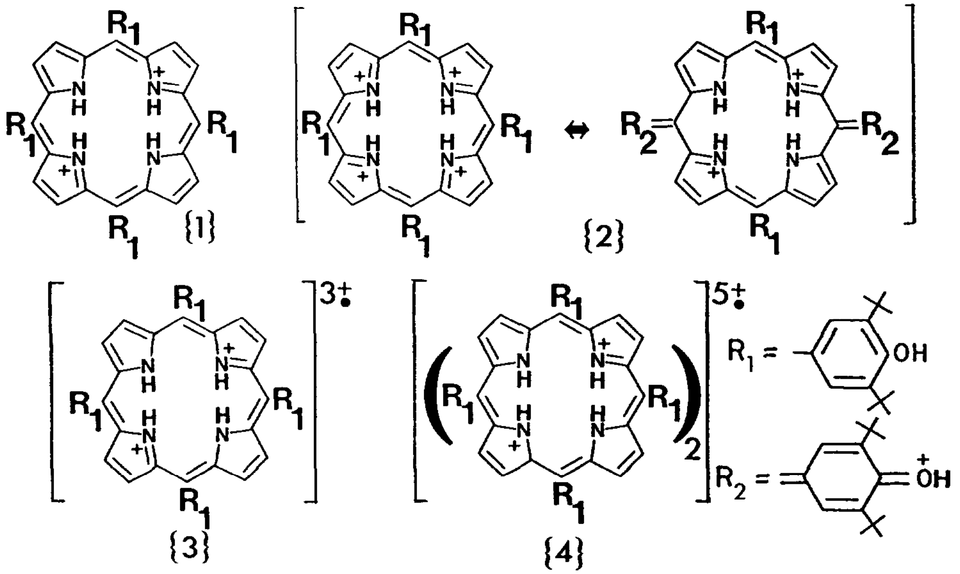
ABSTRACT Addition of acidified 1,1,1-trichloroethane to the oxidised porphyrin 2 produces the porphyrin π-cation radical 3: evidence is presented to show that a long-lived radical produced via the aerial oxidation of porphyrin 1 in TFA, is due to a porphyrin π-cation radical dimer.

Aerial oxidation of mesotetrakis(3,5-di-t-butyl-4-hydroxyphenyl)porphyrin 1 (Scheme 1) occurs in basic[2a] and acidic[3] solutions, to give the two-electron oxidation product 2. In base, esr spectroscopy shows a long-lived porphyrin radical[4,5] (with unpaired electron density localised on a meso-substituent[3]), and hydroxyl radicals.[2] In acid, a different esr spectrum was observed, and interpreted as due to a diprotonated porphyrin π-cation radical 3 with a quasi-$^2A_{2u}$ ground state.[3]



SCHEME 1

We speculated that 3 was produced via conproportionation of protonated 1 and 2. Indeed, equimolar amounts of these compounds produced large concentrations of 3 on addition of degassed trifluoroacetic acid (TFA) -acidified 1,1,1-trichloroethane (TCE).[6] The esr spectrum of 3, however, consisted of only 14 lines, half that obtained by the aerial oxidation of 1 in TFA-acidified TCE (i.e. 29-lines).[3] The difference was interpreted as due to concentration effects.[7]

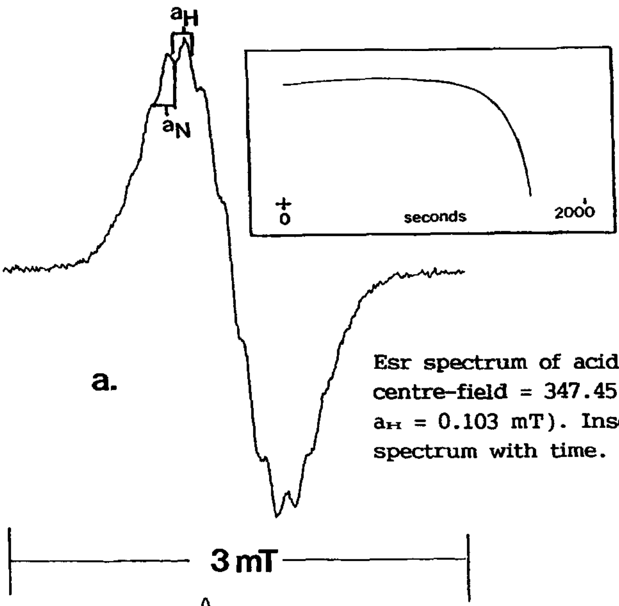
We now report addition of TFA-acidified TCE solutions to the two-electron oxidised porphyrin 2 on its own. Surprisingly, we obtained the radical 3 with the same 14-line esr spectrum as the conproportionation of 1 and 2, but with a shorter life-time. In order to rationalise this behaviour, we reexamined the long-lived radical formed by aerial oxidation of porphyrin 1 in acidified TCE.[3] We conclude that this species is a novel paramagnetic π-radical dimer.

EXPERIMENTAL

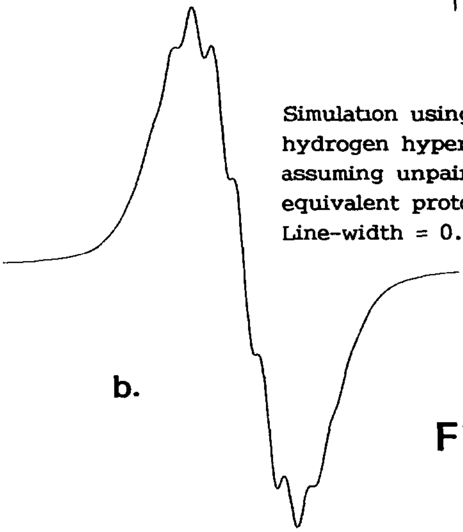
1,1,1-Trichloroethane and dichloromethane were freshly distilled prior to use. The spin traps, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2-methyl-2-nitrosopropane (NtB) were purified by literature methods[7] and added neat to solution. The porphyrin 1 and the oxidised porphyrin 2 were prepared as reported elsewhere.[2b] A solution of TCE acidified with TFA (3 mol dm^{-3}) was prepared and divided into two parts. One part was dried over phosphorus pentoxide, while the other half was used without drying. Esr spectroscopy was performed using a quartz flat cell inside the cavity (20°C) of a Bruker ER 200D esr spectrometer under the following conditions: microwave power, 10 dB; microwave frequency, 9.77 GHz; modulation amplitude, 0.2 mT; scan width and gain are as noted in the text.

RESULTS AND DISCUSSION

To the oxidised porphyrin 2 (10^{-2} mol) was added N_2-degassed acidified TCE (1 ml). The mixture rapidly changed from red to deep emerald green, giving a singlet ESR spectrum (g = 2.006; centre field = 347.45mT), with a 14-line hyperfine structure (a_N = 0.123 mT; a_H = 0.103 mT, Figure 1a). This is the same spectrum as has previously been obtained via conproportionation of 1 and 2 under identical conditions.[3,6] Compared with these long-lived (i.e., > 2 h) spectra, however, this one had decayed within 25 minutes. Addition of water (0.1.ml) to the mixture, immediately after the acidified TCE solution, changed the colour of the lower layer of the now-two-phase system back to red and destroyed the esr spectrum. However, when the acidified TCE was dried over P_2O_5 and added to 2, the resulting ESR spectrum was found to be very weak. From this, we conclude that traces of water are necessary to produce the π-cation radical 3 from 2, but that excess inhibits its formation.



Esr spectrum of acidified 2 (g = 2.006; centre-field = 347.45 mT; a_N = 0.123 mT; a_H = 0.103 mT). Inset shows the decay of spectrum with time.



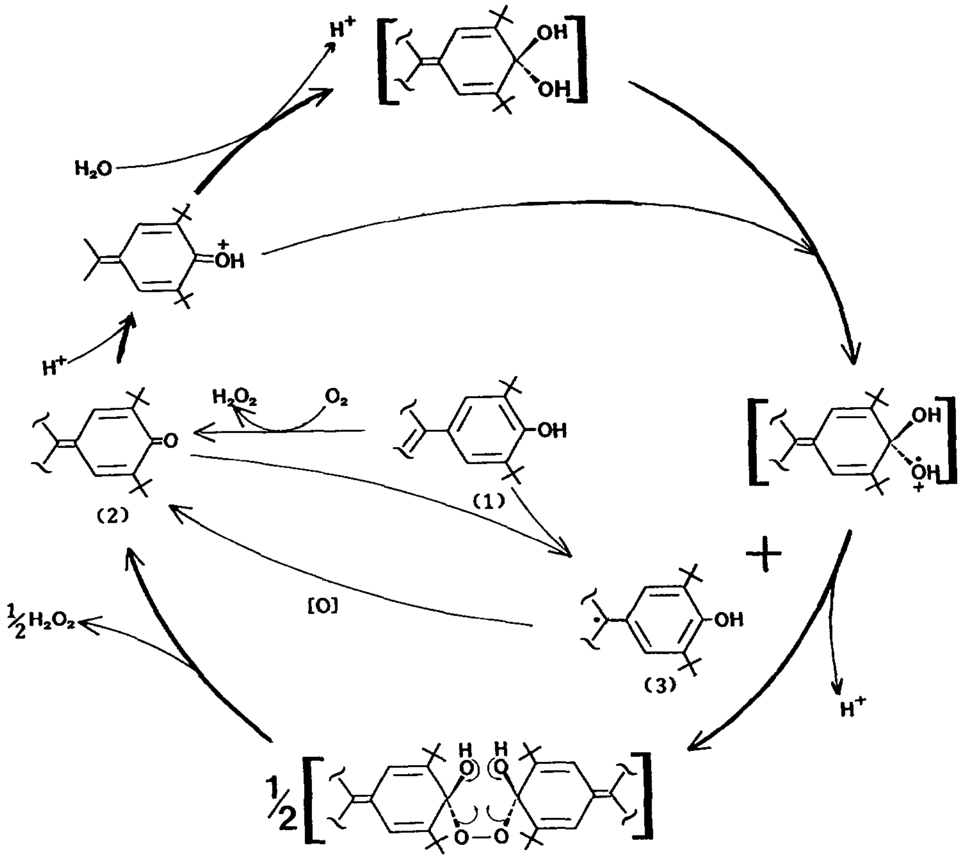
Simulation using experimental nitrogen and hydrogen hyperfine splitting constants and assuming unpaired electron is coupled to four equivalent protons and four equivalent nitrogens. Line-width = 0.09mT cm^{-1}; line-shape 40% Laurentzian

Figure1.

The radical decay profile shows that its concentration remains constant for a time (about 15 min), after which it rapidly disappears (Figure 1a, inset). However, addition of degassed and dried acidified TCE (1 ml) to an equimolar mixture of 1 and 2 yielded the intense, long-lived, 14-line spectrum of 3.[6]
Clearly, two reactions produce 3 in acidified TCE: (i) conproportionation of 1 and 2, and (ii) reaction of 2 with trace water in the solvent. The spectrometer gain needed to produce comparable esr peak-heights approximates to the relative amounts of 3 produced by the two reactions. For reaction (ii) the gain was $8*10^4$, compared to $5*10^2$ for conproportionation (i), which is therefore about 160 times more efficient at forming 3.

We investigated whether the mechanism of (ii) involved radical species (e.g., $\dot{O}H$, solvent-derived carbon-centred species, $\dot{O}OH$, or $\dot{H}$) by repeating reaction (ii) using large concentrations of the spin-traps 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and/or 2-methyl-2-nitroso-propane (NtB),[2,5,9] and acidified DCM as solvent (DCM forms carbon-centred species more readily with $\dot{O}H$ than TCE). No spin-adducts were detected.

The following is a plausible mechanism for reaction (ii), and is the acid analogue of a similar reaction of 2 with base.[2,5]



SCHEME 2

In acidic non-aqueous media, quinones are known to form conjugate acids, which as strong oxidants, readily accept electrons from suitable substrates.[10,11] The oxidised porphyrin 2 has an extended quinonoid structure which should also form a strong oxidising conjugate on protonation. Attack on such a conjugate by trace water will lead to a geminal diol. Excess water, however, would shift the protonation equilibrium back to the unprotonated quinonoid structure.

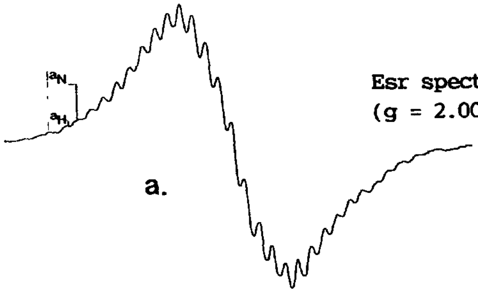
The geminal diol then undergoes one-electron oxidation by protonated 2, generating 3 and a transient radical species that rapidly dimerises. The peroxy dimer would then collapse to regenerate 2 and hydrogen peroxide (stable in acid media), which would rapidly oxidise the π-cation radical back to 2 (Scheme 2). This would explain the disappearance of 3 in reaction (ii). We now compare the π-cation radicals generated in acidified TCE by (a) aerial oxidation of the porphyrin 1[3], and (b) the conproportionation of 1 and 2[6], (i), and the reaction of 2 with trace water in the solvent, (ii).

The differences in the esr spectra of these species lies in the halving of the number of hyperfine lines superimposed on the singlet envelope; 29 in (a) and 14 in reactions (i) and (ii). Also, the hydrogen hyperfine splitting constants (a_H) are doubled: 0.05 mT in (a) and 0.103 mT reactions (i) and (ii). We have been able to simulate the 14-line esr spectrum using the experimental nitrogen and hydrogen hyperfine splitting constants, and assuming a protonated porphyrin π-cation radical 3, in which four central hydrogens are coupled to the four macrocyclic nitrogens (Figure 1b).

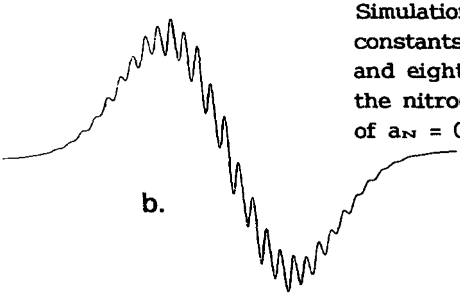
We had previously explained the difference of the 29-line and 14-line esr spectra in terms of concentration effects[6] leading to exchange broadening of the spectra.[7] However, dilution did not change the 14-line into the 29-line spectrum. Another explanation is that in (a), the π-cation radical forms a radical dimer with a molecule of the dicationic porphyrin 1, while in reactions (i) and (ii), no such dimerisation takes place. Consequently, the esr spectra recorded would be for different radical species: (a) represents a π-cation radical dimer 4, while reactions (i) and (ii) produce the undimerised π-cation radical 3.

There are many precedents for aromatic π-cation radicals forming dimers with neutral aromatic molecules,[12] in which the unpaired electron is delocalised over twice the number of carbon atoms, with its spin coupled to twice the number of protons. Also, in vivo studies on chlorophyll radical cations has revealed paramagnetic radical cation dimers.[13] Consequently, we resimulated the 29-line esr spectrum of the π-cation radical formed by aerial oxidation of the dication of 1.[3] We had earlier assumed the experimentally-obtained coupling constants derived from four protons attached to four nitrogen atoms, and eight hydrogens attached to four meso-substituents, best-guessing a value of the nitrogen hyperfine coupling constant. Resimulation, required only experimentally-obtained hyperfine coupling constants[3] originating from eight central nitrogens and hydrogens.

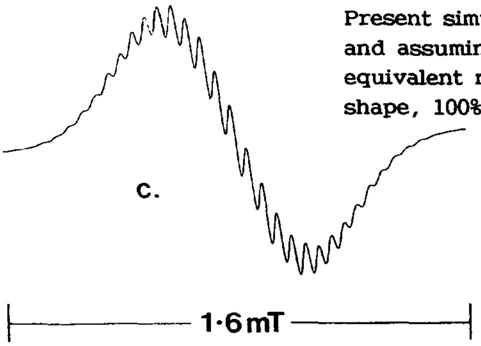
The resulting simulation is shown figure 2 with the original experimental spectrum and the first simulation. As can be seen, the two simulations are virtually identical. The advantage of the new simulation is that only **experimentally-derived hyperfine coupling contants are used: no <u>assumed</u> constants are included in order to make the simulation work.** Occam's razor therefore suggests that the new simulation - and its assumption of a radical dimer 4 - is a better fit for the origin of the 29-line esr spectrum than a π-cation radical 3 with a quasi-$^2A_{2u}$ ground state.



Esr spectrum[3] obtained from acidified 1 ($g = 2.007$; $a_H = 0.0828$mT; $a_H = 0.05$mT).



Simulation[3] using experimental hyperfine splitting constants derived from four equivalent central protons and eight equivalent protons on four meso-susbtituents; the nitrogen hyperfine splitting constant was a best-fit of $a_N = 0.0962$ mT.



Present simulation using $a_N = 0.0828$mT; $a_H = 0.05$mT and assuming the unpaired electron is coupled to eight equivalent nitrogens and eight equivalent protons: line-shape, 100% Gaussian, spectral width = 0.08mT cm^{-1}.

Figure 2.

Although the hydrogen hyperfine coupling constants have doubled on going from the 29-line- to the 14-line spectrum (as expected in changing from a π-cation radical dimer 4 to a π-cation radical 3), the nitrogen hyperfine coupling constants have not[14] (a_N=0.083 mT compared to a_N=1.23 mT). Comparison of the distribution of positive charges on the dimer 4 and monomer 3 is, however, instructive. The former carries five positive charges, while the latter has three. If we make the simplifying assumption that most of these charges are localised on the macrocyclic central nitrogens,[15] then the charge/nitrogen atom for the dimer is 5/8ths, while for the monomer it is 3/4ths. The increase in positive charge over the central nitrogens of 3 compared to 4 would account for the observed lack of doubling of the nitrogen hyperfine coupling constants. Support for this view is found in comparison of the spectral linewidths of 3 with 4. As predicted,[13a] the monomer linewidth ($\Delta H_M = 0.028$ mT) is approximately $\sqrt{2}$*linewidth of the dimer ($\Delta H_D = 0.020$ mT).

Finally, we wish to speculate. The paramagnetic radical dimer 4 proposed here, forms remarkably easily (by simple aerial oxidation of 1 in acid solution) from a porphyrin that is both sterically hindered and positively charged. This could have some bearing on the reasons why chlorophyll dimers[16] were utilised as trapping centres for PS I and PS II during the molecular evolution of the photosynthetic apparatus.[17]

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