Improved Generation of Porphyrin Radicals *via* Conproportionation

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meso-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin **1** undergoes conproportionation with the two-electron-oxidised compound **2** to yield high concentrations of porphyrin radicals in acidified and basified 1,1,1-trichloroethane (TCE).

Recently, we reported the facile aerial oxidation of the porphyrin **1a** in acidified solutions to give (by ESR spectroscopy and simulation studies) a long-lived π-cation radical.[1] We had also previously shown that aerial oxidation of **1b** occurs in basified solutions to yield a porphyrin–phenoxy-radical intermediate **1d**[2] (with unpaired electron density localised on a *meso*-substituent). This decays to the porphodimethene-type compound **2b**, with pseudo-first-order kinetics,[3] in the presence of oxygen, and can be separated by neutralising the reaction solution to give **2c**.[2a]

Speculating on a possible mechanism for the aerial oxidation of **1a** in acidified solutions, we proposed[1] that the porphyrin π-cation radical is not formed directly by aerial oxidation (as is **1d** in basified solutions), but indirectly *via* a conproportionation reaction between the unoxidised dication **1a** and the doubly oxidised protonated compound **2a**, $PH_4^{4+}(OH)_4$, eqn. (1).

$$PH_4^{2+}(OH)_4 + PH_4^{4+}(OH)_4 \rightleftharpoons 2PH_4^{3+\cdot}(OH)_4 \qquad (1)$$

This suggested that it should be possible to generate the porphyrin π-radical cation by simply mixing equimolar amounts of **1c** and **2c** in acid solution. Further, a similar conproportionation reaction in basified solution, might also generate the porphyrin–phenoxy radical **1d**. This paper reports our findings.

Equimolar quantities of **1c** and **2c** were mixed and dissolved in nitrogen-flushed 1,1,1-trichloroethane (TCE, 10^{-2} mol dm^{-3}), acidified with trifluoroacetic acid (3 mol dm^{-3}). This solution immediately gave a singlet ESR spectrum[†] (g = 2.007(85), centre field = 347.62 mT) that was of much greater intensity than the same spectrum produced by aerial oxidation of **1a** in acidified TCE, under similar conditions of solution concentration, and spectrometer conditions [see Fig. 1(*a*)].[1][†]

Significantly, we observed no 29-line hyperfine structure superimposed on the singlet envelope, as we reported earlier for the porphyrin π-cation radical produced *via* aerial oxidation.[1] Ten-fold dilution of the conproportionation reaction solution, however, produced a singlet spectrum with a 14-line hyperfine structure [g = 2.010(8), a_H = 0.12 mT, Fig. 1(*b*)]. Further dilution did not increase the number of hyperfine lines. Presumably, high radical concentrations are causing exchange broadening, leading to loss of hyperfine structure.[4]

Equimolar quantities of **1c** and **2c** were then mixed in nitrogen-flushed TCE (10^{-2} mol dm^{-3}), this time basified with a solution of 1 mol dm^{-3} methanolic tetra-n-butylammonium hydroxide (5 ml in 20 ml TCE). Immediately, a triplet ESR spectrum was obtained, that was of much greater intensity and of highly distorted shape, compared with that obtained by aerial oxidation of **1b** in basified dichloromethane[2] [g = 2.01(1), a_H = 0.15 mT]. Ten-fold dilution of the conproportionation reaction solution improved the resolution so that more accurate hyperfine splitting constants[2d] could be obtained [g = 2.012, a_H = 0.13 mT, centre field = 346.90 mT, Fig. 1(*c*)]. Once again, the high concentration of the radical (much higher than has previously been obtained by direct aerial oxidation) is probably causing exchange broadening, leading to some loss of hyperfine structure.[4]

Precedents for such conproportionation reactions exist in the tetraquinocyclobutane[5] and triquinocyclopropane[6] systems. In the former, the equilibrium is well over to the left hand side of the equation, favouring reactants over radical product (as shown by the weak ESR spectrum). In the latter, the reverse is the case, with the intense ESR spectrum showing the radical product in high yield. Presumably, the cyclopropenium and porphyrin [4*n* + 2] aromatic systems are superior at stabilising unpaired electrons than the antiaromatic [4*n*] cyclobutadiene system. Further, in basic media, **1b** appears to be behaving as a two-stage Würster-type redox system,[3,7] while in acidic media, rapid two-electron oxidation occurs,[1] followed by conproportion of the doubly-oxidised compound **2a** with the unoxidised porphyrin dication **1a**.

Both the tetraquinocyclobutane[5] and the triquinocyclopropane[6] systems also undergo conproportionation in neutral

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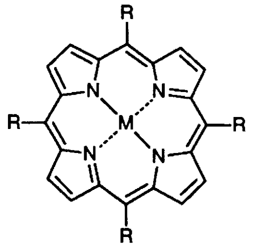
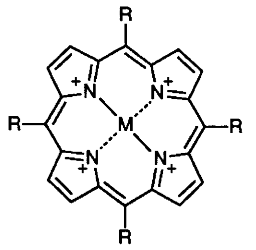
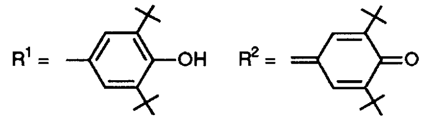
[†] Spectra were recorded on a Bruker ER 200D ESR spectrometer. TCE was deoxygenated by bubbling with nitrogen for several hours. For experiments in neutral solution, the deoxygenated TCE was then stored (with continued nitrogen flushing) over dried sodium carbonate.

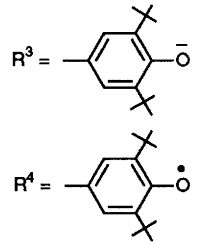


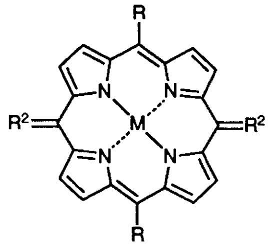
1a; R = R^1, M = 4H(2$^+$)
1b; R = R^3, M = 2H(4$^-$)
1c; R = R^1, M = 2H



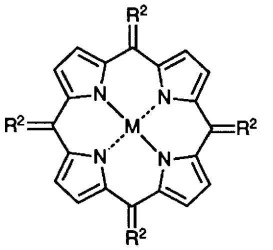
2a; R = R^1, M = 4H(4$^+$)



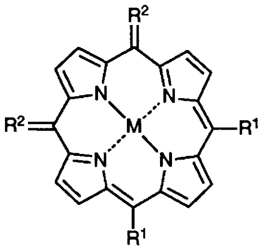




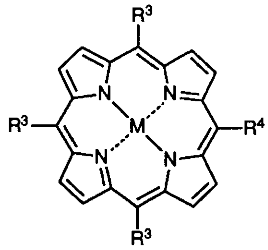
2b; R = R^3, M = 2H(2$^-$)
2c; R = R^1, M = 2H



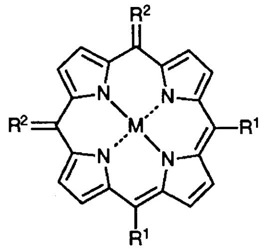
2d; M = 4H



2e; M = 2H



1d; M = 2H(3$^-$)



1e; M = 4H

solution to give neutral radical species. We wished to investigate whether the porphyrin and the doubly-oxidised tetraquinomethide porphyrinogen would react similarly. Consequently, the two species were mixed in neutral nitrogen-flushed TCE. A faint singlet ESR spectrum was obtained [g = 2.01(06); centre-field = 347.13 mT, Fig. 1(*d*)], reminiscent of that observed in acidified TCE, but was too weak for observation of any hyperfine structure.

Though radical formation *via* conproportionation is relatively common (see refs. 5 and 6, for example), and especially between quinones and the corresponding dihydroxybenzene,[8] to the best of our knowledge, this is the first time such reactions have beeen observed in the porphyrin series. We present a steric argument suggesting how conproportionation occurs between **1** and **2**, and why such a reaction appears to be less favoured in neutral TCE.

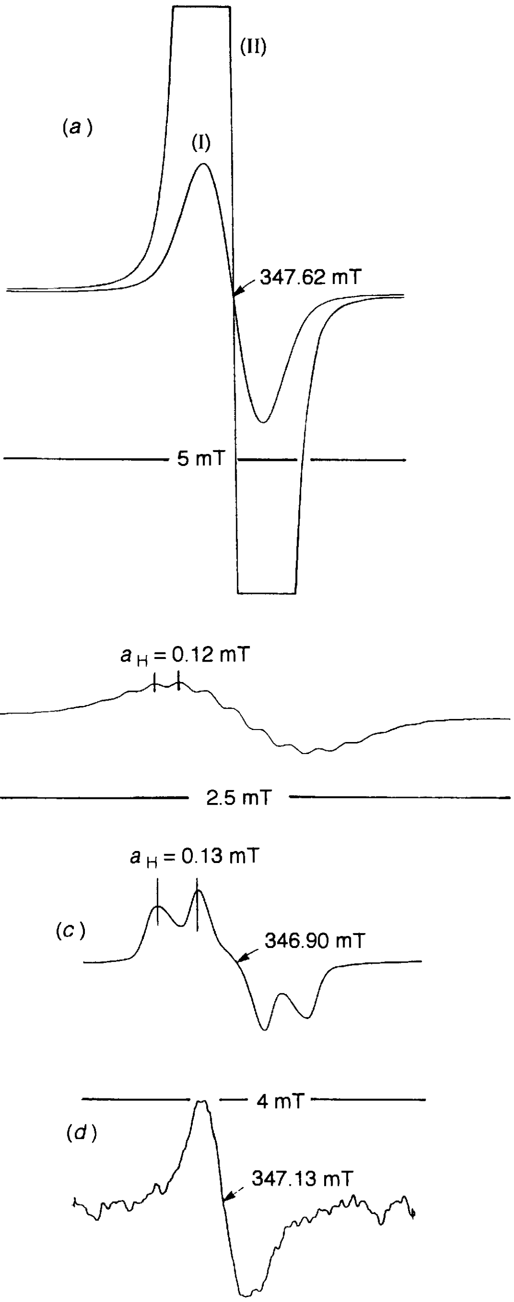


Fig. 1(*a*) Porphyrin radical cation generated *via* aerial oxidation of **1a** in acidified TCE (10^{-2} mol dm^{-3}) (I), and porphyrin radical cation generated *via* conproportionation of **1c** and **2c** in acidified TCE (10^{-2} mol dm^{-3}) under the same spectrometer conditions of receiver gain (4×10^4), modulation amplitude (0.05 mT), modulation frequency (100 kHz) and microwave power (10 dB); g = 2.007(85), centre field = 347.62 mT (II). (*b*) Solution from (*a*) (ii) after ten-fold dilution, g = 2.010(8), a_H = 0.12 mT. (*c*) Triplet ESR spectrum obtained by conproportionation of **1c** and **2c** in basified TCE (10^{-3} mol dm^{-3}), g = 2.012, a_H = 0.13 mT, centre field = 346.90 mT. (*d*) Weak singlet ESR spectrum obtained by conproportionation of **1c** and **2c** in neutral TCE (10^{-2} mol dm^{-3}), g = 2.01(06), centre field = 347.13 mT.

meso-Substituted porphyrin dications are known to have puckered macrocyles with aryl moieties strongly tilted towards the plane defined by the macrocyclic α-carbon atoms.[9] We have also shown that in the solid-state, the doubly-oxidised tetraquinomethide porphyrinogen (**2d**: one of the tautomeric forms of **2**) possesses a highly puckered macrocycle, planar *meso*-substituents, and an extensive network of intermolecular hydrogen bonds.[10] Quinonoid compounds are also well-known for forming bimolecular complexes.[11] We believe, therefore (and molecular models show), that the porphyrin dication **1a** and compound **2a** are isostructural and can approach closely enough (possibly aided by hydrogen bonding) for rapid electron transfer to occur to yield the porphyrin radical cation.

A similar situation would pertain in basified TCE, where molecular models again show that planar *meso*-substituents (the necessary prerequisite for delocalisation of phenoxide negative charge[12]) puckers the macrocycle of **1b**. This tautomer, is again isostructural with **2b**, so that rapid electron transfer can take place to yield the porphyrin phenoxy radical species.

In neutral TCE, however, the *meso*-substituents of **1c** are non-planar, thus sterically hindering close approach of **1c** and any tautomeric form of **2** (*e.g.*, the tautomer **2e**) and therefore electron transfer. However, a trace amount of the tautomer **1e** (with the required planar *meso*-substituents) would cause a little conproportionation with **2e** to occur. This would yield a low concentration of porphyrin π-radical cation and hence the weak singlet ESR spectrum.

Finally, it is interesting to note that aerial oxidation of the porphyrin **1** in TCE affords porphyrin radicals that can apparently be made to switch their unpaired electron from different parts of the molecule, depending on the acidity or basicity of the surrounding medium. Under basic conditions, the unpaired electron is localised on a *meso*-substituent, while under acidic conditions a conproportionation reaction occurs leading to a porphyrin π-radical cation with unpaired electron density delocalised over the macrocycle in a quasi-$^2A_{2u}$ ground state.[1] We are continuing to investigate the mechanism of porphyrin π-radical generation in acid solutions.

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