Tetrahedron Vol. 48, No. 14, pp. 2951-2956, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

FACILE AERIAL OXIDATION OF A PORPHYRIN. PART 12.[1]
SPIN-TRAPPING OF SOLVENT-DERIVED INTERMEDIATES FROM THE ADDITION OF BASE TO AN OXIDISED PORPHYRIN.

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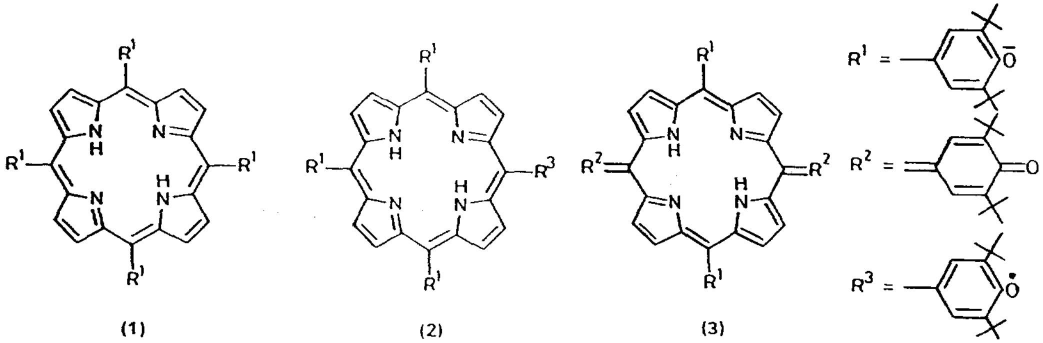
(*Received in UK* 5 *February* 1992)

Abstract. Esr-active adducts are produced on addition of base and a spin-trap to dichloromethane (DCM) solutions of the oxidised porphyrin (3): an explanation is offered in terms of trapped, solvent-derived intermediates undergoing oxidation to esr-active species.

AERIAL oxidation of porphyrin (1),[2] in basified DCM and ethanol (but not in chloroform[2]) is a concerted two-electron process to the porphodimethene-like compound (3) and hydrogen peroxide.[1] Further, (3) reacts with base and (1) to form the long-lived phenoxy-radical (2) in a reaction similar to hydrogen peroxide generation from base and anthraquinones.[3]

Esr spectroscopy and spin-trapping demonstrated production of $\dot{O}H$ (from hydrogen peroxide), and $\dot{C}H_2OH$ (from methanol used in the base) during the aerial oxidation of (1) to (3).[1] We wished to explore further the reaction of (3) with base in DCM, and in this paper we report our findings. Our results demonstrate the production of different solvent-derived intermediates which on trapping become esr-active only on further oxidation.



SCHEME 1

Experimental

Dichloromethane (DCM) and deuterated DCM were freshly distilled and degassed with nitrogen. The spin-traps, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO-Aldrich) and 2-methyl-2-nitrosopropane (NtB-Aldrich) were purified by literature methods[4] and made up into aqueous solutions (DMPO, 1M; NtB, 0.023M). The porphodimethene-like compound (3) was prepared as reported elsewhere,[2b] and samples dissolved in DCM (or d_2-DCM; 1ml). To these solutions were added the spin-traps (0.1 ml) followed (with vigorous agitation) by base (tetra-n-butylammonium hydroxide in methanol, 1M; 0.1 ml). Aliquots of these suspensions were then placed in a quartz flat cell, which was positioned within the cavity (20°C) of a Bruker ER 200D esr spectrometer. Spectra were run under the following conditions: microwave power = 10 dB, microwave frequency = 9.77 GHz, modulation amplitude = 0.2 mT, scan width = 10 mT, and gain = $4*10^5$.

Results and Discussion

Figure 1 shows the esr spectrum obtained on addition of base to a DCM solution containing (3) and DMPO. The triplet (a_H=0.133mT, ΔH_{pp}=0.053mT, g=2.009(6))[2a,e] is due to the phenoxy-radical and strongly suggests that because of its extended quinonoid structure, (3) reacts with base in a similar manner to anthraquinones (which generate hydrogen peroxide).[1,3]

Also present are bands due to a DMPO spin adduct significantly different from those observed by addition of base to DCM solutions of (1) and DMPO.[1] Figure 1 shows that the DMPO bands are clearly symmetric, suggesting a nine-line spectrum with the middle band obscured by the intense triplet of (2). The spectrum is readily assigned to the spin adduct of DMPO with $\dot{H}$ (4),[5] (a_N=1.52mT, a_H=2.013mT, g=2.006(4)).

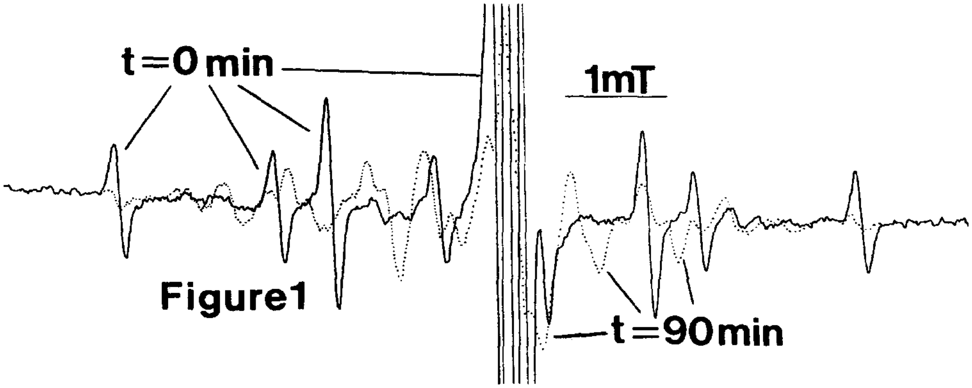


Figure1

Further evidence for this assignment was obtained by repeating the experiment using the spin-trap NtB. The spectrum is shown in figure 2, with one of the central peaks obscured by the triplet of (2) and gives typical values of nitrogen and hydrogen hyperfine splitting constants for an NtB-H spin adduct,[6] (a_N=1.47mT, a_H=1.25mT, g=2.010(1)).

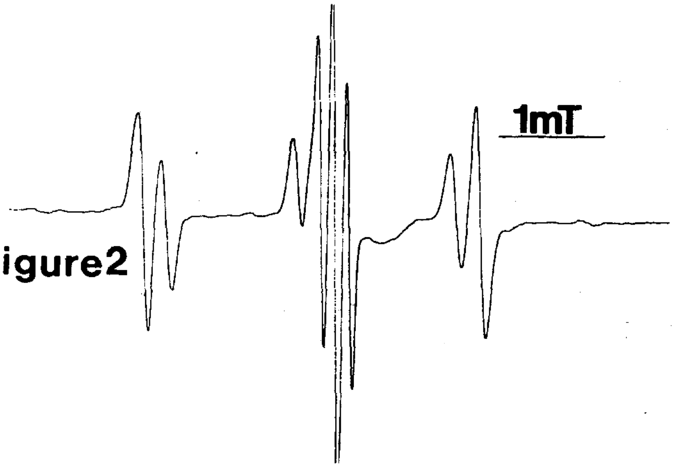


Figure2

Hydrogen peroxide is produced by the aerial oxidation of (1) in basified DCM[1] and most likely by the action of base on (3) under the same conditions. The observation of the DMPO-spin adduct (4) during the latter reaction suggests that $\dot{H}$ is also being produced. Under the circumstances, it is hard to see what the source of $\dot{H}$ might be and, even if $\dot{H}$ were produced, how it could survive long enough in the presence of $\dot{O}H$ (from the disproportionation of hydrogen peroxide in base[7]) to form a spin adduct with DMPO. We now suggest an alternative scheme, for the reaction of base with (3), in which the spin-adduct (4) is an artefact of the use of DCM as solvent.

Dichloromethane is known to undergo nucleophilic substitution in the presence of base to give formaldehyde.[8] Furthermore, formaldehyde undergoes a Cannizarro reaction in base (to give methanol and formate anion,[9]) which is known to involve hydride transfer. We suggest that DMPO intercepts the transfer of hydride anion, forming the esr-silent [DMPO-H]$^-$ adduct, a precedent for which exists in the known borohydride reduction of DMPO.[5] The presence of $\dot{O}H$ (from the reaction of (3) with base) would provide the necessary oxidising power to convert [DMPO-H]$^-$ to the esr-active (4). If this is true, then in the absence of (3), a mixture of DCM, base, and DMPO should be esr-silent. This proved to be the case. On addition of (3) to this mixture, however, the esr spectrum of (4) immediately appeared. Presumably, the rate of hydride transfer and trapping by DMPO is faster than the rate of peroxide formation by the action of base on (3).

Hydride transfer in the Cannizarro reaction of formaldehyde is thought to occur from an intermediate (**5a**). If so, then replacing the geminal hydrogens with deuterium atoms to give (**5b**) should alter the nature of any DMPO adduct. If deuteride transfer occurs, then the spin adduct with DMPO will show a suitably modified esr spectrum.[10] The primary deuterium kinetic isotope effect[11] would also lead to slower rates of deuteride transfer from (**5b**), enabling other intermediates to form DMPO adducts. On oxidation these would become esr-active, leading to a complete change in the esr spin-adduct spectrum. To test these ideas, we repeated the reaction of base with (3) in d_2-DCM containing DMPO. Figure 3 shows the esr spectrum obtained.

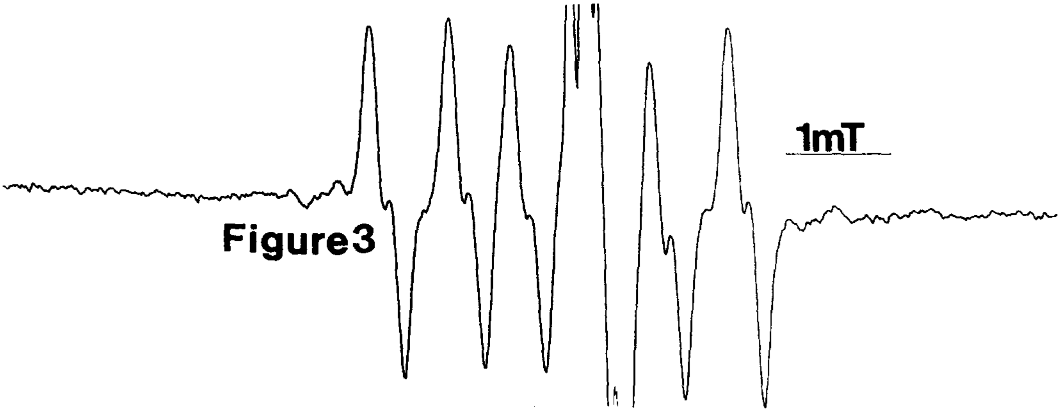


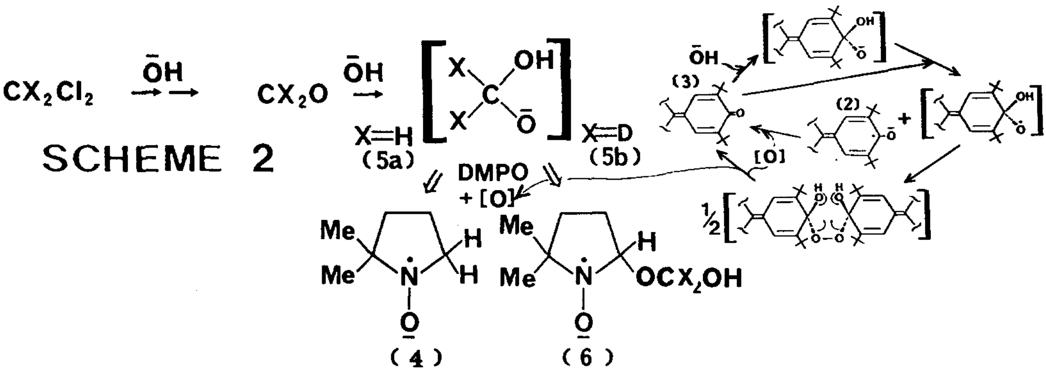
Figure3

Once again, the triplet of (**2**) predominates, obscuring one of the six spin-adduct bands. This DMPO-spin-adduct spectrum is different to that of (**4**) and those obtained from the aerial oxidation of (1) in basified DCM.[1] Analysis of the nitrogen and hydrogen hyperfine splittings (a_N=1.35mT, a_H=0.77mT, a_H =0.11mT, g=2.010(3)) shows them to be typical of those obtained for alkoxy-DMPO spin adducts.[12] We believe that DMPO has trapped the intermediate (**5b**), which has then been oxidised by $\dot{O}H$ to the esr-active DMPO adduct (**6b**, X=D) (Scheme 2).

Interestingly, the spectrum shown in Figure 1 decays after 90 min into a weak spectrum that resembles Figure 3. Presumably, in DCM, $\dot{H}$ competes more successfully than (**5a**) for DMPO. However, a small amount of (**6a**, X=H) is formed which has a longer life-time than (**4**). In d_2-DCM, on the other hand, (**5b**) reacts with DMPO in preference to $\dot{D}$, presumably because the primary deuterium kinetic isotope effect slows down the rate of deuteride transfer, to the extent that it is unavailable for adduct formation with DMPO.

Finally, the esr spectra of (**6a**) and (**6b**) are virtually identical. This may be explained by the equidistance of the δ-OC$\underline{H}_2$- and δ-OC$\underline{D}_2$- groups, respectively, from the unpaired electron making their contributions to nitrogen and hydrogen hyperfine splittings negligible.[12]

In conclusion, we believe that production of DMPO-adducts (4) and (6b) shows that attack by base on the solvent (DCM or d_2-DCM), is substantially faster than production of peroxide from base and (3). This contrasts with the rapid generation of peroxide (and its disproportionation into $\dot{O}H$) from the aerial oxidation of (1) in basified DCM. We continue to study the reactions of (1) and (3) and their possible applications.



SCHEME 2

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