E.S.R. Evidence for Chromium(v) Porphyrinates

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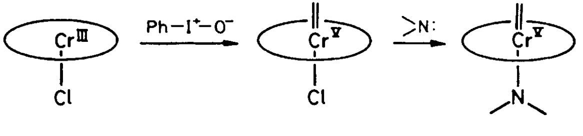
Summary The oxidation of chloro-5,10,15,20-tetraphenylporphyrinatochromium(III) with iodosylbenzene proceeds with oxygen transfer to chromium and two-electron oxidation of the metal to give a chromium(V) porphyrinate complex; the e.s.r. spectra of this complex, its ^{17}O-derivative, and its t-butylamine adduct show strong electron hyperfine interactions with the metal nucleus and the metal ligands and indicate a metal-centred radical as expected for chromium(V).

The facile catalysis of olefin epoxidation and alkane hydroxylation by iron(III),[1,2] manganese(III),[3,4] and chromium(III)[5] porphyrinates has been proposed to involve higher-valent oxo-complexes which readily transfer the oxo-ligand to organic substrates. Such metalloporphyrin species are of interest with respect to the oxidized forms of peroxidase[6] and the oxygen-transfer reactions characteristic of cytochrome P-450.[7] Considerable ambiguity exists regarding the electronic structure of oxidized porphyrins since electrons can be removed either from the metal or from the porphyrin ring. We report here e.s.r. data which indicate that the oxidation of chromium(III) porphyrins with iodosylbenzene leads to oxidation of the metal to a chromium(V) complex.

The treatment of dichloromethane solutions of chloro-5,10,15,20-tetraphenylporphyrinatochromium(III) [Cr(TPP)Cl] with excess of iodosylbenzene at room temperature resulted in the production of an unstable, paramagnetic species (**1**) (equation 1). The reaction was conveniently monitored by



(1)

Cr(TPP)Cl (1) (2)

observing the appearance of a new Soret band at 418 nm (log ϵ 5·03) in the visible spectrum. The α,β-bands of Cr(*TPP*)*Cl* were replaced by weak, broad absorptions throughout the 500—600 nm region. On standing at room temperature, (**1**) decomposed to a bright red, diamagnetic oxochromium(IV) complex [λ_{max} 430 (ϵ 5·29) and 544 (4·29) nm].[8]

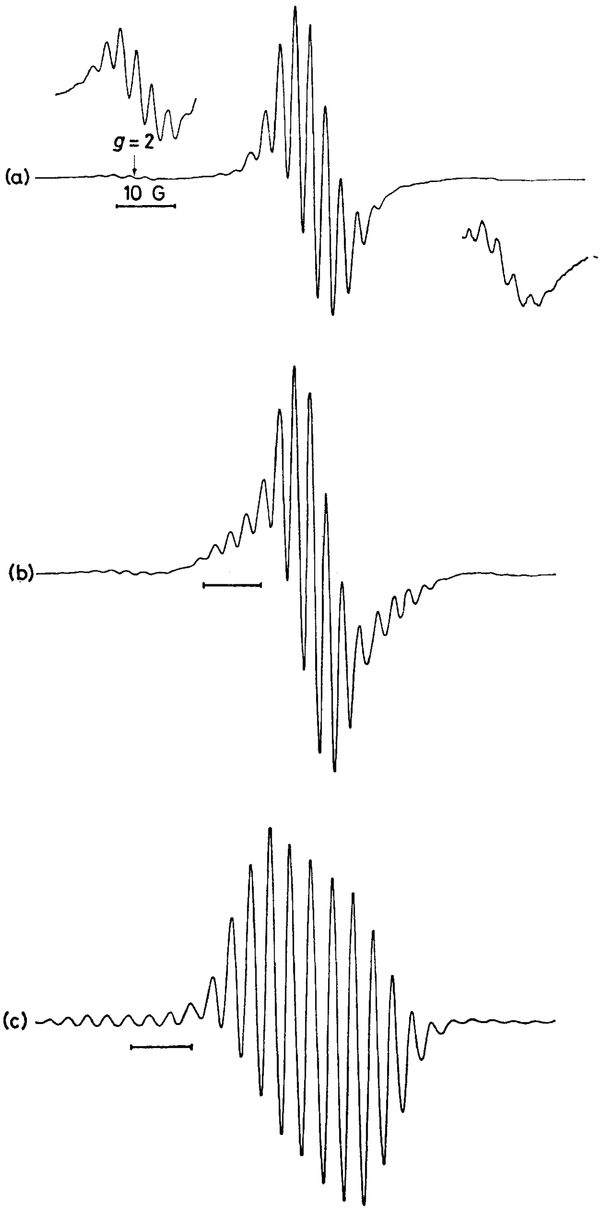


FIGURE. The e.s.r. spectra of (a) (**1**), (b) [^{17}O]-(**1**), and (c) (**2**), g 1·982, a_{Cr} 2·19 mT, determined in toluene at 293 K.

Examination of the reaction of Cr(TPP)Cl with iodosylbenzene in toluene by e.s.r. spectroscopy showed the disappearance of the broad absorbances characteristic of the axially symmetric, $S = 3/2$ chromium(III) and the appearance of a strong, sharp signal near $g = 2$ for (**1**). The e.s.r. spectrum of (**1**) consisted of a well resolved nine-line pattern centred at $g = 1{\cdot}982$, similar to that ascribed by Roček[9] to chromium(V) (Figure). This value also agrees well with e.s.r. spectra reported for d^1 metalloporphyrinate complexes of molybdenum(V)[10] and tungsten(V).[11] Figure (1a) shows electron–nuclear hyperfine interactions with the four equivalent ($I = 1$) ^{14}N nuclei ($a_{N(porph.)}$ 0·285 mT). That (**1**) is primarily a metal-centred radical is supported by the strong coupling of the electron spin to the 9·5% abundant, $I = 3/2$ ^{53}Cr nucleus (a_{Cr} 2·3 mT).

Transfer of oxygen from [^{17}O]iodosylbenzene to Cr(TPP)Cl is indicated by the e.s.r. spectrum in Figure (b). This spectrum could be simulated as a superposition of 56% (**1**) and 44% [^{17}O]-(**1**) ($I = 5/2$, 17 lines) with an isotropic ^{17}O hyperfine coupling constant of 0·54 mT. Addition of t-butylamine to solutions of (**1**) led to the e.s.r. spectrum in Figure (c). The axial nitrogen in this amine adduct (**2**) is coupled strongly to the electron spin ($a_{N(ax)}$ 0·78 mT, $a_{N(porph.)}$ 0·35 mT). Addition of aqueous NaOH to solutions of (**1**) caused a narrowing of the lines in the e.s.r. spectrum consistent with replacement of the axial chloride ($a_{Cl} <$ 0·1 mT) with hydroxide. Likewise, coupling was evident when the chloride was replaced with fluoride.

On the basis of this e.s.r. data, the formulation of (**1**) as a d^1 oxochromium(V) species is indicated. The alternative chromium(IV)–porphyrin π cation-radical would be expected to show significant proton hyperfine interactions and a g value near 2·00. Thus, the two-electron oxidation of Cr(TPP)Cl with iodosylbenzene resulted in the removal of both electrons from the chromium d orbitals and not from the porphyrin π-orbitals. By contrast, the oxidation of chloro-5,10,15,10-tetramesitylporphyrinatoiron(III) with *m*-chloroperoxybenzoic acid leads to a two-electron oxidation product which we have characterized as an iron(IV) π cation-radical species.[12]

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