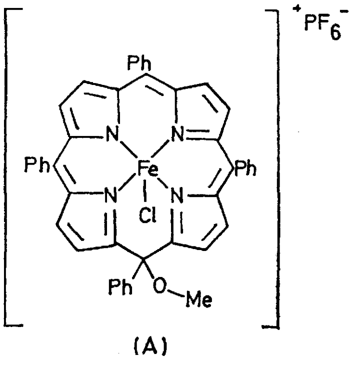
meso-Tetraphenylmethoxyisoporphyriniron(III) Chloride

By James A. Guzinski and Ronald H. Felton*
(*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia* 30332)

Summary The title iron(III) isoporphyrin, prepared by electrolysis, has optical features inconsistent with its identification as a hydroperoxidase, 'Compound I'.

During the catalytic cycle of hydroperoxidases, two-electron oxidation of the ferrihemeprotein yields an enzymatically active species conventionally denoted as Compound I. Among the various structures suggested[1-3] for this intermediate is one in which an iron(III) isoporphyrin[4] is formed from the heme. We describe here the preparation of compound (**A**), a model iron(III) isoporphyrin derived from the synthetic pigment, tetraphenylporphyriniron(III) chloride, $Fe^{III}TPPCl$.

Cyclic voltammetry of $Fe^{III}TPPCl$ dissolved in CH_2Cl_2 with $Pr_4N^+PF_6^-$ as supporting electrolyte displays two one-electron waves, $E_{\frac{1}{2}}(1) = 1{\cdot}05$ V *vs.* SCE (aq.) and $E_{\frac{1}{2}}(2) = 1{\cdot}53$ V. At the first wave iron(IV) porphyrin is formed reversibly.[5] The second wave is polarographically reversible at a scan rate of 3 V/min. Addition of methanol



(A)

leaves the first wave unaltered but causes the second wave to disappear during the reductive sweep.

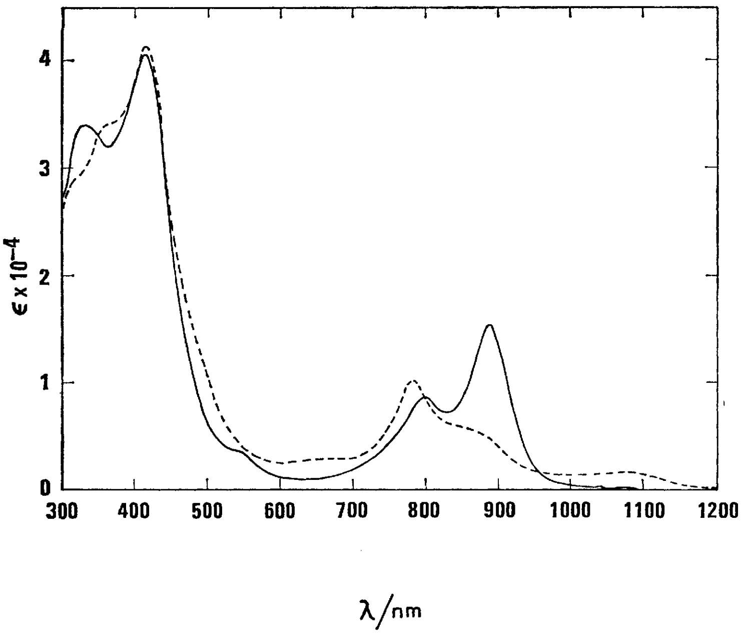


FIGURE. Absorption spectra in CH_2Cl_2: tetraphenylmethoxyisoporphyrin-iron(III) ———, -iron(II) – – – – – .

Upon controlled potential oxidation at 1·40 V in MeOH–CH_2Cl_2 (1% v/v) the spectrum shown in the Figure appears as the Fe^{IV}TPPCl spectrum disappears. The oxidation product isolated as the PF_6^- salt contains high-spin iron (μ_{eff} = 5·7 ± 0·1),[6] and may be electroreduced ($E_{\frac{1}{2}}$ = 0·45 V) to the unstable iron(II) compound whose spectrum is shown in the Figure. The reduced form is oxidized in air to the iron(III) species, but in the presence of a proton source it disproportionates to Fe^{III}TPPCl and the iron(III) form. Reduction of the iron(III) isoporphyrin under acidic conditions with the net uptake of 2 equiv. affords complete recovery of Fe^{III}TPPCl. Electrophoresis demonstrated that the isolated iron(III) compound was positively charged. Incorporation of MeO^- was proved by isolation of the iron(III) isoporphyrin prepared with CD_3OD. The i.r. absorption spectrum (Nujol) possessed the characteristic symmetrical (2072 cm^{-1}) and asymmetrical C–D stretching frequencies (2220 and 2225 cm^{-1}). Shaking of the CD_3O adduct in CH_2Cl_2 with aqueous HCl had no effect on the i.r. absorptions thus demonstrating that the methoxide is incorporated into the porphyrin nucleus and is not an axial ligand. That chloride is present is shown by a satisfactory elemental analysis.

Assignment of methoxy-addition to the *meso*-carbon is inferred from the striking similarity of the near-i.r. and visible absorption spectrum with that of the previously characterized *meso*-tetraphenylmethoxyisoporphyrinzinc-(II).[7] The absorption at 875 nm, so characteristic of interruption of the porphyrin π system, clearly eliminates the idea that Compound I contains an iron(III) isoporphyrin prosthetic group, for neither horseradish peroxidase nor catalase Compound I possess strong near-i.r. bands.

In view of the evidence that isoporphyrins are formed by nucleophillic attack[7,8] upon porphyrin π-dications, we suggest that the primary electrode product at the second polarographic wave is an iron(IV) π-cation radical which forms the π-dication by internal electron transfer following nuclear rearrangement. Rapid-scan spectroelectrochemical studies in progress should permit characterization of the primary product.

We acknowledge support by the National Institutes of Health.

(*Received*, 9*th July* 1973; *Com.* 973.)

---

[1] A. S. Brill, *Compre. Biochem.*, 1966, **14**, 447.

[2] J. Peisach, W. E. Blumberg, B. A. Wittenberg, and J. B. Wittenberg, *J. Biol. Chem.*, 1968, **243**, 1871.

[3] D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 614.

[4] D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, in 'Bioinorganic Chemistry,' ed. R. F. Gould, Advances in Chemistry Series 100, American Chemical Society Publications, 1971, p. 44.

[5] R. H. Felton, G. S. Owen, D. Dolphin, and J. Fajer, *J. Amer. Chem. Soc.*, 1971, **93**, 6332.

[6] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[7] D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, 1970, **92**, 743.

[8] G. H. Barnett, M. F. Hudson, S. W. McCombie, and K. M. Smith, *J.C.S. Perkin I*, 1973, 691.