

Redox Chemistry of Dichlorophosphorus(v)tetraphenylporphine: Isolation and Characterization of a Stable Porphyrin 'Anion' Radical and Possible Evidence for Internal Electron Transfer.

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One-electron reduction of the title complex leads to an extremely stable ring-reduced radical which has been isolated and characterized; addition of a second electron leads to, among other products, the free base tetraphenylporphine *via* an internal electron transfer.

The recent discovery of nonmetal and metalloid porphyrins, specifically phosphorus complexes of octaethylporphyrin (OEP)^{1,2} and tetraphenylporphine (TPP)³ has engendered considerable interest owing to some unique chemical and spectroscopic properties exhibited by these materials. Many of these properties can be traced to the accessibility of two valence states for the central atom⁴ and to structural deformations associated with binding the very small P^V ion.⁵ For these reasons we have investigated the redox chemistry of these systems.

The title complex (1), originally identified as the mixed ligand,⁵ chloro-hydroxo-complex has now been determined to be the dichloro-species. In acetonitrile, this cationic complex, P^V(TPP)Cl₂⁺ Cl⁻, undergoes reversible reduction as indicated by cyclic voltammetry (Figure 1). The two sequential one-electron reductions separated by 379 mV are typical for porphyrin complexes undergoing reduction at the ring.⁶ What is notable however, is the relatively high potential at which these reductions occur. In fact, this is the most easily reduced porphyrin complex yet reported, most porphyrins not undergoing reduction until *ca.* -1.0 V.[†] Fuhrhop, Kadish, and Davis have shown that the redox potentials of

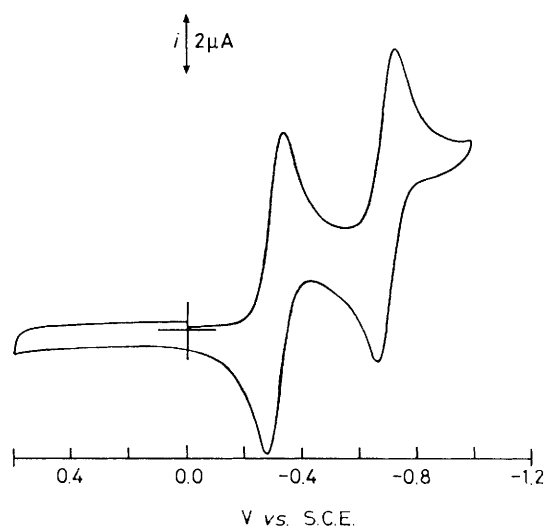
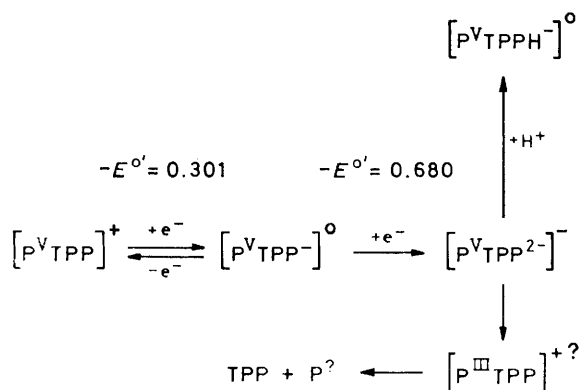


Figure 1. Cyclic voltammogram of dichlorophosphorus(v)tetraphenylporphine on a Pt electrode in acetonitrile, at -3°C , at a scan rate of 0.1 V/s. The electrolyte is 0.1 M tetrabutylammonium hexafluorophosphate.

[†] Prior to discovery of the metalloid porphyrins, the highest ring-based reduction potential reported was that of the Sn^{IV} complex of TPP at -0.9 V. The other metalloid porphyrins such as Sb^VOEP also have relatively high reduction potentials, see ref. 4.

metalloporphyrins can be related to the inductive effects of the central metal ion.⁶ The high reduction potential for the phosphorus(v) complexes is consistent with this idea but most probably contains a structural component as well.



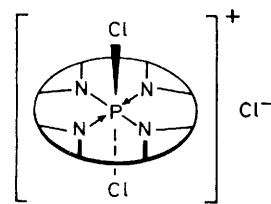
Scheme 1

Exhaustive electrolysis at -0.52 V and -3°C in acetonitrile consumed one electron per mole and resulted in the crystallization of the 'anion' radical.[‡] This crystalline material has been characterized by optical, e.p.r., and i.r. spectroscopy as the mono-ring-reduced species.§ This is only the second time a crystalline one-electron reduction product of a porphyrin has been isolated and characterized.⁷ The radical is extremely stable, with no detectable decomposition observed in air for at least six months, in the solid state. It is also stable for days in undegassed toluene solution but reverts back to starting material within several hours in chlorinated solvents. The ease of isolation, preparation, and stability of this species suggest that a crystal suitable for X-ray diffraction may be obtainable.

Addition of a second electron to the dichloro-complex is chemically reversible on the cyclic voltammetry time scale at low temperatures or at a very fast scan rate, and presumably leads to the two-electron-reduced monoanion. However, exhaustive electrolysis at -0.8 V, even at -3°C , leads to two new major products. These products have been identified by optical spectroscopy as the P^V phlorin anion and the free base tetraphenylporphine. The formation of free TPP upon

‡ Owing to the cationic nature of the starting porphyrin, the radical has overall electroneutrality. The 'anion' radical terminology is used only to facilitate comparison with the porphyrin literature.

§ E.p.r. parameters: $g = 2.0027$, peak-to-peak line width, 7 G; n.m.r. spectroscopy reveals contact shifted resonances consistent with the free radical formulation. Optical data, λ_{max} ($\epsilon \times 10^3$) 434 (68.0), 645 (5.2), 701 (6.3), 726 (6.8), and 830 nm (2.2).



(1)

two-electron reduction can best be rationalized as an internal electron transfer between the direduced porphyrin ring and the central phosphorus atom yielding an unidentified $P^{III}TPP$ complex. Phosphorus(III) complexes of the porphyrins are known to be extremely unstable and to decompose to yield free porphyrin.¹ Internal electron transfers such as that described here have been shown to occur in a few other metalloporphyrin systems.^{8,9} The other major product, the phosphorus(V) phlorin anion, appears to be formed competitively with the internal electron transfer product *via* protonation of the initially formed two-electron ring-reduced species. Such phlorins are common products of porphyrin reductions.¹⁰ The overall reductive electrochemistry of the dichloro-phosphorus(V)TPP complex is depicted in Scheme 1.

The electrochemistry of these phosphorus complexes is strongly controlled by the axial ligation. The analogous dihydroxy-complex gives a completely different electrochemistry.

Received, 23rd August 1982; Com. 1016

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