Cations and Cation Radicals of Porphyrins and Ethyl Chlorophyllide a

Sir:

The polarographic oxidation of a variety of porphyrins has been studied in butyronitrile and in methylene chloride. Oxidation proceeds via two well-defined one-electron abstractions, and cyclic voltmammetry showed these reactions to be reversible and the intermediates to be stable. We describe here the electrolytic and chemical preparation of cation radicals of various porphyrins and of ethyl chlorophyllide a as well as the formation of the dication of magnesium octaethylporphyrin.

Electrolysis of magnesium octaethylporphyrin (MgOEP) in CH2Cl2 at +0.7 V vs. aqueous sodium chloride yielded a blue-green solution, and the resulting species (principal absorption maxima at 378, 392, 585, and 660 nm; see Figure 1) was shown by coulometry to be the product of a one-electron oxidation. Isobestic points, observed as the oxidation was followed spectrophotometrically, were indicative of the smooth course of the reaction. Esr measurements on these solutions showed a single line, g = 2.0028, 2.5 G wide (peak to peak). MgOEP underwent a similar one-electron oxidation when treated with bromine in either methylene chloride or chloroform. The product of the chemical oxidation was spectroscopically similar to the cation radical obtained via electrolysis and was stable in these solvents. Our optical and magnetic data are consistent with those of the radical obtained by Fuhrhop and Mauzerall. Because of its absorption spectrum and its stability, these authors have proposed that the MgOEP radical formed in alcohols is a phlorin derived from the solvent. However, the agreement between the calculated and observed electronic absorption spectra of the cation radicals and our observation of their stability in alcohol-free solvents render this proposal unnecessary.

Additional evidence for a simple cation radical in which an electron has been abstracted from the porphyrin ring is found in the reversible one-electron oxidation of magnesium and zinc tetraphenylporphyrins (TPP). Thus the partially resolved nine-line esr spectrum of ZnTPP+ (Figure 2, second derivative presentation) can readily be assigned to four equivalent nitrogens, hyperfine splitting constants of aN = 1.5 G and aH = 0.25 G (eight β protons of the pyrroles) were obtained by the SCF-MO calculations described below. A computer-simulated spectrum (Figure 2), based on aN = 1.43 and aH = 0.24 G, adequately resembles the experimental data.

Continued electrolysis of MgOEP+ at +0.9 V vs. aqueous sodium chloride resulted in the removal of an additional electron, and the optical spectrum at this stage is shown in Figure 1. The esr signal associated with MgOEP+ decreased during the course of the electrolysis. Two-electron reduction of this new species regenerated 95% of the initial MgOEP. Addition of MgOEP to the oxidized product re-formed the cation radical in accord with the reaction

\[
\text{MgOEP}^2+ + \text{MgOEP} \rightarrow 2\text{MgOEP}^+ + \text{MgOEP}^2-
\]

Electrolysis of MgTPP+ and ZnTPP+ also proceeded to the dication stage. Oxidation of metalloporphins, by the methods described, is not limited to group II metals but may be extended to transition metals. Thus cobalt(II) octaethylporphyrin (CoIIOEP), in chloroform, underwent two distinct one-electron oxidations when treated with bromine. The first step, which required 0.51 ± 0.02 mol of bromine, brought about the oxidation of divalent to trivalent cobalt giving [CoIII(OEP)]^2-Br-. Further oxidation of the trivalent complex used 0.51 ± 0.02 mol of bromine and yielded a green species (Figure 3) formulated as [CoIII(OEP)]^2-2Br-. This formulation is supported by the quantitative conversion of the dication according to

\[
[\text{CoIII(OEP)}]^2-2\text{Br}^- + [\text{CoIII(OEP)}] \rightarrow 2[\text{CoIII(OEP)}]^2-\text{Br}^-
\]

The two-electron oxidation stage could also be reached by electrolysis in CH2Cl2.

The interest shown in the redox products of chloro-

![Figure 1](image1.png)

![Figure 2](image2.png)

Figure 2. (a) Second-derivative esr spectrum of ZnTPP+ in CH2Cl2. (b) Computer-simulated spectrum: 1.22-G line width, Lorentzian line shape, four equivalent nitrogens, aN = 1.43 G, and eight equivalent protons, aH = 0.24 G.

(2) S. W. Feldberg, private communication.
phylls prompted us to study the electrochemical oxidation of ethyl chlorophyllide a. One-electron oxidation at 0.6 V vs. sce yielded a yellow solution whose optical spectrum is shown in Figure 4. The product exhibited a singlet esr signal 9 G wide (g = 2.0028). Attempted chemical oxidation by bromine led to allomerized material.

Stable oxidized products of CdTPP, CoTPP, H₂TPP, zinc tetraphenylchlorin, free base and zinc etioporphyrin I, and ZnOEP have also been prepared by the above techniques. These results will be discussed fully in a later publication.

(3) Controlled potential electrolyses were performed in situ, at platinum electrodes, in either a Cary Model 14 spectrophotometer or a Varian V-4502 esr spectrometer. Methylene chloride solutions of porphyrins (≈10⁻¹ M) and electrolyte (0.1 M (C₂H₅)₃NClO₄) were purged with argon. Potential plateaus were obtained from ref 1. For esr measurements, the anodic potential was slowly raised until a signal appeared.

(4) Errors in the coulometric data do not exceed 10%.

(5) J. H. Fuhrhop and D. Mauzerall, J. Am. Chem. Soc., 90, 3875 (1968), have recently reported the one-electron oxidation of magnesium octaethylporphin by iodine in alcohols.

(6) Open-shell, restricted Hartree–Fock calculations of the optical and esr spectra of the porphyrin cation radical were performed in the Pariser–Parr–Pople approximation. Calculated transitions are at 371, 398, 724, 740 nm. In the same order, dipole oscillator strengths are 0.032, 1.628, 0.014, 0.018.


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R. H. Felton
Department of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

D. Dolphin
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

D. C. Borg, J. Fajer
Brookhaven National Laboratory
Upton, New York 11973
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(8) Although the assignments may not be unique because of the incomplete resolution, the experimental spectrum could not be matched without the proton splittings.

(9) [CoIIIOEP]⁺Br⁻ was isolated, and recrystallized from methylene chloride-ligroin. Satisfactory elemental analyses and mass spectra were obtained.


Communications to the Editor