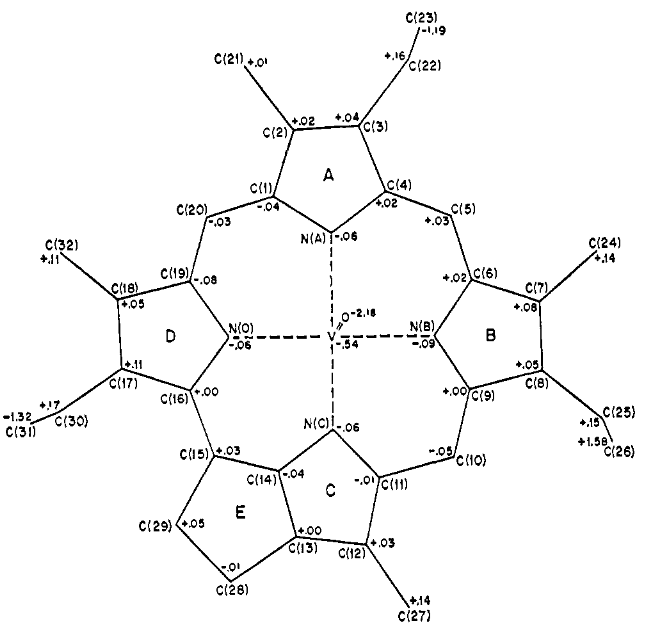

Figure 1. The two-dimensional structure of VO-DPEP projected onto the plane defined by the four nitrogen atoms. The smaller numbers at each atom specify the displacement in ångströms from the best least-squares plane using all the atoms except V, O, and the methyl and ethyl side groups.

b = 13.961 (1), c = 14.090 (3) Å; β = 116.97° (1); Z = 4; empirical formula $C_{32}H_{34}N_4VO \cdot C_2H_4Cl_2$.

The intensities of 1911 independent reflections were measured by the 2θ scan technique using an automated General Electric XRD-5 diffractometer (Cu Kα radiation). The vanadium atom position was uniquely determined from a sharpened three-dimensional Patterson synthesis. The remaining structure was found by successive Fourier syntheses using all the observed intensities with phases calculated from the partial structure. No corrections were made for absorption or extinction. (μl = 0.9 for longest crystal dimension). The vanadium and chlorine scattering factors were corrected for the real and imaginary dispersion in the structure-factor calculations.

The refined structure indicates that the four nitrogens are coplanar within the standard error, and the vanadium atom lies 0.48 Å out of this plane.[4,5] The molecule as a whole is nearly planar but can perhaps be best described as having the shape of a very shallow saucer. In Figure 1 the numbers at the atom positions represent the displacements in ångströms from the best least-squares plane defined by all the atoms except the V=O group and the attached methyl and ethyl groups. The isotropic B's increase with distance from the vanadium atom, being 2.8 Å^2 for the four nitrogens and their 8 adjacently bonded carbon atoms, 3.2 Å^2 for the 14 outer carbon atoms, and 4.3 Å^2 for the substituent methyl and ethyl carbon atoms. These are average values, and no atom has a B greater than 5.5 Å^2. The B's for the ethylene chloride are extremely anisotropic, and it is likely that this thermal motion is the cause of the low limit of observable reflections ($2\theta \leq 80°$).

The results given above suggest that the strain introduced by the ring E is not localized but is transmitted throughout the entire molecule.[6] Bond distances and angles have lost the fourfold symmetry which characterizes many of the porphyrins and porphines.[2] Another effect of the E ring is that it appears to have "pushed" the N(C) atom in toward the vanadium, as the V–N(C) bond distance (1.97 Å) is significantly shorter (about 7 σ) than the other three vanadium–nitrogen distances (2.11 Å average).

Acknowledgment. We acknowledge the support of the U. S. National Institutes of Health, General Grant No. FR-05580-013.

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The One-Electron Oxidation of Magnesium Octaethylporphin

Sir:

The porphyrins are central to the energy-transforming systems of biology: photosynthesis and respiration. Their function in these systems is based on their versatile redox properties. Although the reduction of porphyrins,[1-3] including photoreduction,[4] is partially understood, the behavior of these pigments on oxidation is far less clear.[5,6] We have found conditions for the reversible oxidation of a metalloporphyrin which lead to the formation of a rather stable free radical.

When a methanolic solution of magnesium octaethylporphin is titrated with iodine the pink color changes to green and the porphyrin fluorescence disappears. The spectrum of the product (Figure 1) shows bands at 398 (ϵ 71,000) and 683 nm (ϵ 23,000), with weak absorptions to wavelengths of >1 μm ($\epsilon \lesssim 10^3$); the strong absorption bands resemble those obtained from phlorins.[1-4] The reaction is reversed by simple back-titration with potassium iodide or other mild reducing agents. The redox potential of the system porphyrin–oxidation product is about equal to that of iodide–iodine in the same solvent. The overall form of the titration curve is complex because of the multiple equilibria involved between iodine and the solvent and possibly the por-

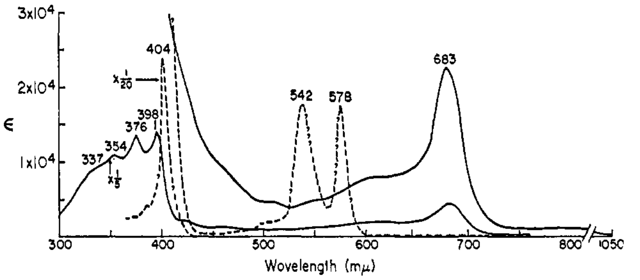

Figure 1. Absorption spectrum of magnesium octaethylporphin in methanol (----); after oxidation with FeCl$_3$ (——).

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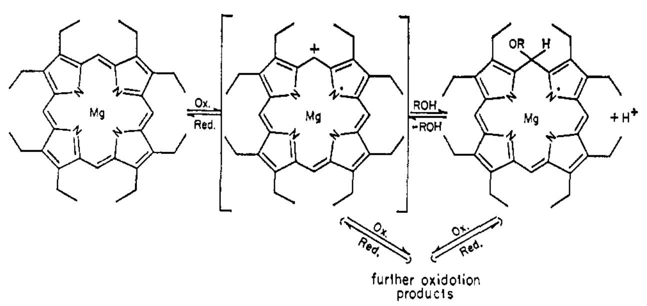

Figure 2.

phyrin. However, the initial part of the oxidation shows a ratio of 1.7 ± 0.3 mol of magnesium porphyrin to 1 mol of iodine. In agreement with this one-electron oxidation, the solution shows an esr spectrum of a single (Gaussian) line of width 4.9 ± 0.1 G and a g value of 2.0026 ± 0.0001. The line width and shape were invariant over a 100-fold range of concentration (10^{-5}–10^{-3} M). Calibration of the esr spectrometer with diphenylpicrylhydrazyl in the same solvent showed that 100 ± 30% of the green product could be accounted for as free radical. Moreover, the correlation of spins and absorbancies at 683 nm on titration with iodine was constant to ±20%, again over a 100-fold range. The esr signal also decreased or vanished on reversal of the reaction with KI or triethylamine.

Essentially the same product is obtained with dichlorodicyanobenzoquinone, bromine, N-bromsuccinimide, ferric chloride, and ferric perchlorate as oxidants of magnesium octaethylporphyrin in methanol. Oxidation with potassium permanganate, ceric sulfate, and sodium periodate gave the product absorbing at 683 nm, together with other products. No reaction occurred with p-benzoquinone or chloranil.

The formation of the green product stable for several hours occurs only in methanol and ethanol, and to some extent in 1-propanol with iodine as oxidant. No products absorbing beyond 620 nm are found in pyridine, chloroform, benzene, dimethyl sulfoxide, dimethylformamide, or petroleum ether. With bromine or N-bromsuccinimide in methanol as oxidant, a peak near 680 nm is observed in chloroform, dimethyl sulfoxide, dimethylformamide, 1- and 2-propanol, 1- and 2-butanol, and 2-methyl-1-propanol. In 2-methyl-2-propanol the absorption peak is at 640 nm. In all these cases the green color vanishes rapidly, yielding brown solutions with complex spectra.

The above properties are best explained by the reaction scheme given in Figure 2.

The formulation of the radical as a phlorin derivative follows from its absorption spectrum and its stability in simple alcoholic solvents. Some evidence for a cationic form, either the porphyrin radical shown or the fully oxidized species, was obtained by observing the cathodic migration of the green product on paper electrophoresis.

Zinc octaethylporphin is not oxidized under these conditions by iodine, but is by bromine. The main oxidation product here has a broad absorption band at 960 nm and is now under more detailed study. The free base and the copper derivative are yet more difficult to oxidize.

The facile oxidation of the magnesium porphyrin as compared with the zinc derivative may help explain why it is the former chelate which occurs in photosynthetic systems. We explain this effect by noting that the spectra indicate the magnesium chelate to be more ionic than that with zinc. We would expect the dianion of the porphyrin to be more readily oxidized; Fischer has shown[7] that porphyrin disodium salts are easily photooxidized.

This class of porphyrin oxidation product may be of interest not only as the first step in the biosynthesis of bile pigments but also for its relation to the radical observed in photosynthetic systems.[8] The radical discussed in this note has a g value the same as that observed in photosynthetic bacteria and similar to that observed in porphyrin and bacteriochlorophyll radicals.[9]

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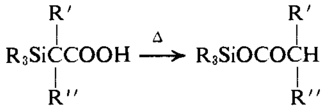
Thermal and Base-Catalyzed Rearrangements of Silylacetic Acids

Sir:

We wish to report that silylacetic acids (β-carboxysilanes), I, undergo thermal rearrangements to the isomeric acyloxysilanes (silyl esters), II, at or above their melting points when heated in sealed Pyrex tubes.



$$\underset{\text{I}}{R_3Si\overset{R'}{\underset{R''}{C}}COOH} \xrightarrow{\Delta} \underset{\text{II}}{R_3SiOCO\overset{R'}{\underset{R''}{C}}H}$$

Related thermal rearrangements have been reported recently for β-keto silanes.[1] Data for the rearrangements of the silylacetic acids are given in Table I.[2]

When base is present, similar rearrangements occur at much lower temperatures, and under some circumstances the silylacyloxysilane, III, accompanies the simpler rearrangement product, II. Compound III, which may arise by attack of carboxylate ion on the rearrangement product, II, as shown, is generally observed in reactions run at high concentrations of acid I or base; the amount of III formed can usually be reduced, sometimes to negligible amounts, by working at low concentrations. Because of the possible complexity of these rearrange-

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[2] Satisfactory analyses and spectra in complete accord with proposed structures have been obtained for all new compounds.