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THE FUNCTIONALISATION OF VANADYL OCTAETHYLPORPHYRIN

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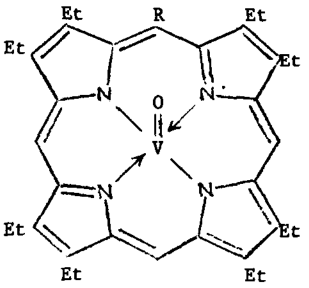
The fossil porphyrins frequently occur in the form of vanadyl complexes.[1] Thus the vanadium content of crude oil, which leads to corrosion problems in furnace operation,[2] commonly exists, in part at least, in the form of vanadyl porphyrins. We are examining the fundamental chemistry of the vanadyl porphyrin system, and have chosen vanadyl octaethylporphyrin (I) as the model substrate.



(I) R = H

(II) R = NO_2

Vanadyl octaethylporphyrin was prepared by metallation[3] of the parent base with vanadyl sulphate in acetic acid. It formed crimson crystals, m.p. >350°, and was characterised by elemental analysis and mass spectrometry (accurate molecular ion). The visible absorption of the metal complex in chloroform showed the normal, essentially two-banded, spectrum: in trifluoroacetic acid (but not in acetic acid) a considerable change, which we ascribe to the formation of the O-protonated species, was observed (figure 1). Spectroscopic changes were also noted when certain amines were employed as solvents. These changes are presumably associated with the introduction of a solvent molecule as an axial ligand, and, indeed, are sensitive to the steric requirement of the base. Thus pyridine, but not 2,6-lutidine, showed the effect; and, as shown in figure 2, the effect diminished in the solvent series:

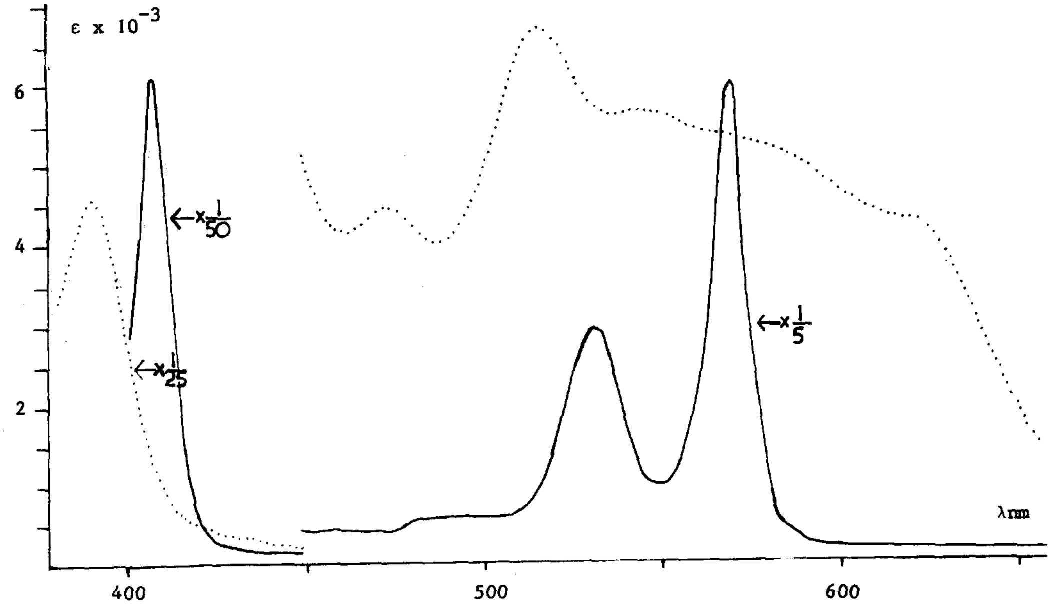


Figure 1. Electronic spectra of vanadyl octaethylporphyrin in $CHCl_3$ (——) and in CF_3CO_2H (·····).

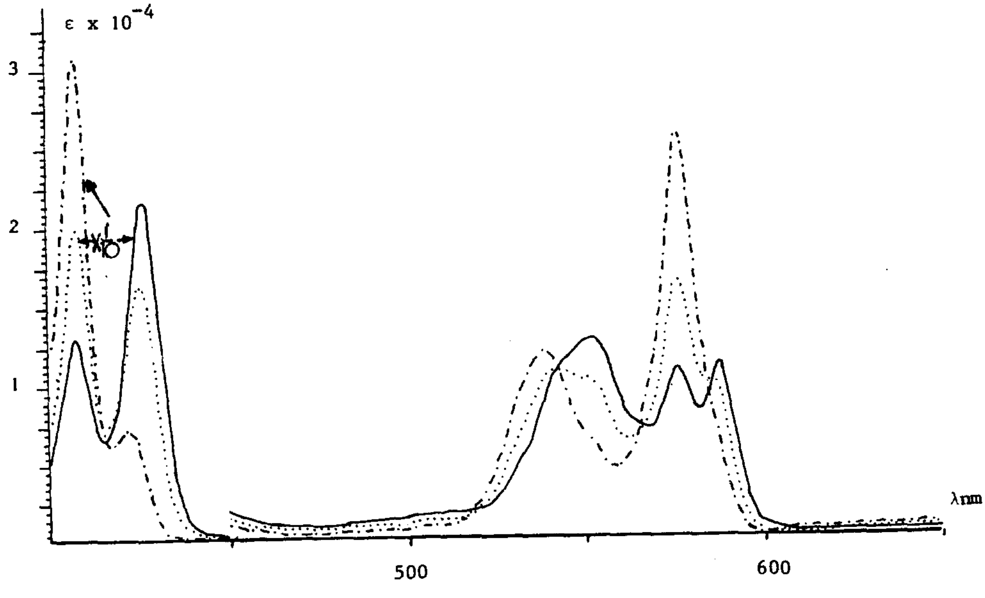


Figure 2. Electronic spectra of vanadyl octaethylporphyrin in n-butylamine (——); in sec-butylamine (·····); and in t-butylamine (-·-·).

n-$BuNH_2$; s-$BuNH_2$; t-$BuNH_2$.

Demetallation of vanadyl octaethylporphyrin could be effected with conc. sulphuric acid (3 min., room temperature) or methane sulphonic acid (1 hr., 100°):[4] partial demetallation occurred with HBr/HOAc[5] (4 hr., 100°), but no demetallation was observed with 50% aqueous sulphuric acid (1 hr., 100°) or with trifluoroacetic acid (18 hr., reflux). Demetallation could also be carried out via various reductive processes (ZnHg/HCl, then DDQ; $Li/NH_2CH_2CH_2NH_2$;[6] $LiAlH_4$). With the last reagent a green intermediate (λ_{max} ~ 462, 495, 585, 613, 650, 734 nm) was detected.

Attempted nitration of vanadyl octaethylporphyrin with HNO_3/HOAc[7] gave green polar materials which have not been identified. The nitration could, however, be controlled when nitric acid in acetonitrile was employed as reagent to give, under various conditions, mono-, di- and tri- substituted derivatives. Thus treatment with 2% nitric acid in acetonitrile at 0° for 5 min. gave vanadyl 5-nitrooctaethylporphyrin (II, 61%) as crimson prisms (analysis, accurate M^+) identical with a sample prepared by metallation of 5-nitro-octaethylporphyrin. It is of interest that, under the conditions of this metallation (i.e. $VOSO_4$/HOAc/Δ) although the main product is the expected one, some protodenitration occurs.

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REFERENCES

[1] A.Treibs, Annalen, 517, 172 (1935).
G.W.Hodgson, B.L.Baker, and E.Peake in "Fundamental Aspects of Petroleum Geochemistry" (Ed B.Nagy and U.Colombo), Elsevier, 1967, p.177.

[2] W.T.Reid, Seventh World Petroleum Congress, Section VII, 151 (1967).

[3] J.G.Erdman, V.G.Ramsey, N.W.Kalenda, and W.E.Hanson, J.Am.Chem.Soc., 78, 5844 (1956).

[4] J.G.Erdman, U.S. 3,190,829. Chem. Abstracts, 63, 5428d (1965).

[5] S.Groenings, Anal. Chem., 25, 938 (1953).

[6] U.Eisner and M.J.C.Harding, J.Chem.Soc., 4089 (1964).

[7] This reagent conveniently nitrates the parent compound.
R.Bonnett and G.F.Stephenson, J.Org.Chem., 30, 2791 (1965).