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Oxovanadium(IV) and Nickel(II) Etioporphyrin I as Models for Petroporphyrins

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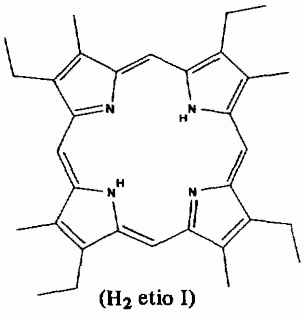
The occurrence of oxovanadium(IV) and nickel(II) porphyrin derivatives in crude oil deposits constitutes a major problem for processing heavy petroleum feeds [1]. In catalytic cracking, for example, the deposition of these metals on the catalyst surface produces several adverse effects, including loss of catalytic activity, detrimental changes in product hydrocarbon composition, and irreversible breakdown of the crystalline pore structure of the zeolite [2]. Removal of these trace contaminants by catalytic hydrotreating is a rapidly expanding segment of refinery processing. Naturally occurring petroporphyrins, present in concentrations of less (and commonly significantly less) than 2000 ppm, are difficult to extract from bitumen in any appreciable quantities: to elucidate the behaviour of these materials, a model compound is required which is readily available by laboratory synthesis and which is chemically, thermodynamically and spectroscopically similar to them. Oxovanadium(IV) and nickel(II) complexes of 2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-21*H*,23*H*-porphine (etioporphyrin I; H_2etio I), [VO(etio I)] and [Ni(etio I)], are readily synthesised in the laboratory [3], and have been used previously as models for petroporphyrins [4]. However, apart from their obvious synthetic attraction, and a skeletal similarity to some recognised components of petroporphyrins, no data have ever been presented to justify their use as model compounds. We present below thermodynamic and kinetic data which convincingly endorse their continued use.

The temperature régime for the mixing of catalyst and feed and subsequent cracking inside a commercial fluid-bed catalytic cracking unit is typically 650 to 800 K [5], with contact times of a few seconds. The thermal degradation of both [VO(etio I)] and [Ni(etio I)] was studied in dodecahydrotriphenylene solution in evacuated Carius tubes at *ca.* 670 K. The kinetics of thermal decomposition (monitored by quenching the reaction mixture, and determining the concentration of unreacted metalloporphyrin by electronic absorption spectroscopy) were found to be first-order: for [VO(etio I)], $k = 2 \times 10^{-4}$ s^{-1} (670 K), $t_{1/2} = 50$ min; for [Ni(etio I)], $k = 1.1 \times 10^{-4}$ s^{-1} (670 K), $t_{1/2} = 105$ min. The Arrhenius constant for [Ni(etio I)] is 0.22 s^{-1}, which compares favourably with the value of 0.20 s^{-1} obtained previously [6] for a petroporphyrin extract from Boscan crude. Under similar experimental conditions, the free porphyrin, H_2etio I, is essentially completely degraded after 90 min. These results signify that the majority of petroporphyrins present in the feedstock of a commercial cracking unit will reach the surface of the zeolite catalyst intact, but that any demetallation process on the surface will lead to a rapid irreversible degradation of the liberated ligand.



(H_2 etio I)

Stability constants are a sensitive measure of the balance of electronic and steric factors governing adduct formation between a complex and a ligating molecule or a surface. [VO(etio I)] forms 1:1 adducts with a wide range of *N*-donor ligands, L, according to:

$$[\mathrm{VO(etio\ I)}] + \mathrm{L} \overset{K}{\rightleftharpoons} [\mathrm{VO(etio\ I)(L)}]$$

K has been determined spectroscopically (see Fig. 1) for a wide range of ligands, and some of these values are compared in Table I with those determined using

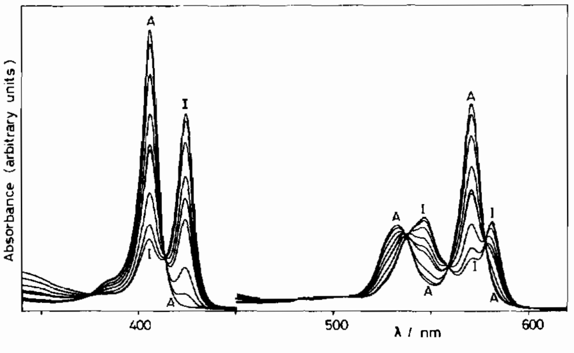


Fig. 1. The effect upon the electronic absorption spectrum of [VO(etio I)] in toluene at 25 °C (A) of the addition of increasing amounts of pyrrolidine (B → I). The total concentration of vanadium present in these solutions was 6.25 × 10^{-6} mol dm^{-3}, and there is an absorbance scale change at 450 nm.

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TABLE I. Stability Constants (l mol^{-1}) Determined for [VO(porphyrin)(L)] at 25 °C

L	[VO(etio I)]	Petroporphyrin
Pyrrolidine	1.19	1.00
Butylamine	0.38	0.39
Piperidine	0.26	0.27
2-Aminobutane	0.12	0.09
Pyridine	0.10	0.09

a sample of a natural oxovanadium(IV) petroporphyrin, extracted from a South American bitumen after a prolonged chromatographic purification procedure [7], and characterised by both electronic absorption and EPR spectroscopy. Despite the fact that natural mixtures of petroporphyrins are believed [8] to contain much longer alkyl side-chains than [VO(etio I)], there is a remarkable agreement between the values obtained for the natural and synthetic materials. Thus, from the kinetics of thermal degradation, stability constant measurements, and spectroscopic (both UV–Vis and EPR) measurements, metalloporphyrins derived from etioporphyrin I are seen to be excellent models for petroporphyrins.

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