On the Origin of Petroporphyrin Homologues: the Transalkylation of Vanadyl Octa-alkylporphyrins

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Summary Transalkylation occurs when vanadyl octaethylporphyrin is heated with alumina, with illite, or with montmorillonite.

RECENT mass spectroscopic studies have established that the petroporphyrins, for long regarded, following Treibs' pioneering study,[1] as essentially a mixture of deoxophyllo-

Transalkylation of octa-alkylporphyrin derivatives

Complex[a]	Support	Conditions[b]	Relative abundance[c] $M + 14$	$M + 28$
Vanadyl EP	—	*ca.* 300°, 12 h	1·2	0
Vanadyl EP	Al_2O_3[d]	300°, 12 h	2·7	3·8
Nickel OEP	—	300°, 12 h	0	0
Nickel OEP	Al_2O_3	300°, 12 h	0	1·7
Vanadyl OEP	—	300°, 12 h	0	0
Vanadyl OEP	Al_2O_3	300°, 12 h	2·0	21·0
Vanadyl OEP	SiO_2[e]	200°, 12 h	0	0
Vanadyl OEP	Montmorillonite[f]	200°, 12 h	5·0	10·5
Vanadyl OEP	Montmorillonite	150°, 12 h	1·1	1·0
Vanadyl OEP	Illite[g]	200°, 12 h	1·2	7·9

[a] EP = aetioporphyrin I, OEP = octaethylporphyrin. [b] All experiments were carried out in the absence of air. [c] M refers to the mass of the molecular ion of the appropriate reactant. [d] Al_2O_3: Hopkin and Williams "Camag" M.F.C. grade, neutral. [e] SiO_2: Hopkin and Williams M.F.C. grade. [f] From Amory, Mississippi; sample number 48W1222. [g] From Morris, Illinois; sample number 48W1536.

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erythroaetioporphyrin (I) and aetioporphyrin III (II), as their metal (vanadyl, nickel) complexes, comprise a complex mixture in which important constituents are members of homologous series related to the two porphyrins named.[2] While the formation of these two porphyrins[1] from chlorophyll a (or b) and haem pigments during diagenesis is plausible, the origin of their homologues—lower and higher —is not clear. Of the suggested explanations,[2] that postulating transalkylation[3] during diagenesis seemed to us most likely, and we now report model experiments which support it. Yen *et al.*[4] have reported that transalkylation occurs when vanadyl aetioporphyrin (I) is heated alone at 420°. However the mass spectrum reported (most intense peak *m/e* 445) does not contain the parent ion (*m/e* 543).

When heated *in vacuo* at *ca.* 300° for 12 h vanadyl octaethylporphyrin (III) was virtually unaffected (mass spectrum, Figure). However, when this vanadyl complex (1 mg) distributed on alumina (250 mg, chloroform slurry taken to dryness) was subjected to the same treatment, the mass spectrum of the product showed a considerable change (Figure). Prominent ions now appeared above the molecular ion (599) of (III) at intervals of 28 a.m.u.: below *m/e* 599 a prominent peak appeared at *m/e* 571 whereas in the spectrum of (III) the most important peak in this region occurred at *m/e* 569 (M^+ − 2Me). Accurate mass measurement on the ions at 571 and 627 showed that they corresponded, respectively, to the vanadyl complexes of heptaethylporphyrin and nonaethylporphyrin (or their isomers). Evidently transethylation had occurred: the appearance of groups of minor peaks around *m/e* 613 and 639 presumably represents a rather less favourable transmethylation (benzylic cleavage) process. With vanadyl aetioporphyrin (I) both transmethylation and transethylation appeared to be important. This and other results, including some with appropriate mineral supports at much lower temperatures (200°, 150°), are recorded in the Table. The reaction is regarded as an acid-catalysed aromatic transalkylation, well known in simpler systems,[5] although the location of the entering alkyl group (presumably *meso*) remains to be confirmed. Transalkylation between the octa-alkylporphyrin system and hydrocarbons (especially aromatic ones) appears to be a likely and relevant possibility and is being investigated.

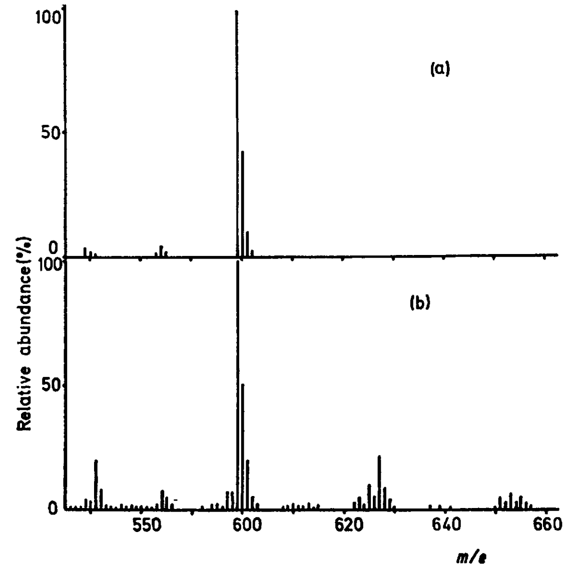
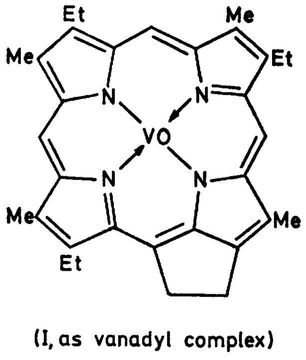
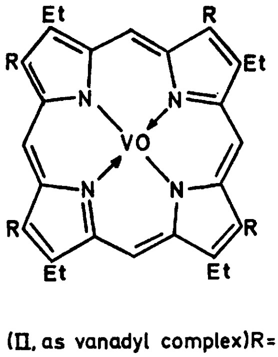


FIGURE. *High mass region of mass spectrum of vanadyl octaethylporphyrin after* (a) *heating alone* in vacuo (ca. 300°, 12 *h*) *and* (b) *heating with alumina under the same conditions.*



(I, as vanadyl complex)



(II, as vanadyl complex) R=Me
(III) R=Et

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[3] E. W. Baker, *J. Amer. Chem. Soc.*, 1966, **88**, 2311; D. J. Casagrande and G. W. Hodgson, *Nature Phys. Sci.*, 1971, **233**, 124; G. Eglinton, personal communication.

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[5] *E.g.*, R. L. Burwell and A. D. Shields, *J. Amer. Chem. Soc.*, 1955, **77**, 2766; A. Streitweiser and L. Reif, *ibid.*, 1964, **86**, 1988.