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Synthesis of Vanadylporphyrins Revisited

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Abstract

The reported methods for porphyrin vanadization were reviewed with the aim of optimizing a synthetic procedure. It was found that 100% metallation was obtained in 2 h with vanadylacetylacetonate in quinoline. The experiments were carried for *m*-tetraphenylporphyrin and octaethylporphyrin, the latter being easier to metallate.

Introduction

Vanadylporphyrins are naturally occurring components in many heavy oil deposits [1]. Trace amounts of this metal contaminant critically affect some of the processes in refinery [2], therefore it must be removed from crude oil.

Synthetic vanadylporphyrins have been widely used as model compounds to study the interactions of petroporphyrins with hydroprocessing catalytic surfaces [3–6]. However after reviewing the literature [7–16], it was found that there has not been reported an expeditious method for vanadyl insertion into the porphyrin macrocycle.

The most common methods for porphyrin vanadyzation were reviewed in trying to optimize a procedure with the following criteria:

(a) Complete metal insertion, to avoid separation from the free ligand.

(b) Minimal reaction times, given it has been reported [10] that the use of high temperatures for prolongued periods causes alteration of reactive side groups in the porphyrin.

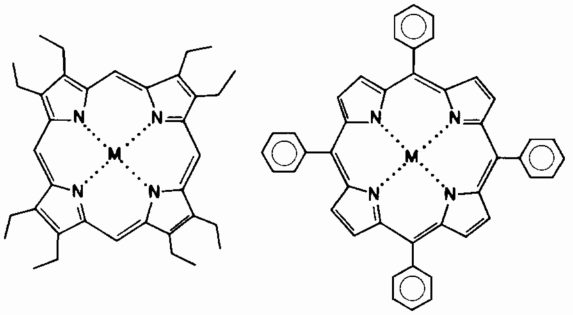
(c) Easy isolation and purification of the product.

In this communication we present a discussion of our results and report an improved synthesis for the vanadyl derivatives of *m*-tetraphenylporphyrins **2** and octaethylporphyrins **1** (Fig. 1).

Experimental

Reagents and Solvents

All reagents and solvents were of reagent grade and used as such, except pyrrole, dimethylformamide, pyridine, quinoline and acetic acid which were distilled before use. TPP was synthesized by Ruthemund's condensation [18] and freed of *m*-tetraphenylchlorine by oxidation with 2,3-dichloro-5,6-dicyano-quinone (DDQ) [19].



1a: OEP, M = 2H
1b: VOOEP, M = VO
2a: TPP, M = 2H
2b: VOTPP, M = VO

Fig. 1. Structures of octaethylporphyrin **1a** and *m*-tetraphenylporphyrin **2a**, and their vanadyl derivatives.

The metallation process was followed by electronic spectroscopy (Varian 2290). The TPP ligand has a very characteristic UV-Vis spectrum. This consists of an intense band at 418 nm ($\log \epsilon = 5.67$) and four satellite bands of lower extinction coefficient ($\log \epsilon \sim 4$) in the region between 500 and 700 nm. Upon vanadyl insertion, the four visible bands of the TPP collapse into one at 547 nm ($\log \epsilon = 4.30$) with two small side bands. Figure 2 presents a comparative UV-Vis spectra of H_2TPP and VOTPP in CH_2Cl_2. The criteria for complete metallation was the total disappearance of the TPP band at $\lambda = 515$ nm from the UV-Vis spectrum of the reaction mixture.

Discussion

Treib's method [9] using VCl_4 in a pressure vessel at 165 °C, was not repeated as it has been reported [10] to lead to chlorination on the porphyrinic meso-carbons.

Erdman *et al.* [10] claimed complete metallation of ethioporphyrin **I** in 3 h using vanadyl sulphate in a solvent mixture of pyridine:acetic acid (2:1).

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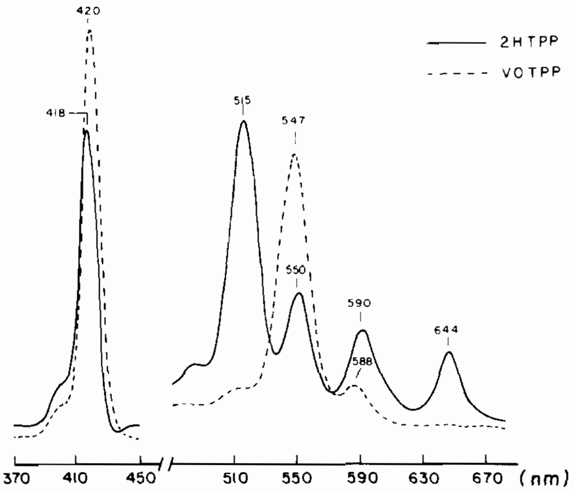

Fig. 2. Comparative UV-Vis spectra of TPP and VOTPP.

Bonnet *et al.* [11] took 7 h to insert vanadium into OEP under refluxing conditions using Erdman's procedure. We only obtained approximately 60% metallation for the TPP ligand after 24 h with the above conditions.

Adler's DMF method [12] using vanadylacetylacetonate [$VO(acac)_2$] as the metallating agent gave only 50% metallation of TPP after 48 h under reflux conditions. An increase of reaction times or addition of larger amounts of $VO(acac)_2$ did not significantly improve the yield. Similar results were reported by Walker [13] and Mitchell [14]. Use of pyridine instead of DMF gave the same yield.

Johnson and Dolphin [15] reported the synthesis of VOTPP in DMF by using vanadylsulphate as metal carrier. After 7 h they obtained only 46% yield. They noted that even upon the addition of more $VOSO_4$ or continued heating at reflux, metallation is never complete. The authors [15] developed an ingenious way to isolate VOTPP from H_2TPP by protonation of the free ligand with CF_3COOH. By solvent extraction they separated VOTPP from the water soluble protonated TPP. This method presents the disadvantage of low yields and it has been reported that CF_3COOH reacts with vanadylporphyrin [11] which is manifested by the change in its UV-Vis spectrum [17]. Bonnett [11, 17] ascribed this change to oxigen-protonation of the vanadyl groups. However Scott [6] observed partial degradation of VOTPP with CF_3COOH under aerobic conditions.

Melting of a thoroughly ground homogeneous 1:10 mixture of TPP:$VO(acac)_2$ at 250 °C, as reported by Buchler *et al.* [16] afforded partial metallation (50%).

Buchler *et al.* [16] reported that VOOEP could be metallated by $VO(acac)_2$ in phenol or quinoline at reflux temperatures (220–240 °C). The experimental procedures for the above syntheses were not described. It was found that phenol is not an ideal solvent because it is solid at room temperature. However, with quinoline 100% metallation was obtained after 2 h reaction in experiments carried out for TPP and OEP.

Results

The optimized procedure is as follows:

A solution of TPP (100 mg, 0.163 mmol) in quinoline (100 ml) was heated to reflux in the dark, under nitrogen atmosphere. $VO(acac)_2$ (0.43 g, 1.63 mmol) was then added and the mixture stirred for 2 h (disappearance of $\lambda = 515$). Quinoline was distilled off at reduced pressure and the crude was extracted with CH_2Cl_2 and then filtered through a short alumina column in order to remove impurities and excess of $VO(acac)_2$. Slow removal of CH_2Cl_2 in a rotary evaporator which induced crystallization with CH_3OH afforded 98 mg of pure VOTPP (90%). Similar results were obtained for VOOEP and for titanil insertion into TPP and OEP.

Conclusion

This method appears to be the best so far available because it requires a short period of reaction time, gives complete metallation and the isolation of the product is straightforward and affords high yields.

Acknowledgements

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