

## REDOX CHEMISTRY OF WATER-SOLUBLE VANADYL PORPHYRINS

PETER HAMBRIGHT<sup>a</sup>, PEDATSUR NETA<sup>b</sup>, MARIE-CLAUDE RICHOUX<sup>b</sup>,  
ZEINAB ABOU-GAMRA<sup>c</sup> and ANTHONY HARRIMAN<sup>c</sup>

<sup>a</sup>*Department of Chemistry, Howard University, Washington, DC 20059 (U.S.A.)*

<sup>b</sup>*Center for Chemical Physics, National Bureau of Standards, Gaithersburg, MD 20899 (U.S.A.)*

<sup>c</sup>*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (U.K.)*

(Received March 26, 1986; in revised form June 4, 1986)

### Summary

In aqueous solution, pulse radiolytic studies have shown that vanadyl porphyrins undergo redox reactions only at the porphyrin ring. The resultant porphyrin radical anions and cations are unstable with respect to disproportionation. Steady state reduction, both radiolytic and photochemical, of the vanadyl porphyrins results in formation of phlorins, porphodimethenes and chlorins depending upon pH and the nature of the porphyrin periphery groups. There is no evidence to show formation of products in which the central vanadyl ion has been reduced.

---

### 1. Introduction

Metalloporphyrins undergo successive electron additions and removals such that the polarograms and cyclic voltammograms exhibit a series of peaks [1, 2]. The redox reactions can occur either at the porphyrin ring or at the central metal ion. In fact, for oxidation processes it is possible to alternate the site of reaction. Thus, one-electron oxidation of lead(II) porphyrins results in formation of the lead(II) porphyrin radical cations [3] but removal of a second electron leads to the formation of the corresponding lead(IV) porphyrins [3 - 5]. In certain cases, manganese(III) porphyrins can be successively oxidized to the manganese(IV) porphyrin and then to the manganese(IV) porphyrin radical cation [6]. Similar examples can be found with oxidation of palladium(II) [7] and nickel(II) [8] porphyrins.

Alternate reaction sites are not so well documented for reduction processes. Under certain circumstances tin(IV) porphyrins can be reduced to the tin(II) porphyrins [9, 10], presumably via intermediate formation of the tin(IV) porphyrin radical anion, but the overall process is poorly characterized. Better examples are to be found with cobalt(II) and manganese(III)

porphyrins where the first electron is added to the central metal ion and further electrons go to the porphyrin ring [11 - 13]. Recent work [14, 15] has shown that certain vanadium(IV) porphyrins can be reduced to the corresponding vanadium(II) porphyrins, although the reaction mechanism remains unclear. This is somewhat surprising because electrochemical studies [16] have shown that vanadyl tetraphenylporphyrin (VOTPP) undergoes redox reactions only at the porphyrin ring. Consequently, it seems that the state of the axially coordinated ligands can influence the reduction product.

In this paper, we describe the redox chemistry of some vanadyl porphyrins in aqueous solution. Emphasis is placed upon reduction processes. In this context, it should be noted that vanadium porphyrins are important contaminants in oil and that they are extremely difficult to remove. Reduction of the central metal ion might render the compound susceptible to acid-catalysed demetallation, hence providing a possible means of removal [17].

## 2. Experimental details

Vanadyl *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (VOTMPyP) (tosylate salt) and vanadyl *meso*-tetrakis(4-sulphonatophenyl)porphyrin (VOTSPP) (sodium salt) were obtained from Midcentury Chem. Co. (The charge on the porphyrin periphery has been omitted for clarity, but it should be recalled that TSPP and TMPyP complexes possess overall electronic charges of  $-4$  and  $+4$  respectively.) The VOTSPP sample was purified by ion chromatography before use. All other materials were of the highest available commercial purity and were used as received.

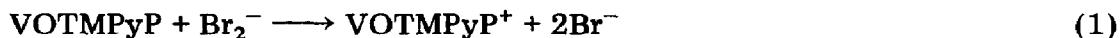
Pulse radiolysis experiments were performed as before [18] using a Febetron 705 accelerator to generate 50 ns pulses of 2 MeV electrons. For oxidations, the aqueous solutions contained metalloporphyrin (about  $10^{-4}$  mol dm $^{-3}$ ), KBr ( $10^{-2}$  mol dm $^{-3}$ ) and buffer (borate, phosphate or HClO $_4$ ;  $10^{-3}$  mol dm $^{-3}$  where possible) and were bubbled thoroughly with N $_2$ O. Under such conditions, Br $_2^-$  radicals are formed [19] with a radiation yield  $G = 6$ . This species is a powerful oxidant and it can be used to oxidize the metalloporphyrin. Solutions for reduction contained metalloporphyrin (about  $10^{-4}$  mol dm $^{-3}$ ), propan-2-ol (2% v/v) and buffer and were purged thoroughly with N $_2$ . Here, solvated electrons ( $G = 3$ ) and 1-hydroxy-1-methylethyl radicals ( $G = 3$ ) can be used to reduce the metalloporphyrin. Steady state radiolyses were performed with a  $^{60}\text{Co}$   $\gamma$  source delivering 10 krad min $^{-1}$ . In all cases, the course of reaction was followed by absorption spectroscopy.

Steady state photolyses were made with a 100 W quartz-iodine lamp filtered to remove light of wavelength shorter than 400 nm. Solutions contained metalloporphyrin ( $10^{-5}$  mol dm $^{-3}$ ), nicotinamide adenine dinucleotide (reduced) disodium salt (NADH) ( $2 \times 10^{-3}$  mol dm $^{-3}$ ) and buffer. The solutions were purged thoroughly with N $_2$  before irradiation and the course of reaction was followed by absorption spectroscopy.

### 3. Results and discussion

#### 3.1. Oxidation

Pulse radiolysis experiments performed at pH 7 showed that the two water-soluble vanadyl porphyrins were oxidized by  $\text{Br}_2^-$  radicals ( $E_{\text{ox}} = 1.69 \text{ V}$ ) [20, 21]:



However, under the conditions of the experiment,  $\text{Br}_2^-$  radicals decay rapidly by disproportionation



( $k = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [21]) and since the rate constant for reaction (1) is low ( $k_1 < 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) the yield of  $\text{VOTMPyP}^+$  was very much less than quantitative. Oxidation of  $\text{VOTSPP}$  was much more efficient ( $k_2 = 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ), despite the electrostatic repulsion between the reactants. The products of reactions (1) and (2) absorb quite strongly in the near IR region and they are assigned to vanadyl porphyrin radical cations by comparison with absorption spectra recorded for many other water-soluble metalloporphyrin radical cations [22]. The absorption spectrum recorded after oxidation of  $\text{VOTSPP}$  at pH 7 is shown in Fig. 1(a).

The pulse radiolysis records showed that  $\text{VOTSPP}^+$  decayed with a first half-life of 3 ms at pH 7. The decay kinetics gave poor fits to both first- and second-order kinetics, as is often the case for metal TSPP radical cations in water [23]. Increasing the pH to 12 decreases the half-life to about 1 ms. These values are roughly in agreement with the stability of  $\text{VOTSPP}^+$  expected from the electronegativity of the central vanadyl ion [23].

Steady state radiolysis using  $\text{Br}_2^-$  radicals as the oxidant at pH 7 showed that the vanadyl porphyrins were irreversibly bleached under oxidative conditions. The absorption spectral profile for oxidation of  $\text{VOTSPP}$  is shown in Fig. 1(b). The final product absorbs weakly at about 670 nm and is assigned to a dihydroxyporphyrin [24]. Thus, decay of  $\text{VOTSPP}^+$  most probably involves reduction by inadvertent impurities and radiation products and disproportionation to form the vanadyl porphyrin dication. This latter species is a strong electrophile and readily reacts with hydroxide ions to form isoporphyrin and dihydroxyporphyrin derivatives.

#### 3.2. Reduction

Pulse radiolysis studies performed in  $\text{N}_2$ -saturated aqueous solution at pH 7 showed that both  $\text{VOTMPyP}$  and  $\text{VOTSPP}$  are reduced by solvated electrons and 1-hydroxy-1-methylethyl radicals. The rate constants for reduction by solvated electrons were very high ( $k > 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) but reduction by 1-hydroxy-1-methylethyl radicals was much slower. The bi-

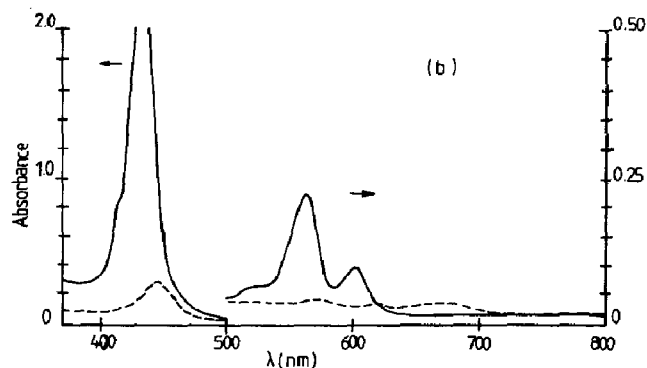
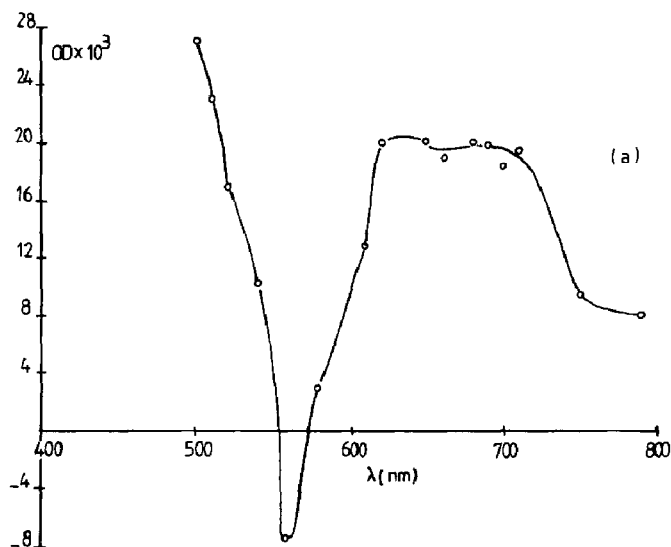


Fig. 1. (a) Differential absorption spectrum observed following pulse radiolytic oxidation of VOTSPP with  $\text{Br}_2^-$  radicals in aqueous solution at pH 7. (b) Absorption spectra recorded before (—) and after (---) steady state radiolysis of VOTSPP in  $\text{N}_2\text{O}$ -saturated aqueous solution at pH 7 containing  $\text{KBr}$  ( $10^{-2} \text{ mol dm}^{-3}$ ).

molecular rate constants for the reactions



and



were determined to be  $1.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $4.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively.

Figure 2 shows the difference absorption spectra recorded at the end of the reduction process (after about  $100 \mu\text{s}$ ). The spectra show absorption peaks between 600 and 700 nm and, by comparison with earlier work [22, 25], they can be assigned to the porphyrin radical anions. For VOTSPP, the differential absorption spectrum was found to be unaffected upon raising

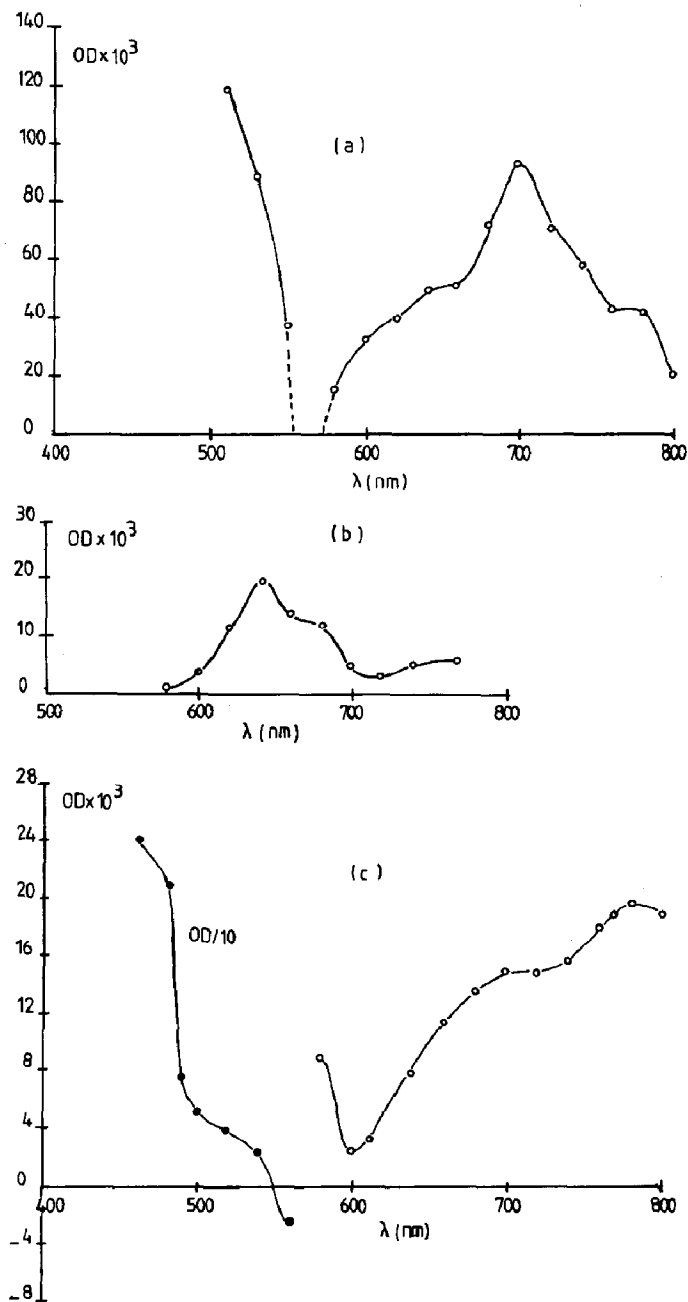


Fig. 2. Differential absorption spectra of the various radical anions as recorded after pulse radiolytic reduction of (a) VOTMPyP at pH 7, (b) VOTSPP at pH 7 and (c) VOTSPP at pH 1 in  $N_2$ -saturated aqueous solution.

the pH to 9 but lowering the pH to 1 caused a marked spectral change. The spectrum observed at pH 1 is shown in Fig. 2(c) and it is quite unlike that found at pH 7. The absorption spectrum of VOTSPP itself shows no changes throughout the range  $0 < \text{pH} < 11$  although there is a slight red shift of the

whole spectrum upon increasing the pH to 13. This latter effect is associated with deprotonation of an axially bound water molecule, for which the  $pK$  is about 14. The large absorption spectral change noted for the radical anion in acidic solution presumably reflects a protonation step. The proton may be added at either the meso position, forming a neutral radical



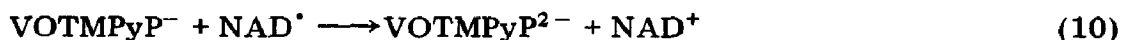
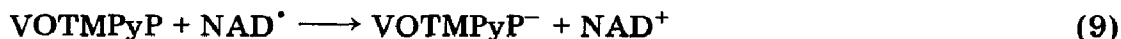
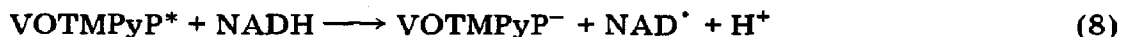
or at the vanadyl ion



Even though protonation of the vanadyl ion does not occur in the ground state complex at pH 0, the increased electron density residing on the porphyrin ring in the radical anion might raise the  $pK$  for this process. Consequently, we cannot really distinguish between these two sites for protonation but, based upon the electronegativity of the vanadyl ion [25], reaction (6) should become pronounced at  $\text{pH} < 3$ .

On longer time scales the radical anions decayed. For  $\text{VOTMPyP}^-$ , the absorbance at 700 nm decayed rapidly via second-order kinetics for which the first half-life was only 0.5 ms at pH 7. Under such conditions, there was a corresponding absorption growth at 650 and 800 nm. In neutral and acidic (pH 1) solutions,  $\text{VOTSPP}^-$  also decayed by second-order kinetics, decay being much faster at lower pH. Presumably, the major decay route, in all cases, involves disproportionation to form the metalloporphyrin dianion.

Normally, metalloporphyrin dianions are unstable with respect to protonation [26], even in alkaline solution, and the final products are phlorins. (A phlorin is a porphyrin  $\pi$  dianion, as formed by addition of two electrons to the porphyrin  $\pi$  system, which is monoprotonated. The single proton resides at one of the meso carbon atoms.) Steady state photolysis of  $\text{VOTMPyP}$ , in the presence of NADH as an electron donor [27], showed that, indeed, the phlorin is the major reaction product at  $\text{pH} > 7$ .



The triplet excited state lifetime of  $\text{VOTMPyP}$  was measured by laser flash photolysis to be about 350 ns. No fluorescence could be detected at 80 or 298 K but low temperature phosphorescence with a maximum around 750 nm was observed in water-glycerol mixtures. These findings imply that reaction (8) occurs via the excited triplet state manifold.

The phlorin ( $\text{VOTMPyPH}^-$ ) absorbs strongly at 820 and 510 nm, as shown in Fig. 3. There are no obvious changes in the absorption spectrum of

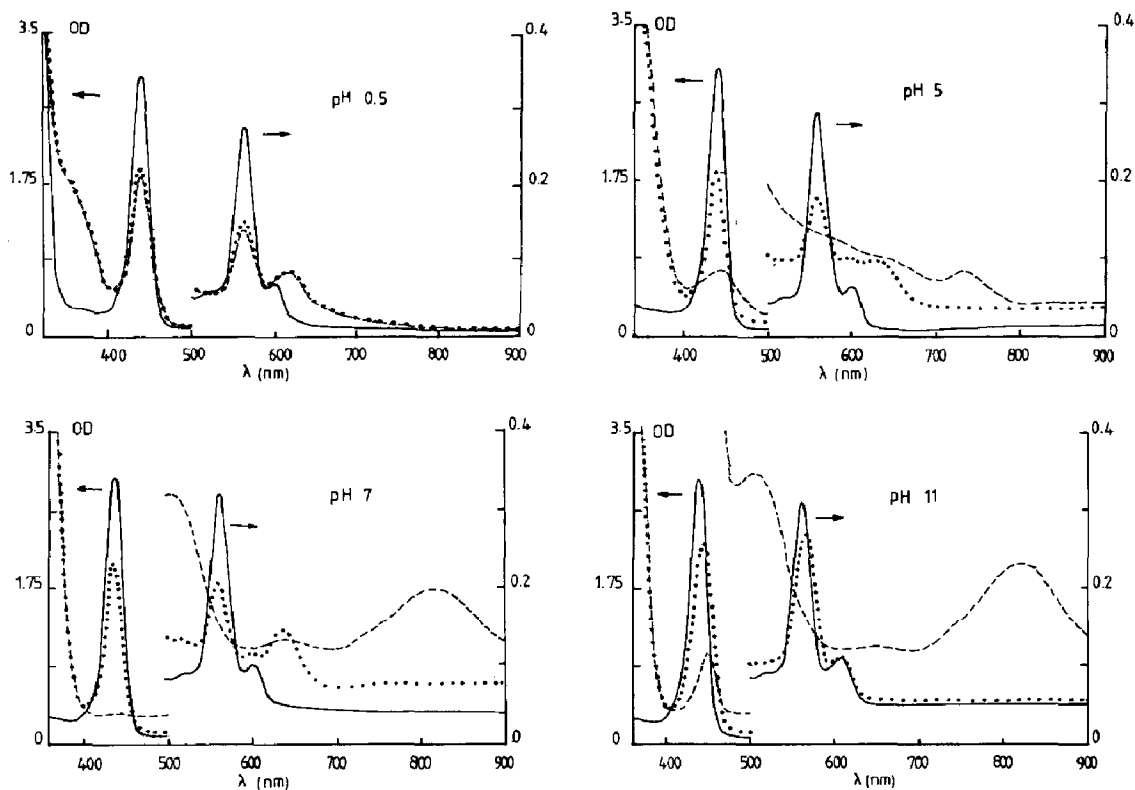


Fig. 3. Absorption spectra recorded before (—) and after (---) visible light photolysis of VOTMPyP in  $N_2$ -saturated aqueous solution containing NADH ( $2 \times 10^{-3}$  mol  $dm^{-3}$ ) at the given pH. Also shown (...) are the absorption spectra observed after aeration of the photolysed solution.

the phlorin between pH 7 and 13 although there is a progressive increase in absorbance around 650 nm relative to 820 nm as the pH approaches 7 (Fig. 3). Aeration of the final solution restores the original VOTMPyP but at pH < 8 aeration results in partial formation of a reduced metalloporphyrin ( $\lambda_{max} = 638$  nm). This latter product is a chlorin or an isobacteriochlorin [28]. (A chlorin is a porphyrin with hydrogen atoms added to two adjacent carbons on one of the pyrrole rings whilst an isobacteriochlorin is formed by addition of two further hydrogen atoms to an adjacent pyrrole ring.) Photo-reduction at pH 5 gave no phlorin but a product possessing weak absorption across the 600 - 750 nm region was formed (Fig. 3). Aeration of this product gave mostly reduced porphyrin ( $\lambda_{max} = 638$  nm). Photoreduction at pH 1.4 and 0.5 gave only reduced porphyrins ( $\lambda_{max} = 638$  nm and  $\lambda_{max} = 620$  nm respectively). Steady state radiolytic reduction at pH 7 gave an absorption spectrum almost identical with that observed after photoreduction and both phlorin ( $\lambda_{max}$  of 820 nm and 520 nm) and 650 nm species could be detected clearly. The identity of the product absorbing at 650 nm was not established for certain but it was not the radical anion. More likely, it is a phlorin having a different degree of protonation since addition of deoxygenated KOH

solution to a solution photolysed at pH 7 resulted in quantitative formation of the phlorin. The extra proton is probably added at the meso position forming a porphodimethene [29] (this is a diprotonated porphyrin  $\pi$  dianion with the protons residing on opposite meso carbon atoms) rather than at the vanadyl ion since the latter effect seems unlikely to cause such a large change in the absorption spectrum.

In most cases, aeration of the phlorin results in re-formation of the original porphyrin with little overall loss:



However, it is not clear how aeration at lower pH causes formation of chlorin. Possibly, the chlorin arises from a small amount of tetrahydroporphyrin that might be present but the mechanism of the reaction has not yet been established.

Similar photoreductions were performed with VOTSPP. Here, photolysis at  $\text{pH} > 10$  bleached the porphyrin but the product showed only diffuse absorption between 600 and 750 nm (Fig. 4). Aeration gave a reduced porphyrin with  $\lambda_{\text{max}} = 638$  nm but little restoration of the original VOTSPP. Photolysis at pH 9 (Fig. 4) gave rise to an absorption spectrum stretching right across the visible spectrum but there was a clearly resolved peak at 520 nm. Aeration gave some reduced porphyrin ( $\lambda_{\text{max}} = 638$  nm) but the major product was the original porphyrin. Similar spectra were observed for photoreduction at pH 7 and pH 5 although there was progressively less of the 520 nm product and more reduced porphyrin as the pH was lowered. Photolysis at  $\text{pH} < 5$  gave only reduced porphyrin. Again, steady state radiolytic reduction in the presence of propan-2-ol gave absorption spectral changes in very good agreement with those found in the photoreduction experiments.

It was found that the yield of the 520 nm product was optimal at pH 8. Photoreduction at this pH showed that the product could be oxidized quantitatively back to VOTSPP upon aeration of the solution. Addition of small amounts of  $\text{O}_2$ -saturated water showed that the re-oxidation step involved a two-electron change. Addition of deoxygenated  $\text{HNO}_3$  or KOH solutions to the solution photoreduced at pH 8 resulted in formation of the chlorin (or isobacteriochlorin) with  $\lambda_{\text{max}}$  at 638 nm or the diffuse spectrum respectively. Even dropping the final solution pH to below 1 did not cause demetallation.

For VOTMPyP, the observed reductive chemistry is consistent with known trends [25]. The electronegativity of the vanadyl ion is somewhat similar to that of aluminium(III) and the two metalloporphyrins show quite similar behaviour [25, 30]. At all pH values, the radical anion is unstable with respect to disproportionation and the phlorin is formed. At low pH, the radical anion may be protonated and disproportionation of the neutral radical might lead directly to formation of the chlorin. The phlorin also shows a pH dependence, owing to addition of a second proton at the meso position and, possibly, to the acid-base properties of an axially bound



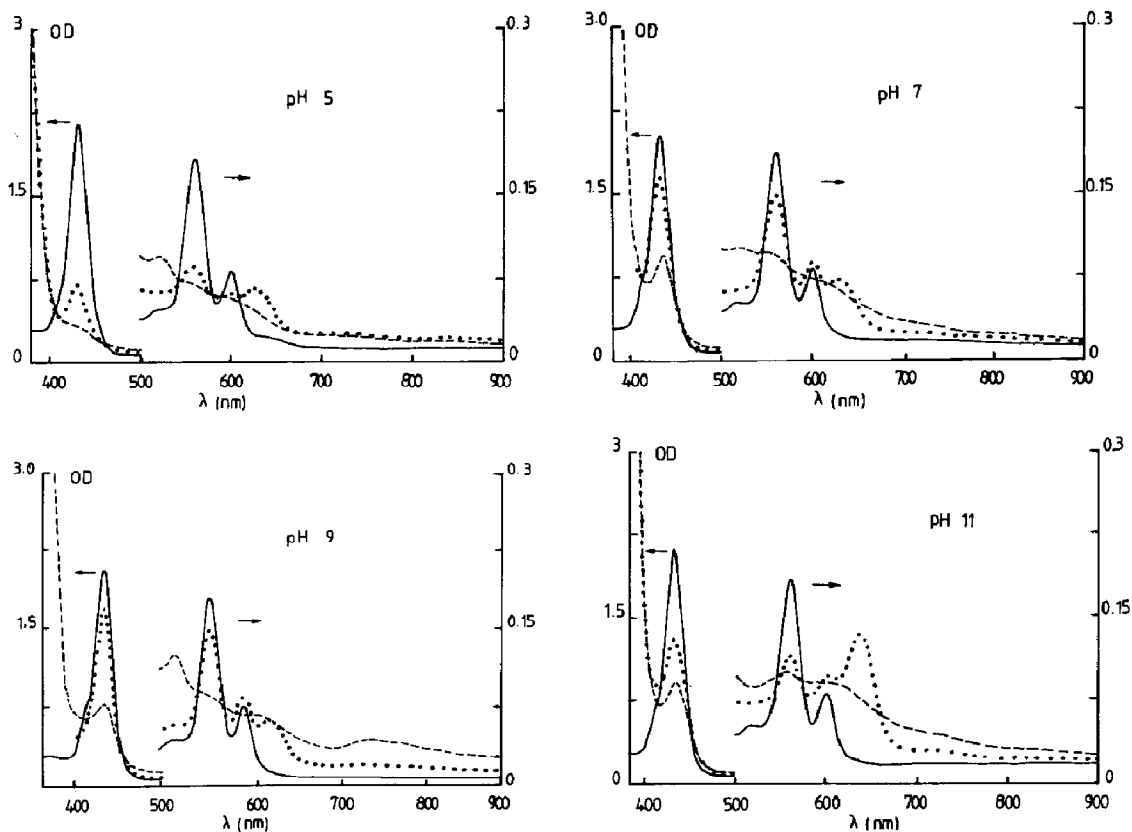


Fig. 4. Absorption spectra recorded before (—) and after (---) visible light photolysis of VOTSPP in  $N_2$ -saturated aqueous solution containing NADH ( $2 \times 10^{-3}$  mol  $dm^{-3}$ ) at the given pH. Also shown (...) are the absorption spectra observed after aeration of the photolysed solution.

water molecule. Clearly, the 820 nm product is the phlorin and the 638 nm product is most likely a chlorin. Previous work [31] has shown that the chlorin formed by reduction of VOTPP has an absorption maximum at 632 nm. The reduction product absorbing around 650 nm is less well identified but it is almost certainly a vanadyl porphodimethene.

With VOTSPP, the same type of reductive chemistry is observed but the water-solubilizing group causes the electron density residing on the porphyrin ring to be considerably higher than in VOTMPyP. This results in higher  $pK$  values for all the relevant species and chlorin formation occurs even in alkaline solution. The phlorin is not observed clearly, even at pH 13. Instead, the vanadyl porphodimethene seems to be the preferred reduction product. This species shows an absorption peak at 520 nm and a long tail stretching as far as 800 nm.

In no case is there any evidence to show formation of a reduction product having the reducing equivalents sited on the vanadium ion. This finding is in agreement with the reported [16] electrochemical properties of VOTPP. Thus, the redox chemistry of vanadyl porphyrins involves electron

addition and removal only at the porphyrin ring. Reports [14, 15] that vanadium(IV) porphyrins, stabilized by axial coordination with donor ligands, can be reduced to vanadium(II) porphyrins contrast sharply with these findings. The difference in reactivity must be associated with the nature of the axial ligands, but it is important to note that the only really stable vanadium porphyrins are based on the vanadyl ion. This ion appears to be extremely resistant to both oxidation and reduction.

### Acknowledgments

We thank the Science and Engineering Research Council, General Electric Co. (Schenectady) and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support. One of us (Z.A-G.) thanks the Egyptian Department of Education for the award of a research scholarship.

### References

- 1 R. H. Felton, in D. Dolphin (ed.), *The Porphyrins*, Vol. V, Academic Press, New York, 1978, Chapter 3.
- 2 D. G. Davis, in D. Dolphin (ed.), *The Porphyrins*, Vol. V, Academic Press, New York, 1978, Chapter 4.
- 3 J. A. Ferguson, T. J. Meyer and D. G. Whitten, *Inorg. Chem.*, **11** (1972) 2767.
- 4 D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, **7** (1974) 26.
- 5 M. C. Richoux, P. Neta and A. Harriman, *J. Chem. Soc., Faraday Trans. I*, **82** (1986) 201.
- 6 P. A. Christensen, A. Harriman, G. Porter, K. M. Morehouse, P. Neta and M. C. Richoux, *J. Chem. Soc., Faraday Trans. I*, **82** (1986) 3215.
- 7 J. W. Buchler, K. M. Lay and H. Stoppa, *Z. Naturforsch. Teil B*, **35** (1980) 433.
- 8 A. Wolberg and J. Manassen, *Inorg. Chem.*, **9** (1970) 2365.
- 9 L. Edwards, D. Dolphin, M. Gouterman and A. Adler, *J. Mol. Spectrosc.*, **38** (1971) 16.
- 10 M. Gouterman, F. D. Schwarz, P. D. Smith and D. Dolphin, *J. Chem. Phys.*, **59** (1973) 676.
- 11 H. Kobayashi, T. Hara and Y. Kaizu, *Bull. Chem. Soc. Jpn.*, **45** (1972) 2148.
- 12 H. Kageyama, M. Hidai and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **45** (1972) 2898.
- 13 K. M. Morehouse and P. Neta, *J. Phys. Chem.*, **88** (1984) 1575.
- 14 P. Richard, J. L. Poncet, J. M. Barbe, R. Guillard, J. Goulon, R. Rinaldi, A. Cartier and P. Tola, *J. Chem. Soc., Dalton Trans.*, (1982) 1451.
- 15 J. L. Poncet, J. M. Barbe, R. Guillard, H. Oumous, C. Lecomte and J. Protas, *J. Chem. Soc., Chem. Commun.*, (1982) 1421.
- 16 C. M. Newton and D. G. Davis, *J. Magn. Reson.*, **20** (1975) 446.
- 17 T. F. Yen, in T. F. Yen (ed.), *The Role of Trace Metals in Petroleum*, Ann Arbor Science, Michigan, 1975, Chapter 1.
- 18 P. A. Christensen, A. Harriman, G. Porter and P. Neta, *J. Chem. Soc., Faraday Trans. II*, **80** (1984) 1451.
- 19 M. S. Matheson, W. A. Mulac, J. L. Weeks and J. Rabani, *J. Phys. Chem.*, **70** (1966) 2092.
- 20 W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12** (1973) 962.
- 21 L. J. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61** (1957) 1089.

- 22 A. Harriman, M. C. Richoux and P. Neta, *J. Phys. Chem.*, **87** (1983) 4957.
- 23 A. Harriman, P. Neta and M. C. Richoux, *J. Phys. Chem.*, **90** (1986) 3444.
- 24 J. A. S. Cavaleiro, B. Evans and K. Smith, in F. R. Longo (ed.), *Porphyrin Chemistry Advances*, Ann Arbor Science, Michigan, 1979, Chapter 26.
- 25 P. Hambright, S. Baral, A. Harriman, M. C. Richoux and P. Neta, *J. Phys. Chem.*, in the press.
- 26 J. G. Lanese and G. S. Wilson, *J. Electrochem. Soc.*, **119** (1972) 1039.
- 27 J. Handman, A. Harriman and G. Porter, *Nature*, **307** (1984) 534.
- 28 G. R. Seely and M. Calvin, *J. Chem. Phys.*, **23** (1955) 1068.
- 29 J. W. Buchler and H. H. Schneehage, *Tetrahedron Lett.*, (1972) 3803.
- 30 S. Baral, P. Neta and P. Hambright, *J. Phys. Chem.*, **88** (1984) 1595.
- 31 C.-W. Hung and J. Wei, *Ind. Eng. Chem. Process Des. Dev.*, **19** (1980) 257.