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Oxidation products of VO(T(*m*-NO_2)PP): EPR and cyclic voltammetric studies

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Abstract

The EPR study of VO(T(*m*-NO_2)PP)$^+$ at 77 K is reported. A triplet state spectrum of VO(T(*m*-NO_2)PP)$^+$ at 77 K is obtained. The ZFS parameters are obtained from the computer simulation. An inter-electron distance of 3.57 ± 0.05 Å between the two unpaired electrons is obtained. This is attributed to an a_{2u} ground state of the porphyrin. Also, room temperature EPR of the pre-oxidized species of VOTPP with $SbCl_5$ are reported. The effect on the oxidation potentials due to substitution is also reported.

Keywords: Oxidation products; VO(T(*m*-NO_2)PP); Electron paramagnetic resonance (EPR); Cyclic voltammetry; Triplet state; Inter-electron distance

1. Introduction

The possible occurrence of metalloporphyrin π-cation in nature such as in photosynthesis [1–7], cytochrome, heme catabolism [8,9], catalase and peroxidase [7,10] were studied, compared and reported in the literature. Therefore, metalloporphyrin π-cation serve as biological model system.

EPR studies on the oxidation products of VOTPP were done by a number of workers [11–14,16,17]. The redox properties of VOTPP were studied by different electrochemical methods such as polarography [15] and cyclic voltammetry [16] and the reports are available in the literature. The unoxidised VOTPP possesses an unpaired electron in the $3d_{xy}$ orbital of the vanadium atom. One electron oxidation removes an electron from the ligand [14] generating another unpaired electron giving rise to a triplet state ($S = 1$). In a metalloporphyrin with D_{4h} symmetry, the two highest occupied π-molecular orbitals are very close lying with symmetry levels a_{1u} and a_{2u}. The question is in which orbital the unpaired π-electron spin density is localized? Generally, a cation of MTPP (M = metal atom), the unpaired π-electron is assigned to an a_{2u} ground state [17] while it is assigned to a_{1u} for MOEP type. However, our experimental results indicate that the demarcation may not be very rigid.

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The effect of ring substitution on the oxidation and reduction potentials of MTPP were widely studied and reported in the literature [18–20]. So far, the EPR and cyclic voltammetric studies of the oxidation products of VO(T(m-NO_2)PP) are not reported in the literature. In this paper we present the EPR and cyclic voltammetric studies of one electron oxidation products of VO(T(m-NO_2)PP). We also present the room temperature EPR spectra of the oxidation products of VOTPP which were not reported earlier.

2. Experimental

2.1. Chemicals

TPP and VOTPP were synthesized and purified according to the standard method reported in the literature [21–23].

(T(m-NO_2)PP) was synthesized and purified according to the literature [24]. Also, a good product was obtained by taking freshly distilled pyrrole (1.70 ml), 3.775 g of m-NO_2 benzaldehyde (Sigma chemicals) and 300 ml of reagent grade propionic acid and refluxed for 30 min. The reaction mixture was cooled to room temperature and kept standing for 18 h. The tarry material was filtered and extracted the product in chloroform and kept in the dark at room temperature for about 36 days. Chloroform was recovered followed by washing the product with methanol and hot water till the filtrate was colorless. The product was extracted with chloroform, dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The product thus obtained was chromatographed using a mixture of chloroform and benzene. The purity of the sample was checked by TLC and visible spectra.

VO(T(m-NO_2)PP) was prepared and purified by the same method used for the preparation of VOTPP as reported in the literature [23].Tetra-n-butylammoniumperchlorate was prepared by the reaction of sodium perchlorate with tetra-n-butylammonium iodide (Aldrich chemicals) and recrystallized from methanol. The purity was checked by recording cyclic voltammogram in dichloromethane. Antimonypentachloride (Sigma chemicals) was used as received.

2.2. EPR measurement

EPR measurements were done with X-band E109 (Varian) spectrometer. A cold finger dewar was employed for the liquid nitrogen measurements. All measurements were done after deaerating with N_2 gas.

2.3. Computer simulation

A computer program QCPE 134 for the simulation of EPR spectra of single crystal was modified for PC systems. Simulated spectra were obtained using WINEPR graphics.

2.4. Cyclic voltammetric measurements

Cyclic voltammogram were obtained using polarographic analyzer model 174A, PARC and a universal programmer model 175, PARC coupled with a digigraphic 2000XY recorder. A platinum plate electrode and a platinum wire were used as working electrode and auxiliary electrode, respectively. A saturated calomel electrode was used as reference electrode. All measurements were carried out after deaerating by bubbling N_2 gas through the solution in the cell.

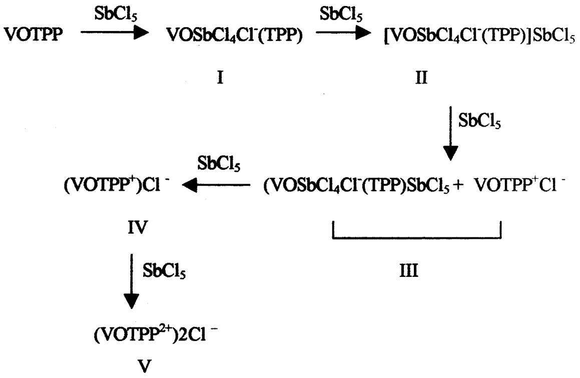
2.5. UV–Vis measurement

UV–Vis measurements were done with DU* 650 spectrophotometer (Beckman) using a quartz cuvette.

3. Results and discussion

3.1. EPR studies

Firstly, we report here the room temperature EPR spectra of VOTPP oxidation with $SbCl_5$ which were neither observed nor reported earlier. The oxidation of VOTPP can be represented as follows:



The preoxidized species I and II are observable at room temperature (Fig. 1a–d). The EPR signal of the species IV, i.e. VOTPP$^+$ do not vanish completely but broadens out. This is observable at higher modulation as a broad signal at room temperature (Fig. 1e). We have not measured it at 77 K because these reports are available in the literature [12]. The formation of monocation is further supplemented by IR [25,26] spectrum which shows a new band at 1272.76 cm^{-1}. The spectrum a (Fig. 1) show splitting giving additional lines on both ends. Further addition of SbCl$_5$ have produced the spectrum b and c (Fig. 1) and subsequently produces the spectrum d (Fig. 1) exhibiting inversion of the intensity and linewidth as well. The spectrum a is attributed to complex I while spectrum b and c to complex II. The spectrum d is attributed to complex III which is a mixture of the complex II and the monocation. The hyperfine coupling constant of the spectrum d (Fig. 1) is 71 G. This spectrum seems to indicate the presence of VOTPP$^+$ having some amount of a$_{1u}$ species. Linewidth and intensity inversion are also observed at room temperature although not

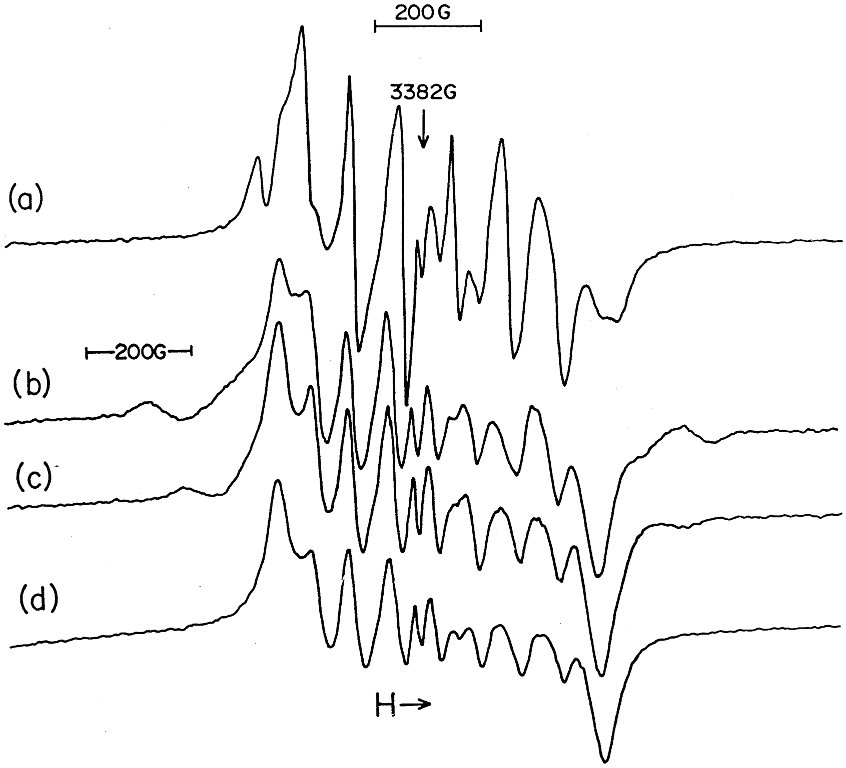


Fig. 1. Room temperature X-band EPR spectra of VOTPP in dichloromethane oxidized with SbCl$_5$, (a) species I; (b) and (c) species II; (d) species III; (e) species IV and (f) species V. Experimental conditions: modulation frequency, 100 KHz, microwave power, 2 mW, microwave frequency, 9.33–9.4 GHz, scan range, 1600 G, scan time, 8 min, spectrum; (A) modulation amplitude, 0.8 × 10 G; (B) and (C) modulation amplitude, 1.6 × 10 G, (D), (E) and (F) modulation amplitude, 2.0 × 10 G.

significantly as in the case of VO (OEP) cation [27] and VO (*Meso*) cation [28]. The spectrum **e** (Fig. 1) is attributed to VOTPP$^+$ having dominant a_{2u} species and hence broadens out. The hyperfine coupling constant of the dication (spectrum f in Fig. 1) is 80 G (lesser than the unoxidized VOTPP).

It has been observed that most of the substituted VOTPP undergo oxidation in the similar pattern as that of the VOTPP. Oxidation of [VO(*m*-NO_2TPP)]$^+$ exhibits a very broad EPR signal at room temperature (Fig. 2a). On freezing it to 77 K gives a triplet state spectrum (Fig. 2b). Half-field signal characteristic of ^{51}V nucleus is also observed (Fig. 2d).

The spin Hamiltonian for such a system has been discussed elsewhere [29]. Diagonalization of the Hamiltonian was done considering the system to be of axial symmetry while the powder spectrum is obtained by averaging over all angular orientations using gaussian quadrature method. The value of *A* and *D* were varied so as to match the experimental spectrum. The spin Hamiltonian parameters are presented in the Table 1.

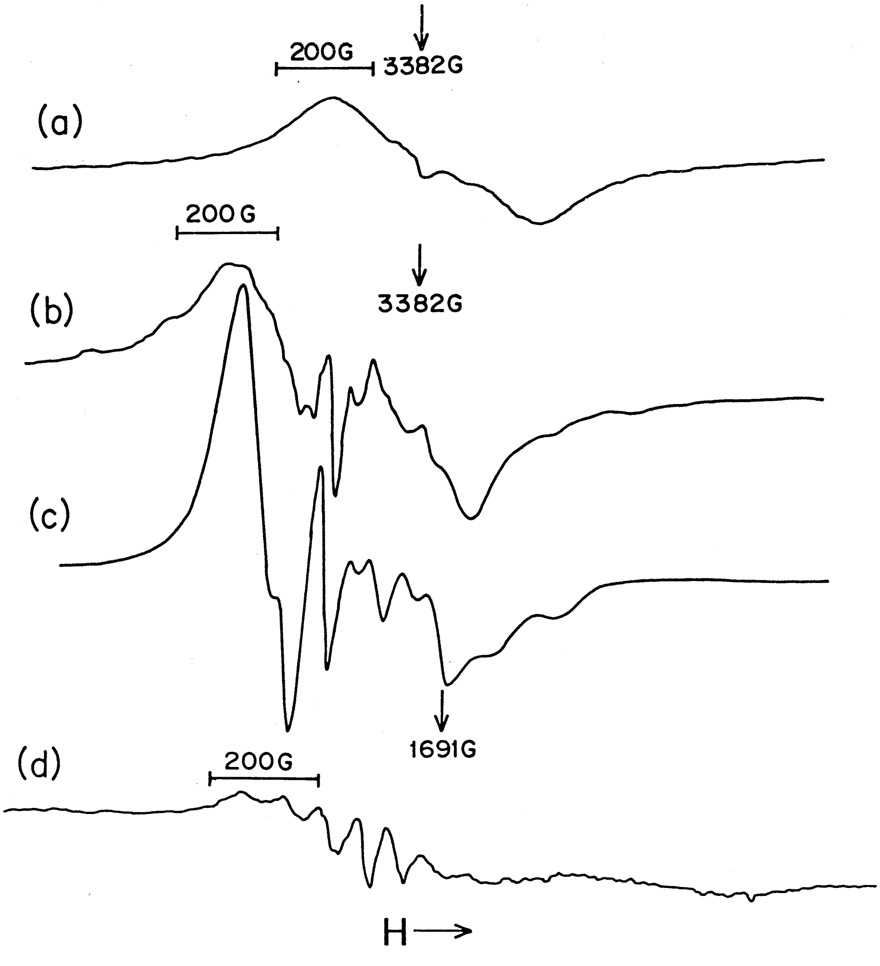


Fig. 2. X-band EPR spectra of VO(T(*m*-NO_2)PP) in dichloromethane oxidized with $SbCl_5$ at, (a) room temperature; (b) 77 K, (c) computer simulated spectrum and; (d) Half-field spectrum ($g \approx 4$). Experimental conditions: modulation frequency, 100 KHz, microwave power: 2 mW, scan range, 1600 G, scan time, 8 min. Spectrum (a) microwave frequency, 9.33–9.4 GHz, modulation amplitude, 0.5 × 0.1 G; (b) microwave frequency, 8.89–9.1 GHz; modulation amplitude, 0.5 × 0.1 G; and (c) microwave frequency, 8.89–9.1 GHz, modulation amplitude, 2.0 × 10 G.

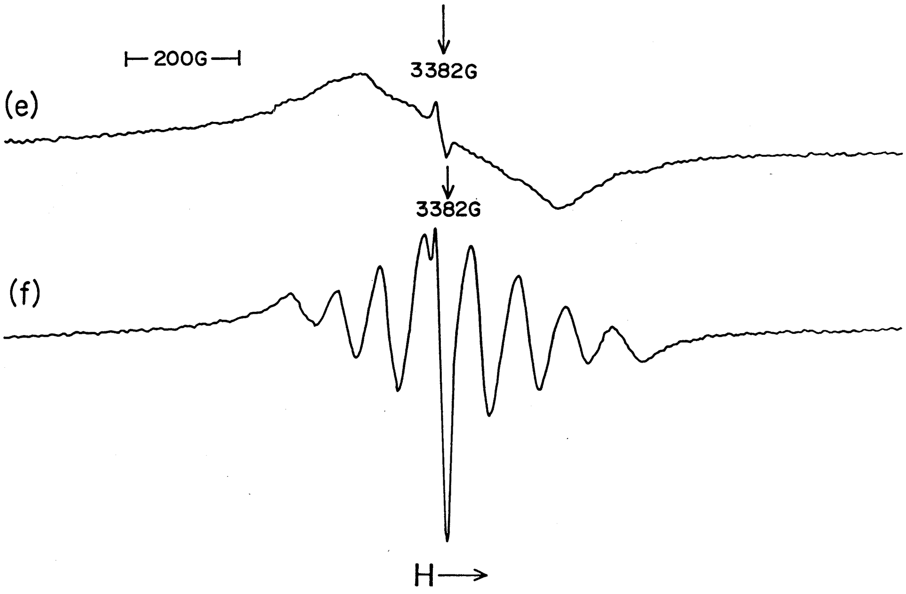


Fig. 2 (*Continued*)

The parameter D obtained from the spectrum is considered as follows: The inter-electron vector is considered parallel to the plane of the ring and normal to the 4-fold axis of the molecule. The D and g tensors are obtained in the same principal axis system with the Z-axis parallel to the 4-fold symmetry axis. Thus, the ZFS tensor is rewritten with the inter-electron axis on the Z-axis.

For an axially symmetric system the ZFS tensors along the inter-electron axis, (Z′)(Zeeman and zero field interaction only):

$$D_{x'x'} = D_{y'y'} = \frac{-D_{z'z'}}{2}$$

and

$$D_{\parallel} = D_{x'x'} = D_{y'y'} = \frac{-D_{z'z'}}{2}$$

$$D_{z'z'}\ (\text{in MHz}) = 1.298 \times 10^4 \frac{g^2}{R^3}$$

where R is expressed in angstrom and

$$g^2 = g_{\parallel}^2 + 0.5 g_{\perp}^2$$

Here, we consider the dipolar interaction as the only factor contributing to the entire zero field splitting (ZFS). This is a crude approximation only

Table 1
Parameters of triplet state ESR spectra of some metalloporphyrin

Complex	$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})	Reference
V(IV)OTPP	(1.97–2.0)	0.036 (a_{1u})		
			0.048 (a_{2u})	[11]
V(IV)OEP$^+$	1.973	1.970	> 0.04	[12]
Ni complex			0.0004	[30]
ZnTPP			0.031	[31]
MgTPP			0.031	[32]
VO(T(m-NO$_2$)PP)	1.919	1.98	0.04	[a]

[a] Present work.

and is not conclusive in determining the inter-electron distance between the two unpaired electrons. Thus, inter-electron distance of 3.575 ± 0.05 Å is obtained. It is to be noted that the dipolar interaction contribution in the case of Nickel isobacteriochlorins the Ni(I)–N is reported [30] to be around 1.2 MHz (0.0004 cm^{-1}) only. The D value we obtained is in between 0.036 and 0.048 cm^{-1}. Considering a smaller D value of 0.036 cm^{-1} an inter-electron distance of 3.73 ± 0.05 Å is obtained but no appreciable change in the simulated spectrum is observed. This may be due to the unpaired π-electron density is more in a_{2u}. This is in agreement with the earlier report[7]. The non-vanishing EPR spectrum of the π-cation at room temperature points to a possibility of having considerable unpaired π-electron density in a_{1u}. However, the shorter inter-electron distance obtained is in good agreement with that of the VOTPP^+.

3.2. *UV–Vis spectra*

In order to ascertain the ligand oxidation and the reversibility of the oxidation, UV–Vis measurements are done. VO(T(m-NO_2)PP) on oxidation with $SbCl_5$ shows decrease in the intensity of the soret band while the visible band (Q-band) broadens out (Fig. 3). It indicates that the porphyrin ligand is oxidized. Reducing the oxidized product with dimethylamine regenerate the neutral VO(T(m-NO_2)PP) but no demetallation is observed.

3.3. *Cyclic voltammetric studies of VO(T(m-NO₂)PP)*

To further supplement the EPR studies cyclic voltammetric measurements are carried out. The voltammogram exhibiting two oxidation peaks with 1.287 and 1.511 V as their $E_{1/2}$ values are obtained (Fig. 4). These potentials are assigned to the two successive one electron oxidations of the ligand. The oxidation steps were assigned according to the following scheme:

$$\mathrm{VO}(m\text{-}\mathrm{NO_2TPP}) \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{E_{1/2}=1.287\ \mathrm{V}}{\mathrm{VO}(m\text{-}\mathrm{NO_2TPP})^{+}} \underset{+e}{\overset{-e}{\rightleftharpoons}} \times \underset{E_{1/2}=1.511\ \mathrm{V}}{\mathrm{VO}(m\text{-}\mathrm{NO_2TPP})^{++}}$$

The oxidation potentials are shifted more positively as compared with that of the VOTPP. The $E_{1/2}$ of the first oxidation is shifted by 0.289 V while that of the second oxidation potential by 0.288 V. The shifts are quite uniform and large. The difference (ΔE) between the oxidation potential and the reduction potential of each redox couple are found to be 0.098 and 0.109 V, respectively. These values are rather large for one-electron oxidation steps. It seems that these peaks are overlapped of very close redox couples.

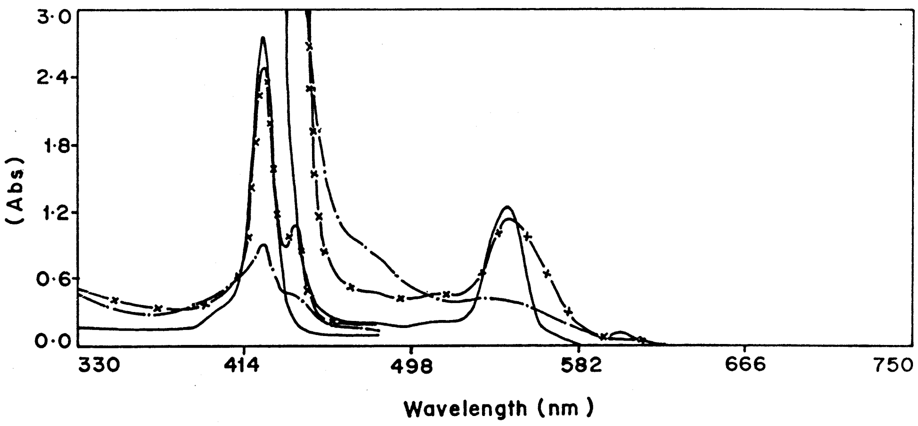


Fig. 3. Visible spectra of VO(T(m-NO_2)PP) in dichloromethane containing 0.1M $SbCl_5$ Neutral—, Oxidation—·—·, Reduction—×—×.

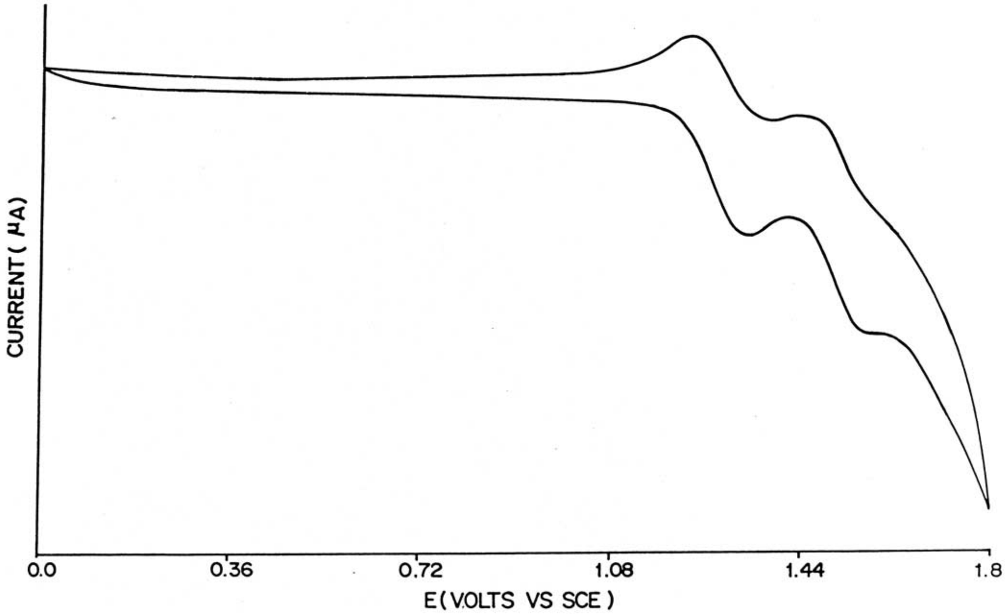


Fig. 4. Cyclic voltammogram of VO(T(m-NO_2)PP) in dichloromethane containing Tetra-n-butyl ammonium perchlorate. Scan rate 50 mV s^{-1}.

However, the ratio of the cathodic peak and the anodic peak seems to be unity.

4. Conclusion

The EPR spectra of the oxidation of VOTPP exhibits a triplet state at room temperature. This may suggest to a considerable amount of unpaired spin density in a_{1u}. Similar trends were observed for VO(T(m-NO_2)PP). This may be the reason for observing large ΔE values in the voltammogram. The electron withdrawing substituents in the phenyl ring of the porphyrin does affect the oxidation potentials of the vanadyl porphyrin (shifted to higher positive potentials). Similar trends were observed by some earlier workers [14].

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