CHAPTER VI

CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES

OF TETRABROMO MESO TETRAPHENYL PORPHYRIN
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VI.1 INTRODUCTION

The redox potentials of metalloporphyrins can be tuned to one's requirement by modifying the substituents in the periphery of the metalloporphyrin.\(^1,2\) Substituents could be introduced in the ortho or para positions of the phenyl rings in the meso positions or in the \(\alpha\) and \(\beta\) positions in the pyrrole ring. A number of studies have been reported on the redox potentials of phenyl substituted meso tetraphenyl porphyrin.\(^3,4\) The redox potentials have been correlated with the Hammet constants of the substituents.\(^3,4\) The effect of substituents on the phenyl ring on the redox potential is only moderate since the phenyl ring is twisted out of the plane of the porphyrin ring to some extent. When the substituent is in the beta position the effect on the redox potential is quite marked. Very few studies on the redox potentials of such systems are available.\(^5,6\) The results indicate that with electron withdrawing substituents the shift in the reduction potentials is quite large compared to that in the oxidation potential. As an example, for tetra cyano TTP\(\text{P}\) the oxidation potential for the copper complex is shifted
Fig. VI.1. Structure of metalloporphyrin (MBr₄TPP system)

$M = \text{VO}, \text{Cu}, \text{Zn}, \text{Ni}$

$X = \text{Br}$
from 1.06V (for Cu(TPP)) to 1.41V while the corresponding first reduction potential is shifted from -1.35V to -0.35V. This has been interpreted on the basis that the sites for oxidation and reduction are different.

The redox potential data are available for some metal complexes of porphyrins with mono substituents in the beta position and with symmetric tetracyano TPP.\(^5,6\)

We have in the present work attempted cyclic voltammetric studies on some metal complexes of symmetric tetrabromo substituted TPP. Only the oxidation potentials have been obtained and wherever possible the optical and esr spectra of the one-electron oxidation product have been recorded for the possible assignment of the product obtained on oxidation.

VI.2 EXPERIMENTAL DETAILS

The synthesis of symmetric tetrabromo TPP and its metal complexes is discussed in detail in chapter II. The procedure for cyclic voltammetric studies is the same discussed in chapter II and IV. Dichloromethane and tetrabutylammonium perchlorate were used as solvent and supporting electrolyte respectively. Cyclic voltammetric studies were done on the following systems: Zn(II), Cu(II), Ni(II) and VO(II) complexes of tetrabromo TPP.
### TABLE VI.1

Cyclic voltammetric data for Br₄TPP systems at room temperature.

Solvent: CH₂Cl₂  
Concentration: 10⁻³ M  
Supporting Electrolyte: TBAB  
Reference electrode: SCE  
Sweep rate: 100 m V/s

<table>
<thead>
<tr>
<th>System</th>
<th>Oxidation potential in volts</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th>Reversibility</th>
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<tr>
<td></td>
<td>( E^a_p(I) )</td>
<td>( E^c_p(I) )</td>
<td>( E_{1/2}(I) )</td>
<td>( E^a_p(II) )</td>
<td>( E^c_p(II) )</td>
<td>( E_{1/2}(II) )</td>
<td></td>
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<tr>
<td>CuBr₄TPP</td>
<td>0.980</td>
<td>0.860</td>
<td>0.920</td>
<td>1.296</td>
<td>1.220</td>
<td>1.258</td>
<td>0.338</td>
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<tr>
<td>NiBr₄TPP</td>
<td>0.880</td>
<td>0.764</td>
<td>0.822</td>
<td>1.240</td>
<td>1.092</td>
<td>1.166</td>
<td>0.344</td>
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<tr>
<td>VoBr₄TPP</td>
<td>1.264</td>
<td>1.184</td>
<td>1.224</td>
<td>1.454</td>
<td>1.372</td>
<td>1.413</td>
<td>0.189</td>
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<tr>
<td>ZnBr₄TPP</td>
<td>0.866</td>
<td>0.754</td>
<td>0.810</td>
<td>1.172</td>
<td>1.008</td>
<td>1.090</td>
<td>0.280</td>
</tr>
</tbody>
</table>
Fig. 1.2. Cyclic voltammogram (oxidation steps) of Zn(Br4TPP) in CH2Cl2 at room temperature. Sweep rate 100 mv/s.
Fig. VI.3. Cyclic voltammogram of CuBr$_4$TPP
Fig. VI.4. Cyclic voltammogram of NiBr$_4$TPP
Fig.VI.5. Cyclic Voltammogram of VOBr₄TPP
VI.3 RESULTS AND DISCUSSION

The cyclic voltammograms are presented in figures VI.2, VI.3, VI.4, VI.5. The half-wave potentials for the metalloporphyrins studied in the present work are listed in Table VI.1. The half-wave potentials of the corresponding TPP and tetracyano TPP systems are also presented for comparison. The tetrabromo system is expected to lead to a significant change in the pi acidity of porphyrin system. But the oxidation potentials indicate no significant change from the unsubstituted TPP. The oxidation potentials however lie in the intermediate range between those of TPP systems and tetracyano TPP systems. The difference between the first and second oxidation potentials is in the range 20 to 30 millivolts which is indicative of oxidation at the porphyrin site. We have also attempted to identify the first oxidation product by optical and esr spectroscopy. Oxidation of Zinc and Nickel tetrabromo TPP leads to the formation of radical cations as indicated by esr spectra (see figures VI.6 and VI.7). The oxidation was done using antimony pentachloride as oxidising agent. Interestingly we have observed that the esr spectrum of the radical cation of Zn(II) tetrabromo TPP is quite different from that of the corresponding system from Zn(TPP). Zn(TPP) on oxidation with antimony pentachloride yields a twelve-line spectrum with a spacing of about 1.4 Gauss. Normally one expects a
Fig. VI.6.(b). ESR spectrum of oxidized ZnBr₄TPP with SHCl₅ at room temperature.
nine line spectrum which arises from the coupling of four equivalent nitrogen atoms. The twelve line spectrum may be interpreted as arising from four equivalent nitrogen atoms and one nucleus having spin 3/2 having the same coupling as the nitrogen. This nucleus could be a chlorine atom coming from the antimony pentachloride ion which is present as the counterion. In the case of Zn(II)tetrabromo TPP, we do not observe well-resolved lines. A broad three hump-pattern is observed in this case with an approximate spacing of four gauss. The contributing nuclei to the hyperfine structure could be the four nitrogen atoms, the four bromine atoms and the chlorine atom from counterion. Since there are too many parameters for adjustments we have not attempted any simulation of this spectrum.

The oxidation of Ni tetrabromo TPP is also assigned on the ligand. The esr and optical spectra of the species obtained on oxidation of the nickel complex with antimony pentachloride are presented in figures VI.7 and VI.8 respectively. The spectra indicate only the presence of a free radical species.

The oxidation potentials for vanadyl tetrabromo TPP occur at about 200 millivolts higher than the corresponding values of vanadyl TPP. The difference between the first and second oxidation potentials indicate that oxidation occurs in the ligand site as expected for vanadyl porphyrins.
Fig. VI.7. ESR spectrum of NiBr$_4$TPP with SbCl$_5$ at room temperature
Fig. VI.8. (---) visible absorption spectrum of NiBr$_4$TPP in CH$_2$Cl$_2$ (10$^{-4}$M), (----) visible absorption spectrum of NiBr$_4$TPP in CH$_2$Cl$_2$ oxidized with SbCl$_5$
VI.4 CONCLUSIONS

The foregoing cyclic voltammetric studies indicate that tetrabromo substitution increases the oxidation potentials of metalloporphyrins only to a marginal extent, compared to the tetracyano system. In general it has been observed that electrophilic substituents in the beta positions of the porphyrin ring changes the redox potentials significantly as compared with substitution on the phenyl ring in the meso positions. In the present cases, however, the effect of tetrabromo substitution on the oxidation potentials is only marginal.
REFERENCES


