ESR AND ELECTROCHEMICAL STUDIES ON THE OXIDATION PRODUCTS OF SOME METALLOPORPHYRINS

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TO

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PREFACE

This thesis deals with the electron spin resonance studies on the oxidation products of some vanadyl porphyrins and supporting cyclic voltammetric studies on these systems. It consists of six chapters.

Chapter I consists of a review on the esr and other structural studies on the oxidation products of TiO, VO, Cr, Mn, Fe, Cu and Ni porphyrins. The material presented in this chapter gives an overall picture about the structural aspects of the oxidation products of transition metal porphyrins. Oxidation products of Mn and Fe porphyrins are considered to be active intermediates in the biological reactions catalysed by enzymes like catalase, peroxidase etc. This review also provides a backdrop for the esr studies on the oxidation products of vanadyl porphyrins presented in the later chapters of this thesis.

The details of the experimental procedures adopted in the present work are described in Chapter II.

In Chapter III, the esr studies of the one-electron oxidation products of vanadyl octaethylporphyrin at liquid nitrogen temperature are presented. The radical cation has been found to exists as a dimeric species in triplet state. From the triplet state esr spectrum the distance between the two vanadium atoms in the dimer has been obtained.

Cyclic voltammetric studies on zinc, Cu and vanadyl complexes of proto- and mesoporphyrins are presented in Chapter IV. Evidence for the existence of dimers in solution has been obtained in the case of Zn, and VO protoporphyrins. The oxidation potentials for the monomeric and dimeric forms of VO mesoporphyrin have been obtained.

In Chapter V detailed esr studies on the oxidation products of vanadyl protoporphyrin-IX dimethylester and mesoporphyrin IX dimethylester are presented. ESR spectra of the samples at room temperature and liquid nitrogen temperature and at about 10K are presented. Wherever possible, computer simulations of the esr spectra have been included. Monomeric radical cations ($S = 1$) and dimeric radical cations ($S = \frac{3}{2}$) have been identified in solution at room temperature. Different types of dimeric species have been shown to exist at low temperatures. A monomeric radical cation has also been identified at 10K. The results presented in this chapter are amply supported by the cyclic voltammetric studies discussed in Chapter III.

The results of cyclic voltammetric studies on some metal complexes of tetrabromo tetraphenyl porphyrin (Cu, Ni, VO and Zn) are discussed in Chapter VI. Wherever possible, the oxidation products were characterised by esr and optical spectroscopy.

The oxidation products of transition metal porphyrins offer challenging structural problems to the chemist and a study of these systems is important to understand the redox reactions occuring in biological system. In this thesis an attempt has been made to identify the products obtained on oxidation of vanadyl porphyrins which are the simplest systems among the transition metal porphyrins.

CONTENTS

CHAPTER I

A BRIEF REVIEW ON THE ESR STUDIES ON THE OXIDATION PRODUCTS OF TRANSITION METAL PORPHYRINS

I.1 INTRODUCTION

The aim of this review is to provide the background material which has motivated us to undertake the esr and electrochemical studies of the oxidation products of some transition metal porphyrins, especially vanadyl porphyrins. The oxidation products of transition metal porphyrins are being investigated currently by many groups using magnetic resonance techniques (NMR, ESR and Mössbauer) and magnetic susceptibility measurements.[1] The interest in these system is two-fold. The magnetic resonance data, especially the esr spectra require the development of new theoretical approaches for their interpretation. Apart from this challenging aspect, these systems play important roles as intermediates in heme enzyme - catalyzed reactions.[2] A Fe(IV) porphyrin is postulated as an intermediate in the reaction involving catalase and peroxidase. In the present review we shall restrict ourselves mainly to the magnetic resonance studies on the oxidation products of transition metal porphyrins. A systematic review is not available in the literature, though the esr of oxidation products of iron porphyrins have been discussed in detail.[3,4] Since a large number of reviews[5,6,7] have appeared on dioxygen adducts of metalloporphyrins this aspect is not included in this review.

I.2 Titanium and Vanadium porphyrins

Till now there has been no report in the literature on the oxidation products of titanium porphyrins. In the course of our own investigations on vanadyl porphyrins, we had observed that treatment of titanyl octaethylporphyrin with trifluoroacetic acid leads to the appearance of single line esr signal at room temperature (width $\simeq$ 20G) and a radical cation type optical absorption spectrum. No further esr studies have been made on this system.

Vanadyl porphyrins also lead to the formation of radical cation on one-electron oxidation (oxidation potential $\simeq$ 1.0V vs SCE).[8,9] Of the various vanadyl porphyrins that have been studied, namely, vanadyl octaethylporphyrin, vanadyl protoporphyrin, vanadyl mesoporphyrin and vanadyl tetraphenylporphyrin, the esr spectra of the oxidation products of these systems are quite different from each other. The following is a summary of the previous work on esr studies on the oxidation products of vanadyl porphyrins.

Vanadyl octaethylporphyrins on oxidation forms a radical cation.[9] This system is monomeric containing two unpaired electrons per molecule, one on the d-orbital and the other in the porphyrin π orbital. The esr spectrum of this radical cation at room temperature consists of eight lines with the spacing being one-half of the value obtained for the unoxidised product. Unusual linewidth effects have also been observed with this spectrum, the outer lines being narrow and the inner lines very broad. The esr spectrum has been analysed in terms of a spin Hamiltonian

$$H = \frac{(g_1 + g_2)}{2} \beta B_o (S_{z1} + S_{z2}) + a \hat{I}.\hat{S}_1 + J \hat{S}_1.\hat{S}_2 \qquad \ldots \quad (I.1)$$

Where S_1 and S_2 correspond to the unpaired spin in the vanadium d-orbital and the one in the porphyrin π orbital respectively. The isotropic hyperfine coupling constant of the ^{51}V in the radical cation has been reduced to one-half of its original value in the unoxidised species. This indicates that the exchange interaction J is larger than microwave frequency i.e., $J \gg 0.3$ cm^{-1}. Analysis of the linewidth effects by relaxation matrix theory has yielded the value of zero-field splitting between the two electrons as 2810 Mrad s^{-1}. Assuming that this arises entirely from dipolar interaction, a distance of 4Å was obtained between the two unpaired electrons. In terms of the molecular structure, this information means that the unpaired π electron is confined to the pheripheral positions of the porphyrin framework. The actual estimates of J has not been made so far. Attempts to obtain a correct estimate of zero-field splitting by recording esr spectrum at low temperature have not been successful. In frozen solutions around liquid nitrogen temperature, the radical cation of vanadyl OEP dimerises to yield a new triplet state.[10] This dimer has one unpaired electron each on the V-orbital. The two π electrons seems to have paired up. A distance of 4.2 Å has been obtained between the two vanadium nuclei. A detailed discussion of the esr of this system is presented in Chapter III. Similar work on vanadyl etioporphyrin has been reported by Selyutin _et al_[11]. No detailed analysis of the spectra has been reported by the authors. In the present thesis detailed studies have been made on the electrochemical and esr behaviour of the oxidation products of the vanadyl complexes of protoporphyrin-dimethylester and mesoporphyrin dimethylester.

A triplet state esr spectrum has been reported for γ-irradiated VO(TPP) in tetrachloro ethane.[12] Only the half-field lines were observed since the $\Delta m_s = \pm 1$ transitions were marked by the strong esr signal of VO(TPP). The half-field signal consists of 8 lines indicating that the irradiated product is monomeric vanadyl porphyrin in a triplet state. This species has been assigned as the one-electron oxidation product of VO(TPP), on the basis of its optical spectrum. An approximate estimate of $D \leqslant 0.024\ cm^{-1}$ has been made from the H_{min} value in the half field spectrum.

I.3 Chromium porphyrins[13-28]

The most stable oxidation state for Cr in chromium porphyrins is 3. Oxidation of Cr(III) porphyrins leads to Cr(IV) and Cr(V) porphyrins. Reduction leads to Cr(II) porphyrins. Interestingly, the oxidation products of Cr(OH) porphyrins and CrCl (porphyrins) are different.[13,14] Cr(III) porphyrins with hydroxyl group as the axial ligand, on oxidation in alkaline medium with sodiumhypochlorite yield CrO(porphyrin) where Cr is in Cr(IV) state. CrO(TPP) and CrO(OEP) have been isolated in the solid state. The optical spectra of these compounds are very similar to that of vanadyl porphyrins. The magnetic susceptibility as measured by Evans method indicate that these system are diamagnetic. X-ray structure of the oxo chromium(IV) TPP has also been reported.[13,15] CrCl (porphyrins) on oxidation with hypochlorite or iodosylbenzene form Cr(V)O porphyrins.[16-19] A nitrido chromium(V) porphyrin CrN(TPP) has also been reported.[20] Cr(V)O porphyrins exhibit esr spectra typical of

d^1 systems.[23] The following esr parameters have been obtained in solution at room temperature for $CrO(TPP)^{\overset{+}{\bullet}}$, $g_{av} = 1.982$, $a_N = 0.285mT$, a_{cr} (^{53}Cr) = 2.3mT. The esr parameters are very similar to vanadyl porphyrins and hence a similar orbitally non-degenerate ground state has been proposed for Cr(V) porphyrins (d^1_{xy}). A d_{xy} ground state is obtained for the unpaired electron, if we assume a co-ordinate system in which x and y axes are perpendicular to the plane. Treatment of Cr(V)P with t-butylamine leads to axial ligation involving the amine. ESR spectrum also indicates the presence of hyperfine coupling from the axial nitrogen ligand (0.78mT) which is much larger than that of porphyrin nitrogen. Nitride Cr(V) porphyrins also shows hyperfine coupling from the axial nitrogen which is about the same as that from the in-plane nitrogen nuclei. ENDOR measurements that have also been made on these systems, indicate slight differences between the axial and porphyrin nitrogen coupling.[24] The esr data for CrNTPP are as follows.[24] a_N(isotropic) = 0.28mT; a_o (^{53}Cr) = 2.83mT; $a_{\parallel}$ (Cr) = 4.01mT; $g_{\parallel} = 1.9583$; $g_{\perp} = 1.9945$. The closeness of $g_{\perp}$ value to that of free electron g-value indicates that the energy gap between the d_{xy} ground state and the nearest excited state (d_{xz}, d_{yz}, e) is quite high. This might also be the reason why Cr(IV) (porphyrin) is diamagnetic though it is a d^2 system.

Reduction of Cr(III) porphyrins leads to the formation of Cr(II) porphyrin which irreversibly reacts with dioxygen to form Cr(IV)OP.[25,26,27].

I.4 Manganese porphyrins

In the last five years, considerable amount of work has been done on the synthesis and structural evaluation of oxidation products of Mn(III) porphyrins. Electrochemical oxidation of Mn(III) porphyrins lead to the formation of Mn(III) porphyrin radical cations[4]; chemical oxidation products have been identified as Mn(IV) porphyrin μ -oxo bridged Mn(IV) dimer, Mn(IV) porphyrin adducts of oxidant, Mn(V) nitrido porphyrins. The products of chemical oxidation of Mn(III) porphyrins seem to depend on the nature of the oxidant and the medium.

I.4.1 Mn(III) porphyrin radical cations

Electrochemical oxidation of MnTPPCl, Mn Tetrakis (p-methoxy tetraphenyl porphyrin) Cl and Mn(OEP)Cl have been reported.[4] The one-electron oxidation product for each of these systems ($\simeq$ 1.1V Vs SCE) had been isolated. The pmr spectrum of the oxidised species indicates that the pyrrole protons (α, β, protons) signals are shifted upfield and broadened. ESR spectra of these systems consist of strong absorption at $g = 2$ (linewidth $\simeq$ 300-500G) and a weak and very broad signal around $g = 3$. A magnetic moment of 4.7BM was obtained for TPPMn(Cl)(ClO_4) which was found to be invariant with temperature in the range -50°C to 29°C. All the oxidation products are formulated as Mn(III) porphyrin radical cations. The $g = 2$ signal is assigned to the π radical. The broadening of this signal is considered to arise from spin-spin interactions between the d-electrons and the π-electron. Assignment of Mn(III) π radical cation is also consistent with the broadening and loss of intensity of Soret band and increase in the intensity of long wavelength region.

I.4.2 Higher Valent Mn porphyrins

Chemical oxidation of Mn(III) porphyrins has been studied extensively.[29-36] Mn(III) porphyrins have been found to be versatile synthetic oxidation catalysts for alkane oxidation. The activation of C-H bond is accomplished in nature by heme mono oxygenase type of enzymes. Higher valent Mn porphyrins have also been effeciently used to oxidise water thermally and photochemically. Hence the oxidation products of Mn(III) porphyrins are of great importance as unique catalysts for oxidation reactions. Some early papers in the literature contain ambiguous assignments to the oxidation state of Mn in oxidised Mn(III) porphyrins based on insufficient experimental data. Clean synthesis, isolation and structural elucidation have been reported for Mn(IV) (porphyrin) X_2 and (Mn(IV) porphyrin $X)_2O$.[37,38] Oxidation of Mn(III)TPPX in alkaline methanolic solutions by iodosyl benzene or sodium hypochlorite leads to the formation of Mn(IV)$TPPX_2$, where X is OCH_3^-, N_3^- or NCO^-. Oxidation of Mn(III)PX in an inert medium like chloro benzene by iodosyl benzene results in the formation of dimeric species XPMn(IV)-O-Mn(IV)PX, ($X = N_3^-$, OCN^-). Oxidation of Mn(III)PX by sodium hypochlorite or iodosyl benzene in the presence of excess ammonia results in the formation of Mn(V)NP. The crystal structures of all the three types of species have been reported.

I.4.3 Monomeric Mn(IV) porphyrin[29-40]

ESR of Mn(IV) porphyrins have been reported. ESR spectra were recorded for Mn(IV)P$(NCO)_2$, Mn(IV)P$(N_3)_2$ in dichloromethane solution at 12K.[36] Interestingly, the esr spectrum depends on the nature of the two axial ligands Mn(IV)TPP$(NCO)_2$ exhibits a strong signal at $g = 3.92$ and a resolved ($a_{Mn} = 69G$) structure at $g \cong 2$. This indicates that the ligand field is axially symmetric and the zero field splitting, $D \gg h\nu$ for the $S = \frac{3}{2}$ system. On the other hand, Mn(IV)TPP$(OCH_3)_2$ yields g values as 5.46, 2.4 and 1.0. The signal at $g = 5.46$ is very strong and resolved ($a_{Mn} = 72G$). This signal indicates highly rhombic character of the $S = \frac{3}{2}$

system. Using the available-theoretical models for the ESR of $S = \frac{3}{2}$ systems, an approximate estimate of $D \simeq 1.7\ cm^{-1}$ has been made for the Mn(IV) porphyrins. In contrast to Cr(III) porphyrins $(S = \frac{3}{2})$ the ZFS value in Mn(IV) porphyrins is quite high. This has been attributed to contraction along the axial bonds in Mn(IV)P due to smaller ionic radius of Mn(IV) ion compared to that of Cr(III) ion. A monomeric Mn(IV) porphyrin containing two molecules of iodosylbenzene has also been reported.[40] A similar esr spectrum ($g = 3.52$, $g = 2$) was reported for the species obtained during γ irradiation of Mn(III)TPPCl containing equimolar amount of TCNE (Tetracyano ethylene). This species has been assigned as Mn(IV)P on the basis of its optical and esr spectra.

A recent study[43-44] on the interconversion of Mn(III)P radical cation and Mn(IV) porphyrin clearly demonstrates the effect of axial ligand on the valence state of Mn. With weak axial ligands like ClO_4^-, Mn(III)P radical cation is favoured. Replacement of perchlorate ion by OCH_3^-, leads to the formation of $Mn(IV)P(OCH_3)_2$.

I.4.4 μ -oxo Mn(IV) porphyrins

It has been established that basic medium is required to generate monomeric Mn(IV)P during the oxidation of Mn(III)P with iodosyl benzene. Instead, if the oxidation performed in a neutral medium like chlorobenzene, PMn(IV)-O-Mn(IV)P dimer is formed. This subtle difference in the synthetic procedure is not clearly discussed in the literature. Camenzind et al[37,45] point out that treatment of Mn(III)TPP(OAC) in dichloromethane with iodosyl benzene leads to very little oxidation in about half-an-hour, but the reaction is instantaneous when sodium methoxide is added to the system. The same authors claim that the Mn(IV)oxo-dimer is formed when the oxidation is done in an inert medium. The exact conditions for the formation of the oxodimer are not very clear but the species has been identified and its crystal structure and magnetic data have been reported.[45] The μ -oxo dimer has -Mn(IV)-O-Mn(IV)-moiety with an effective magnetic moment μ_{eff} = 2BM. No epr signal has been observed down to 8K. This system can oxidise water to H_2O_2 in a thermal or photochemical process. Oxidation of hydrocarbons has also been reported. A report on Mn(V)=0 porphyrins in the literature does not contain adequate data for the assignment of the Mn = 0 vibrations in the IR and the similarity of the optical spectra to μ-oxo Mn(IV) system point to the fact that the species is not Mn(IV) = 0 system but is very likely to be PMn(IV)-O-Mn(IV)P. A μ -oxo Mn(IV) system as an adduct of iodosyl benzene has also been reported (μ_{eff} = 1.5BM). This compound is also epr-silent. The low magnetic moment in the μ -oxo system indicates strong antiferro magnetic coupling of the d-electrons ($J \simeq 250\ cm^{-1}$). Mossbauer study of ^{127}I in the iodosyl benzene adduct have also been reported[48]. The complexes $[(N_3)Mn(IV)TPP]_2O$ and $[(OCN)Mn(IV)TPP]_2O$ are thermally unstable and decompose slowly.[50] When solutions of these systems are allowed to decompose partially and frozen at liquid nitrogen temperature, a 16-line esr spectrum is obtained. The epr spectrum is shown to be very similar to the known mixed valence Mn(III)-O-Mn(IV) systems.[51,52] In equivalence of the Mn atoms have also been observed in the hyperfine couplings. The epr spectra of the mixed valence Mn porphyrins are similar to those observed when spinach chloroplasts are flashed with a pulse of light and frozen.[52] A coupling of $S = \frac{3}{2}$ [Mn(IV)] and $S = 2$ [Mn(III)] leads to a ground state $S = \frac{1}{2}$ in the mixed valence dimer. The theory of the esr of this system is discussed in detail for Mn(III)-O-Mn(IV) dipyridyl systems.[53]

I.4.5 Mn(V) porphyrins

Craig *et al*[54] and Buchler *et al*[55] have independently reported the synthesis of Mn(V) nitrido porphyrin. Treatment of Mn(III)TPP or OEP systems with sodium hypochlorite or iodosyl benzene in the presence of excess of ammonia leads to the formation of $PMn(V) \equiv N$. Optical spectra

($\lambda_{max}^{(nm)}$ = 424, 538, 626nm), crystal structure and magnetic data have been reported. This system is diamagnetic. Mn(V) is a d^2 system and apparently the ground state is non-degenerate and does not have any low lying excited states. A similar situation is observed for PCr(V)$\equiv$N (d^1) which gives a sharp line epr spectrum in solution at room temperature, indicating that the d-orbital energy levels are similar for Mn(V) and Cr(V).

I.4.6 MnP-O_2 complexes[56-59]

Mn(II) porphyrins bind irreversibly to dioxygen. The esr data clearly indicates that Mn exists as Mn(IV) in the dioxygen complex. A typical set of esr parameters are:[56] D = 2.46 cm^{-1}, $E/_D$ = 0.3291 cm^{-1}, A (^{55}Mn)= 52.6 x 10^{-4} cm^{-1}, B (^{55}Mn) = 86.4 x 10^{-4} cm^{-1} for MnTPP(O_2) system. A hyperfine coupling for ^{17}O in the O_2 moiety was found to be equal to 2 x 10^{-4} cm^{-1}. The adduct is accordingly formulated as Mn(IV)P-O_2^{--} . An edge-on geometry for O_2 moiety has been proposed on the basis of EHT calculations.[60] Recent ab initio calculations also support the same view.[61]

I.5 Iron porphyrins[62-95]

Much has been said on the nature of oxidation products of iron porphyrins. A recent review summarises the earlier results upto 1982.[3] The early studies[2,62-65] on the esr and magnetic susceptibility studies on the products obtained on the electrochemical oxidation of iron porphyrins were interpreted on the assumption that the oxidised product is a Fe(IV)P species. More detailed reports have appeared in recent years on the detailed optical, and nmr studies on the oxidation products of Fe(III) porphyrins obtained both by chemical and electrochemical oxidations. Fe(IV) porphyrins are formed when an oxo ligand is present. The species (FeO)P has been identified as Fe(IV) porphyrins.

I.5.1 Electrochemical oxidation of Fe(III) porphyrins

Oxidation of the iron in the iron(III)-porphyrin to Fe(IV)O group is well established for enzymes like catalase and peroxidase where superoxide or peroxide species are involved respectively. There are also other classes of enzymes containing isobacterio chlorin (sirohydro chlorin) which have very low oxidation potentials.[66,67] On the basis of the esr and optical spectra of the oxidised species at room temperature, this species has been identified as Fe(III)P radical cation. In the following paragraphs, the available structural information on each type of oxidised species of Fe(III) porphyrins is summarised.

I.5.2 Fe(III)P radical cation

One electron oxidation of Fe(III) porphyrins is being investigated for the past twenty five years.[65] Early electrochemical studies by Wolberg and Manassen[66] as well as by Felton *et al.*[62,63] were not very conclusive about the assignment of structure to the species, which was not completely characterised. Chemical oxidations of Fe(III) porphyrins, using iodosylbenzene,[76] chloroperoxy benzoic acid,[93] antimony pentachloride[71] or $Fe(ClO_4)_3$[82] have been reported in recent years. The products of chemical oxidation depend on the nature of oxidising agent. Oxidation product obtained by using iodosylbenzene has been shown to be Fe(IV) species. The product obtained with chloroperoxy benzoic acid has been described as Fe(IV)P π cation radical.[93] Oxidation with $Fe(ClO_4)_3$ or $SbCl_5$ lead to Fe(III)P cation radicals. Electrochemical oxidation in the presence of perchlorate as counter-ion has been studied in detail with Fe(III) porphyrins and $(Fe(III))_2O$.[68,69] The products have been isolated on a synthetic scale and detailed magnetic measurements, Mössbauer and nmr studies have been performed on these systems. Solution magnetic measurements using nmr method has lead to a value of 5.5 BM for $TPP(OCH_3)Fe(ClO_4)$ and the corresponding OEP system over a temperature range of 215-300K. A similar oxidation product obtained by using $SbCl_5$ as oxidant, exhibits a magnetic moment of 5.1 BM over a temperature range 5-300K. Mössbauer data shows increased isomer shifts in comparison with the Fe(III)P, whereas decreased shifts are expected for Fe(IV) species. The oxidised species is esr-silent. In the visible electronic spectrum, Soret band is shifted with diminished intensity and a broad absorption is noticed around 870nm. The oxidised monomeric species yield well-resolved pmr spectra which differ from the parent Fe(III)P spectra in terms of larger phenyl proton isotropic shifts. The large shifts for the phenyl protons which are observed for any transition metal porphyrins had been taken as indicative of the presence of π radical cation. Approximate correlation have been made using the phenyl proton shifts in $(TPP)FeClO_4$ and the mesoproton shifts in $OEPFeCl(ClO_4)$ in assigning the ground state of the unpaired π electron as a_{2u} and a_{1u} respectively. On the basis of above data, the electrochemical oxidation products of FeP had been assigned as Fe(III)P cation radical .

A recent work by C.A. Reed and co-workers report the preparation of analytically pure $FeCl(TPP)SbCl_6$, $Fe(TPP)(ClO_4)_2$ using radical cations of thianthrene and phenoxathiin.[70,71] Detailed magnetic susceptibility measurements and X-ray crystal structure have been reported for these two systems. The temperature dependent-magnetic susceptibility data for FeCl (TPP)$SbCl_6$ has been interpreted as arising from strong antiferro magnetic coupling of $S = \frac{5}{2}$ iron atom and $S = \frac{1}{2}$ porphyrin radical, leading to $S = 2$ ground state. A value of J between -125 to -250 cm^{-1} has been estimated. On the other hand, $Fe(ClO_4)_2TPP$ radical cation exhibits a magnetic susceptibility of 6.50 BM at room temperature. A maximum value of 6.75 BM is reached at 100K. This value is greater than the spin only value for $S = \frac{5}{2}, \frac{1}{2}$ uncoupled system. A ferromagnetic coupling between $S = \frac{5}{2}$ iron and $S = \frac{1}{2}$ porphyrin radical has been postulated to explain the observed susceptibility data, with $J \simeq 40$ cm^{-1}. ESR spectra were not observable for both these systems down to 4.5K. The crystal structure data indicated that the Fe atom is out-of-plane of porphyrin ring in FeClTPP($SbCl_6$) and in the plane, in $Fe(ClO_4)_2TPP$. In the later situation the orthogonality of the d-orbitals with $a_{2u} - \pi$ orbital of porphyrin could lead to $S = 3$ state. The overlap in $FeTPPSbCl_6$ could lead to strong antiferromagnetic interaction between unpaired electrons on the metal and the ligand resulting in $S = 2$ state. The magnetic susceptibility data for $FeTPP(ClO_4)_2$ reported by Boersma and Goff[74] ($\mu = 4.8$ BM) differs considerably from the value of 6.75 BM obtained by Gans et al[71]. The latter authors have done the measurement in the solid state using SQUID susceptometer while the former measurement was done using nmr method in solution. At present it is difficult to rationalise the observed difference in the susceptibility for the same compound.

Radical cations of the type $[\mathrm{Fe(III)TPP}]^{2+}$, $[\mathrm{Fe(III)OEP}]^{2+}$ with Fe in the low-spin state have also been generated and studied by nmr.[72] The low spin systems have been obtained from the corresponding high spin systems generated electrolytically, by adding directly excess of imidazole into the nmr tube. Thus $[\mathrm{Fe(III)TPPIm_2}]^{2+}$ and $[\mathrm{Fe(III)OEPIm_2}]^{2+}$ had been identified by solution nmr. The magnetic susceptibilities of these two systems obtained by nmr method are 2.8 BM and 3.3 BM respectively, indicating the presence of a triplet state. These systems have been found to be esr silent.

I.5.3 μ -oxo iron porphyrins

One and two-electron oxidation products of μ-oxo iron porphyrins have been reported.[69] The one - electron oxidation product yields a single line esr signal at 77K with g = 2. The doubly oxidised dimer is esr silent. IR spectra of both monomeric and dimeric species show diagnostic absorption at $\simeq$ 1290 cm^{-1} characteristic of porphyrin π-cation radicals. The magnetic susceptibilities of the one- and two-electron oxidation products (ClO_4^- as the counter ion) are respectively 3.2 and 1.7 BM indicating the presence of strong antiferromagnetic exchange in these systems.

Other Fe(III)P radical cations reported involve the ligand sirohydrochlorin (isobacteriochlorin).[66,67] The free base 2,4 dimethyl gem octaethyl isobacteriochlorin (DMOE-iBC) and its metal complexes (Free base : 0.37V vs SCE Zn complex : 0.07V vs SCE) have much lower oxidation potentials than the corresponding porphyrin systems. Oxidation of Fe(II)(DMOE-iBC)(pyridine)(CO) yields a π cation characterised by visible electronic and esr spectrum at room temperature. Fe(II)(DMOE iBC)Cl on one-electron oxidation, yields a radical type visible electronic spectrum and is esr silent. These radical cations are considered to be models for the active sites in sulphite reductase and nitrite reductase. An iron oxophlorin radical system has also been identified by esr.[75]

I.5.4 Fe(IV) porphyrins

A clear identification of Fe(IV)P was probably made for the first time by Chang and Kuo[76] and also by LaMar et al.[77-81] The later group had obtained [Fe(IV)OP(base by treating [Fe(III)P-O-O-P Fe(III)] with imidazole type bases at low temperatures (-50°C). The Fe(IV) species was identified by its typical two-banded visible electronic spectrum and nmr spectrum. The magnetic susceptibility of this species was obtained as 2.9 BM corresponding to low-spin Fe(IV) state (S = 1). The same species was found to be active catalysts involved in the oxidation of triphenyl phosphane in the presence of Fe(II)P oxygen.

Chang and Kuo[76] had obtained a green species on oxidation of Fe(III) starpped porphyrin with iodosylbenzene in neutral medium. This was identified as Fe(IV)OP in the high spin state (μ = 4.9 BM). The optical spectrum of this species was observed to be very similar to that of the active site in catalase enzymes. The nmr spectra of Fe(IV)OP (high spin) and (NMeImFe(IV)OP) (low spin) show significant differences in the contact shift of pyrrole and phenyl protons of porphyrin.

The considerations which govern metal centered-oxidation vs ligand oxidation in Mn-porphyrin apply in the case of Fe porphyrin also. Oxidation of Fe(III)P in the presence of ligands of the type ClO_4^- lead to the formation of π radical cation. If oxo ligands are present then Fe(IV) is the preferred species. It has been shown in recent years that treatment of the radical cation, $(Fe(III)P)(ClO_4)_2$ with OCH_3^- ion leads to the formation of $Fe(IV)P(OMe)_2$. This species has been isolated in the solid form.[82,83]

The nmr, magnetic and Mössbauer data are reported for this system. The dimethoxy system is low spin Fe(IV) (μ = 2.9 BM). But its nmr spectrum is different from that of [Base Fe(IV)OP] which is also a low spin Fe(IV). The reasons attributed are that in the former, Fe may be in the plane of P ring, while Fe(IV)O may be a pyramidal system. To clarify the situation further, electrochemical oxidation of Fe(III)P(OH) has been done in CH_2Cl_2 around -70°C to obtain a species characterized as Fe(IV)OP.[84] The same species is also obtained by chemical oxidation with iodosyl benzene in presence of methanol. Further, treatment of Fe(IV)PO with perchloric acid affords the π-radical cation, Fe(III)P$(ClO_4)_2$. Thus, a reasonably clear picture have emerged out of the confusion prevailing over a decade. Fe(IV) porphyrins are also esr silent.

I.5.5 Fe(IV)P radical cation

This species has been postulated as the active center in HRP-compound I.[85-92] Mössbauer data of the HRP-I indicates the presence of Fe(IV).[88] NHR results point to the presence of π-radical cation.[91-92] ESR and ENDOR studies have also been made on this system. These latter studies indicate a free radical system, strongly coupled to a paramagnetic metal center.[97] The overall magnetic susceptibility accounts for $S = \frac{3}{2}$ state. On the basis of these data, the present explanation for HRP-I is that it is Fe(IV)$P^{+\bullet}$ with Fe in the low spin state (S = 1) coupled to a π radical cation ($S = \frac{1}{2}$). Fe(IV)$P^{+\bullet}$ is reported to be formed during the oxidation of Fe(III)P by chlorobenzoic acid in methylene chloride-methanol system at -78°C.[93] This product is epr silent, and its magnetic susceptibility is 4.2 BM. Though this system is distinctly different from Fe(III)$P^{+\bullet}$ in its nmr spectrum, it is not identical to compound I of HRP. Further characterisation of the chemically obtained species is necessary.

An iron porphyrin containing Fe-C bond has been oxidised to Fe(IV) porphyrin.[95] Phenyl Fe(III)(p-tolyl TPP) was oxidised with bromine. The product was identified by nmr data as Fe(IV) porphyrin.

Using a chemical oxidising agent, N-N dimethylaniline-Noxide, a facile oxidation of Fe(III)TPP has been observed.[96] The oxidation product has been assigned as Fe(V)P. No detailed structural assignments are available.

I.6 Nickel porphyrins

One electron oxidation product of nickel porphyrins were reported to undergo valence tautomerism.[98,99] The oxidation product at room temperature was identified as the cation radical while at 77K the colour changed from green to red with a strongly anisotropic esr spectrum ($g_\perp = 2.286$, $g_\parallel = 2.086$). This species was identified as d^7Ni(III) system. It was also observed that when the oxidation was done using Br_2 as the oxidant no spectral changes occured at low temperatures. When the oxidation had been carried out in the presence of PF_6^- ion, Ni(III) species was observed at low temperatures. A recent resonance Raman study of the system also confirms the above observation. Apparently PF_6^- stabilises Ni(III) whereas Br^- does not.[100]

I.7 Cu porphyrins

Cu(II) porphyrins on oxidation form the radical cations. In solution the oxidised species has two unpaired electrons ($\mu = 2.4$ BM).[101,102] Deuterium nmr of Cu(TPP)$^{\dot{+}}$ has also confirmed the presence of radical cation. The crystalline of one-electron oxidation product of Cu(TPP), with $SbCl_6$, is diamagnetic while in solution $\mu = 2.4$ BM.[103] This value matches with that for two non-interacting $S = \frac{1}{2}$ magnetic centers. From the nmr data the ground state for the unpaired π electron in Cu(TPP)$^{\dot{+}}$ was assigned as a_{2u}.[104]

Cu(OEP) and Cu(OEC) (octaethyl chlorin) on one-electron oxidation lead to the formation of cation radicals which are esr-silent at ambient temperatures. In frozen solutions at 77°C, dimeric species have been observed with S = 1 state, dimer has one electron each on the Cu atoms and distance between the Cu atoms had been obtained as 3.7 Å from the observed epr spectrum.[105] Another type of oxidised species was detected by epr when a frozen solution of Cu(TPP) was irradiated by γ-rays. This species gave a characteristic triplet state epr spectrum, corresponding to only one Cu center. The radiation induced oxidation has most likely yielded a monomeric Cu radical species.[106]

I.8 Ag porphyrins

Silver(II) porphyrins have unusually low oxidation potentials. The first one-electron oxidation product of Ag(II)OEP and Ag(II)TPP were shown to be diamagnetic and no π- radical spectrum was observed.[107-110] On this basis, the oxidised species has been assigned as Ag(III)P. A recent deuterium nmr study on the same system also confirms this assignment.[111]

A selective review has been presented above on some of the recent work on the oxidation products of transition metal porphyrins as studied by magnetic resonance, optical spectra and magnetic susceptibility measurements. It is clear from the material presented, that no single physical technique is adequate to understand the structural features of the systems discussed. A number of problems still remain to be solved regarding the magnetic properties of oxidised porphyrins. In the work presented in this thesis, an attempt is made to understand the magnetic properties of the oxidation products of some simple transition metal porphyrins, namely vanadyl porphyrins. ESR had been the main technique used, supported by visible absorption and cyclic voltametric data.

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