CHAPTER IV

EPR studies on one-electron oxidation products of Ni(II) porphyrins

IV 1 Introduction

The oxidation products of transition metal porphyrins have evinced considerable interest in the past twenty years since they serve as (i) catalysts for oxidation reaction, (ii) Models for heme oxygenase Metalloporphyrins containing iron, manganese, chromium and other transition elements can be oxidized by chemical or electrochemical methods. Two broad conclusions have been reached from the studies on iron and manganese porphyrins (i) The oxidation can be either metal-centered or ligand-centered depending upon the condition (ii) Conversion from ligand-centered oxidation to metal centered oxidation is possible by adding a strong nucleophile like methoxide ion.

The reports on oxidation studies on nickel porphyrins are less extensive than those available on iron and manganese porphyrins. In the present work some systematic observations on the one-electron oxidation products of nickel porphyrins are reported.

Among the earliest studies on the oxidation of Ni(II) porphyrins, Wolberg and Manasson have reported the cyclic voltammetric and EPR measurements on Ni(II) tetraphenylporphyrin, Ni(II)TPP in 0.1M tetrabutylammonium perchlorate (TBAP)-benzonitrile medium. Although EPR-silent at room temperature, the oxidized complex has a spectrum characteristic of Ni(III)TPP⁺ at liquid nitrogen temperature. Dolphin and co-workers examined the oxidation of Ni(II)TPP in the presence of TBAP and tetrabutylammonium hydroxide (TBAH) or Br⁻. One-electron oxidation at room temperature afforded a green solution whose UV-Visible and EPR spectra are
characteristic of Ni(II)TPP$: An orange red solid is obtained when the green solutions containing TBAB or TBAH is frozen at 77K. On the basis of EPR and optical spectra of the solid, it has been suggested that an internal electron transfer has occurred to yield Ni(III)TPP$^+$. This change did not occur in the presence of Br$^-$ or small amount of water. Resonance Raman data presented by Spiro and coworkers$^{11}$ provided further evidence for the change in the site of oxidation upon freezing.

Kadish$^{12-14}$ investigated the oxidation of several nickel porphyrins in various solvents and supporting electrolytes. Three different mechanisms are found to occur. The first was consistent with Dolphin's observations. Ni(III)$^+$ is obtained upon freezing the one-electron oxidation product, Ni(II)$^+$. Further oxidation of Ni(II)$^+$ yielded the dication Ni(II)$^{2+}$. In the second mechanism, the initial product is the cation radical Ni(II)$^+$. Cooling to 77K did not induce internal electron transfer. The second oxidation has yielded the Ni(III)$^{2+}$. Nickel (III) is inaccessible in the third mechanism. The site of oxidation is determined by number of factors including the substituents, solvent, electrolyte, temperature and oxidant.

Stolzenberg$^{15}$ had investigated the chemical and electrochemical oxidation of nickel porphyrin, chlorn, and isobactenochlorin complexes in the octaethyl and methyl substituted octaethyl series. The first oxidation of all the compounds have yielded Ni(II) cation radical. The site of oxidation has remained the same upon freezing. Unlike Ni(II)TPP$^+$, the cation radical complexes (Ni(II)OEP$^+$) did not undergo internal electron transfer to form Ni(III) complexes at low temperatures. Instead, they formed Ni(II) dication complexes (Ni(II)OEP$^{2+}$). The second oxidation of nickel isobactenochlorins have afforded Ni(III) cation radical complexes.
Morishima and coworkers\textsuperscript{16} had reported that Ni(II) substituted myoglobin and horseradish peroxidase upon oxidation yielded Ni(II) cation radicals. Oxidation of Ni(II)OEP and Ni(II)protoporphyrin in the presence of pyridine or imidazole afforded Ni(III) complexes at low temperatures. Ni(II)TMP-N-O(porphyrins N-oxide) was oxidized with trifluoro acetic acid in dichloromethane. Three iso-electronic one-electron products were identified. They are identified as a Ni(III) porphyrin (5 co-ordinate), Ni(II)P\textsuperscript{+} radical cation and Ni(III) porphyrin (6 co-ordinate). Rhombic g-values are reported for the Ni(III) species.\textsuperscript{17}

The valence isomerisation of Ni(II)P\textsuperscript{+} radical cation to Ni(III) porphyrin has not been systematically studied by earlier workers. We have also observed that the nature of the products depend on the oxidizing agents. A careful study has been done on the oxidation of Ni(II)TPP by Br\textsubscript{2}, I\textsubscript{2}, trifluoroacetic acid and antimony pentachloride. Conversion of Ni(II)TPP\textsuperscript{+} radical cation to Ni(III)TPP by the addition of sodium methoxide has also been studied and this behaviour is very similar to that reported for Fe(III)TPP\textsuperscript{+} and Mn(III)TPP\textsuperscript{+} systems.

IV.2 Experimental section

Dichloromethane was used as solvent for optical and EPR spectral measurements. It was refluxed over phosphorous pentoxide and distilled just before use. Tetrakis(3,4-dimethoxy)\(\alpha,\beta,\gamma,\delta\)-tetraphenyl porphyrin (DMTPP) was synthesized by propionic acid method using pyrrole and 3,4-dimethoxybenzaldehyde. 2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl porphyrin (H\textsubscript{2}TPP(\text{Br})\textsubscript{4}), 2,3,12-tribromo-5,10,15,20-tetraphenyl porphyrin (H\textsubscript{2}TPP(\text{Br})\textsubscript{3}), 2,3,12,13-tetracyano-5,10,15,20-tetraphenyl porphyrin (H\textsubscript{2}TPP(CN)\textsubscript{4}) and 2,12,13-tricyano-5,10,15,20-tetraphenyl...
porphyrin(H$_{2}$TPP(CN)$_{3}$) were synthesized by the procedure described by Callot et al. The Ni(II) complexes are prepared by refluxing the porphyrin with excess anhydrous nickel chloride in chloroform-methanol (80:20) medium. The nickel porphyrins were purified by column chromatography using neutral alumina. Purity of the compounds was checked by TLC and Optical spectra.

EPR measurements are done using JEOL FX-100 EPR spectrometer, operating at X-band with 100KHz field modulation. Measurements at liquid nitrogen were done using a cold finger dewar. Computer simulations of epr spectra were done using the program 'POWDER' developed in our laboratory which has been discussed in chapter III. Lineshape function was calculated using the frequency sweep mode.

One-electron oxidation of nickel porphyrins was done using various reagents like bromine in dichloromethane, iodine in dichloromethane, trifluoroacetic acid, antimony pentachloride and BF$_{3}$-etherate. About 1mM of oxidizing reagent in de-aerated solutions of dichloromethane was used. Purified nitrogen from nitrogen generator (Model-NG2504 Peak Scientific, UK) was used for purging the solutions.

IV 3 Results and discussions

IV 3 1 Oxidations with Bromine and Iodine

The results obtained when bromine or iodine was used as oxidant were similar. When less than half equivalent mole of bromine was used, a strong free radical type signal ($g = 2.005$) is obtained at room temperature with a very broad small signal on the low field side of the free radical signal. With increased amount of bromine, this broad signal has become stronger. The development of the broad signal is followed for a period of thirty minutes. The signal intensity increases, reaches maximum, then slightly
decreases and remains constant thereafter Fig IV 1. It appears that some precipitate formation has taken place, which increases with increasing bromine concentration. This perhaps reaches a maximum over a period of time and when the precipitate settles down in the epr tube the signal decreases. If more than one equivalent of bromine was added the precipitate formation could clearly be seen.

Fig VI 1 EPR spectra of one-electron oxidation of Ni(II)TPP with bromine (0.5 mM) at room temperature at 5 minutes interval ($\nu = 9.1427$ GHz)
The broad line spectrum gives a rhombic pattern at liquid nitrogen temperature while the free radical signal remains isotropic at the same temperature.

Fig IV 2 EPR spectra of oxidation product of Ni(II)TPP in dichloromethane at 77K with Br₂ (a) Experimental (b) Simulated \( (\nu = 91221 \text{ GHz}) \)

Computer simulation of the rhombic signal led to the g-values, \( g_x = 2.32, g_y = 2.255, g_z = 2.105 \) indicating a strong Ni(III) character (Fig IV 2) For a \( d^7 \) system in an octahedrally elongated geometry, \( g_\parallel < g_\perp \) or \( g_z < g_x, g_y \). The broad EPR signal at room temperature was quite strong when the oxidation with Br₂ was carried out in the presence of imidazole.
Addition of sodium methoxide to the product obtained on oxidation with bromine, leads to an axially symmetric EPR signal at liquid nitrogen temperature. Very little signal was seen at room temperature. The axially symmetric signal was quite strong and was very similar to that reported by Wolberg and and Manassen for Ni(III)TPP. The $g$ values are also very similar. Addition of methoxide apparently converts Ni(II)TPP to Ni(III)TPP involving valence tautomerism. This behaviour is already known in the case of Fe(III)TPP and Mn(III)TPP. The broad signal obtained with bromine oxidation of Ni(II)TPP also disappears with the addition of methoxide. Experimental and simulated spectra are presented in the Fig. IV 3.

A different EPR behaviour was observed when methoxide was added after the oxidation of Ni(II)TPP in the presence of imidazole. Fig. IV 4.
Fig IV 4 EPR spectra of oxidation product of Ni(II)TPP in dichloromethane at 77K
(i) with Br2/Imidazole, (ii) After adding NaOMe (a) Experimental (b) Simulated
(ν = 9 1512 GHz)

The rhombic signal remains along with the axially symmetric EPR spectrum characteristic of Ni(III)TPP⁺. Addition of less than required amount of methoxide ions leads to the presence of broad rhombic signal, axially symmetric signal and the free
radical type of signal at liquid nitrogen temperature. This indicates that the conversion of Ni(II)TPP$^+$ to Ni(III)TPP$^+$ is slow. The axially symmetric signal was likely to be at least a five coordinated Ni(III) species.

Fig. IV.7: 1. UV-VIS spectrum of one-electron oxidation of Ni(II)TPP with Br$_2$ at room temperature. 2. UV-Visible spectrum of Ni(II)TPP after adding bromine. 3. UV-Visible spectrum of Ni(II)TPP after adding bromine at 5 minutes interval. 4. UV-Visible spectrum of Ni(II)TPP after adding bromine at 10 minutes interval. 5. UV-Visible spectrum of Ni(II)TPP after adding bromine and sodium methoxide.

The optical spectra were recorded for Ni(II)TPP oxidized with bromine and the product obtained on the addition of sodium methoxide to the oxidized product. The product obtained on oxidation with bromine is identified as the radical cation. The optical spectrum obtained after the addition of methoxide to the radical cation is identified as Ni(III) porphyrin. These assignments have been made on the basis of earlier literature.
Structures of the various species

(i) Free radical species The radical cation of Ni(II)TPP is likely to be a five coordinated species with Br\(^-\) as axial ligand. This model is similar to the structures of Mg or Zn porphyrin radical cations.\(^{19}\)

(ii) Species giving rise to rhombic EPR When bromine was used as the oxidant, a rhombic EPR signal was observed. At room temperature along with the radical signal, this signal intensity increases with bromine concentration. This species has been identified as a precipitate in the earlier section. It is difficult to propose a structure for this system. Tentatively, we propose that it could be having a bromide ion as the axial ligand and perhaps a bromine molecule or a nucleophilic solvent molecule, which may be present as impurity in dichloromethane, as the sixth ligand. In the presence of imidazole, another rhombic species was observed which is attributed to a Ni(III) system with an imidazole molecule as an axial ligand and a bromide ion as the sixth ligand.

The EPR results obtained with iodine, as an oxidising agent, are very similar to those obtained with bromine.

IV 3 2 Oxidation with I\(_2\)/AgClO\(_4\) and trifluoroacetic acid

The oxidation species in this situation is supposed to be the I\(^+\) ion. The rhombic EPR signal obtained at earlier situation (bromine or iodine as oxidants) did not appear. Only a free radical signal was observed which is isotropic both at room and liquid nitrogen temperatures. Addition of sodium methoxide to the free radical species leads to an axial EPR signal at liquid nitrogen temperature (\(g_\parallel = 2.125, g_\perp = 2.311\)). Controlled amount of addition of methoxide leads to the appearance of both the free radical signal.
and the rhombic Ni(III)TPP\(^+\) signal at liquid nitrogen temperature. The relevant spectra are presented in Fig. IV 5.

Fig. IV 5 EPR spectrum of oxidation product of Ni(II)TPP in dichloromethane at 77K with I\(_2\)/AgClO\(_4\) after adding NaOMe (a) Experimental (b) Simulated \((v = 91321 \text{ GHz})\)

Similar results are obtained when either trifluoroacetic acid or BF\(_3\) etherate are used as oxidants. With trifluoroacetic acid as the oxidant a small amount of methanol was added. The EPR spectrum of the resultant species indicates the presence of both the free radical and the axially symmetric Ni(III) species (Fig. IV 6).

Substituent effects

Different types of Ni(II) porphyrins were studied in the present work. Ni(II)TPP(CN)\(_4\), Ni(II)TPP(CN)\(_3\), (Ni(II)DMTPP) and Ni(II)TPP(Br)\(_4\) porphyrin, were all subjected to the oxidation by bromine in dichloromethane. Nearly identical EPR results were obtained at room temperature and at liquid nitrogen temperature in the presence and absence of methoxide ions.
Fig. IV.6: EPR spectrum of oxidation product of Ni(II)TPP in dichloromethane at 77K with trifluoroacetic acid/Methanol. (a) Experimental; (b) Simulated. ($\nu = 9.1110 \text{ GHz}$)
V 4 Conclusion

The EPR studies on the oxidation products of Ni(II) porphyrins have clearly indicated that the valence tautomerism has been clearly established. The switching of Ni(II)P⁺ (radical cation) to Ni(III)P⁺ is possible with strong nucleophilic ligand like methanol or methoxide ion. This behaviour is similar to those observed for the cases of Fe(III) porphyrins and Mn(III) porphyrins. In the light of our results, the earlier EPR observations of Wolberg and Manassen and others could have been interpreted in terms of the presence of small amount nucleophilic solvent impurity (like methanol) in their solvents.

V 5 References


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