MECHANISM OF PHOTOREDUCTION AND STEREOCHEMICAL ASPECTS OF AXIAL LIGATION IN SOME IRON-PORPHYRINS MONITORED BY RESONANCE RAMAN SPECTROSCOPY

NABO KUMAR CHAUDHURY
DEPARTMENT OF PHYSICS
SCHOOL OF PHYSICAL SCIENCES
NORTH-EASTERN HILL UNIVERSITY
SHILLONG - 793003

SYNOPSIS OF THE THESIS SUBMITTED
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG - 793 001
INDIA

NOVEMBER, 1990

SYNOPSIS

SYNOPSIS

Porphyrin complexes have long been considered materials of great importance because of their ubiquitous properties and significant role in a variety of physico-chemical functions. Heme-proteins have therefore been investigated on multi and interdisciplinary levels. All these proteins containing an iron-porphyrin as the prosthetic group are responsible for oxygen transport (hemoglobin, myoglobin and cytochromes b, c), oxygen reduction (cytochrome oxidase), hydrogen peroxide utilization and destruction (peroxidases and catalases) and many other functions. The active site in each case contains, most often, an iron protoporphyrin-IX and obviously these diverse functions must be dictated by various stereochemical parameters like oxidation and spin states, the nature of axial ligands, state of coordination and, of course, the environment. The essential biochemical processes, however, require the reduced state of iron as in cooperative binding of oxygen in hemoglobin. In recent years, reduction of iron-porphyrin complexes has been achieved by chemical[1], electrochemical[2] or photochemical[3] methods and monitored by different spectroscopic techniques. But so far it has not been possible to delineate the various steps involved in the reduction and electron transfer processes in these systems. Therefore, in order to understand the functioning of heme-related proteins, it is important to delineate the basic mechanism of oxido-reduction processes including studies of the intermediate transient species involved in the activation process alongwith possible structural changes which may take place during the biophysical changes.

Since vibrational spectroscopy is one of the very powerful tools to gain insight into the nature of chemical bonds and geometrical structure of molecules in solution, Raman spectra of metalloporphyrins have been extensively investigated.[4] Resonance Raman (RR) technique offers a means of selectively enhancing certain vibrational modes of the porphyrin chromophore only in a complex heme-protein which are sensitive probes of the changes in the oxidation, spin and coordination states of the central iron atom and reflect the structural and bonding changes as well. Therefore extensive RR studies on many heme-proteins and model complexes have been carried out in the recent past and have resulted in useful correlations between Raman frequencies and various stereochemical parameters.

This thesis describes systematic RR studies for understanding the mechanism of photoreduction of some iron-porphyrins in the presence of biologically relevant 2-methylimidazole (2-MeIm), 1,2-dimethylimidazole (1,2-Me_2Im) and imidazole (Im) as axial ligands and stereochemical aspects of axial ligation in these systems. We have measured action spectrum and have carried out systematic RR studies to explore the detailed mechanism of photoreduction process in iron porphyrins. We have performed similar studies at low temperatures upto ~20K which have further substantiated our proposed mechanism on photoreduction and also revealed temperature dependent changes in axial ligation. Solvent dependence on the yield of photoreduction of iron porphyrin has been initiated with the aim of understanding the specific role of environment on the photoreduction process. Our RR studies on the stereochemical aspects of axial ligation in the photoreduced iron-porphyrins have revealed the coexistence of both the upright and tilted configurations of axial ligand $Fe-N_{Im}$ bond with respect to the normal to the porphyrin plane. The different aspects of these studies are given in individual chapters.

This thesis is divided into seven chapters.

In Chapter I, we review RR and other related studies on iron porphyrins. Some of the important stereochemical parameters of iron porphyrins have been discussed because of their direct influence on the reactivities of porphyrin complexes as a whole. The increasing importance of photoreduction technique employed here for obtaining reduction of iron porphyrin complexes and in situ monitoring by RR technique have been emphasized over other conventional methods.

We have presented relevant theoretical background to understand the electronic absorption and resonance Raman (RR) spectra of iron porphyrins in Chapter II.

Chapter III presents pertinent details of the different experimental techniques that have been used in this study. A brief description of the method of sample preparation, lasers and laser Raman spectrometer have been incorporated, apart from details of other instruments and accessories used in this work.

In Chapter IV, we present our detailed RR studies on the mechanism of photoreduction of iron protoporphyrin-IX dimethyl ester chloride in the presence of biologically relevant axial ligands.[5] In this study, we have discovered the important catalytic role of trace amount of alcohol (primary or secondary) as "directing ligand", which facilitates the ligation of nitrogenous bases to the fifth coordination site by replacing the tightly bound halide ion from the coordination sphere of iron porphyrins. The dependence of photoreduction on excitation wavelength and coincidence of the maximum of quantum yield of photoreduced species with the Soret transition has been observed, indicating that photoreduction process is driven by absorption in the Soret region. From the action spectra of $Fe^{III}PPDME(2\text{-}MeIm)$ complex obtained by irradiation with a white light source for different times in the presence of a short-cut filter L-38, we have obtained the rate constant for photoreduction as $k_R^{-1} = 10$ minute. We have identified ligand free, four coordinated, $Fe^{II}PPDME$ as the transient species involved in the photoreduction of $Fe^{III}PPDME(2\text{-}MeIm)$ complex from concentration dependent RR studies of photoreduction on axial ligand (2-MeIm). On the basis of these results, a mechanism for photoreduction of iron porphyrins has been proposed. Light irradiation in the Soret region excites the $Fe^{III}PPDME(2\text{-}MeIm)$ complex to the $e_g(\pi^*)$ or to the antibonding d_z2 orbital where ligated 2-MeIm dissociates donating its charge to the iron centre. The resulting 2-MeIm$^+$ then diffuses away from the coordination sphere of iron porphyrins. The ligand free, Fe^{II}PPDME, transient species is stabilized by coordination with another 2-MeIm molecule from solution giving five coordinated, high spin, reduced Fe^{II}PPDME(2-MeIm) complex as the final photoreduced species.

In Chapter V, we discuss our RR studies on Fe^{III}PPDME(1,2-Me$_2$Im) complex at low temperatures. In this temperature dependent RR study[6], we have observed photoreduction of this complex in soft dimethyl sulfoxide (DMSO) matrix at ~100K by excitation in the Soret absorption region and have characterized the photoreduced product as six coordinated, intermediate spin, Fe^{II}PPDME(DMSO)$_2$ complex. Non-photoreducibility in the hard glassy DMSO matrix at ~20K indicates that the long-range quantum-mechanical electron tunneling plays insignificant role while the short-range electron transfer is the primary process involved in the photoreduction of iron porphyrin complexes. Temperature dependent changes in the axial ligation have been observed where in cold solution at ~250K 1,2-Me$_2$Im coordinates at the fifth ligand position by replacing DMSO. The photoreduced species has been characterized as five coordinated, high spin, Fe^{II}PPDME(1,2-Me$_2$Im) complex at this temperature. We also report our preliminary RR studies on the solvent dependent yield of photoreduction where it appears that the yield of photoreduction depends on the polarity of the solvent which facilitates the solvent-induced dissociation of ion-pairs created by electron transfer, although other solvent parameters also play important role.

In Chapter VI, we give the details of stereochemical aspects of axial ligation in the photoreduced iron-porphyrins.[7] During concentration dependent RR studies on axial ligands of FeOEP and FePPDME complexes, we have observed doublet structure in the Fe-N_{Im} stretching region in these complexes with 2-MeIm and 1,2-Me_2Im as axial ligands due to coexistence of the upright and tilted configurations of the Fe-N_{Im} bond with respect to the normal to the porphyrin plane. With 2-MeIm complexes of iron porphyrins, the upright configuration is the predominant species. The frequency of the Fe-N_{Im} stretching mode shows an upshift with increase in the concentration of 2-MeIm axial ligand due to H-bonding between the N_δ-proton of free 2-MeIm and ligated 2-MeIm. However, a larger frequency shift in the case of Fe^{II}PPDME(2-MeIm) complex is attributed to non-bonded interactions between the vinyl groups of Fe^{II}PPDME complex and methyl groups of ligated 2-MeIm. With more sterically hindered ligand 1,2-Me_2Im, we have once again observed that the non-bonded repulsive interaction is responsible for stabilizing the upright configuration of Fe-N_{Im} bond in the Fe^{II}PPDME(1,2-Me_2Im) complex, where as in the Fe^{II}OEP(1,2-Me_2Im) complex, it is the tilted configuration which is the predominant species.

Chapter VII presents summary and conclusions from our RR studies described in this thesis for understanding the mechanism of photoreduction of iron porphyrins and stereochemical aspects of axial ligation. Suggestions for extension of this work in future studies are also made which may help to confirm our proposed mechanism of photoreduction and other aspects discussed in this thesis.

References

1. Donhoe, R.J.; Atamian, M.; Bocian, D.F. *J. Am. Chem. Soc.* 109, 5593, 1987.

2a. Seely, G.R.; Talmadge, K. *Photochem. Photobiol.* 3, 195, 1964.

b. Kim, D.; Miller, L.A.; Rakhit, G.; Spiro, T.G. *J. Phys. Chem.* 90, 3320, 1986.

c. Bottomely, L.A.; Kadish, K.M. *Inorg. Chem.* 20, 1348, 1981.

3a. Bortocci, C.; Maldotti, A.; Traversso, O.; Bignozzi, C.A.; Carassitti, V. *Polyhedron,* 2, 97, 1983.

b. Bizet, C.; Morliere, P.; Brault, D.; Delgado, O.; Bazin, M.; Santus, R. *Photochem. Photobiol.* 34, 315, 1981.

4a. Spiro, T.G. in *"Iron Porphyrins"* Lever, A.B.P.; Gray, H.B. Eds., Adision-Wesley, Reading, M A Part II, p. 91, 1983.

b. Kitagawa, T.; Ozaki, Y. *"Structure and Bonding"*, 64, 71, 1987.

5a. Verma, A.L.; Chaudhury, N.K.; Saini, G.S.S. in *"Recent Trends in Raman Spectroscopy"* Banerjee, S.B.; Jha, S.S. Eds., World Scientific Publishing Co., Singapore, p. 192, 1989.

b. Verma, A.L.; Chaudhury, N.K.; Saini, G.S.S. *"XIIth International Conference on Raman Spectroscopy"* Durig, J.R.; Sullivan, J.F. Eds., John Wiley and Sons, New York, p. 592, 1990.

c. Verma, A.L.; Saini, G.S.S.; Chaudhury, N.K. *Proc. Ind. Acad. Sci. (Chem. Sci.)* 102, 291, 1990.

5d. Verma, A.L.; Chaudhury, N.K. *J. Raman Spectrosc.* (Submitted).

6. Chaudhury, N.K.; Saini, G.S.S.; Verma, A.L. (Submitted).

7. Chaudhury, N.K.; Saini, G.S.S.; Verma, A.L. *Inorg. Chem.* (Submitted).