METALLOPORPHYRIN CATALYZED OXIDATION REACTIONS: SYNTHESIS, STRUCTURE AND MECHANISM

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Metalloporphyrin Catalyzed Oxidation Reactions: Synthesis, Structure and Mechanism

By

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CERTIFICATE

This is to certify that the thesis entitled, "**Metalloporphyrin Catalyzed Oxidation Reactions: Synthesis, Structure and Mechanism**" being submitted by **Mr. Vivek Bagchi** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Vivek Bagchi has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which, to my knowledge has reached requisite standard.

The results contained in the dissertation have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

31st July, 2009

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Dedicated to my
Parents and Teachers

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Guru Saaksaat Param Brahma
Tasmai Shri Guruve Namaha
Guru Is Brahmaa (Who plants the qualities of goodness), Guru Is Vishnu (Who nurtures and fosters the qualities of goodness), Guru Is Maheswara (Who weeds out the bad quality), Guru Is Supreme Brahman Itself, offer thy adorations unto that peerless Guru.

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ABSTRACT

The reactions catalyzed by Cytochrome P-450 family of enzymes have been encouraging the scientists for more than three decades. Alkane hydroxylation and alkene epoxidation in particular have attracted a sustained world-wide effort to understand the details of biological oxygen activation and the development of new catalysts of considerable interest to the scientific and industrial community. The interests towards porphyrin and metalloporphyrins is not only limited to catalysis but also extended in the field of photo-sensitizers, building blocks for electronic devices and porphyrin based superstructure. The advances in our understanding of the mechanisms of the remarkable oxygenation reactions mediated by oxometalloporphyrins in both enzymatic and in small molecule model systems are of exceptional importance in science and technology.

Chapter I give a brief review on the chemistry of enzymatic systems belonging to the class of hemoproteins. Various model systems developed for mimicking the reactions of these enzymes have also been summarized. The current understanding of the nature of reactive intermediates involved in the iron (III) and manganese (III) porphyrin catalyzed oxidation of organic and organometallic compounds using *tert*-butyl hydroperoxide and the scope of the present work has as well been delineated in this chapter.

Chapter II describes the purification of solvents and substrates along with the detailed synthesis of all the iron, manganese, chromium and vanadium porphyrins used in this work. These metalloporphyrin compounds have been used as catalysts, peracids, hydroperoxides, iodosylbenzenes were used as terminal oxidants. Among hydroperoxides, *tert*-butyl hydroperoxide and cumene hydroperoxide are commercially available and were used without further purification. In selected cases dioxygen was also used as terminal oxidant.

Chapter III describes a detailed study of dioxygen activation in the oxidization of organic compounds. The dioxygen activation using several iron and manganese porphyrins as catalyst was carried out in dry acetonitrile at room temperature using cyclohexene as the diagnostic probe substrate and anhydrous inorganic phosphates as co-catalyst. The objective of this study was to demonstrate the active participation of phosphate salts in dioxygen activation.

In Chapter IV, the role of aqueous phosphate in the selective hydroxylation obtained by using Mn and Fe porphyrins as catalysts and *t*-BuOOH as terminal oxidant under ambient conditions has been discussed. In the hydroxylation of cyclohexane by *t*-BuOOH using $F_{20}TPPMn^{III}Cl$ as the catalyst cyclohexanol was formed in 60% yields. In order to achieve this selective transformation a special solvent matrix comprising of 40μM of K_2HPO_4 in 2% aqueous acetonitrile was required. In case the transformation was attempted in the solvent system of CH_3CN-H_2O without any phosphate, no oxidation of cyclohexane was observed. In this special solvent matrix when cyclohexene was used as the substrate, selectively 2-cyclohexene-1-ol was formed in 98% yields with no epoxide formation. In this system the evolution of $F_{20}TPPMn^{IV}=O$ species was confirmed by UV-Visible, NMR, EPR and Mass spectrometric measurements. The possible formations of phosphate adduct of $F_{20}TPPMn^{V}=O$ and its oxygen transfer to the substrate resulted the hydroxylation has been proposed.

That this solvent matrix is not a special case for the manganese catalyst has also been demonstrated by performing the oxidation of cyclohexane with $F_{20}TPPFe^{III}Cl$ where cyclohexanol was formed in 68% yields, which is appreciably high as compared with the reported literature.

In previous studies, a few selected organopalladium compounds were found to act as diagnostic probes to identify the possible reaction intermediate formed from iron (III) porphyrin. Thus the

synthesis of a series of organopalladium compounds has been carried out to see the generality of the reaction. Hence chapter V is divided into two parts:

In Chapter VA, an exploration towards synthesis and crystal packing of azo-benzene based cyclo-palladated compounds have been done. A systematic study of non-bonded interactions seems to influence the crystal packing of the solids. The Pd atom in all these compounds, aquires approximately square-planar geometry. Usually the unoxidized molecules are found to dimerize through a non-bonded S --- S interaction [S --- S ~ 3.4 – 3.5 Å] but oxidation at sulfur centre or switching the substituent from methyl to ethyl obliterate such interaction. The role of secondary interactions such as CH --- O, CH --- Cl, π --- π and CH --- π interactions and its change with substitution on "S" centre, has also been shown to influence the crystal packing. Cl-LPdCl exhibits polymorphism in different solvent system. The role of solvent in aggregation of the molecules in solids has also been discussed.

Chapter VB highlights the mechanistic aspects of manganese (III) porphyrin catalyzed oxidation of simple cyclopalladated compounds (I) and its derivatives. The cyclopalladated 2-(alkylthio)azobenzene complex ($L_{1a}PdCl$) has three sites for oxidation of which the thioether fragment and the Pd – C bond were found to be easily oxidizable. It has been observed that pentafluoroiodosyl benzene (C_6F_5IO) selectively oxidizes Pd – C bonds of a series of cyclopalladated 2-(alkylthio)azobenzene complexes in excellent yields in absence of any catalysts. However in presence of $F_{20}TPPMn^{III}Cl$ catalyst, the site of oxidation was changed and instead of C – Pd bond, the thioether fragment was selectively oxidized. Results revealed that in this oxidation process, PMn (V) species to be the major reactive intermediate in the oxidation of exclusive sulfur center.

Chapter VI describes the Synthesis of metal-organic framework (MOF) based on tetra-pyridyl porphyrin and palladium (II) salt is described in this chapter. In a reaction of a tetrapyridyl porphyrin with Na_2PdCl_4 in DMF resulted in the formation of palladium oxide nano-crystals embedded in a 3D network. The UV-Visible spectroscopy reveals that palladium is not inserted in the porphyrin macrocycle but is coordinated to the peripheral nitrogen of tetra-pyridyl porphyrin. The palladium oxide nano-crystals were characterized by Powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Electron Diffraction (ED), Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The particle size obtained from TEM was found to be in the range of 4-7 nm. The PXRD and HRTEM data supported the formation of palladium oxide nano-crystals. Upon aging the dispersion, tetra-pyridyl porphyrin and palladium undergo polymerization and resulted in the formation of a deep red gel, which is stable in presence of oxidants such as pentafluoro iodosylbenzene, *meta*-chloroperbenzoic acid and hydrogen peroxide. A plausible mechanism for the in-situ generation of nano-crystals and the formation of gel has been proposed.

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