THE REACTIONS OF IRON(III) PORPHYRINS WITH HYDROPEROXIDES/HYDROGEN PEROXIDE: REACTIVE INTERMEDIATE(S) IN SOLUTION

By

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CERTIFICATE

This is to certify that the thesis entitled, **"THE REACTIONS OF IRON(III) PORPHYRINS WITH HYDROPEROXIDES/HYDROGEN PEROXIDE: REACTIVE INTERMEDIATE(S) IN SOLUTION"**, being submitted by **Mr. Parvesh Wadhwani** 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. Parvesh Wadhwani has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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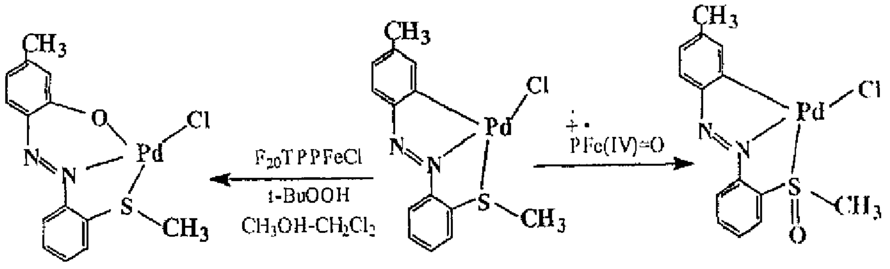
ABSTRACT

The metalloporphyrin catalyzed hydroxylation of alkenes and epoxidation of alkenes has been a subject of considerable interest for last few decades. It has been established that electronegatively substituted iron(III) porphyrins are oxidatively robust and also very efficient catalyst in these reactions. Peracids, hydroperoxides, hydrogen peroxide and iodosylbenzenes are the major terminal oxidants used in these studies. There was limited success in the use of hydroperoxides and hydrogen peroxide as oxidants. The present study is focussed on the iron(III) porphyrin catalyzed oxidation reactions by *tert*-butyl hydroperoxide and hydrogen peroxide.

Chapter I describes a brief literature on the known chemistry of the enzymatic systems belonging to the class of hemoproteins. Various model systems that are developed for mimicking the reactions of these enzymes are also summarized. The current understanding of the nature of the reactive intermediates involved in the iron(III) porphyrin / *tert*-butyl hydroperoxide oxidizing system and the scope of the present work has been delineated in this chapter.

In chapter II, the detail synthetic procedures of the compounds such as the synthesis of various porphyrins ($TMPH_2$, Cl_8TPPH_2, $F_{20}TPPH_2$), metalloporphyrins (PFe(III)Cl, PMn(III)Cl and PCr(III)Cl) and the oxidants (MCPBA and C_6F_5IO) are described. The procedures for the assay of the oxidants have also been described.

Three compounds are mainly used as substrates: (a) an organopalladium compound **1**, (b) 2,4,6-tri-*tert*-butylphenol (TTBP) and (c) 1,4-dipbenyl-butadiene (DPBD).



L_3PdCl 2 **L_1PdCl 1** **L_2PdCl 3**

Chapter III describes the detail reactions of compound **1** with *tert*-BuOOH and H_2O_2 catalyzed by the various iron(III) porphyrins. Compound **1** smoothly reacts with *tert*-BuOOH in CH_3OH-CH_2Cl_2 in presence of *meso*-tetrakis(pentafluorophenyl) porphynato iron(III)chloride to give compound **2** in 100 % yields. This reaction does not proceed in pure dichloromethane. The maximum yield of compound **2** is observed in 33% of methanol in dichloromethane. Similar solvent effect has been observed for the oxidation of 2,4,6-tri-*tert*-butylphenol by the same oxidizing system. The oxidation of TTBP is not perturbed by the presence of compound **1** in the medium. Thus the rate and yield of the $TTBP^{\bullet}$ radical production remained unaffected by the presence of compound 1. Based on these results a scheme for the oxidation of these two substrates has been presented in this chapter.

In chapter IV various reactive intermediates such as oxoiron(IV) porphyrin cation radical(oxene), *tert*-$BuOO^{\bullet}$ radical and oxoiron(IV) porphyrin have been generated by the literature methods and their reactions with compound **1** and TTBP have been investigated. The basic objective was to critically analyze the scheme presented in chapter III. Thus $P^{\bullet+}Fe(IV)=O$ (oxene) has been generated by the reaction of the iron(III) porphyrins with MCPBA or C_6F_5IO. The reactivity of these oxene samples with compound 1 and TTBP under different reaction conditions have been explored. The *tert*-BuOO$^\bullet$ radical has been generated by reacting C_6F_5IO with *tert*-BuOOH and its quantitative trapping has been achieved by using compound 1. TTBP did not react with this radical in methanolic medium. The oxoiron(IV) porphyrin was found to be inert to both the substrates (1 and TTBP). TTBP was found to be the best trap for the oxene whereas organometallic compound 1 is found to be the ideal trap for *tert*-BuOO$^\bullet$ radical.

In the oxidation of the C-Pd bond, the involvement of oxopalladium(IV) has been proposed, though it has never been isolated. Chapter V describes the detail kinetics of the platinum analogue of 1. The reaction of L_1PtCl with C_6F_5IO proceeds smoothly in CH_3CN at the rate of 0.73 $M^{-1}s^{-1}$ at 20°C. The oxidized product is not the platinum analogue of 2 as has been observed from its UV-visible spectrum. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values obtained from the variable temperature kinetic measurements are 53.57 ± 0.18 kJ mol^{-1} and -64.86 ± 0.60 eu respectively. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values for the oxidation of compound 1 by C_6F_5IO under identical reaction conditions were 55.5 ± 3.5 kJ mol^{-1} and -75.7 ± 11.5 eu respectively. In the oxidation of L_1PtCl we have been successful to identify the platinum(IV) species. The subsequent reaction of this high valent oxoplatinum with compound 1 has produced 2. This observation has indicated that the observed oxo-transfer reactions may be intermolecular in nature.

In the final chapter the results obtained in the reaction of $F_{20}TPPFeCl$/ *tert*-BuOOH have been extended to the olefin epoxidation. Preliminary results in the oxidation of 1,4-diphenyl-1,3-butadiene has been described. This substrate is also oxidized by the same oxidizing system and a very similar solvent effect has been observed however the quantitative trapping of the reactive intermediate has not been possible. The significant observation, which has never been observed before, is that upon using a higher initial concentration of the diene the oxidation reaction stops almost completely. This probably indicates the role of the diene coordination to the catalyst and this might block the coordination site of the oxidant to the catalyst. Lower concentration of the oxidant and the diene are found to be the suitable conditions for its oxidation.

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