## CONTENTS

### Chapter 1

**INTRODUCTION**

1.1 Oxygen Atom Transfer Reactions Catalyzed by Metal Complexes  
1.1.1 Oxygen Atom Transfer Reactions Catalyzed by Metal-Porphyrin Complexes  
1.1.2 Oxygen Atom Transfer Reactions Catalyzed by Metal-Salen Complexes  
1.2 Oxygen Atom Transfer to Organic Sulphides Catalyzed by Metal Complexes  
1.3 Oxidation of Organic Sulphides by Other Oxidants  
1.4 Electron Transfer Reactions  
1.4.1 Theories of Electron Transfer  
1.5 Structure-Reactivity Relationships  
1.6 Scope of the Present Investigation

### Chapter 2

**MECHANISM OF OXIDATION OF ORGANIC SULPHIDES BY (SALEN)Mn^{III}/PhIO SYSTEM**

2.1 Oxidative Conversion of Manganese(III) to Oxomanganese(V) Species  
2.2 Stoichiometric Oxidation of Organic Sulphides with Oxo(salen)manganese(V) Complexes  
2.3 Kinetics of Oxidation of Alkyl Aryl and Dialkyl Sulphides with Oxo(salen)manganese(V) Complexes  
2.3.1 Dependence of Rate on [Reactants]₀  
2.3.2 Effect of Pyridine N-Oxide
2.3.3 Substituent - Effect Studies
  i) With aryl methyl sulphides
  ii) With oxo(salen)manganese(V) complexes

2.3.4 Steric - Effect Studies
  i) With alkyl phenyl sulphides
  ii) With oxo(salen)manganese(V) complexes

2.3.5 Oxidation Studies with Dialkyl Sulphides

2.3.6 Mechanism of Oxygen Atom Transfer from
  Oxo(salen)manganese(V) Complexes to Alkyl Aryl Sulphides

2.4. Kinetics of Oxidation of Diaryl Sulphides with
  Oxo(salen)manganese(V) Complexes

2.5 Application of Marcus Theory of Electron Transfer
  2.5.1 Estimation of Redox Potential of MnV/MnIV Couple
  2.5.2 Estimation of Rate Constants

2.6 Applicability of Reactivity-Selectivity Principle
  2.6.1 RSP Studies with Aryl Methyl Sulphides
  2.6.2 RSP Studies with Diaryl Sulphides

Chapter 3

MECHANISM OF OXIDATION OF ORGANIC SULPHIDES BY
(SALEN)MnIII/H2O2 SYSTEM

3.1 Dismutation of Hydrogen Peroxide by (salen)MnIII Complexes

3.2 Preliminary Spectral Studies

3.3 Stoichiometric Oxidation of Organic Sulphides with H2O2 in
  Presence of (salen)MnIII Complexes

3.4 Kinetics of Oxidation of Alkyl Aryl Sulphides with
  Hydrogen Peroxide in Presence of (salen)MnIII Complexes
  3.4.1 Dependence of Rate on [Reactants]o
  3.4.2 Effect of Nitrogenous Bases
3.4.3 Effect of Free-Radical Inhibitor
3.4.4 Effect of Solvent Composition
3.4.5 Mechanism of (salen)Mn\textsuperscript{III} Catalyzed Hydrogen Peroxide Oxidation of Alkyl Aryl Sulphides
3.4.6 Substituent - Effect Studies
   i) With aryl methyl sulphides
   ii) With (salen)Mn\textsuperscript{III} complexes
3.4.7 Steric - Effect studies
   i) With alkyl phenyl sulphides
   ii) With (salen)Mn\textsuperscript{III} complexes
3.5 Kinetics of Oxidation of Diaryl Sulphides with Hydrogen Peroxide in Presence of (salen)Mn\textsuperscript{III} Complexes

Chapter 4

EXPERIMENTAL

4.1 Materials
4.1.1 Preparation of Schiff Base Ligands
4.1.2 Preparation of (salen)Mn\textsuperscript{III} Complexes
4.1.3 Preparation of Sulphides
   4.1.3.1 Aryl methyl sulphides
   4.1.3.2 Diaryl sulphides
   4.1.3.3 Alkyl phenyl sulphides
4.1.4 Preparation of Other Reagents
4.1.5 Purification of Solvents
4.1.6 Purification of Nitrogen Gas

4.2 Instrumentation

4.3 Methods
4.3.1 Oxidation of Sulphides by (salen)Mn\textsuperscript{III}/PhIO System
   4.3.1.1 \textit{In situ} generation of [(H\textsubscript{2}salen)Mn\textsuperscript{V}=O\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-}] complex
4.3.1.2 Kinetic measurements
4.3.1.3 Product analyses

4.3.2 Oxidation of Sulphides by (salen)MnIII/H2O2 System
4.3.2.1 Kinetic measurements
4.3.2.2 Product analyses

4.4 Tables of Kinetic Runs

SUMMARY

LIST OF PUBLICATIONS

REFERENCES

APPENDIX - I Evaluation of errors in kinetic data