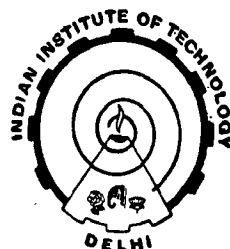


# **KINETICS AND MECHANISMS OF SOME REACTIONS INVOLVING METAL IONS**

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SUBMITTED  
IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**



**TO THE**  
**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**  
**MARCH 1984**

TO

MY PARENTS

## ACKNOWLEDGEMENTS

I express my deep regards to Dr. Rajagopala Varadarajan for his unflinching guidance, and encouragement throughout the progress of this work.

I thank Professor R.P. Gandhi and Professor N.K. Jha, for providing facilities to carry out this work.

I am indebted to several of my friends and colleagues especially Mrs. Mary Joseph, Mr. K.S. Reddy and Mr. R.K. Dhar for their help and encouragement.

I am grateful to the members of the supporting staff especially Mr. Baladutt Phuloria and Mr. Durga Singh of the Instrumentation Laboratory who helped to record the spectral data.

I appreciate Mr. P.M. Padmanabhan Nambiar for his excellent typing of the manuscript.

I thank the authorities of the Indian Institute of Technology Delhi, for financial assistance.

  
(Dasaraju Raghavendra Raju)

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## ABSTRACT

The thesis describes in detail the kinetic and mechanistic studies on the oxidation of some substituted piperidones with manganese(VII), manganese(IV) and manganese(III) in sulphuric acid media in the acidity range of 0.3 to 0.5 M. The substrates investigated are 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one.

Kinetics were followed by studying the decrease in optical density of Mn(VII) at 525 nm, Mn(IV) at 380 nm and Mn(III) at 420 nm respectively. The concentration of Mn(VII) or Mn(IV) or Mn(III) was determined titrimetrically. Stoichiometries were also determined by titrimetry. The products of oxidation were identified by GC/MS analysis and qualitative tests.

Mechanisms of the reaction are found to be similar in all the cases studied. The rate equation generally takes the form

$$K_o = a + b [H^+]$$

where a and b are constants,  $K_o$  the observed rate constant and  $[H^+]$  the molar acidity.

In all these studies, there was no spectroscopic or kinetic evidence for complex formation.

Thermodynamic parameters have been determined for the reactions according to the mechanisms proposed. The results of these studies have been compared with the findings of other investigators for similar compounds involving mainly Mn(VII) and Mn(III) ions.

A linear relationship has been found to exist between enthalpies and entropies of activation for all the cases. This phenomenon has been attributed to the structurally related series of compounds and solvent effects.