MECHANISTIC INVESTIGATIONS OF ELECTROLYTICALLY GENERATED MANGANESE(III) SULPHATE FOR THE OXIDATION OF SOME ORGANIC SUBSTRATES

THESIS SUBMITTED TO THE UNIVERSITY OF MYSORE
FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

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JANUARY 1998

Dedicated to My Parents

Smt. & Sri. S.Nagaraj

and Husband C.S.Sudhir

DECLARATION

I hereby declare that the thesis entitled *"MECHANISTIC IWESTIGATIONS OF ELECTROLYTICALLY GENERATED MANGANESE(III) SULPHATE FOR THE OXIDATION OF SOME ORGANIC SUBSTRATES"* submitted to the *UNIVERSITY OF MYSORE* for the award of degree of *DOCTOR OF PHILOSOPHY* is the result of my own study and was composed independently by me, under the guidance of *Dr. K.S. RANGAPPA,* M.Sc.,Ph.D., Reader in Chemistry, Department of Studies in Chemistry, University of Mysore, Mysore and that it has not been submitted before for the award of any degree, diploma associateship, fellowship or other similar title.

Date : . (N. ANITHA)

Place : Mysore

CERTIFICATE

This is to certify that the research work of Smt. N. Anitha, M.Sc., *entitled "MECHANISTIC INVESTIGATIONS OF ELECTROLYTICALLY GENERATED MANGANESE(III) SULPHATE FOR THE OXIDATION OF SOME ORGANIC SUBSTRATES" was carried out and completed under my supewision. The candidate has completed the research work and is hereby permitted* to *submit the thesis to the University of Mysore for the award of the Ph.D. degree.*

The material presented in this thesis has not been used by the candidate for the award of any degree, diploma, associateship, fellowship etc., of any other similar title.

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ACKNOWLEDGEMENT

I wish to place my profound sense of gratitude to my esteemed guide Dr.K.S.Rangappa, Reader in Chemistry, Department of studies in Chemistry, Manasagangotri, University of Mysore, Mysore, who initiated me to explore this interesting field. His constant encouragement, inspiration and guidance at every stage of the present investigations, have been invaluable.

I am indebted to Dr. D.S.Mahadevappa, Rtd. Professor of Physical Chemistry, University of Mysore and K.M.Lokanath Rai, Reader in Organic Chemistry, university of Mysore for their guidance, valuable suggestions, sound counsel and sustained interest during my research work.

I owe my special thanks to Prof. A.S.Ananda Mm-thy, Chairman, Prof. B.Keshavan former chairman, Department of Studies in Chemistry, for providing necessary facilities required for my research work.

It is a privilege for me to thank the University of Mysore, for providing the necessary facilities during the course of my studies at the Department of studies in Chemistry, Manasagangotri, Mysore.

I express my gratitude to Prof. K.N.Thimmaiah, Dr. S.Ananda and other teaching staff of the Department of studies in Chemistry, University of Mysore, Mysore for their co-operation and useful suggestions.

I wish to thank B.M.Vishakante Gowda and other non-teaching staff of the Department of studies in Chemistry, Manasagangotri, Mysore for their help during my research period.

I am highly thankful to Dr. S.Chandraju, M.Ayesha Nikath, Dr. M.P.Ragavendra, Ere Gowda, H.N.Kalpana, K.R.Prasad, H.Mallesh, N.V.Anil Kumar and other friends for their help extended during my research period.

I would like to take this opportunity to express my gratitude and thanks to my parents, husband. brothers, grand father and parent in laws for their constant encouragement and my daughter's co-operation throughout, without which I could not have come this far.

Finally, I wish to thank softouch computer center, saraswathi puram, Mysore for the elegant typing and for the neat output of my thesis

Lastly I thank one and all who encouraged me directly or indirectly during my research work

(N. ANITHA)

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PREFACE

The thesis describes the elucidation of reaction mechanisms of oxidation of some organic substrates, such has hexoses, pentoses, uronic acids, 6–deoxyhexoses and substituted phenethyl alcohols by electrolytically generated manganese(III) sulphate in sulphuric acid medium. Methods of preparation of stable solutions of manganese(III) are designated and evaluated for suitability. Characterization has done by using the electronic absorption spectra and by the measurement of redox potentials of Mn(III)–Mn(II) couples.

The thesis is divided into five chapters and each chapter contains several sections .

Chapter 1 is of general nature dealing with the introduction to reaction kinetics, review of manganese(III) oxidations, biochemical significance, preparation of manganese(III) in aqueous sulphuric acid medium, estimation of manganese(III), spectrophotometric investigations, stability of manganese(III) in aqueous sulphuric acid , redox potentials of Mn(III)–Mn(II) couple in aqueous sulphuric acid, isotope studies, linear free energy relationship (LFER), experimental details and objective and scope of the present work.

Chapter 2 gives a detailed report on the kinetics and mechanism of oxidation of four hexoses namely D-glucose, D-fructose, D-mannose and L-sorbose and three pentoses namely D-xylose, L-arabinose and D-ribose by manganese(III) sulphate in the presence of sulphuric acid at 30°C. The first section of this chapter gives a brief introduction to monosaccharides, while section 2.2 reviews the available kinetic data on the oxidation of monosaccharides. Section 2.3 describes the actual kinetics and mechanism of oxidation of four hexoses and three pentoses by manganese(III).

Chapter 3 deals with kinetics and mechanism of oxidation of two uronic acids namely D-giucuronic acid and D-gaiacturonic acid by manganese(III) sulphate in acid

medium. Section 3.1 gives a general introduction to uronic acids. Section 3.2 report the actual kinetics and mechanism of oxidation of two uronic acids by manganese(III) sulphate in suiphuric acid medium at 30°C.

Chapter 4 describes the kinetics and mechanism of oxidation of two 6–deoxyhexoses namely L-fucose and L-rhamnose by manganese(III) sulphate in acid medium. Section 4.1 briefly describes a general introduction to the 6–deoxyhexoses. Section 4.2 gives a description of the kinetics and mechanistic investigation of oxidation of the two 6–deoxyhexoses by manganese(III) sulphate in presence of sulphuric acid at 30°C.

Chapter 5 deals with the kinetics of oxidation of phenethyl alcohols by manganese (III) sulphate in acid medium . Section 5. I gives a general introduction to the phenethyl alcohols. Section 5.2 gives a review of oxidation of phenethyl alcohols by other oxidants. Section 5.3 explains the results of oxidation of the phenethyl alcohols by manganese(III) sulphate in presence of suiphuric acid at 30°C.

A brief summary of the present investigations is given after the reference.

Appendix 1 gives an explanation of statistical methods employed in the interpretation of experimental data obtained in the present investigation.

LIST OF ABBREVIATION USED

Aqueous	aq	Observed rate constant	k_{obs}
Concentration	[ ]	Oxidant	ox
Dielectric constant	D	Percentage volume / volume	% v/v
Equilibrium constant	K	Phenethyl alcohol	PEA
Electron volts	eV	Rate constant	k
Enediol	E	Rate determining step	rds
Energy of activation	E_a	Reactant state	RS
Entropy of activation	$\Delta S^{\#}$	Reaction constant	P
Enthalpy of activation	$\Delta H^{\#}$	Regression co-efficient	r
Formal redox potential	E_o	Saturated calomel electrode	SCE
Faraday	F	Standard deviation of point	
Frequency factor	A	from regression line	s
Free energy of activation	$\Delta G^{\#}$	Substituent constant	σ
Gas constant	R	Temperature	temp
Ionic strength	I	Transition state	TS
Initial concentration	[lo	Wavelength in nanometers	
Isokinetic temperature	β	at maximum absorption	λ_{max}nm
Linear free energy relationship	LFER	Uronic acid	UA
Methanol	MeOH	Zero point energy	ZPE
Molar extinction coefficient	ε		

LIST OF PUBLICATIONS

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   Paper presented at the conference on X I I carbohydrate conference held at the department of Chemistry, University of Lucknow Nov 20-21, 1997

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