

***KINETICS AND MECHANISM OF OXIDATION OF
SOME ORGANIC SUBSTRATES WITH
N-CHLORO-p-TOLUENESULPHONAMIDE***

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

*DOCTOR OF PHILOSOPHY
IN
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BY

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DECLARATION

I hereby declare that the thesis entitled "**KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC SUBSTRATES WITH N-CHLORO-p-TOLUENESULPHONAMIDE**" submitted to the **UNIVERSITY OF MYSORE** for the award of degree of **DOCTOR OF PHILISOPHY** 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.

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CERTIFICATE

This is to certify that the research work of **Shri. H. MANJUNATHASWAMY**, entitled "**KINETICS AND MECHANISM OF OXIDATION OF SOME ORGANIC SUBSTRATES WITH N-CHLORO-p-TOLUENESULPHONAMIDE**" was carried out and completed under my supervision. 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.

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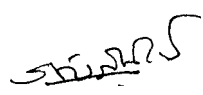
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2. Crystal structure of 1 -(anilino)-1 (-phenyl methylino) pentacarbonyl chromium, (C₁₉H₁₈N₂)(Cr(CO)₅).

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3. Kinetics and mechanism of oxidation of neutral α -aminoacids by sodium N-chloro-p-toluenesulfonamide in Acid medium.

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4. Mechanistic studies of oxidation of 3-dimethylamino-1-propanol by sodium N-chloro-p-toluenesulfonamide in Acid medium.

Asian Journal of Chemistry (Submitted)

5. Ruthenium (III) catalyzed kinetics and mechanism of oxidation of 2-dimethylamino ethanol by sodium N-chloro-p-toluenesulfonamide in HCl medium.

Indian Journal of Chemistry (Submitted)

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PREFACE

The thesis describes the elucidation of reaction mechanism of oxidation of some organic substrates, neutral α -amino acids such as D-glycine, DL-valine, L-alanine and L-phenylalanine, threose series (pentoses and hexoses) D-galactose, L-sorbose, D-xylose and D-lyxose and tertiary amino alcohols 2-dimethyl amino ethanol and 3-dimethylamino-1-propanol by N-metallo-N-arylhalo sulphonamides. N-metallo-N-arylhalo sulphonamides are compounds containing positive halogen which behaves as mild oxidising and halogenating agents. They are finding increasing applications as oxidants, disinfectants and antiseptics. One of the important members of this class of compounds is chloramine-T.

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

Chapter I contains eight sections, Section 1.1 and 1.2 give general introduction to sulphonylhaloamines. Section 1.3. briefly describes some of the salient features of reaction kinetics. Section 1.4 explains the use of isotopes in studying reaction mechanisms. Section 1.5 explains the effect of change in the thermodynamic parameters in reaction rate. Section 1.6 give a brief account on the kinetic investigations with chloramine-T. Section 1.7 explain the scope of the present work. The experimental details are described in section 1.8.

Chapter 2 gives a detailed report on the oxidation of neutral α -amino acids in perchloric acid by CAT. Section 2.1 gives a brief introduction to α -amino acids. Section 2.2 gives a review of oxidation of α -amino acids. Section 2.3 describes the oxidation of **D-glycine**, **DL-valine**, **L-alanine** and **L-phenylalanine** in perchloric acid medium at 303K.

Chapter 3 deals with the kinetics of oxidation of threose series pentoses and hexoses by CAT. Section 3.1 gives a brief introduction to monosaccharides. Section 3.2 gives a review of oxidation of monosaccharides. Section 3.3 explains the results of oxidation of **D-galactose**, **L-sorbose**, **D-xylose** and **D-lyxose** by chloramine-T in presence of **NaOH** at 308 K.

Chapter 4 explains the kinetics of oxidation of tertiary aminoalcohols by CAT in **HCl** medium with **Ru(III)** as catalyst at 313 K. Section 4.1 gives a brief introduction to DMAE and DMAP. Section 4.2 gives a review of oxidation of primary alcohols. Section 4.3. Explains the results of oxidation of **2-dimethyl amino ethanol** and **3-dimethylamino-1-propanol**.

A brief summary of the present investigation is given at the end.

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

LIST OF ABBREVIATIONS USED

CAT	Chloramine-T
DCT	Dichloramine-T
Ts	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$
ZPE	Zero Point Energy
TS	Transition state
RS	Reactant state
β	Isokinetic temperature
I	Ionic strength
PTS	p-toluenesulphonamide
TLC	Thin layer chromatography
DNP	di-nitro phenylhydrazine
DMAP	3 -dimethyl amino- 1 -propanol
DMAE	2-dimethyl amino ethanol
r	Regression Co-efficient
S	Standard deviation of points from regression line.