

MECHANISTIC INVESTIGATIONS OF THE
REACTIONS OF SOME IMPORTANT ORGANIC
SUBSTRATES WITH N-HALOARYL **SULPHONAMIDES**

hæ "N-metallo-N-haloaryl Sulphonamides"

THESIS SUBMITTED TO THE
MYSORE UNIVERSITY
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DEDICATED TO
MY GRAND MOTHER
Smt. DEVAMMA.

DECLARATION

*I hereby declare that the thesis entitled "MECHANISTIC INVESTIGATIONS OF THE REACTIONS OF SOME IMPORTANT ORGANIC SUBSTRATES WITH N-HALOARYL SULPHONAMIDES " submitted to the MYSORE UNIVERSITY 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, Mysore University, Mysore** and that it has not been submitted before for the award of any Degree , Diploma, Associateship or other similar title.*

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CERTIFICATE

The research work by Shri **H. RAMACHANDRA**, Lecturer in Chemistry, P.E.S College of Engineering , Mandya , entitled **“MECHANISTIC INVESTIGATIONS OF THE REACTIONS OF SOME IMPORTANT ORGANIC SUBSTRATES WITH N-HALOARYL SULPHONAMIDES”** was carried out and completed under my guidance. The candidate has completed the research work and is hereby permitted to submit the thesis to the **Mysore University** 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 or any other similar title.



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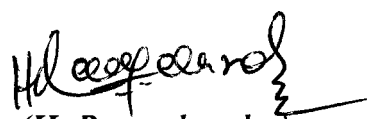
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List of Publications

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Presentations at Conferences / Symposia.

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5. "*Biphasic Hammett rho for the reaction of diphenylmethanols with organic haloamines in presence of ruthenium (III) catalyst : Oxidation mechanism*".

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PREFACE

The thesis describes the elucidation of reaction mechanisms of oxidation of some organic substrates, a heterocyclic compound such as **indole** and substituted **indoles**, an aromatic primary alcohol phenethyl alcohol and substituted phenethyl alcohols and an aromatic secondary alcohol benzhydrol and substituted benzhydrols by N-metallo-N-aryl halo sulphonamides. N-metallo-N-arylhalo sulphonamides are compounds containing positive halogen which behave as mild oxidising and halogenating agents. They are finding increasing application as oxidants, disinfectants and antiseptics. The important members of this class of compounds are chloramine-T (CAT), chloramine-B (CAB), bromamine-T (BAT) and bromamine-B (BAB) and the corresponding dihalo compounds.

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

Chapter 1 contains seven sections. Sections 1.0 and 1.1 give general introduction to the organic haloamines. Section 1.2 briefly describes some of the salient features of reaction kinetics. Section 1.3 explains the use of isotopes in studying reaction mechanisms. Section 1.4 gives a brief introduction to the linear free energy relationships and their interpretation. Section 1.5 indicates the scope of present studies. The experimental details are described in section 1.6.

Chapter 2 gives a detailed report on the kinetics of oxidation of **indoles** by the organic haloamines. Section 2.0 briefly describes a general introduction to the **indoles**. Section 2.1 gives a review of oxidation of **indoles** by other oxidants. Section 2.2 describes the results obtained with the oxidation of **indoles** by CAT, CAB, BAT and BAB in alkaline medium catalysed by OsO_4 at 303K.

Chapter 3 deals with the kinetics of oxidation of phenethyl alcohols by CAT, CAB, BAT and BAB. Section 3.0 gives a general introduction to the phenethyl alcohols. Section 3.1 gives a review of oxidation of phenethyl alcohols by other oxidants. Section 3.2 explains the results of oxidation of the phenethyl alcohols by

the organic haloamines in presence of HCl at 308K . The experimental results are explained on the basis of a suitable mechanism.

Chapter 4 explains the kinetics of oxidation of benzhydrols by CAT , CAB , BAT and BAB in HCl medium with RuCl_3 as catalyst at 308K. Section 4.0 gives a general introduction to the benzhydrols. A review of the oxidation of benzhydrols by other oxidants is given in section 4.1. The results obtained by oxidation of benzhydrols with organic haloamines are explained in section 4.2

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

Appendix 1 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
CAB	-	Chloramine-B
BAT	-	Bromamine-T
BAB	-	Bromamine-B
DCT	-	Dichloramine-T
DCB	-	Dichloramine-B
DBT	-	Dibromamine-T
DBB	-	Dibromamine-B
Ts	-	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-}$
Ph	-	$\text{C}_6\text{H}_5\text{-}$
In	-	Indole
PEA	-	Phenethyl alcohol
BH	-	Benzhydrol
PTS	-	p-toluenesulphonamide
BSA	-	Benzenesulphonamide
MeOH	-	Methanol
ZPE	-	Zero point energy
TS	-	Transition state
RS	-	Reactant state
LFER	-	Linear free energy relationship
TLC	-	Thin layer chromatography
temp	-	Temperature
w.r.t	-	With respect to
ox	-	Oxidant
ρ	-	Reaction constant
σ	-	Substituent constant
β	-	Isokinetic temperature
r	-	Regression coefficient
μ	-	Ionic strength