

MECHANISTIC INVESTIGATIONS OF REACTIONS OF N - METALLO-N-HALOARYL SULPHONAMIDES

THESIS SUBMITTED TO THE UNIVERSITY OF MYSORE

FOR THE AWARD OF DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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SEPTEMBER 1991.

DECLARATION

I hereby declare that this thesis is the result of my own study and was composed independently by me under the supervision of Dr. K.S.Rangappa M.Sc., Ph.D., Lecturer 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

The research work by Mrs. C. K. Mythily, entitled "**Mechanistic Investigations of Reactions of N-Metallo-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 University of Mysore for the award of the Ph.D. degree.

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



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ACKNOWLEDGEMENTS

I am highly grateful to Dr. K.S. Rangappa, M.Sc., Ph.D., Lecturer in Physical chemistry, Department of studies in Chemistry, Manasagangothri, Mysore for suggesting the problem and for guidance and supervision during the research studies. I owe my sincere gratitude to him for his suggestions and encouragement throughout the present investigations.

I am indebted to Dr. D.S. Mahadevappa, M.Sc., Ph.D., (Sask, Canada), F.N.A.Sc., Professor of Physical Chemistry, University of Mysore, for his guidance rendered during my research tenure. I am thankful for his fruitful suggestions and for his valuable guidance during the preparation of my thesis. I also thank the Chairman, Department of studies in Chemistry for providing me the necessary facilities required for my research work.

I express my sincere thanks to Dr. N.M.M. Gowda, Assistant Professor, Western Illinois University, Macomb, U S A for important suggestions.

I wish to thank the Teaching and non-teaching staff and my research colleagues for their suggestions and help extended during my research period.

I owe great depth of gratitude to my parents, brothers, sisters, grand parents, parents-in-law, brothers-in-law and sisters-in-law whose constant encouragement helped me to complete my research work. I am highly thankful to my

husband Mr. Narasimha Rangan for his sacrifice a n d for t h e help extended during my research period.

Finally, I wish to thank "Comptek Compute4 Systems" Mysore, for elegant typing and for the neat out put of my thesis.

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K.S. Rangappa, C.K. Mythily, D.S Mahadevappa and N.M.Made Gowda.
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Polyhedron (in press) 1993

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PREFACE

The thesis describes the elucidation of reaction mechanisms of some organic substrates such as an α, β -unsaturated aromatic aldehyde (cinnamic aldehyde), aliphatic esters, secondary aliphatic alcohols, **indole** and substituted **indoles** by aromatic sulphonyl haloamines. Aromatic sulphonyl haloamines are compounds containing positive halogen which behave as mild oxidising and halogenating agents. They are finding increasing applications as oxidants, disinfectants and antiseptics. The important members of this class of compounds are, chloramine-T, chloramine-B (**CAB**), bromamine-T (**BAT**), bromamine-B (**BAB**) and the corresponding dihalo compounds.

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

Chapter I gives an outline of the preparation and properties of N-metallo-N-aryl halosulphonamides, with special emphasis on CAT, CAB and BAB. It also includes an introduction to the subject of reaction kinetics, a review of the kinetic work carried out with CAT, CAB and BAT and the experimental procedures employed in the present investigation.

Chapter II reports the kinetics and mechanism of oxidation of cinnamic aldehyde by CAT. The first section

reviews the available kinetic data on the oxidation of cinnamic aldehyde. The subsequent four sections include the results and discussion on the oxidation of cinnamic aldehyde by CAT in different media, namely HClO_4 , HCl , H_2SO_4 and NaOH .

Chapter III deals with the studies on kinetics of oxidation of secondary alcohols, **propan-2-ol**, **butan-2-ol**, **pentan-2-ol**, **hexan-2-ol** and **heptan-2-ol** by CAB in presence of HCl at 40°C . It includes two sections. The first section gives the review on the oxidation of secondary alcohols by other oxidants and the other section reports the kinetic results obtained in the present study.

Chapter IV reveals the kinetics of oxidation of some aliphatic esters, methyl, ethyl, propyl, isopropyl and butyl acetates by BAT in HCl medium at 40°C .

Chapter V gives a description of the kinetic study of oxidation of **indole** (In) and substituted **indoles** namely **5-chloroindole**, **5-bromoindole** and **5-methoxyindole** by CAT in NaOH medium catalysed by OsO_4 . It contains four sections. The first section gives a brief introduction to the properties **indole**. The second section describes a review of oxidation of **indole** by other oxidants. The third section deals with results of oxidation of **indole** at low concentrations of hydroxide and **indole** and the fourth section contains the results and describes the discussion of oxidation of **indole** at high concentrations of $[\text{OH}^-]$ and $[\text{In}]$.

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

Appendix I 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	-	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ -
Ph	-	C_6H_5 -
ZPE	-	Zero point energy
TS	-	Transition state
RS	-	Reactant state
LFER	-	Linear free energy relationship
σ^*	-	Polar substitution parameter in Taft treatment
E_s	-	Steric substitution parameter in Taft treatment
ρ^*	-	Polar constant in Taft and Pavelich - Taft equation
δ	-	Steric constant in Taft and Pavelich - Taft equation
β	-	Isokinetic temperature
CA	-	Cinnamic aldehyde
PTS	-	p - toluenesulphonamide
BSA	-	Benzenesulphonamide
MA	-	Methyl acetate
EA	-	Ethyl acetate
PA	-	Propyl acetate
IPA	-	Isopropyl acetate
BA	-	Butyl acetate
In	-	Indole
r	-	Regression coefficient
s	-	Standard deviation of the points from regression line.