

KINETIC AND ANALYTICAL **INVESTIGATIONS** WITH ORGANIC HALOAMINES

THESIS SUBMITTED TO THE UNIVERSITY OF MYSORE
FOR THE AWARD OF DEGREE OF
D O C T O R O F P H I L O S O P H Y

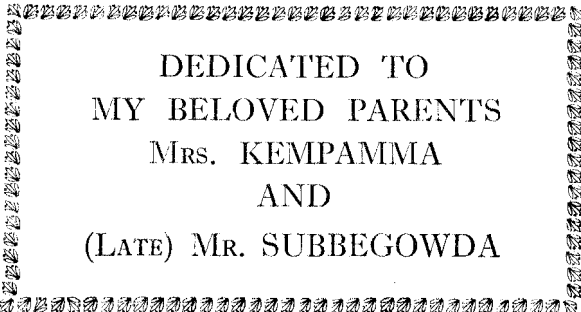
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APRIL 1982



DEDICATED TO
MY BELOVED PARENTS
Mrs. KEMPAMMA
AND
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DECLARATION

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I hereby declare that this thesis is the result of my own study and was composed independently by me, under the guidance of Dr. D.S. Mahadevappa, M.Sc., Ph.D. (Sask, Canada), Professor of Physical Chemistry, Department of Post-graduate Studies and Research 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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C E R T I F I C A T E

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The research work by Shri K.S. Rangappa entitled "KINETIC AND ANALYTICAL INVESTIGATIONS WITH ORGANIC HALOAMINES" 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 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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1. Kinetic and mechanistic studies on the oxidation of arginine and histidine by chloramine-T in hydrochloric acid medium.
Reaction Kinetics & Catalysis Letters (Hungary), 15, 13-19 (1980).
2. Sodium N-chlorobenzenesulphonamide (Chloramine-B) as an Analytical Reagent: Estimation of thiosemicarbazide alone and in its metal complexes
Indian Journal of Chemistry, 20, 102-104 (1981).
3. Kinetic and Mechanistic Studies of Oxidation of Arginine and Histidine by Sodium N-chloro-4-methyl benzene sulphonamide (Chloramine-T) in hydrochloric acid medium.
Indian Journal of Chemistry 20A, 263-268 (1981).
4. Some Analytical application of Aromatic Sulfonyl Haloamines: Estimation of indigocarmine by chloramine-B, Bromamine-T and Dibromamine-T.
Microchemical Journal (U.S.A.), 26, 132-140 (1981).
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5. Some Analytical Applications of Aromatic Sulfonyl Haloamines: Determination of Thiocyanate and Cyanide ions in Metal Complexes and Salts and Thiosemicarbazide in Metal Complexes with Bromamine-T.
Microchemical Journal (U.S.A.), 26, 375-386 (1981).
6. Kinetics and Mechanism of Oxidation of L-threonine in acid media by Sodium N-chloro-p-toluene sulfonamide.
Journal of Physical Chemistry (U.S.A.), 85, 3651-3658 (1981).

7. Some Analytical Applications of Aromatic Sulfonyl Haloamines: Determination of Thiocyanate and Cyanide ions in Metal Complexes and Salts with Bromamine-B and Dichloramine-B.

Microchemical Journal (U.S.A.), (in press). 27, 77-86 (1982)

8. Some Analytical Applications of Aromatic Sulfonyl Haloamines: Determination of Thiosemicarbazide alone and in its Metal Complexes with Bromamine-B and Dichloramine-B.

Microchemical Journal (U.S.A.), (~~in press~~). 27, 254-264 (1982)

9. N,N-Dibromobenzene-sulfonamide as an analytical reagent: Determination of Thiocyanate and Cyanide ions in Metal Complexes and Salts and Thiosemicarbazide alone and in its Metal Complexes with Dibromamine-B.

Microchemical Journal (U.S.A.), (in press).

10. Oxidimetric Determination of Methionine and its Complexes with Chloramine-B and Dichloramine-B.

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(Also presented at the 69th Session of the Indian Science Congress Association held at Mysore, Jan 3-8, 1982).

11. Kinetic and Mechanistic studies of Oxidation of Arginine, Histidine and Threonine in alkaline Medium by Chloramine-T.

International Journal of Chemical Kinetics (U.S.A.), (in press).

12. Kinetic and Mechanistic Studies of Oxidation of Arginine and Histidine by Chloramine-T in Perchloric and Sulfuric acid Media.

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P R E F A C E

Organic haloamines are compounds containing positive halogen and the chemistry of aromatic sulphonyl haloamines has received considerable attention. The latter have diverse properties and behave as oxidants and halogenating agents. They have been extensively employed as oxidimetric reagents in kinetic studies and in the determination of a variety of reductants in solution. The prominent member of this class of compounds is chloramine-T, ($p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NClNa} \cdot 3 \text{H}_2\text{O}$, abbreviated as CAT). The present investigations centre around the kinetics and mechanism of oxidation of three amino acids, arginine, histidine and threonine by CAT in presence of mineral acids and NaOH. Analytical applications of other sulphonyl haloamines such as bromamine-T ($p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NBrNa} \cdot 1.5 \text{H}_2\text{O}$; BAT), dibromamine-T ($p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{NBr}_2$; DBT), chloramine-B ($\text{C}_6\text{H}_5\text{-SO}_2\text{NClNa} \cdot 1.5 \text{H}_2\text{O}$; CAB), bromamine-B ($\text{C}_6\text{H}_5\text{-SO}_2\text{NBrNa} \cdot 1.5 \text{H}_2\text{O}$; BAB), dichloramine-B ($\text{C}_6\text{H}_5\text{-SO}_2\text{NCl}_2$; DCB) and dibromamine-B ($\text{C}_6\text{H}_5\text{-SO}_2\text{NBr}_2$; DBB), in the estimation of thiosemicarbazide, cyanide ion, thiocyanate ion and their metal complexes, methionine and its metal complexes and indigocarmine are also described.

The thesis has been divided into six chapters, and each chapter contains several sections.

Chapter I gives an introduction to the chemistry of chloramine-T. Section 1 describes the general characteristics of this haloamine while Section I-(2) discusses the elements of

reaction kinetics. Mechanistic interpretations of oxidation of diverse substrates with CAT forms the subject matter of Section I-(3). A review of literature on the oxidation of amino acids by different oxidants is presented in Section I-(4), while the scope of the present work is indicated in Section I-(5). Section I-(6) describes the experimental method adopted for studying the oxidation kinetics of arginine, histidine and threonine by CAT.

Chapter II deals with the kinetics of oxidation of arginine by CAT and is divided into three sections. The first two sections describe the oxidation of amino acid in presence of HCl, HClO₄ and H₂SO₄. Suitable mechanistic interpretations for the results are given. Section II-(3) reports the results of oxidation of arginine in presence of sodiumhydroxide. A OH⁻ ion dependent path and a path independent of OH⁻ ion are noted.

A detailed kinetic investigation of the oxidation of histidine by CAT is given in Chapter III, which is divided into four sections. Detailed mechanistic pathways for the oxidation of the amino acid in presence of HCl, HClO₄, H₂SO₄ and NaOH are presented in these Sections.

Chapter IV reports the kinetics of oxidation of another amino acid, L-threonine and the results in HCl, HClO₄, H₂SO₄ and NaOH media are presented in two sections. Oxidation of threonine by CAT in acid media follow more or less identical kinetics, while the rate of reaction is independent of [OH⁻].

Some analytical applications of organic haloamines are

presented in Chapter VI, with an introduction to the subject in Chapter V. Oxidation of methionine and its metal complexes with CAB and DCB forms the subject matter of Section VI-(1). The amino acid could be estimated by these reagents in (1) a direct titration with potentiometric and visual end-points and (2) a back titration procedure, involving excess oxidant.

Indigocarmine, thiosemicarbazide and its metal complexes, thiocyanate and cyanide ions in salts and metal complexes are estimated using organic chloramines and bromamines employing back titration procedures. These results are described in Sections VI-(2) to VI-(5).

C O N T E N T S

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