

KINETICS AND MECHANISMS OF SOME
OXIDATION REACTIONS

By

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DEDICATED

TO THE MEMORY OF MY BELOVED FATHER

C E R T I F I C A T E

This is to certify that the thesis entitled 'Kinetics and Mechanisms of Some Oxidation Reactions' being submitted by Md.Amjad Hossain to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr.M.A.Hossain has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T S

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A B S T R A C T

The thesis describes in detail the kinetic and mechanistic studies involving the oxidation of some amino poly carboxylic acids and aminoalcohols with aqueous cobalt(III) perchlorate in perchloric acid-sodium perchlorate media at two different ionic strengths viz. 5.0 M and 7.0 M at acidity series 1.0 M to 5.0 M and 5.0 M to 7.0 M respectively. The substrates investigated are glycine, iminodiacetic acid, nitrilotriacetic acid, ethylenediamine tetraacetic acid, N-2-(hydroxyethyl)-ethylene diamine-N,N',N'-triacetic acid, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propane diol and 2-amino-2-hydroxymethyl-1,3-propane diol.

Kinetics were followed by studying the decrease in optical density of Co(III) at 270 nm. The cobalt(III) concentrations were determined indirectly at 260 nm or directly at 250 nm. Stoichiometries were determined for all the reactions spectrophotometrically. The products of oxidation were identified by thin layer chromatography, paper chromatography, paper electrophoresis and qualitative tests.

Mechanisms of the reactions have been found to vary at the two acidity series. In the acidity series 1.0 M to 5.0 M, the rate equation takes the form

$$k_o = a + b [H^+]^{-1}$$

and at the acidity series 5.0 M to 7.0 M it assumes the form

$$k_o = a + b [H^+]$$

where a and b are constants, k_o the observed rate constant and $[H^+]$ the molar acidity. Michaelis-Menten kinetics have been found to be operative in all these studies.

Thermodynamic parameters have been determined for the reactions according to the mechanisms proposed and these have been discussed in the light of the stabilities of the complexes and cobalt(III) species involved. The results of these studies have been compared with the findings of other investigators for similar compounds involving Co(III) ion mainly.

The thermodynamic parameters have been found to show linear relationship between enthalpies and entropies of activation for all the cases. This phenomenon has been attributed to the structurally related series of compounds and solvent effects.

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