MECHANISMS OF OXIDATION OF ORGANIC COMPOUNDS BY METAL IONS

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TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled "Mechanisms of Oxidation of Organic Compounds by Metal Ions" being submitted by Mrs. Mary Joseph to the Indian Institute of Technology, Delhi for the award of the Degree of Doctor of Philosophy in Chemistry is a record of bona fide research work carried out by her. Mrs. Mary Joseph 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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ABSTRACT

The thesis describes in detail the kinetic and mechanistic studies on the oxidation of some aminocarboxylic acids and aminoalcohols with aqueous manganese(III) perchlorate in perchloric acid-sodium perchlorate media in the acidity range of 3.0 M to 6.0 M. The substrates investigated are glycine, threonine, iminodiacetic acid, 2-amino-2-methyl-1,3-propanediol and 2-amino-2-hydroxymethyl-1,3-propanediol. The oxidation of threonine by cobalt(III) perchlorate has also been studied at two different ionic strengths of 5.0 M and 7.0 M in the acidity ranges of 1.0 M to 5.0 M and 5.0 M to 7.0 M respectively.

Kinetics were followed by studying the decrease in optical density of [Mn(III)] or [Co(III)] at 270 nm. The concentration of Mn(III) or Co(III) was determined indirectly at 260 nm. Stoichiometries were determined spectrophotometrically. The products of oxidation were identified by paper chromatography, thin layer chromatography and qualitative tests.

Mechanisms of the reactions have been found to vary with substrates. The rate equation generally takes the form

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

where a and b are constants, k_o the observed rate constant and $[H^+]$ the molar acidity. In the case of certain

substrates, the observed rate constant has been found to depend on the inverse square of the hydrogen ion concentration. For the cobalt(III) oxidation of threonine, the rate equation takes the above form in the acidity range of 1.0 M to 5.0 M while in the acidity range of 5.0 M to 7.0 M it assumes the form

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

In most of these studies, there was no spectroscopic or kinetic evidence for complex formation. Michaelis-Menten kinetics were found to be operative only in the case of 2-amino-2-hydroxymethyl-propane-1,3-diol.

Thermodynamic parameters have been determined for the reactions according to the mechanisms proposed. The results of these studies have been compared with the findings of other investigators for similar compounds involving mainly Co(III) and Mn(III) ions.

A linear relationship has been found to exist 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.

The second part of the thesis deals with the oxidation of alcohols using anodically prepared cobaltic sulphate. The oxidations have been carried out at different acidities to determine the optimum conditions of oxidation.

The products of oxidation have been identified and the yields of carbonyl compound obtained have been reported. Some oxidation studies involving peroxo complexes of thorium and zirconium, in the presence and absence of picolinic acid have been included and the yields for these oxidation studies have been reported.

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