ABSTRACT

Investigation of the nature and mechanism of oxidation of amino acids by different oxidising agents continue to be an interesting field of research for the last decade. The oxidation of amino acids is important, not only from the point of view of product formation, but because they represent the sources of much of the free energy utilised in biological processes. The knowledge of the mechanism of oxidation is fundamental to an understanding of amino acid metabolism. Biochemical reactions taking place in various physiological processes of human body are estimated to have resemblance with the simple chemical reactions. This feature may provide an opening scope in controlling the products and the reaction step by a suitable manipulation of the experimental technique.

Despite the biological significance of catalytic functions of Fe(II) and its formation of complex during amino acid metabolism, diverse and scanty observations have been reported in the literature on oxidations of amino acid by hydrogen peroxide catalysed by Fe(II). The present investigation describes the kinetic methods in greater detail.
with a view to show how the experimental results can be utilised to formulate the mechanism.

Accordingly, the present thesis deals with "Kinetics of oxidation of some organic compounds by hydrogen peroxide" and is divided into eight chapters.

Chapter I of the thesis is introductory in nature and gives a brief account of the development of hydrogen peroxide as an oxidant and the importance of ferrous sulphate as a catalyst. It also outlines in detail the existing literature on the oxidation of amino acids. The object of the work done is also reported.

Chapters II, III, IV, V and VI describe the experimental studies in the oxidation of glycine, \( \beta \)-alanine, serine, aspartic acid, glutamic acid and arginine by hydrogen peroxide in the presence of ferrous sulphate as a catalyst in acid medium. The effects concentration of oxidant, substrate, catalyst and neutral salt are reported with each of the six amino acids separately in these chapters. The various activation parameters namely energy of activation \( E \), enthalpy of activation \( \Delta H^\pm \), free energy of activation \( \Delta S^\mp \) for the reactions have also been evaluated. The reaction series is found to follow the isokinetic phenomenon. This suggests that the reactions are entropy controlled. This also indicates a
similar type of mechanism operative in the oxidation of all the amino acid.

The reactions are studied in 0.04M perchloric acid which has been kept constant throughout the investigation. An explanation has been offered on the basis of the facts available in literature. It is found that the rate of oxidation increased with decrease in the $pK_a$ values or increase in the dissociation of amino acids. The order of the rates of oxidation is glutamic acid > serine > glycine > $\beta$-alanine > aspartic acid. A broad conclusion is that with the presence of electron withdrawing groups at $\alpha$-carbon such as $-\text{CH}_2\text{OH}$ increases the rate whereas electron releasing group such as $-\text{CH}_3$ decreases the rate. The order of the relative reactivities of the amino acids is supported by the views of Pokrovskaya.

The data interpreted in the Chapter VIII deals with detailed discussion of the results obtained. The conclusions drawn on the basis of this study may be summarised as follows:

(i) The rates of oxidation of various amino acids studied have been found to depend linearly on substrates and initial concentration of the catalyst, whereas they are independent of hydrogen peroxide concentration.

(ii) Ionic strength of the medium has no effect on the rate of reactions.
(iii) The products of oxidation were characterised as the corresponding aldehydes, carbon dioxide and ammonia.

(iv) The stoichiometry was found to be 1:1 (oxidant : substrate).

(v) Arrhenius law is obeyed and a large negative value of entropy of activation is observed for each reaction.

(vi) The reaction series follows isokinetic phenomena suggesting that the reactions are entropy controlled.

These facts together with similar nature of these reactions lead to the conclusion that these reactions follow a common general mechanism. The rate law comes out to be

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- \frac{d[H_2O_2]}{dt} = k [Fe^{+2}] [amino acid]
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which substantiates the rate data obtained. The product analysis, observed stoichiometry and induced polymerisation of acrylonitrile supports the chain mechanism proposed. Further, the fact that the rate of reaction is independent of the ionic strength of the medium is also accounted for.

The present work has therefore contributed in confirming the free radical mechanism of the oxidation of amino acids studied.