Study of Kinetic Stability and Oxidation of Some Amino Acids in Acidic Oxidant

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***Abstract*—Amino acid being a versatile chemical entity its oxidation is very important from a chemical point of view and it has more impact on the mechanism of metabolism by amino acid. Various kinetic investigations on the oxidation of amino acids have been carried out under various oxidants and varying experimental conditions. This paper focuses on the kinetic and mechanistic approach of the oxidation of various amino acids. The future scope of this study has also been stated at the end of this paper.**

Keywords— Oxidation of amino acids, Kinetic study, Oxidants, Amino acid metabolism.

I. INTRODUCTION

Amino acids are the complex molecules which contains both amine and carboxylic acid groups. Amino acids served as the building block of body as they are the main constituent of the protein. Protein needed by human body for growth and well development of body. Proteins on hydrolysis give the mixture of amino acids which acts as chemical messengers for communication between cells. When the diet of high content of proteins is consumed then there is increase in the volume of urine which is the indication of oxidation of amino acid as the body is unable to store excess of proteins. The two groups of research scholar have been studied that the oxidation of amino acid is facilitated and amino group is excreted to the liver [1, 2].Excess of amino acids converted into many useable products through deamination which converts nitrogen of amino acids into ammonia and liver converts it into urea in the excretory cycle. With the view of this, oxidation of amino acids is very important as per the chemical point is concern. Various kinetic investigations have been performed on the oxidation of amino acids by various oxidants under different experimental conditions [3, 4]. However, the mechanism is different in different reaction system. These oxidation reaction evidences the profound mechanism of decarboxylation and oxidative deamination [5].Most of the amino acid contains the alkyl groups, but only the amino and carboxyl functional groups brought about the changes that made them useful in many of the chemical transformations and thus hydrocarbon moiety remains intact during these chemical changes. There are many different types of chemical reactions and wide variety of techniques may be employed to investigate the mechanism of oxidation of amino acids. Considerable amount of efforts have been performed to study the kinetics and reaction mechanism in solution phase. In many ways the investigations provides the most satisfactory way of testing of basic theories of reactions. The maximum attention of the chemists and researchers has been gained by the reactions in liquid phase as these reactions are more feasible and produce excellent result [6]. Oxidation of amino acids in solid phase needs more attention as limited amount of work has been done in this era [7].

II. RESULTS AND DISCUSSION

The major kinetic investigations are concerned with the reactions whose rates can be measured without the use of instrumental methods [8]. During recent years, due to development of new electronic techniques, a sound deal of efforts has been devoted to study the reactions that are very difficult to study by conventional methods. In general there are two kinds of problems that arise in any kinetic investigations, first is the establishment of the relationship between the velocity and various factors such as concentration, solvent , catalyst , ionic strength ,temperature etc. and the second is to arrive at interpretations of the empirical laws in terms of reaction mechanisms. There are two key factors that decide the productivity of the reaction, Thermodynamics which explains the extent of reaction whereas the kinetic provides the information about the mechanism of the reaction.

Radhey S. Verma and co-workers [9] studied the rate of oxidation of various amino acids in aqueous sulphuric acid and perchloric acid solutions .It has been observed that the order of the reaction is two for a given concentration of listed acids. Various hypotheses for the mechanism of acid catalysis have been studied and found that Brunett's hypothesis worked excellent. The remarkable observation was that the amino acids with an even number of atoms in carbon chain are more easily oxidized in acidic media than those with odd number of atoms in carbon chain, which was in good agreement with the view of Pokrovskaya. S.K.Joshi et al.[10] have been examined the kinetics of oxidation of amino acids such as Glycine, Alanine and Valine by Manganese (III) acetate in aqueous sulphuric acid medium. The rate law equation have been derived which shown that the reaction was first order in substrate, second order in Mn(III) and inverse first order in sulphuric acid. The inverse dependence on the concentration of sulphuric acid might be resulted from formation of protonated species of the substrate which is non-reactive in oxidation process.

Rao et al.[11] has investigated the kinetics of oxidation of glycine , alanine, serine, threonine ,aspartic acid, glutamic acid by permanganate in the presence and absence of silver

ion. The order of the reaction was found to be one with respect to substrate and oxidant. The silver ion was responsible for catalyzing these reactions. B.Thimme Gowda and Mahesh Shetty[12] had employed twelve sodium salts of N-Chloroarylsulphonamide as oxidants for investigating the mechanism of two amino acids i.e. aspartic acid and glutamic acid. The reaction was found to follow second order kinetics in oxidant, fractional order in amino acid and shown the inverse dependence of concentration of hydrogen ions. In these entire Cl^+ ion was an effective oxidizing species. From the study it has been observed that introduction of electron-withdrawing group enhance the ease of Cl^+ions which further increases the oxidizing strength of the employed substrates.

Shanu Mathur et al.[13] has studied the kinetics of oxidation of Lysine with Chromium(VI) in perchloric acid medium. The order of reaction with respect to lysine was less than one and for chromium (VI) it was found to be one. It was also observed that increase in concentration of acid accelerates the rate of reaction. The final oxidation Products were identified as chromium (III) and 5-aminopentaldehyde. Dhan Raj , Manju Bala Yadav &Vijay Devra [14] studied the oxidation of serine by cerium(IV) in presence of Mn(III) as a catalyst. From the study it has been observed that formerly rate of reaction was slow in acidic media but when catalyst was introduced the reaction rate increased significantly. $Ce(SO_4)_2$ was found to be a reactive species. S.Parimala Vaijayanthi & N.Mathiyalagan[15] has carried out the oxidation of various amino acids by novel oxidant N-chloropyrazinamide (NCPZA) in acetic acid medium in presence of hydrochloric acid. The study revealed that the reaction was first order in novel oxidant and H+ and Cl-. The order with respect to amino acid was zero. One significant observation was noted that on addition of novel oxidant the rate of reaction retarded.

T. Sumathi et al.[16] have been investigated kinetic and mechanistic study of oxidation of L-methionine and N-acetyl L-methionine by Cerium (IV) in sulfuric acid medium. The sulfoxide forms of the substrate were found to be major oxidation products. Increase in concentration of acidic medium did not have any effect on the reaction rate. Under inert atmospheric condition polymerization process initiated which shown the generation of the free radicals. C.S.Chidan Kumar[8] and other investigated the kinetics of Mn(III)-Ala reactions in acid solutions. The stoichiometry in the reaction was found to be 2:1. It has been also investigated that the reaction was proceeds through the formation of transition state and the state was rigid and reaction was entropy controlled. K. Vivekanandam &R.Lakshmi Narayanan[17] has worked on the oxidative decarboxylation and deamination of essential amino acids by Nicotinium Dichromate (NDC) in perchloric acid medium. The reaction was found to be temperature dependent and follow pseudo-first order kinetics. B. L.Hiran and others [6] has found that the final oxidation product was aldehyde when oxidation of phenylalanine was carried out by PCC in DMF-water mixture in the presence of perchloric acid . The reaction was found to be first order in all respect and also it followed the Michelis-Menten mechanism. M.Sundar et al[18]. has studied the oxidation of lysine by oxone in a buffered medium concluded the non-existence of autocatalysis. Due to this further formation of Schiff base was discarded.

III. CONCLUSION

All the discussions made above emphasize the thermodynamic as well as catalytic dependency of oxidations of amino acids**.** From the literature survey it can be concluded that researcher can focus on the kinetic study of mixture of essential and non-essential amino acids, Research can be carried out in future with the view of following aspects:

a) A conclusive evidence for reaction pathway

b) Deciding the plausible mechanism of reaction

c) Verifying the order of reaction

d) Deciding various thermodynamic parameters such as activation energy, Gibb's free energy, effect of ionic strength, effect of change in temperature etc.

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