Volume: 2017 Issue: onference Month of publication: September 15, 2017

DOI:

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor:6.887
Volume 5 Issue IX, September 2017- Available at www.ijraset.com

Kinetic Study of Oxidation of Certain Amino-Acids by $KMno_4$ in Moderately Concentrated Acidic Media: A Review

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Abstract: In the study of kinetics of oxidation of glycine, alanine, phenylalanine, serine threonine, aspartic, glutamic acid and valine and by acid permanganate it was observed that, the mechanism of the reactions was elucidated. The reactions were found to be acid catalyzed, and the kinetic data indicate the participation of the water molecules in the rate-determining step as a proton-abstracting agent from the substrate, as per Bennett's hypothesis. It has been observed in another paper that, Twelve sodium salts of N-chloroarylsulphonamides were employed as oxidants for studying the kinetics of oxidation of two acidic amino acids (aspartic and glutamic acid) and their monoamides (aspargine and glutamine)in aqueous acidic medium under various conditions, to see how the oxidative strength of these reagents vary with substitution. After reviewing another paper, study ofthe Kinetics of Oxidation of amino acids glycine, alanine and valine by manganese (III) acetate in aqueous sulphuric acid, it is found that, the formation of intermediate complex. This shows an inverse dependence on $[H_2SO_4]$***. The reaction has second order dependence with respect to Mn (III) and first order dependence with respect to substrate. The mechanism consistent with rate data has been proposed.***

It is also observed that, the rate of oxidation of glycine, DL-alanine, DL-valine, and DL-leucine by potassium permanganate in aqueoussulphuric and perchloric acid solution is proportional to the concentration of the amino-acid. For each amino-acid, the total order of the reaction is two at a given concentration of sulphuric and perchloric acid. The rate of oxidation of the amino-acids is greater in sulphuric than in perchloric acid for the same concentration. It is learnt that, various hypotheses for the mechanism of acid catalysis have been tested and it has been found that the rate is related to the activity of water in accord with Bunnett's hypothesis

Key Words: Kinetics of Oxidation, amino acids, first order reaction, ionic strength,

I. INTRODUCTION

In view of this, many literature surveys has been done for systematic kinetics study of the oxidation of glycine, alanine, valine and leucine by $KMnO_4$ in acidic medium to get an insight in to the mechanism. This is by no means of an exhaustive review, nor can it be taken as a definitive guide, as the nature of the described. It is, however, hoped that the information provided will permit educated choices of systems to use, and potentially limit the inappropriate use and interpretation of data obtained from these techniques. In this paper many investigations for kinetics & mechanism of oxidation of non essential were studied. The purpose of this review is to study the literature and to understand further scope of investigation of kinetics &mechanism of oxidation of some essential, non essential& mixed amino acids.

II. DISCUSSION

V. Surender Rao et al studied the kinetics of oxidation of some amino acids by $KMnO_4$ in a moderately concentrated H_2SO_4 medium in the presence and absence of Ag$^+$[1],the expected oxidizing species in of permanganate oxidation in acid solutions wereMn(III), Mn(IV), and Mn(VII) .If Mn(III) or Mn(IV) were to be the reactive species, the addition of complexing agents like fluoride, sulfate, and pyrophosphate ions should have decreased the rate. It is revealed that, there is no effect of these ions on the rate and the absence of an induction period show that only Mn(VII) is the most probable reactive species. The increase in the rate, with an increase in $[H^+]$, could be due to theprotonation of the oxidant resulting in the formation of a more powerful oxidant, namely, HMnO4, according to the following equilibrium:

$$H^+ + MnO_4^- \rightleftharpoons HMnO_4$$

The addition of an Ag^+ ion to the reaction system increased the rates, and in the presence of Ag^+, the order in [amino acid] changed from unity to fractional, indicating that it might be involved in complexation either with Mn(VII) or with Ag+. Plots of log $k_0$versus log [H_2SO_4] and log $k_0$versus - H_0were found to be linear, indicating that the reactions are acid catalyzed, but none of the above plots gave an ideal slope of unity. In view of the departure from the ideal behavior, the applicability of Bennett’s hypothesis was tested. According to Bennett’s observations, if the slope of such a plot is greater than -2, it indicates the involvement of a water molecule in the rate-determining step as a proton-abstracting agent from the substrate. As Ag+ was found to catalyze these reactions, the oxidation of glycine and glutamic acid was carried out in the presence of Ag+. In the presence of Ag+, the order in [$KMnO_4$] was 1 and that in [amino acid] and [Ag+] was fractional. Two probable mechanisms, one involving a two-electron transfer process and the other a one-electron transfer mechanism, found discussed.
S .K .Joshi and colleagues studied the Oxidation of amino acids by manganese (III)[2, 3, 4] in suphuric acid [5], the results of the study werefound summarized as below:

A. The reactions have second order dependence with respect to manganese (III)because the time versus [manganese (III)] plots is linear in nature. The value of linearity always found greater than 0.95.
B. The order with respect to the substrate concentration is always first as confirmed by a linear plot between [substrate] versus k_{obs}values, which passed through origin.
C. The reaction rate is retarded by H_2SO_4. The reaction shows an inverse dependence on[H_2SO_4] and the plot of 1/[H_2SO_4] versus $k_{obs}$is linear which didn’t pass through the origin.This highlights the point that it is the unprotonated species, which takes part into the reaction.
D. The concentration of Mn (II) in the reaction mixture is 0.1 mol dm^{-3}. Below this concentration the variation of Mn (III) has no effect on reaction rate. In the study the Mn (II) promotes the stability of Mn (III) in the solution through the established equilibrium.
E. The absence of polymerization in the reaction mixture in presence of acrylonitrile indicatesthe absence of free radical formation in the oxidation process. It reveals that the reactiontakes place through the formation of intermediate complex.

Radhey S Verma et al studied the ‘Kinetic of Homogeneous Acid Catalysed Oxidation of certain Amino Acids by $KMnO_4$ in Moderately conc. Acidic Medium [6]’.Crystalline glycine, DL-alanine, DL-valine, and DL-leucine were used. Potassium permanganate, sulphuricacid,etc were used. Stock solutions of sulphuric and perchloric acid were standardized against previously standardized sodium hydroxide solution. Solutions of the substrate,sulphuric or perchloric acid, and of salt were mixed and the mixture broughtto constant temperature. An appropriate volume of potassium permanganate solution, previously thermos tatted, was then mixed rapidly with the solution. Zero time was taken when half the permanganate solution had been added. The kinetics was measured using a Lange colorimeter; model J, at 525 nm. Portions (2 ml) of there action mixture were withdrawn at known intervals and the reaction was quenched by adding it to a known excess of ice-cold distilled water (2') in the optical cell. The absorbance due to unchanged permanganate was read directly from the colorimeter. The absorbance at 525nm of products in reactions which were 99%complete was negligible. It was seen that at constant concentrations of sulphuric or perchloric acid and substrate, the order of reaction with respect to permanganate is one.Plots of rate constants against amino-acid concentrations gave straight lines passing through the origin for both sulphuric and perchloric acid, thus showing thatthe order of reaction with respect to substrate is one inboth the acidic media. It has also been revealed that, there were no kinetic evidence for intermediate complex formation between substrate and permanganate
B. Thimme Gowda and Mahesh Shetty studied the ‘Kinetics of Oxidation Acidic Amino Acid and their Monoamide by N-ChloroarylSulphonamides in Aqueous Acid Medium[7]’’ .The study indicated thatSodium salts of N-chlorobenzenesulphonamide and its substituted compounds (NCSBS)[8,9] were fairly strong electrolytes in aqueous solution and they furnished different reactive species depending on the pH of the medium. The second-order kinetics in [NCSBS], fractional order in [AA] and higher inverse order dependence of the rate on [H^+] and other effects for the oxidation of Asp, Glu, Asn and Gln[10] by all the N-chloroarylsulphonamides may be explained by a two-pathway mechanism which was also supported by the fact that the direct plots of rate constants versus [AA] gave better correlations than the double
reciprocal plots The applicability of the Hammett equation was tested for the oxidation of all four amino acids by all of the values. Further, the enthalpies and entropies of activations for the oxidations of all the four amino acids by all the N-chloroarylsulphonamides were correlated.it is found that, pure samples of amino acids (aspartic acid, glutamicacid, aspargine and glutamine) were employed [11].They were further assayed by the acetic acid–perchloric acid method.Aqueous stock solutions of

these compounds (0.10 mol dm^{-3}) are found used. The ionic strength of the medium was found maintained at0.30 mol dm^{-3} using a concentrated aqueous solution of sodium nitrate.

It's noted that, DNP was filtered off, dried andrecrystallized from ethanol. The product was found tobe identical (melting-point) with an authentic sample of the DNP of formylacetic acid. In similar experiments with other amino acids, the corresponding carbonyl compounds were identified as their DNPs of carbonyl compounds.

III. CONCLUSION

The above discussions indicates that Under the conditions of [amino acid] >> [$KMnO_4$] in particular concentration of H_2SO_4, plots of log (absorbance) versus time were linear, showing that the reaction is first order in [$KMnO_4$]. This was also confirmed by varying [[$KMnO_4$], which did not show any change in the pseudo-first-order rate constants k**.** The reactions also exhibited a first-order dependence in [amino acid] However, in the presence of Ag+ the order of [$KMnO_4$] was 1 and that of [amino acid] and Ag+] was fractional [1] , The decrease in reaction rate of amino acids with increase in sulphuric acid concentration may attribute to the formation of protonated species of the substrate which is non reactive in oxidation process[12]. The rates of oxidation of amino-acids in moderately concentrated sulphuric and perchloric acid by potassium permanganate are in the order DL-leucine> glycine > DL-valine> DL-alanine. It has also been observed that amino-acids with an even number of atoms in the carbon chain are more easily oxidized in acidic media than those with an odd number of atoms [13].This makes an important to study the kinetics of the reactions in the absence of Ag^+ and also their effects on various parameters such as ionic strength, P^H etc**.** This also emphasize to study the reaction rates and kinetics of various amino acids in different acidic medium having various concentrations.

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