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Kinetics and Mechanism of Oxidation of Acidulated Amino Acids by Various Oxidizing Agents: A Review

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Abstract: ***The kinetics of oxidation of some non essential amino acids by $KMnO_4$ in acidulated medium was investigated to elucidate the mechanism of the reactions. An attempt to correlate the rate of oxidation with acid concentration, various hypotheses for mechanism of acid catalysis was tested. The Bunnetts hypothesis is useful in elucidating the mechanism of reaction and chemical role of water in rate controlling step. The oxidations of Non essential amino acids like Glycine, Alanine, Aspartic acid, Glutamic acid, Serine and Cysteine by acidified permanganate are first order with respect to amino acid concentration. The plot of inverse of rate constant versus inverse of nonessential amino acid concentration is straight line with intercept on y-axis indicating that there is an intermediate complex formation between Nonessential amino acids and permanganate.***

Key Words: Kinetics, Oxidation, non essential amino acids, first order reaction

I. INTRODUCTION

Though the $KMnO_4$ is extensively used as an oxidizing agent, the kinetics of oxidation of organic compounds in moderately concentrated acid solutions has received small attention. It has been reported by Verma and et al that[1], the oxidation of glycine, alanine, valine and leucine by $KMnO_4$ in acidicmedium, proceeds by free radical mechanism. Further literature survey reveals that the kinetics and mechanism of oxidation of some amino acid by various oxidising agents such as chromium peroxy-dichromate [23] Cerium (IV) [24], Bromanine [25], Alkaline mercuric iodide[26], sodiuin-N-bromobenzene[27], copper (II) [28], potassium bromate[29], Thallic perchlorate[30] Vanadium (V) [31] etc. were investigated in acidic and alkaline medium. An attempt to correlate the rate of oxidation with acid concentration, various hypotheses for mechanism of acid catalysis was tested. The Bunnetts hypothesis is useful in elucidating the mechanism of reaction and chemical role of water in rate controlling step. 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 permiteducated 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

The paper published on "Kinetics of Oxidation of some Essential Amino Acids by N-Chlorosaccharin in Aqueous Acetic Acid medium" was studied. In this paper it has been observed that, the kinetics of oxidation of some essential amino acid namely, valine, leucine and phenylalanine by N-Chlorosaccharin in Aqueous Acetic Acid medium in the presence of perchloric acid have been investigated. The observed rate of oxidation is the first order in [AA], N-Chlorosaccharin (NCSA) and of increase fractional order in $[H^+]$. The main product of oxidation was the corresponding aldehyde. The ionic strength on the reaction rate has no significant effect. The effect of changing the dielectric constant of the medium on the rate indicates the reaction to be of dipole-dipole type. Hypochlorous acid has been postulated as the reactive oxidizing species. The reaction constant involved in the mechanism was derived. The activation parameters were computed with respect to slow step of the mechanism.[1]

The paper "Kinetics and mechanism of oxidation of L-Cysteine by Hexacyanoferrate (III) in alkaline medium". The following observations were observed that, the oxidation of L-Cysteine was done in alkaline medium at 30 ^{0}C. The reaction was followed spectrophotometrically at λ_{max} = 420nm. The reaction was found to be first order dependence each on [HCF(III)] and [Cysteine]. It

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has been observed that, the rate of reaction increases with increase in [OH^-]. The oxidation product of the reaction was found to be cystic acid. To account for the experimental result a plausible mechanism was proposed.[2]

The paper "Mechanism of oxidation of L-methionine by iron [III]-1,10-phenanthroline complex- A kinetic study" the following observations were noted. Oxidation of L-methionine was carried out in acidic medium by using perchloric acid. The reaction was first order each in iron [III] and methionine. Increase in [Phenanthroline] increases the rate of reaction while increase in [HLO_4] decreases in rate was observed. While the reactive species of the substrate was the zwitterions form, that of oxidant was $[Fe(Phen)_2(H_2O)_2]^{3+}$. The proposed mechanism leads to the rate law:

$$\frac{d[Fe9Phen)_3{}^{2+}]}{dt} = \frac{K_2K_4K_3K_2{}^2\,[Fe^{III}]\,[Phen]^{2+}\,[Met]}{(1+K_1[H^+][H^+]^2+K_4K_3K_2{}^2\,[Phen]^2)}$$

In the conclusion statement it has been noted that, Methione is a sulphur containing amino acid and it has three coordinating centre, oxygen, nitrogen and sulphur. The oxidation product of Mthionine depends on the nature of the oxidants.[3]

The paper is "Kinetica and Mechanism of the oxidation of methionine by Quiolnium Chlorochromate". It has been noted from the paper that, the oxidation of methionine by Quiolnium Chlorochromate [QCC] has been studied in the presence of chloroactic acid, and in water – acetic acid mixture of varying mole fractions. The reaction was first order with respect to methionine , QCC and acid.The reaction rate were determined at three different temperature (25, 35 and 45 ^oC) and the activation parameters were computed. The rate of reaction was found increased with increase of mole fraction of acetic acid in the mixture and specific solvent – solvent – solute interactions were found to predominate (81%). A salvation model and a suitable mechanism for the reaction are postulated.

It has been also observed that, the reaction was highly influenced by the amount and nature of the organic co-solvent added to the mixture. From the regression coefficients, information on the solvent – reactant and the solvent – transition state interaction was obtained and salvation model were proposed.[4]

"Kinetics and Mechanism of oxidation of DL - α – alanine by permanganate ion in acid percholorate media." While reviewing this paper it has been observed that, the permanganate oxidation of DL -α – alanine is carried out in aqueous perchloric acid solution at a constant ionic strength of 2.0 mol dm^{-3} has been investigated spectrophotometrically. The reaction was found to show second order kinetics overall with respect to each of the reactants in the slow initial stage; the second order kinetics are not, however, maintained throughout the relatively fast final stage of reaction. The added salts lead to the prediction that Mn(III) and (or) Mn(IV) play very important role in the reaction kinetics.

From the experimental observations it has been suggested that, the oxidation of DL-α –alanine by permanganate ion proceeds by a successive one electron transfer mechanism of inner sphere nature throughout two distinct stages. In initial slow stage, manganese (III) is formed as a transient species. Then, the Mn (III) formed is attacked by the substrate to give the reaction products via intermediate complex formation throughout the auto acceleration period. It has been also noted that, it does not possible to obtain direct evidence for detection of the intermediate complex ions. But this failure is, however, not contrary to the proposed mechanism of this reaction since the subsequent oxidation of the intermediates was slow in comparison with their formation. [5].

Where as "Kinetics and Mechanism of oxidation of L-cystine by Manganese (III) in sulfuric acid medium." It has been observed that, the mechanism of oxidation has been studied in sulfuric acid medium at 30 ^oC. The reaction was followed spectrophotometrically at λ_{max} = 500 nm. The reaction shows first order dependence on both [^{MnIII}] and [Cystine]. It was found that the rate of reaction decreases with increase of [H^+] up to a certain point and the remained unchanged. The oxidation product of the reaction was found to be cystic acid. A plausible mechanism has been proposed to account for the experimental results. In most of these studies cystic acid was found to be the product of oxidation.[6]

Paper "Kinetics of oxidation of amino acids by some free stable Hydrazyl Radicals". Amino acid represents for organism forerunners of essential bimolecules such as proteins, hormones, enzymes, etc; also, they may serve as energy source, losing their amino group by two path ways: transmination or oxidative deamination.

The kinetics of amino acid viz. serine, praline, leucine, tryptophane, threonine, phenylalanine, methionine and histidine oxidation was carried out by sodium salts of 2 – P- phenylsulfonic acid, 2- phenyl-1-picrylhydrazyal (I)and 2,2-di-p-phenylsulfonic acid, 2-phenyl-1-picrylhydrazyal (II) at isoelectric point of amino acids, over the temperature range 298-318 K. The kinetics as followed by monitoring the disappearance of I and II, spectrophotometrically at 520 nm and 514 nm respectively. The activation parameters were determined from rate constant dependence on temperature.

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It has been observed that, the amino acids with aromatic structures like histidine, tryptophane, and phenylalanine were oxidized more rapidly than the others. A mechanistic pathway for amino acid oxidation was proposed and discussed, similarly with their enzymatic degradation, which have as final products α – keto acids and ammonia. The study also presents some importance I understanding of natural ageing and oxidative stress process mainly due to the generation of free radicals in vivo. [7]

"Kinetics and mechanism of the Oxidation of some neural and acidic amino acids by tetrabutylammonium tribromide". The following points were noted during the reviewing the paper. Total eleven amino acids were oxidized by tetrabutylammonium tribromide (TBATB) in aqueous acetic acid medium and result in the formation of corresponding carbonyl compounds and ammonia. The reaction observed is of first order with respect to tetrabutylammonium tribromide. The presence of ammonia in the reaction mixture was detected by the test with p-nitrobenzene-diazonium chloride. Michaelis-Menten type kinetics was observed with some of the amino acids, while others exhibits second order dependence.

It failed to induce polymerization of acrylonitrile. The effect of solvent composition indicates that, the rate of reaction increases with increase in the polarity of the medium. Addition of tetrabutylammonium chloride has no effect on the rate of oxidation. Addition of bromide ion causes decrease in the oxidation rate but only to a limiting value. The reaction is susceptible to both polar and steric effects of the subsistent. The values of the reaction constant support the proposed mechanism. The negative polar reaction constant is in accordance with the net flow of electrons towards the oxidants. An increase in the electron density at the reaction centre facilitates the flow of electrons from substrates towards the oxidants. The negative steric reaction constant indicates a steric acceleration. This may well be due to high ground statenergy of the more substituted amino acids.[8]

The next paper related to oxidation of amino acid reviewed is "Kinetics and mechanism of oxidation of Methionine by Chromium (VI): EDTA Catalysisation". Following observations were made in the above reviewed paper. Methionine is naturally occurring sulphur containing amino acid and has three coordinating centers viz. oxygen, nitrogen and sulphur. Sulphur is more susceptible to attack by Cr^{VI} . Methionine is a methyl donor and this process in the body is activated by adenosine triophosphate (atp).

The kinetics of the oxidation of DL- metionine to sulphoxide by Cr^{VI} has been studied in aqueous acetic acid in the presence of sodium salt of Ethylene Diamine Tetr Aactetic acid (EDTA). It appears that Cr^{VI} – EDTA is the active electophil. The low dielectric constant of the medium favors the reactivity. Ionic strength and Mn^{II} have no significant effect on the conversion. The ratio K (D_2O) / K (H_2O) ≈ 1 does not seem to indicate any significant solvent isotope effect. Highly negative $\Delta S^{\#}$ values indicate a structured transition state. A ternary intermediate has been envisaged for describing the enhanced reactivity. It appears that the presence of EDTA decreases the enthalpic barrier to the reaction. [9]

While reviewing the paper "Kinetics and Mechanism of the oxidation of L-α – amino – n – butyric acid in moderately concentrated sulfuric acid medium", following observations were made. The oxidation of L-α – amino – n – butyric acid was made with permanganate in moderately strong acid medium using a spectrophotometer technique. It has been also observed that an auto-catalytic effect, due to Mn^{+2} ions formed, as a reaction product. Both catalytic and non catalytic process was determined to be first order with respect to the permanganate ion and the amino acid. The overall rate of equation for the process is:

$$\frac{-d[MnO_4^-]}{dt} = K'_1[MnO_4] + K'_2[MnO_4^-].[Mn^{+2}]$$

Where, K'_1 and K'_2 are pseudo – order rate constants for the non catalytic reactions, respectively. The influence of the factors such as temperature and reactant concentration on the rate constant has been studied and the activation parameters were found calculated. Reaction mechanism was found satisfying observations for both rates. [10].

III. CONCLUSION

The observed rate of oxidation is the first order with respect to the ion of oxidants and the amino acid.

The amino acids with aromatic structures like histidine, tryptophane, and phenylalanine were oxidized more rapidly than the others.

The reaction was highly influenced by the amount and nature of the organic co-solvent added to the mixture.

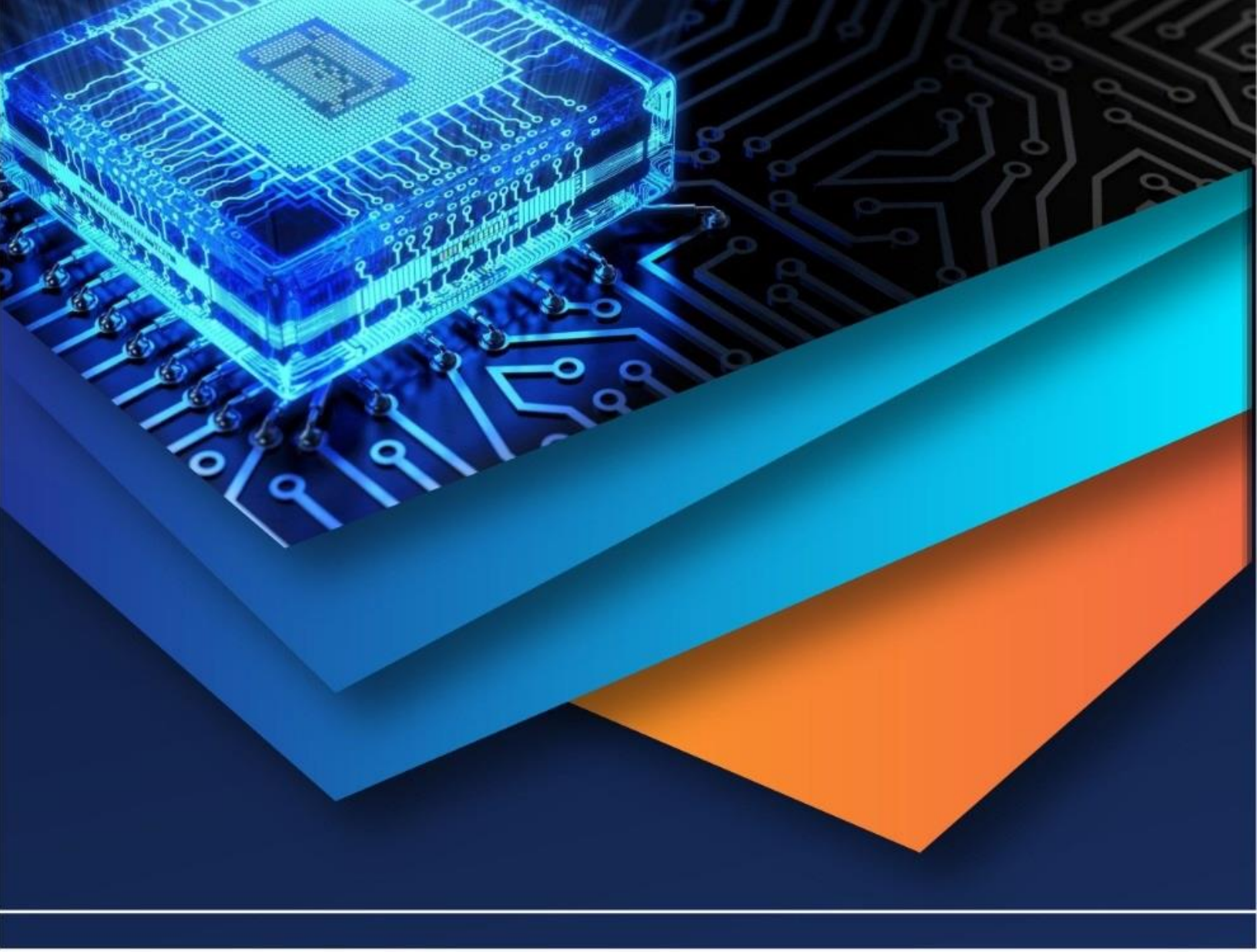
REFERENCES

[1] Mohamed farook N.A., Sayed Dameen G.A., Murugesan A and Kangaraj M, e-journal of chemistry (ISSN: 0973:4945). Vol.1 (2), pp 132-136, 2004.
[2] Annapurna Nowduri, Kalyankumar Adari, Nageswara Rao Gollapalli and vani Parvataneni, e-journal of chemistry (ISSN: 0973:4945). Vol.6 (1), pp 93-98, 2009
[3] Vani P, Krisna kishore K, Rambabu R and Dikshitulu L.S.A., Proc. Indian Acad. Sci. (Chem Sci), Vol. 113 (4), pp 351-359,2001
[4] Pandeeswaran M., Bincy John, Bhuvaneshwari D.S., Elango K.P. and J. Serb, Chem. Soc.(JSCS-3257), Vol. 70(2), pp 145-151, 2005
[5] Refat M. Hassan, Canadian journal of chemistery, 69, pp 2018-2023, 1991
[6] Nowduri Annapurna, Adari Kalyan kumar, Parvataneni Vani and Gollapalli Nageswara rao, Transition Met. Che., 33, pp 691-696, 2008
[7] Gabriela Ionita, Victor Em Sahini, Gheorghe Semenescu and Pitor Ionita, Acta Chem. Slov., 47, pp 111-119, 2000

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[8] Raghvendra Shukla, Pradeep K, Sharma and Kalyan K. Banrji, Journal of Chemical Sciences, Vol. 116(2), pp 101-106, 2004
[9] Subbiah Meenakshi Sundaram and Rajgopal Vinothini, CCACAA (ISSN-0011-1643, CCA - 2855) 76(1), pp 75-80, 2003
[10] Homayoon Bahrami and Mansour Zahedi, Canadian Journal of Chemistry (doi 10-1139/V03-181), 82, pp 430-436, 2004
[11] Loredano pollegioni, Bernd Langkau, Wilhem Tischer, Sandro Ghisals and Mirella S. Pilone, Journal of Biological Chemistry, 268 (19), pp13860-13857, 1993
[12] S. Huo, C. Song, J. Shan, S. Shen and H. Sun, Journal of Indian Chemical Society, Vol. 6 (2), pp 243-250, 2009
[13] J.R.Clamp and L. Hough, Biochem journal, 94 (17), 1965
[14] Raghavendra Shukla, Pradeep Sharma, Laszlo Kotaj and Kalyan Banerji, Ind. Acd. Sci.(Chem. Sci.) Vol.115 (2), pp 129-134, 2003.

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