

Kinetics and Mechanism of Ion Catalyzed Oxidation of Asparagine, Glutamine and Phenylalanine by Permanganate in aquo-acidic Medium

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Abstract: The kinetics of oxidation of Asparagine , Glutamine and Phenylalanine by permanganate in aqueous acidic medium showed that the reaction was first order with respect to each reactant. The H⁺ ion concentration and ionic strength have significant effect on the reaction rate. The effect of varying concentration of substrate and oxidant, on the rate has been confirmed. The observed value of ΔG , ΔH , E_A were determined in KJ mole^{-1} ΔS in $\text{JK}^{-1} \text{mole}^{-1}$. The activation parameters were computed with respect to slow step of mechanism. There was good agreement between the observed and calculated rate constant with respect to various effect. The catalytic effect of bromide and ferrous ion were examined in detailed.

Key Word : kinetics of oxidation, aqueous acidic medium, activation parameter.

Introduction :

Potassium permanganate widely used as oxidizing agent play key role in the kinetics of number of organic and biological active compounds¹⁻⁵. Although a great deal of work has been done on the kinetics and mechanism of oxidation of various amino acids by permanganate ion. The kinetics and oxidation of Asparagine, Glutamine and Phenylalanine MnO_4^- ion in presence of anion and cation catalyzed oxidation has received little attention. Present paper deals with kinetics behavior of the above amino acids in presence anion and cation. Amino acids make upto 75% of human body .Kinetics investigation of the oxidation of amino acids are important because of their biological significance. Some oxidation of amino acids by catalyzed oxidation studied by Kulkarni and coworker¹¹. The Kinetics and mechanism of the permanganate oxidation of some amino acids have been reported¹². Literature survey reveals that permanganate ions are widely used as oxidizing agent in synthetic and analytical chemistry¹³.

Material and Method

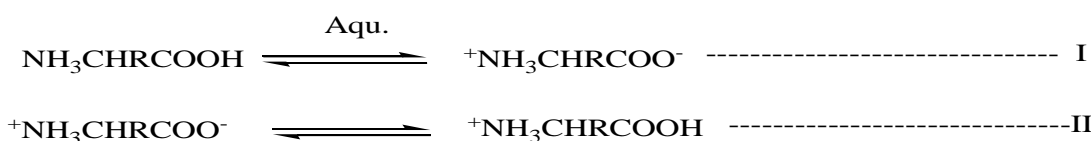
All the chemicals were used of AR grade. The solutions were prepared in glass distilled water. Sulphuric acid, hydrochloric acid, potassium chloride and potassium bromide were of qualigen. Hydrochloric acid and Sulphuric acid were used to maintain the acidic medium. Sodium sulphate (Thomas becker) and potassium chloride were used to maintain constant ionic strength

Potassium permanganate was prepared and standardized by a standard method describe by vogel⁶.the reaction was initiated at 298 K by adding to an equilibrated mixture of asparagines ,potassium bromide, hydrochloric acid and requisite quantity of pre-equilibrated solution of potassium permanganate .the idea in utilization of hydrochloric acid was to examine to oxidative nature of chlorine for reaction involving

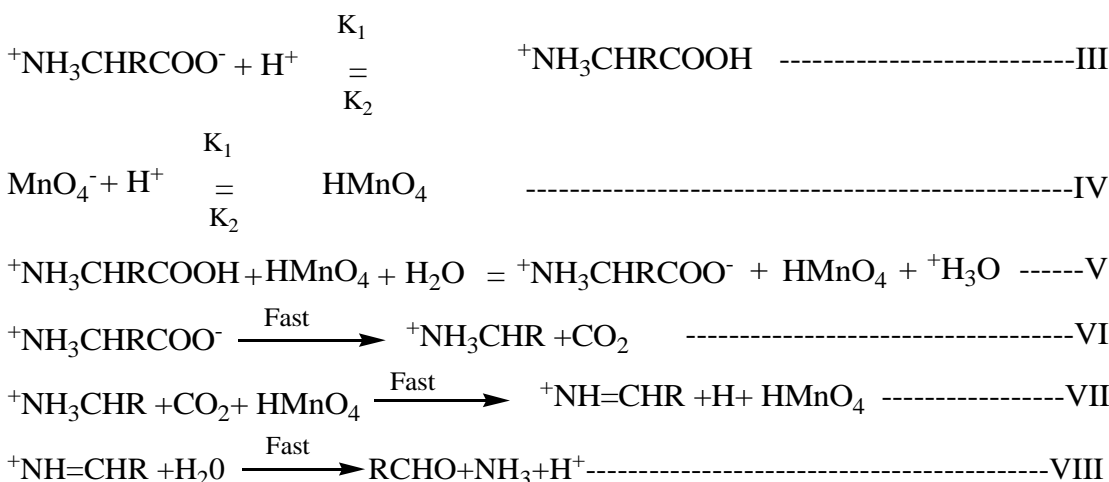
asparagines and glutamine. The effect of Cl⁻ on MnO⁻⁴ ions was negligible in absence of amino acid (observed light pink color with ppt in 24 hours)⁷. The progress of reaction was followed by measuring the optical density of remaining permanganate at 545nm a shimadzu UV-VIS 1601 spectrophotometer . It was confirmed that there is no interference due to other reagents at this wavelength. Similar procedure is repeated for glutamine and phenylalanine. While performing the kinetic runs, the concentration of substrate was kept in large excess and the pseudo first order rate constant were evaluated from plots of log (a-x) versus time. The initial rates were determined by verifying permanganate concentration and fixing substrate and by fixing permanganate and varying substrate concentration for all the amino acid in the present investigation . The ionic strength of the medium was adjusted with potassium chloride and sodium sulphate .the reaction mechanism proposed as follows.

Reaction Mechanism :

The amino acid exist predominantly as a protonated species in concentrated acidic medium⁸⁻⁹. It can be presented according to the following equilibrium .



It is evident from experimental result that increase the rate of reaction of all the Amino acids studied¹⁰. The following schemes have been proposed to account for the observed rate data.



The kinetics of oxidation of amino acid studied in aqueous medium at 298K obeys the following rate law;

$$\frac{d[\text{MnO}_4^-]}{dt} = K [\text{Amino Acid}] [\text{MnO}_4^-] \text{-----IX}$$

Result and Discussion :

The kinetics of oxidation of amino acid amides has been studied at various concentration of Asparagine ,Glutamine and Phenylalanine (0.024to 0.05M) keeping the [MnO₄⁻] constant i.e. 2.4 × 10⁻⁴ M, than keeping the concentration of substrate constant and varying the concentration of [MnO₄⁻] i.e.1.6 × 10⁻⁴M Carbon dioxide , ammonia and respective aldehyde were identified as the reaction product using their spot test evaluation of CO₂ and NH₃ was detected by lime water and Nessler's reagent respectively. The reaction to be very slow and not possible to measure the absorbance. However in presence of excess amino acid, the reaction rate was reasonably fast. The rate of reaction K_{mean} was good agreement with K_{Graph} (slope of log (a-x) verses time) . The rate of reaction indicate the first order dependence on [H⁺] concentration under the condition of constant [Amides] and [MnO₄⁻] with 7 oxidation state of Mn . The rate of reaction was found to be one in all the system studied. There was no kinetics evidence for intermediate complex formation between amino acid and permanganate ion . The possibility of complex formation was extremely small . The rate of reaction has been studied exhaustively in presence of Fe⁺⁺⁺ Br⁻ ions. The experimental result of kinetics investigation has been presented in Table 1 and Table 2 along with pseudo first order rate constant.

Table 1: Effect of concentration of cation on rate of reaction.

$$[\text{Asp}] ; [\text{Glu.}] ; [\text{Phe.}] = 5.0 \times 10^{-2} \text{ M} \quad [\text{MnO}_4] = 2.4 \times 10^{-4} \text{ M}$$

[Fe II] × 10 ⁵ M	K _{obs} × 10 ⁻² min ⁻¹ [Asp.]	K _{obs} × 10 ⁻² min ⁻¹ [Glu.]	K _{obs} × 10 ⁻² min ⁻¹ [Phe.]
0.8 2.7	2.330	2.573	0.16
1.6 5.2	4.860	5.036	0.32
2.4 9.9	8.106	9.224	0.48
3.2 14.3	12.390	13.25	0.64

Table 2: Effect of concentration of anion on rate of reaction.

$$[\text{Asp}] ; [\text{Glu.}] ; [\text{Phe.}] = 5.0 \times 10^{-2} \text{ M} \quad [\text{MnO}_4] = 2.4 \times 10^{-4} \text{ M}$$

[Br ⁻] × 10 ⁴ M	K _{obs} × 10 ⁻² min ⁻¹ [Asp.]	K _{obs} × 10 ⁻² min ⁻¹ [Glu.]	K _{obs} × 10 ⁻² min ⁻¹ [Phe.]
0.8 6.02	4.080	4.123	0.8
1.6 9.0	6.940	7.148	1.6
2.4 12.1	9.570	9.783	2.4
3.2 13.9	11.97	12.46	3.2

in Table 1 and Table 2 the cation and anion exert specific effect on the oxidation . The evaluation of thermodynamic parameter $\Delta E, \Delta H$ and ΔG , the reaction at 298K,308K,313K and 318K. the final result have been presented in Table 3

Table 3: Effect of concentration of anion on rate of reaction.

$$[\text{Asp}] ; [\text{Glu.}] ; [\text{Phe.}] = 5.0 \times 10^{-2} \text{ M} \quad [\text{MnO}_4] = 2.4 \times 10^{-4} \text{ M}$$

Amino Acid	ΔE	ΔG	ΔH	ΔS
Asparagine	48.13	19.29	45.65	--64.61
Glutamine	49.78	19.27	47.30	-64.51
Phenylalanine	47.36	19.48	44.88	-65.25

Fairly high values of negative ΔS and of positive ΔH suggest the formation of transition state , which is more restricted in geometry compare to the reactant . the negative ΔS and positive ΔH values observed in all system were attributed towards the formation of more ordered activated complex state, and the transition state is highly solvated.

Acknowledgements

We are very much thankful to Late Dr .V.G.Dongra Professor, Department of Chemistry, Mumbai University ,Mumbai and Late Dr .V.W.Kamble , Deputy Director, Forensic Lab, Aurangabad,India for his valuable guidance and supports for research work .

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