Kinetic measurements of oxidation of Amino acids in acidic, Neutral & alkaline medium

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Abstract

Literature survey shows that the stability constants of amino acids have been the subject of study by many workers [2] and there is ample scope for the spectrophotometric and kinetic study of amino acids [2-7]. But, no systematic attempt has been made so far on the chemical kinetic and spectrophotometric investigations of amino acids in presence of anions, cations, micelles and catalysts.

In view of the importance and growing interest in the field of chelation, kinetics and mechanism of oxidation of amino acids in presence of different oxidants, catalysts and micelles [8-12], it is thought worthwhile to study in detail the title investigation.

In the present investigation, kinetic measurements of oxidation of various amino acids in acidic, neutral and alkaline medium were studied. The K_{obd} value for the reactions obtained from calculations and from graphical representations was evaluated. The order of reaction was confirmed from the slopes of plots of log K_{obd} Vs log C.

In all the systems studied, the order was found to be one with respect to each reactant. The rates of reactions were evaluated by using the usual expression. The effect of varying concentration of amino acids, oxidants, Br^-, Fe^{++}, surfactants like T-80 and T-X-100 on rate of reaction has also been studied. In order to study the effect of ionic strength and temperature on K_{0bd}, the systems were studied at different concentrations of the electrolyte and at elevated temperatures.

KEYWORDS:- The oxidation of amino acids viz. glycine, DL-alanine, DL-leucine, DL-aspartic acid, DL-glutamic acid, L-lysine and L-arginine by potassium permanganate in sulphuric acid.

Introduction:

Biologically active compounds like amino acids, proteins and vitamins containing hetero atoms are receiving considerable attention in various fields like nutrition, pharmaceutical, clinical and biochemical research. The amino acids have received considerable attention as possible constituent of proteins. These biologically important amino acids have been used as chelating agents, with certain metal ions at different experimental conditions [1]. An exhaustive work has been carried out on the thermodynamics and complexometric investigations of these chelating reagents. There has been a great deal of interest in the reactions between the amino acids and metal ions because of their importance in chemistry and biology. Simple and mixed complexes of amino acids with certain metal ions in solution have also been studied by some workers [2]. The binary and ternary chelates of some amino acids have been studied exhaustively in aqueous and aquo organic media by few workers [2-5] using

pH metry, potentiometry and polarography. However no systematic study of the chemical kinetics of oxidation of amino acids in aqueous acidic, neutral, alkaline medium has been done so far in presence of surfactants, cations, anions and at elevated temperatures.

Methods:

Chemical kinetics is gaining importance in pure and applied fields and it leads to find out optimum conditions required to get desired product which is economically viable. In practice the decrease in concentration of a reactant or increase in concentration of a product can be measured with time. Numbers of methods are available for the measurements of kinetic parameters, few of which are summarised as under:

(i) Periodic or continuous spectral measurement: The reaction mixture under investigation can be subjected for kinetic measurements using spectrophotometric (UV, VIS, IR, NMR, ESR), chromatographic, polarographic methods.

(ii) Quenching and analysing: Series of reactions can be performed at different experimental conditions either by lowering the temperature or by adding an inhibitor. The reaction mixture can be then subjected for analysis using usual procedures, depending upon the nature of the reactants or product formed.

(iii) Removal of aliquots at intervals: Each aliquot from the reaction mixture can be subjected for analysis.

(iv) Measurement of change in total pressure for gas phase reactions [6, 7].

(v) Spectrophotometric methods: of the methods available for the kinetics of oxidation of amino acids, spectrophotometric method is most suitable since it finds wide applications because of its quick, precise and continuous means of monitoring changes in concentration of the reactants and or products.

EXPERIMENTAL RESULTS

Part - A: Kinetic Measurements of Oxidation of Amino Acids in Acidic, Neutral and Alkaline Medium:

The kinetic measurements of the oxidation of amino acids viz. glycine, DL-alanine, DL-leucine, DL-aspartic acid, DL-glutamic acid, L-lysine and L-arginine by potassium permanganate in sulphuric acid medium keeping excess of amino acids have been studied spectrophotometrically using Shimadzu UV-VIS-160-1A Spectrophotometer in aqueous acidic, neutral and alkaline medium in presence and absence of anions, cations and surfactants. Sulphate ions and bromide ions were used as anions in the form of Na_2SO_4 and KBr. Fe(III) and copper(II), Ag(l) were studied in presence of few amino acids. Polyoxyethylene sorbitan monooleate, octyl phenoxy polyethoxy ethanol and sodium dodecyl sulphate were used to study the effect of surfactant on the rate of reaction. The dependence of ionic strength, on the rate of reaction has been studied using sodium sulphate, sodium perchlorate and potassium nitrate as electrolytes.

The effect of $[H^+]$ ion concentration has also been studied for all the systems selected in the present investigation.

The kinetic runs were carried out at 0.1 M Na_2SO_4 ionic strength and at 298°K in'a thermostatic serological waterbath (± 0.1 °C). Some of the systems, which were

investigated earlier, were reinvestigated here to get the kinetic data under identical experimental conditions maintained for present kinetic runs. The reaction was initiated by adding to an equilibrated mixture of respective

amino acid, sodium sulphate, sulphuric acid requisite quantity of preequilibrated solution of potassium permanganate. The experimental details of first order rate constants with respect to amino acids and potassium permanganate are given here in a tabular fonm (Table 3.1al- 3.1.f-40) for some representative systems. However, since the experimental conditions were the same for the remaining systems they are not described to avoid duplication.

Kinetics of oxidation of amino acids in aqueous acidic, neutral and alkaline medium:

The kinetic runs were carried out spectrophotometrically in aqueous acidic medium (2 - 3.0 M H2SO4) at 0.1 M ionic strength by preparing a series of solutions. Initially four sets of solutions were prepared separately with excess and varying amount of respective amino acid (0.05 - 0.1 M) keeping the oxidant concentration constant (104 to 10-5M). The experimental solutions of the reactants were kept in thermostatic water bath for some time. After equilibration at constant temperature, the substrate / amino acid solution was mixed into the potassium permanganate solution and the reaction mixture was filled in quartz cuvettes and absorbance was measured immediately with one minute time interval. The total volume of the reaction mixture was made to 12.5 ml and in some cases it was 25 ml. The ionic strength was maintained by addition of sodium sulphate and/or potassium nitrate.

The effect of ionic strength on rate of reaction was also studied though it has a negligible effect in the lower concentration range studied.

The progress of the reaction was followed by measuring the absorbance at 545 nm on a Shimadzu UV-VIS 160-1 Spectrophotometer. Since the conditions maintained for DL-alanine, DL-leucine, DL-aspartic acid, DL-glutamic acid, L-lysine and L-arginine were the same. Same procedure was adopted for the kinetic runs.

The procedure was repeated for rest of the kinetics of oxidation of amino acids in neutral and alkaline medium and the effect of varying concentration of substrate and oxidant was studied in detail. The rate of decrease of concentration was found to be first order with respect to each reactant in all the systems studied. The initial rates were found to be reproducible within the limits of experimental error. (1%.). The plots of log Kobserved Vs log C are linear passing through the origin, suggesting the first order dependence of the rate on both the reactants.

Measurements for first order rate constants of Amino acids:

The data was utilized for the evaluation of rate of reaction using usual expression given in chapters I and II and the first order rate of reaction (Kmean and Kgraphical) are presented in tables 3.1.a-l - 3.1.f-40.

The plots of x Vs time, log (a-x) Vs time and IogKobd Vs logC for few representative systems are also plotted and presented in Fig. 3.1 .a-1 to 3.1.a-20, 3.l.e-1, 3.1.c.2, and 3.1.d-l - 3.1.d-2. The reaction was also studied at 30°C, 35°C, 45°C and 50°C, and the thermodynamic data required for energy of activation, enthalpy and

entropy has been presented in table 3.1.a-l to 3.1 f-40. The effect of catalysis and surfactants has also been studied in almost all the amino acids and oxidants.

Table 3.1.G-1. Measurements for the first order rate constant of Glycine at constant concentration of oxidant.

[Oxi] = 0.8 x 10^{-4} M — Medium = Acidic
T = 298°K — [H_2SO_4] = 2M

Time (in min)	O.D. [Glycine]			
	0.08M	0.16M	0.2M	0.24M
0.0	0.135	0.135	0.135	0.135
10.0	0.131	0.129	0.128	0.127
20.0	0.129	0.127	0.124	0.125
30.0	0.128	0.125	0.122	0.120
40.0	0.127	0.123	0.121	0.120
50.0	0.126	0.122	0.120	0.119
60.0	0.125	0.121	0.119	0.117
70.0	0.124	0.120	0.118	0.115
80.0	0.124	0.120	0.118	0.114
90.0	0.123	0.119	0.117	0.113
100.0	0.122	0.118	0.117	0.112
110.0	0.122	0.118	0.116	0.111
120.0	0.121	0.117	0.115	0.110
130.0	0.120	0.116	0.114	0.110
140.0	0.119	0.115	0.114	0.109
150.0	0.119	0.114	0 113	0.108
160.0	0.118	0.114	0.112	0.107
170.0	0.118	0.113	0.112	0.106
180.0	0.117	0.112	0.111	0.105
190.0	0.116	0.111	0.110	0.104
200.0	0.116	0.111	0.110	0.103
210.0	0.115	0.110	0.109	0.103
220.0	0.115	0.109	0.108	0.102
230.0	0.114	0.109	0.108	0.101
240.0	0.114	0.108	0.108	0.100
	K_{mean}= 1.796x10^{-3} Sec^{-1}	K_{mean}= 2.305x10^{-3} Sec^{-1}	K_{mean}= 2.917x10^{-3} Sec^{-1}	K_{mean}= 3.679x10^{-3} Sec^{-}
	K_{graph}= 1.701x10^{-3} Sec^{-1}	K_{graph}= 2.299x10^{-3} Sec^{-1}	K_{graph}= 3.034x10^{-3} Sec^{-1}	K_{graph}= 3.611x10^{-3} Sec^{-1}

Table 3.1 .G-2. Measurements for the first order rate constant of Glycine with varying concentration of oxidant.

[Gly] = 0.2M — Medium = Acidic
T = 298°K — [H_2SO_4] = 2M

Time (in min)	O.D. [Oxi]			
	4 x 10^{-5} M	8 x10^{-5} M	1.2 x 10^{-4} M	1.6 x 10^{-4} M

0	0.114	0.134	0.154	0.195
10.0	0.110	0.128	0.148	0.185
20.0	0.108	0.124	0.142	0.175
30.0	0.107	0.122	0.137	0.168
40.0	0,106	0.121	0.133	0.160
50.0	0.106	0.120	0.129	0.154
60.0	0.105	0.119	0.125	0.148
70.0	0.105	0.118	0.121	0.141
80.0	0.104	0.118	0.119	0.136
90.0	0.104	0.117	0.117	0.130
100	0.103	0.117	0.114	0.125
110	0.103	0.116	0.112	0.121
120	0.102	0.115	0.110	0.119
130	0.102	0.114	0.108	0.116
140	0.102	0.114	0.107	0.114
150	0.101	0.113	0.106	0.112
160	0.100	0.112	0.106	0.110
170	0.100	0.112	0.105	0.109
180	0.100	0.111	0.104	0.107
190	0.099	0.110	0.104	0.106
200	0.099	0.110	0.103	0.105
210	0.099	0.109	0.102	0.104
220	0.098	0.108	0.101	0.102
230	0.098	0.108	0.100	0.100
240	0.098	0.108	0.100	0.099
	K_{mean} =	K_{mean} =	K_{mean} =	K_{mean} =
	2.2111 x10^{-3} Sec^{-1}	2.917x10^{-3} Sec^{-1}	3.912 x 10^{3} Sec^{1}	4.951 x $10'^{3}$ Sec^{1}
	K_{graph} =	K_{graph} =	K_{graph} =	K_{graph} =
	2.210 x 10^{3} Sec^{1}	3.199 x 10 Sec	3.814 x 10^{J} Sec^{1}	4.948 x 10^{3} Sec^{1}

Table 3.88.G-3. Effect of varying concentration of KBr on the first order rate constant of Glycine at 298°K.

[Gly] = 0.2M — Medium = Acidic
[Oxi] = 0.8 x 10^{-4} M — [H_2SO_4] = 2M

Time (in min)	O.D. [B r]			
	4x 10^{-5} M	8x10^{-5} M	TT2 x 10^{-4} M	1.6 x 10^{-4} M
0.0	0.135	0.135	0.135	0.135
2.0	0.133	0.131	0.129	0.127
4.0	0.131	0.128	0.126	0.122
6.0	0.129	0.125	0.121	0.116
8.0	0.126	0.122	0.118	0.110
10.0	0.124	0.119	0.113	0.103
12.0	0.121	0.115	0.109	0.098
14.0	0.119	0.111	0.104	0.093

16.0	0.117	0.107	0.098	0.087
18.0	0.115	0.103	0.093	0.080
20.0	0.112	0.099	0.089	0.072
22.0	0.109	0.095	0.084	0.065
24.0	0.108	0.092	0.080	0.059
26.0	0.106	0.089	0.076	0.054
28.0	0.104	0.085	0.073	0.050
30.0	0.102	0.082	0.070	0.046
32.0	0.100	0.080	0.066	0.043
34.0	0.098	0.078	0.063	0.040
36.0	0.097	0.076	0.061	0.038
38.0	0.095	0.074	0.059	0.035
40.0	0.094	0.072	0.057	0.032
	K_{mean} = 7.587×10^{-3} Sec^{-1}	K_{mean} = 1.279×10^{-2} Sec^{-1}	K_{mean} = 1.833×10^{-2} Sec^{-1}	K_{mean} = 2.538×10^{-2} Sec^{-1}
	K_{graph} = 7.593×10^{-3} Sec^{1}	K_{graph} = 1.267×10^{-3} Sec^{1}	K_{graph} = 1.799×10^{-3} Sec^{1}	K_{graph} = 2.438×10^{3} Sec^{1}

Table 3.1.G-4. Effect of varying concentration of T-80 on the first order rate constant of glycine at 298°K.

[Gly] = 0.2M Medium = Acidic

[Oxi] = 0.8×10^{-4} M $[H_2SO_4]$ = 2M

Time (in min)	O.D. [T-80] %			
	4×10^{-3}	8×10^{-3}	1.2×10^{-2}	106×10^{-2}
0.0	0.135	0.135	0.135	0.135
2.0	0.125	0.118	0.110	0.100
4.0	0.114	0.107	0.100	0.090
6.0	0.107	0.100	0.092	0.081
8.0	0.101	0.095	0.086	0.071
10.0	0.097	0.091	0.080	0.065
12.0	0.093	0.085	0.075	0.060
14.0	0.089	0,082	0.070	0.052
16.0	0.085	0.077	0.064	0.046

18.0	0.081	0.072	0.057	0.040
20.0	0.078	0.069	0.051	0.034
22.0	0.074	0.064	0.047	0.028
24.0	0.071	0.060	0.041	0.024
26.0	0.068	0.057	0.035	
28.0	0.064	0.054	0.030	
30.0	0.060	0.052		
	K_{mean} =	K_{mean} =	K_{mean} =	K_{mean} =
	3.876×10^{-2} Sec^{-1}	5.004×10^{-2} Sec^{-1}	6.393×10^{-2} Sec^{-1}	8.514×10^{-2} Sec^{-1}
	K_{graph} =	K_{graph} =	K_{graph} =	K_{graph} =
	3.811×10^{-2} Sec^{-1}	4.499×10^{-2} Sec^{-1}	6.383×10^{-2} Sec^{-1}	8.502×10^{-2} Sec^{-1}

Table 90.1.G-5. Effect of varying concentration of T-X-100 on the first order rate constant of glycine at 298°K.

[Gly] = 0.2M
[Oxi] = 0.8×10^{-4} M
Medium = Acidic
[H_2SO_4] = 2M

Time (in min)	O.D. [T-X-100] %			
	4×10^{-5}	8×10^{-5}	1.2×10^{-4}	1.6×10^{-4}
0.0	0.135	0.135	0.135	0.135
2.0	0.124	0.117	0.109	0.099
4.0	0.113	0.106	0.099	0.089
6.0	0.108	0.101	0.091	0.079
8.0	0.102	0.094	0.084	0.070
10.0	0.098	0.090	0.078	0.064
12.0	0.094	0.084	0.073	0.058
14.0	0.090	0.081	0.068	0.050
16.0	0.086	0.076	0.062	0.044

18.0	0.082	0.071	0.055	0.038
20.0	0.077	0.068	0.049	0.032
22.0	0.073	0.063	0.095	0.026
24.0	0.070	0.059	0.039	0.022
26.0	0.069	0.056	0.033	
28.0	0.063	0.053	0.028	
30.0	0.059	0.51		
	K_{mean} = $3.719x10^{-2}$ Sec^{-1}	K_{mean} = $4.834x10^{-2}$ Sec^{-1}	K_{mean} = $6.576x10^{-2}$ Sec^{-1}	K_{mean} = $8.931x10^{-2}$ Sec^{-1}
	K_{graph} = $3.712x10^{-2}$ Sec^{-1}	K_{graph} = $4.814x10^{-2}$ Sec^{-1}	K_{graph} = $6.612x10^{-2}$ Sec^{-1}	K_{graph} = $8.899x10^{-2}$ Sec^{-1}

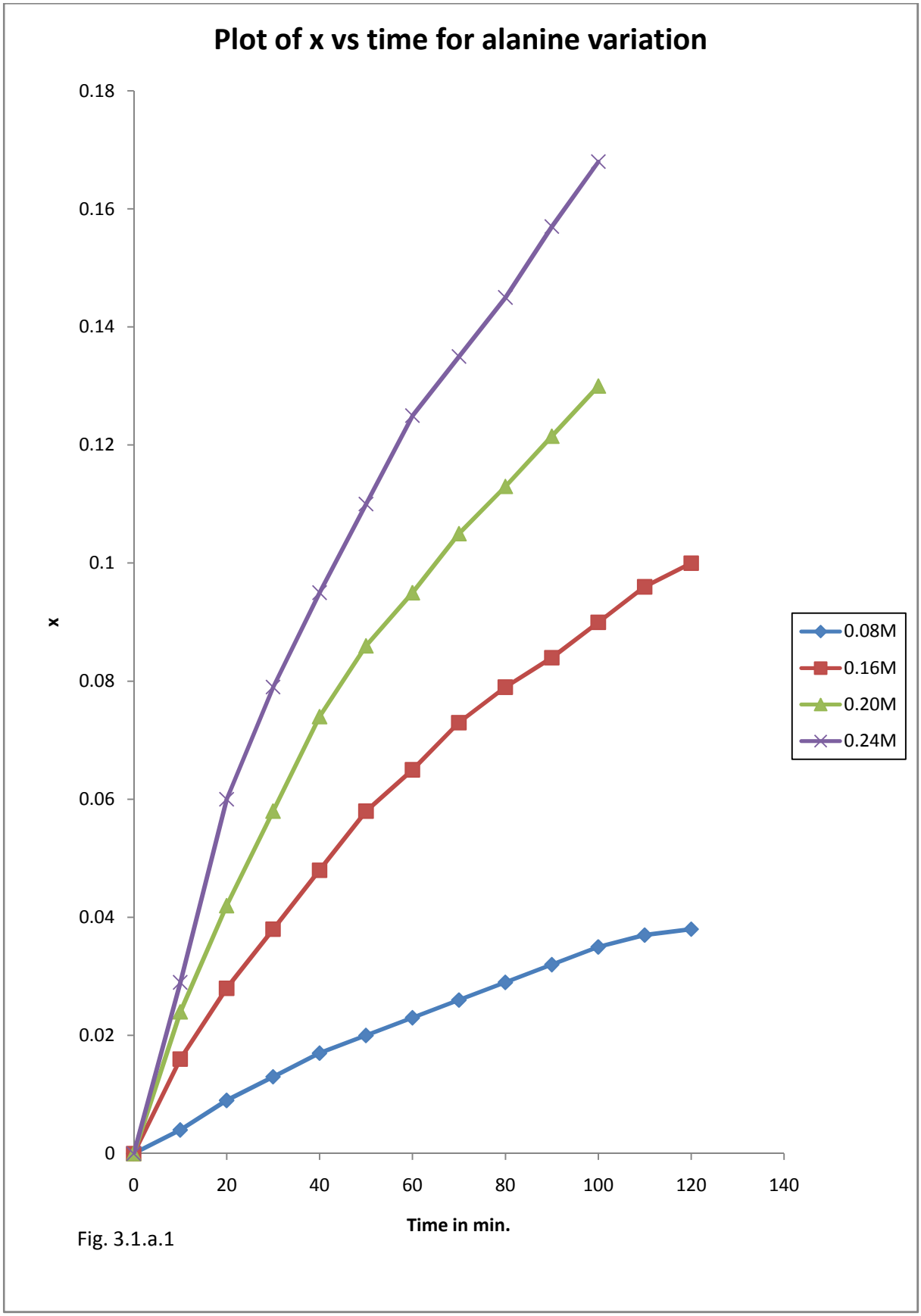

Fig. 3.1.a.1

DISCUSSION OF THE RESULTS

Part - A: Kinetics of oxidation of amino acids in aqueous acidic, neutral and alkaline medium.

The methods and experimental results related with the kinetics of oxidation of amino acids and the stability constants of L-lysine and L-arginine at various experimental conditions are given in Chapters I and II.

Chemical kinetics is receiving considerable attention in recent years due to the role of anions, cations, micells and different catalysts in biological systems. It is also a known fact that the role of metal ions in biological systems is gaining significant attention since last few decades.

Keeping in mind the importance of amino acids, it was decided to undertake systematic study of oxidation of amino acids using some oxidants in aqueous acidic, neutral and alkaline medium.

The literature survey reveals that there is an ample scope for the title investigation. Thus in view of the role of metal ions and importance of amino acids in biological and medicinal research, the spectrophotometric and kinetic study of glycine, DL-alanine, DL-leucine, DL-aspartic acid, DL-glutamic acid, L-lysine and L-arginine in aqueous acidic, alkaline and neutral as well as in aquo-organic media has been undertaken.

Literature survey also reveals that the amino acids are playing a key role as complexing reactants and are useful in number of biological systems[2]. It was observed from the literature survey that the kinetics of oxidation of some amino acids has been studied in aqueous acidic medium using some anions and cations[3-6]. The order and rate of reaction has been a subject of study by many workers[7-40].

However very little is known about the spectrophotometric and kinetics of oxidation of amino acids in presence of cation, anions, micelles and other catalysts.

Kinetic measurements of oxidation of glycine by MnO_4^- in aqueous acidic medium with varying concentration of oxidant.

The kinetics of oxidation of glycine by MnO_4^- has been reinvestigated by carrying out the kinetic runs in aqueous H_2SO_4 medium at 298 K in order to get the data under identical experimental conditions. The measurements of absorbance with time are given in Table 3.1.G-1 a10ng with the first order rate constants. The results are in agreement with the literature values. However, slight differences are observed which may be accounted towards changes in experimental conditions. The kinetic measurements were carried out at different concentrations of glycine ranging from 0.08 M to 0.24 M, keeping constant concentration of MnO^-_4 (8×10^{-5} M) and also at different concentrations of oxidant with fixed concentration of substrate. The observed first order rate constants are given in table 4.1.a-l.

Table 4.1.a-l.

[Gly]	$K_{obd} \times 10^{-2}$ min^{-1}	$[MnO^-_4]$	$K \times 10^{-3}$ min^{-1}
0.08 M	1.796	4×10^{-5} M	2.111

0.16 M	3.727	8×10^{-5} M	3.127
0.20 M	4.605	12×10^{-5} M	3.912
0.24 M	5.343	16×10^{-5} M	4.951

The system has also been studied in presence of Br^- ion. The bromide ion catalysed rate constants are given in table 4.l.a-2.

Table 4.1.a-2. Effect of varying bromide ion concentration on the rate of oxidation.

[Gly] = 0.2 M, $[MnO_4] = 8 \times 10^{-5}$ M, T = 298 K^o

$[Br^-]$	$K_{obd.} \times 10^{-2}$ Sec^{-1}
4×10^{-5}	0.7587
8×10^{-5}	1.279
12×10^{-5}	1.833
16×10^{-5}	2.530

The effect of surfactants on rate of reaction has also been studied. The results are summarised and are presented in table 4.l.a-3.

Table 4.1.a-3. Effect of varying surfactant concentration on the rate of oxidation.

[Gly] = 0.2 M, $[MnO_4] = 8 \times 10^{-5}$ M, Medium = H_2SO_4, T = 298 K.

T – 80 (%)	$K_{0bd} \times 10^{-2}$ sec^{-1}	T-X-100 (%)	$K_{obd} \times 10^{-2}$ sec^{-1}
$.4 \times 10^{-3}$	3.876	4×10^{-5}	3.719
8×10^{-3}	5.004	8×10^{-5}	4.834
12×10^{-3}	6.393	12×10^{-5}	6.576
16×10^{-3}	8.514	16×10^{-5}	8.930

In order to avoid duplication, particularly for this system, the data at different ionic strengths and temperatures are not given.

The plots of 2+ log OD Vs time and log K_{obd} Vs log C were drawn and are presented in Figs. 3.1.a-l to 3.1.a-3. It was inferred from the plots that the order of the reaction was one with respect to each reactant and it was also observed that the rate of reaction was enhanced in presence of anions i.e. Br^- and SO_4^- ion as well as the effect of surfactant was found to be prominent on the K_{obd} values. The reaction is first order each with respect to permanganate ion and glycine. The rate of reaction was proportional to $[H^+]^{-1}$ at low temperature while H^+ ion has a pronounced effect on K_{obd} at high temperature $[H^+]^{-2}$. The oxidation products were identified as carbon dioxide, ammonia and formaldehyde by their respective spot tests[33].

The plots of log K_{obd} Vs log [MnO^-_4] or log [gly] was found to be linear with a slope of one. The K_{obd} values were found to be in good agreement with the $K_{graphical}$ values in all the sets studied. The bromide and iron(II) ion concentration was varied from 4×10^{-5} M to 16×10^{-5} M and 0.4×10^{-5} M to 1.6×10^{-3} M respectively.

The plots of first order rate constants with log Br^- ion concentration at different temperatures were linear with intercepts on Y axis (rate axis) suggesting that there must be a term in the rate law independent of bromide ion concentration corresponding to the
uncatalysed reaction. The rate law must therefore be of the form of $K_{obd} = A + B [Br]$, where A and B are constants which include rate constants and concentration terms. Similar form of the rate law can be expressed in terms of variation of glycine and permanganate ion
concentration i.e, $K_{obd} = C + D [gly]$, where C and D are constants which include rate constant and concentration terms.

All the kinetic runs were carried out at different concentrations of Br^-, SO_4^- and Fe(II) at 25°C in the range of 298 K to 318 K and an increasing trend of the reaction rate was observed with increase in concentration.

It is well known that the amino acids exhibit Zwitter ion character, the equilibrium constant K may be expressed as:

$$NH^+_3\ CH_2COO^- + H^+ \overset{K_1}{\rightleftharpoons} NH_2CH_2COOH.$$

The increase in rate with [H^+] suggests that some active species i.e.

$$MnO_4^-\ H^+ \overset{K_1}{\rightleftharpoons} HmnO_4$$ is generated[41] plot of K_{obd} Vs $\sqrt{\mu}$ was a linear suggesting that the rate determining step is between two neutral molecules or between a neutral molecule and an ion[43]. The positive salt effect (electrolyte), further suggests that at least one of the rate determining steps involves a molecule and a positive ion[42]. Thus the generation of $HMnO_4$ and $^+NH_3\ CH_2COOH$ as reactive species is in accordance with the observed salt effect.

The absorbance of glycine, MnO_4^- and bromide were measured independently at the same conditions maintained for the oxidation study. Br^- absorbs significantly at 198 nm while glycine absorbs to a lesser extent. Moreover the absorbance of equimolar composition of glycine and Br^- was found to be less than that of Br^- Although the absorbance pattern remains more or less unaltered. This decrease in absorbance may be attributed towards the following factors:

(1) Due to some weak interaction between the amino acid and Br^-/ Fe(II), there must be formation of ion pair or a weak complex species, which does not absorb at this wave length.

(2) Secondly the (ε), extinction coefficient of the complex species or ion pair may be different than that of the Br alone.

Since the formation constant is very small[42], it is expected that the ion pair must be

predominant over complex species. In the present investigation it is proved beyond doubt that there is no complex formation between permanganate and Br^- or the respective amino acids because there was no change in absorbance of MnO_4^- by the addition of the amino acid or the anion. However, in case of Fe(II), though there is

some weak complex formation but at the present experimental condition (pH <<< 0), this possibility is also ignored.

The plots of K_{obd} Vs bromide ion concentration at constant amino acids were found to be linear. The respective intercepts and slopes are given as:

$It_{Br^-} = K_1$ [gly] and

$S1_{Br^-} = K_1 + K_2$ [gly].

While from the plot of K_{obd} Vs [gly] in presence of Br^- it can be given as:

$It_{gly^-} = K_3$ [Br] and

S1 [gly] = $K_1 + K_2$ [Br]

The intercepts and slopes were determined in each set in the range of 25°C to 45°C to confirm the reactive species and the rate determining steps.

The activation parameters for catalysed and uncatalysed oxidation of glycine was evaluated by adopting usual procedure. The E_a and $\Delta S\neq$ associated with K_1 in the present work are in the range of 10.5 to 11 Kcal per mole ±0.5 K cal $mole^{-1}$ and 40 ± 2 Kcal K^{-1} $mole^{-1}$ respectively for catalysed reaction while E_a associated with K_2 (uncatalysed) was found slightly higher by two units ± 0.5 Kcal $mole^{-1}$ and $\Delta S\neq$ as 32.0 Cal K^{-1} $mole^{-1}$ to 35 Cal K^{-1} mole respectively which are in good agreement with the reported values[51-52]. The effect of ionic strength on rate of the reaction was also studied by varying the concentration of Na_2SO_4, and KNO_3 in the medium, keeping other conditions constant. The observed results reveal that increase in μ causes slight decrease in the rate. Effect of varying acid concentration was also studied. The results are in agreement with the general observation that increase in acid concentrations of the medium increases the rate of oxidation by MnO_4^-.

Kinetics of oxidation of DL-alanine in aqueous acidic and alkaline medium:

The kinetics of oxidation of DL-alanine system was studied in aqueous acidic and alkaline medium. The kinetic measurements made are given in chapter III. The observed data for first order rate constant at different experimental conditions are depicted in tables 4.1.a-4 and 4.l.a-5.

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