Research Article

Kinetics and Mechanism of Oxidation of DL-alanine and L-alanyl-l-glutamine by Manganese (III) Acetate in Aqueous Sulfuric acid medium

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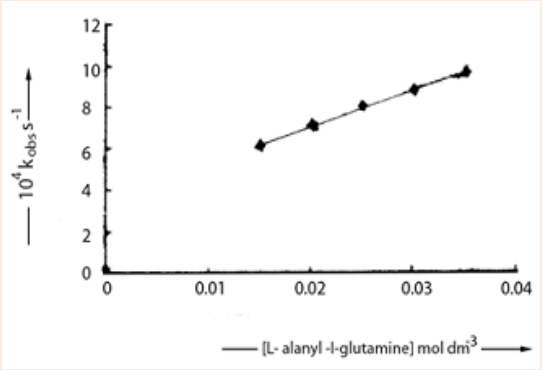
Abstract

The kinetics of oxidation of DL-alanine and L-alanyl-l-glutamine by manganese(III) acetate have been studied spectrophotometrically over the range $1.5 \leq 10^2$ [DL-alanine]$_T$ / [L-alanyl-l-glutamine]$_T \leq 3.5$ mol dm^{-3}, $1.0 \leq [H^+] \leq 2.5$ mol dm^{-3}, I = 0.5 mol dm^{-3}, [Mn(III)] = 0.003 mol dm^{-3}and 295 K $\leq$ T $\leq$ 310 K in the presence of aqueous sulfuric acid. The main products of the reaction were acetaldehyde and L-alanyl-l-aspartate respectively. The thermodynamic parameters H^0(kJ mol^{-1}) and S^0(J K^{-1} mole^{-1}) for the redox reactions of DL-alanine and L-alanyl-l-glutamine from the equilibrium constants were found to be 24.5 ± 5.0, 6.9 ± 1.76 and 87.5 ± 17.2, 14.6 ± 5.20 respectively. The activation parameters H$^{\#}$(kJ mol^{-1}) and S$^{\#}$(J K^{-1} mole^{-1}) for the redox reactions of DL-alanine and L-alanyl-l-glutamine from the composite rate constants were found to be 55.10 ± 3.0, 23.27 ± 3.90 and - 24.5 ± 9.94, -143.22 ± 12.38 respectively.



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Keywords: DL-alanine, Redox reaction, L-alanyl-l-glutamine, Manganese(III) acetate, Spectrophotometer

Introduction

Metal ion promoted radical reactions have found widespread use in organic syntheses, one of the well known examples of this application is the manganese(III) acetate mediated reactions. Mn (III) oxidation of amino acids and their derivatives and peptides is gaining special importance due to its biological relevance[1, 2]. A medium can influence the reaction rate, due to its polarisability, hydrogen bonding ability, electrophilicity, nucleophilicity and specific orientation including associative or dissociative nature. It is a specific character of manganese (III) that it can form different reactive species in presence of different acids. There were a number of reports on the kinetics of oxidation of various substrates by manganese(III) in perchlorate[3] , sulfate [4], acetate[5,6] and pyrophosphate media[7], including oximes[8], vitamins[9] and amino acids[10 - 15]. Manganese(III) sulphate has been scarcely used[16,17] in redox studies due to difficulty in obtaining it in the pure and stable form but the manganese (III) acetate is found in pure and stable form. As part of a broad investigation of the oxidation of amino acids by transition metal ion, this paper represents the kinetics and mechanism of oxidation of DL-alanine and L-alanyl-l-glutamine by manganese(III) acetate in sulfuric acid medium. This study will show the path how the amino acid and peptide is oxidized by metallo enzymes under physiological conditions.

Experimental

Materials and Methods

The reactant complex $Mn(OAc)_3$ (Aldrich product) having 90% purity. It was used as such. DL-alanine and L-alanyl-l-glutamine (SRL, extra pure) were used as such without further purification. Ionic strength was maintained with NaOAc. NaOAc not only enhances the conductivity but also increases the solubility of $Mn(OAc)_3$ due to the formation of $[Mn(OAc)_4]^-$. All other reagents used were AnalaR grade. The solution was prepared in freshly prepared double distilled water using an all glass distillation apparatus containing $KMnO_4$. During kinetic investigation a constant ionic strength 0.5 mol dm^{-3} (NaOAc) was maintained.

Kinetic Studies

The kinetics of oxidation of DL-alanine and L-alanyl-l-glutamine by $Mn(OAc)_3$ were studied spectrophotometrically under pseudo-first order conditions by keeping the concentration of substrate at least ten times in excess over [Mn(III)]. [Substrates] were varied from 1.5 x 10^{-2} to 3.5 x 10^{-2} mol dm^{-3} and $[H^+]$ were varied from 1.0 to 2.5 mol dm^{-3}. The decreased of absorbance with time was monitored at 450 nm for DL-alanine (**Figure 1a**) and L-alanyl-l-glutamine (**Figure 1b**). The kinetic studies were carried out in Systronic 2202 UV-Vis spectrophotometer. The detail experimental procedure of kinetic study was reported in our recent published paper[18].

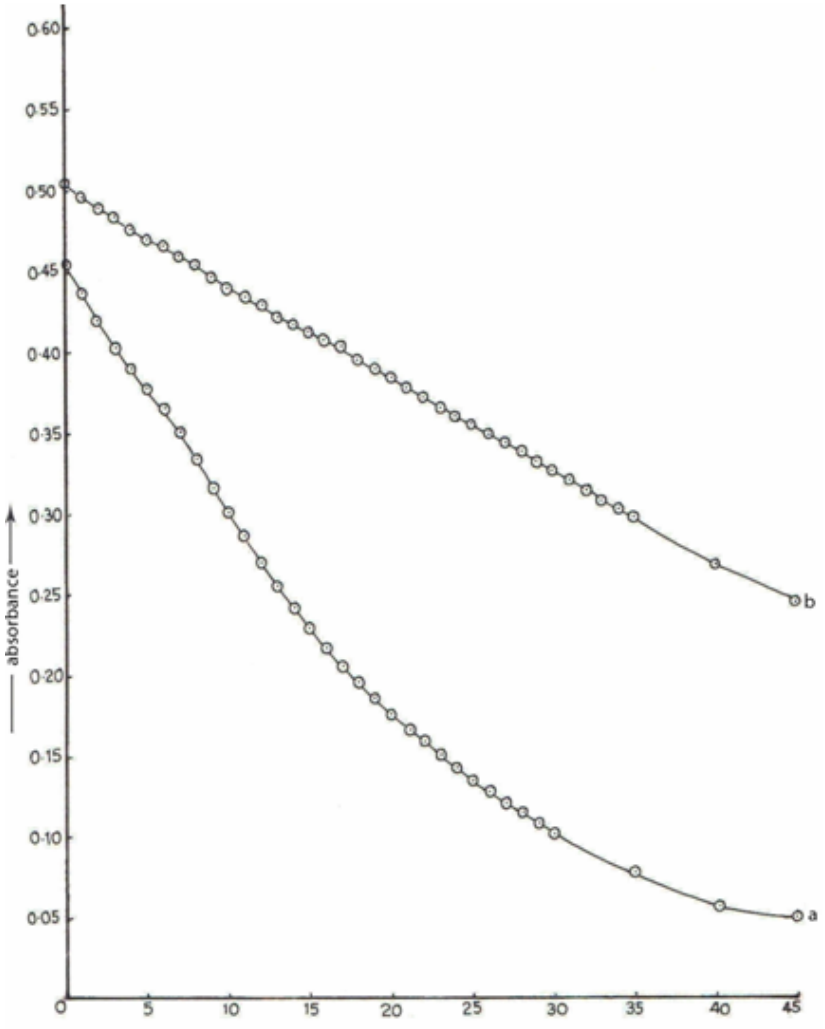

Figure 1 Plot of absorbance versus time (min)
(a) DL- alanine (b) L-alanyl -1 –glutamine

The progress of the reaction was monitored spectrophotometrically by measuring decrease of absorbance of Mn(III) at 450 nm (**Figure 2**).

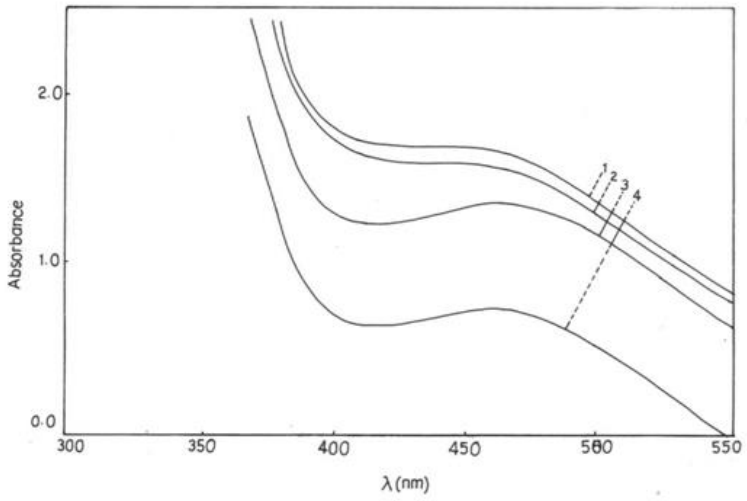

Figure 2 UV – Vis spectral scan of the reaction mixture of [Mn $(OAc)_3$] = 2 x 10^{-3} mol dm^{-3}, [Dl-alanine]/[L-alanyl-L-glutamine] = 3 x 10^{-3} mol dm^{-3}, [H_2SO_4]= 1.0 mol dm^{-3}, I(NaOAc) = 0.3 mol dm^{-3} at 305K, (1) Immediate after mixing, (2)Δt = 5 mins, (3)Δt = 10 mins, (4)Δt = 30 mins.

Stoichiometry and Identification of Product

The reaction mixture containing DL-alanine / L-alanyl-l-glutamine = 0.002 mol dm^{-3}, H_2SO_4 = 0.1 mol dm^{-3}, $Mn(OAc)_3$ = 0.02 mol dm^{-3} were allowed to react at 305K for 24h. After completion of the reaction, the remaining unused Mn(III) was analysed spectrophotometrically. Results showed that two moles of Mn(III) consumed one mole of substrate (DL-alanine / L-alanyl-l-glutamine) leading to formation of aldehyde/acid, NH_3, CO_2 and Mn(II).

The above stoichiometry study showed that the reaction exhibited a 2:1 stoichiometry for Mn(III) with DL-alanine / L-alanyl-l-glutamine.

Stoichiometric determination indicated the following overall reaction for the oxidation of different substrates.

$2Mn(III) + CH_3CH(NH_2)COOH + H_2O \rightarrow 2Mn(II) + CH_3CHO + NH_3 + CO_2 + 2H^+$
$2Mn(III) + H_2NCOCH_2CH_2CH(COOH)NHCOCH(NH_2)CH_3 + 3H_2O \rightarrow 2Mn(II) +$
$HOOCCH_2CH(COOH)NHCOCH(NH_2)CH_3 + NH_3 + CO_2 + 6H^+$

In order to get the reaction product 5 ml of 0.2 mol dm^{-3} of substrate mixed with 10 ml of 0.02 mol dm^{-3} of oxidant Mn(III) and 70% glacial acetic acid were mixed separately in a container along with 10 ml of 0.2 mol dm^{-3} [H^+]. The reaction mixture was allowed to stand for about 24h at 305K for the completion of the reaction. The crystalline products so formed were isolated by filtration and the product was recrystallised. The oxidation product of DL-alanine and L-alanyl-l-glutamine were separately dried in a desiccator. The yield of the products was nearly 70%. FTIR spectra of products were recorded in a Perkin- Elmer (UK) FTIR spectrophotometer.

The FTIR spectra of oxidation product of DL – alanine (**Figure 3**) shows a broad peak at 3417 cm^{-1} is due to coordinated water molecule. Lack of absorption above 3000 cm^{-1} excludes the presence groups seen as –OH, NH_2, NHR and aromatic system. The band at 2887cm^{-1} is due to asymmetric stretching vibration of methyl group as well as C-H stretching of aliphatic aldehyde group. The nature of the aldehyde was confirmed by its FTIR spectrum[19],

carbonyl stretching appear at 1739 cm^{-1}. Moderate intensity band at 1375cm^{-1} is consistent with C-H in plane bending vibration and 1405cm^{-1} corresponds to C-H bending in CH_3 group. Peak at 1067cm^{-1} is due to C-H out plane bending vibration of aldehyde. All the above FTIR data corresponds to acetaldehyde. Hence the oxidation product of DL-alanine is identified as acetaldehyde.

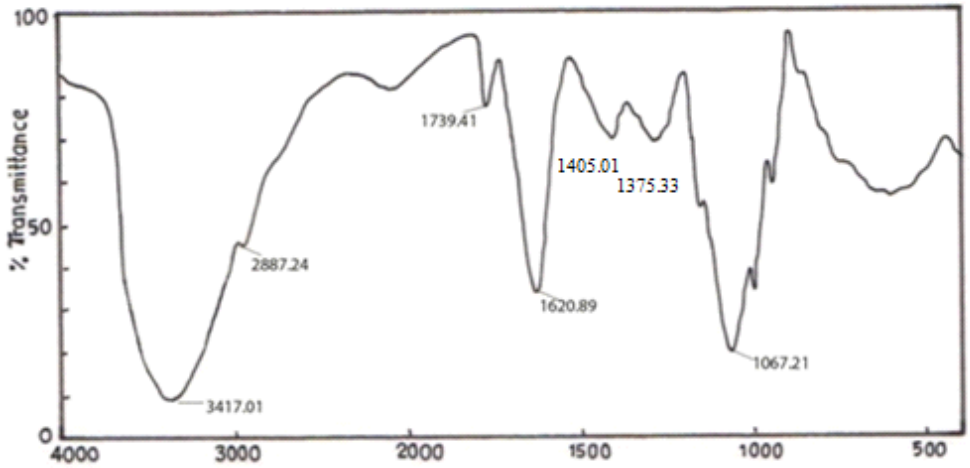

Figure 3 FTIR Spectra of oxidation product of DL-alanine.

The FTIR-spectra of oxidation of L-alanyl-l-glutamine **(Figure 4)** shows the band at 1615cm^{-1} which is the peptide carbonyl group. The shifting of the peptide carbonyl stretching band from 1645 cm^{-1} to 1615 cm^{-1} may be due to the ionization of the peptide NH, since such ionization results in the resonance of O-C-N system, a band at 3429 cm^{-1} indicating the presence of primary amine. The other peaks of the product were 3086 cm^{-1}(C-vinyl stretching), 1734 cm^{-1}(aldehydic CO stretching), 2928 cm^{-1} (aldehydic CH stretching), 1389 cm^{-1} (COO stretching), 1103 cm^{-1} (NH_3^+). An asymmetrical stretching band was observed at 1650 cm^{-1} for carboxylate ion and a weaker symmetrical stretching band is observed at 1400 cm^{-1}. It is concluded that the oxidation product of L-alanyl-l-glutamine is L-alanyl-l-aspartate or {(2S)-2-[[(2S)-2-amino propanoyl]-amino]-butan-1, 4-dioic acid}.

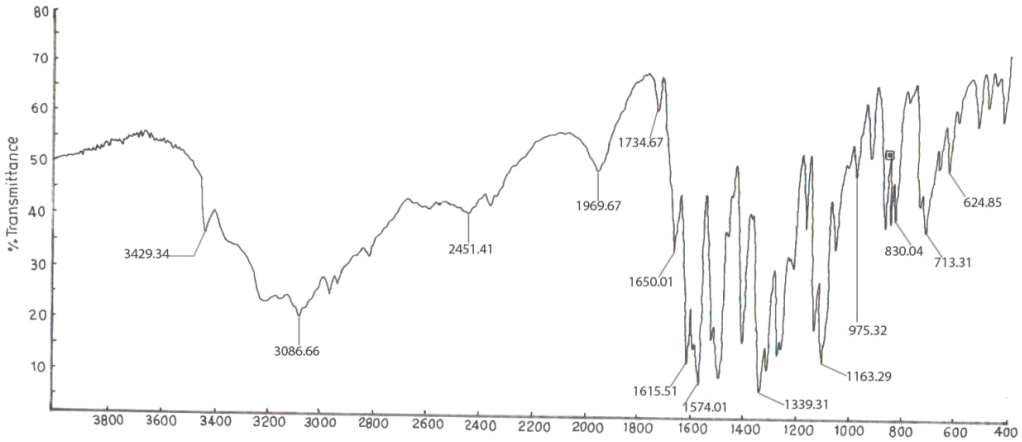

Figure 4 FTIR Spectra of oxidation product of L-alanine-l-glutamine.

Results and Discussion

The UV-VIS spectral scan (**Figure 2**) shows the redox reaction of Mn(III) by free amino acid and dipeptide. The rate constant of the redox reaction was measured spectrophotometrically at 450nm and 350nm respectively. The following effects were studied on the rate constants of the above redox reaction.

Effect of [DL-alanine]

At 305K with Mn(III) = 0.003M, $[H^+]$ = 1.0M, 10^2 [DL-alanine] was varied from 1.5 mol dm^{-3} to 3.5 mol dm^{-3}, the observed pseudo-first order rate constant 10^3 k_{obs} (s^{-1}) changed from 16.15 to 26.33 mol dm^{-3}(**Table 1**).

Table 1 Pseudo-first order rate constants(k_{obs}) for the reaction of $Mn(OAc)_3$ with DL-alanine and L- alanyl – l - glutamine at different $[H^+]$ and different temperature.[Mn(III)] = 3 x 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaOAc) and λ = 450 nm (DL-alanine), 350nm (L- alanyl - glutamine)

Substrate mol dm^{-3}	$10^{-1}[H^+]$ Mol dm^{-3}	$10^3k_{obs}(s^{-1})$			
		295K	300K	305K	310K
DL-alanine					
0.015	1.0	07.50	12.63	16.15	20.93
0.015	1.5	04.50	10.50	13.91	17.87
0.015	2.0	03.80	07.60	10.96	13.27
0.015	2.5	02.45	06.40	07.89	10.20
0.020	1.0	08.88	15.21	20.13	23.81
0.020	1.5	07.85	12.55	15.90	18.51
0.020	2.0	05.15	09.95	13.25	14.00
0.020	2.5	04.59	07.40	09.40	11.01
0.025	1.0	12.51	17.17	21.63	25.63
0.025	1.5	09.30	14.83	17.98	19.50
0.025	2.0	07.06	11.98	13.50	15.50
0.025	2.5	05.85	08.28	10.21	11.51
0.030	1.0	16.85	19.00	22.88	27.00
0.030	1.5	13.41	16.67	19.56	21.68
0.030	2.0	10.11	12.50	15.45	17.85
0.030	2.5	07.95	09.09	10.68	12.15
0.035	1.0	20.95	21.50	26.33	29.93
0.035	1.5	15.50	18.85	22.00	22.50
0.035	2.0	12.22	13.45	16.81	18.81
0.035	2.5	09.50	10.26	12.20	13.10
L – alanyl – glutamine					
0.015	1.0	05.58	06.05	06.85	08.32
0.015	1.5	05.05	05.62	06.25	07.65
0.015	2.0	04.60	05.15	05.73	06.93
0.015	2.5	04.35	04.65	05.10	06.22
0.020	1.0	06.47	07.18	08.22	10.21
0.020	1.5	05.45	05.91	06.93	08.32
0.020	2.0	04.81	05.25	05.96	07.21
0.020	2.5	04.40	04.75	05.45	06.64
0.025	1.0	07.35	08.13	09.34	11.76
0.025	1.5	05.68	06.46	07.15	09.08

0.025	2.0	05.38	07.15	06.05	07.78
0.025	2.5	04.45	04.97	05.62	07.03
0.030	1.0	07.98	08.84	10.35	12.98
0.030	1.5	06.04	07.05	07.92	10.16
0.030	2.0	05.52	05.58	06.38	08.61
0.030	2.5	04.38	05.11	05.98	07.44
0.035	1.0	08.63	09.70	11.27	14.17
0.035	1.5	06.33	07.45	08.25	10.97
0.035	2.0	05.76	06.23	06.96	09.23
0.035	2.5	04.71	05.36	06.16	07.75

The pseudo – first order rate constant increases with increase in initial concentration of the substrate. A plot of [substrate] *versus* k_{obs} is linear (**Figure 5a**). This shows that the order with respect to the [substrate] i.e. [DL-alanine] is first order.

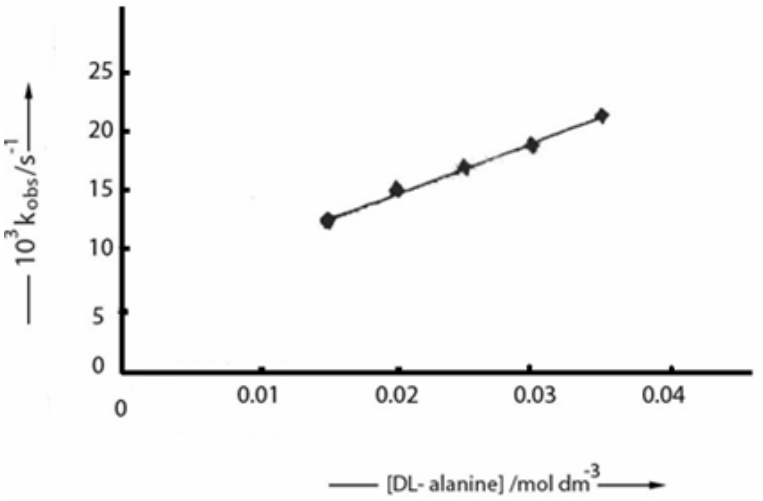

Figure 5(a) Plot of k_{obs} *versus* [DL-alanine] at 300K. [DL-alanine]= 3 x 10^{-3} mol dm^{-3}.

Effect of [L-alanyl-l-glutamine]

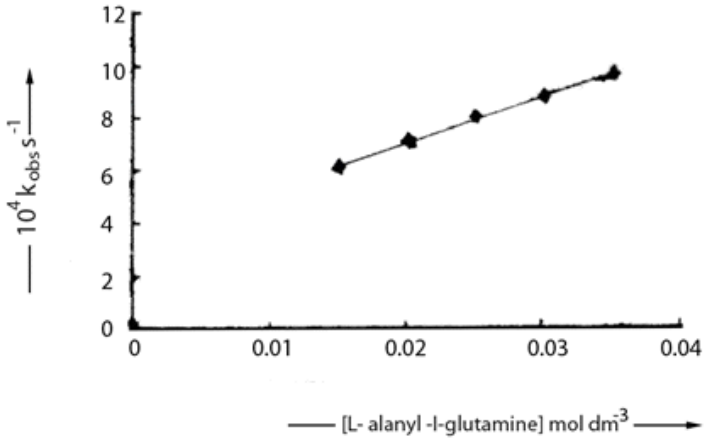

Figure 5b Plot of k_{obs} *versus* [L-alanyl-l-glutamine] at 300K. [L- alanyl-l-glutamine] = 3 x 10^{-3} mol dm^{-3}

Keeping all other conditions constant, the concentration of dipeptide was varied to observe its effect on redox reaction. At 305K with [Mn(III)] = 0.003 mol dm^{-3}, $[H^+]$ = 1.0 mol dm^{-3}, 10^2 [L-alanyl-l-glutamine] was varied from 1.5 to 3.5 mol dm^{-3}, the observed pseudo-first order rate constant 10^4 k_{obs} (s^{-1}) changed from 6.88 to 11.27 mol dm^{-3}**(Table 1)**. Plot of k_{obs} *versus* [L-alanyl-l-glutamine] (**Figure 5b**) is linear indicating first order dependence of the rate with respect to the [L-alanyl-l-glutamine].

Effect of $[H_2SO_4]$

Keeping the constant concentration of substrate constant i.e. [DL-alanine]/[L-alanyl-l-glutamine] = 2 x 10^{-2} mol dm^{-3}, [Mn (III)] = 0.003 mol dm^{-3}, at 305 K. The concentration of sulfuric acid was varied from 1.0 to 2.5 mol dm^{-3}, the observed pseudo-first order rate constant 10^3 k_{obs} (s^{-1}) for DL-alanine decreased from 16.15 to 7.89 mol dm^{-3} and 10^4 k_{obs} for L-alanyl-l-glutamine was also decreased from 6.88 to 5.10 mol dm^{-3} (**Table 1**).This indicates that reaction rate is retarded by increasing $[H_2SO_4]$. The reaction showed an inverse dependence on $[H_2SO_4]$ and the plot of k_{obs} / [substrate] *versus* $[H^+]$ is linear, not passing through the origin, (**Figure 6a and 6b)**. This highlighted that the unprotonated species of the substrate participated in the electron transfer reaction.

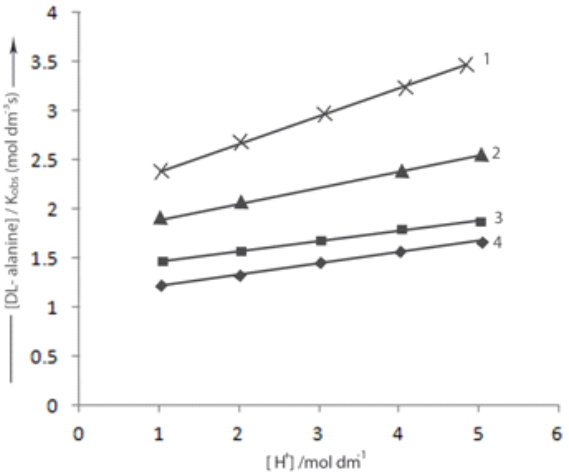

Figure 6 a Plot of [DL-alanine] / k_{obs} *versus* $[H^+]$ at different temperatures,[DL- alanine] = 2 x 10^{-2} mol dm^{-3}, Temp = 295K (1), 300K(2), 305K(3), 310K(4).

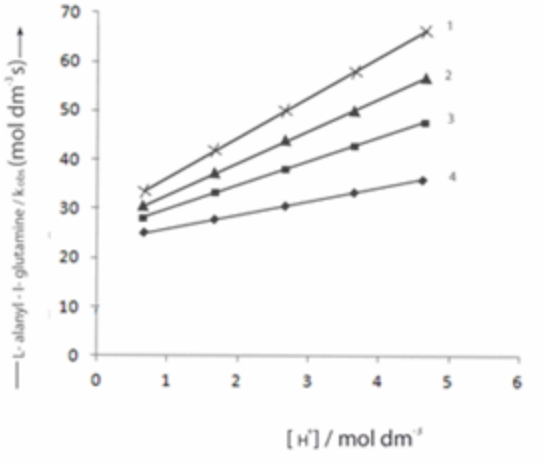

Figure 6b Plot of [L-alanyl-l-glutamine] / k_{obs} *versus* $[H^+]$ at different temperatures,[L-alanyl-l-glutamine] = 2 x 10^{-2}mol dm^{-3}, Temp = 295K (1), 300K(2), 305K(3), 310K(4).

Effect of temperature

The temperature variation was carried out in the range 295K to 310K, with [Mn(III)] = 3 x 10^{-3} mol dm^{-3},$[substrate]_T$ = 2.5 x 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaOAc), the observed pseudo-first order rate constant 10^3k_{obs} (s^{-1}) was found to increase from 12.51 to 25.63 mol dm^{-3} for DL – alanine and 10^4k_{obs}(s^{-1}) was found to change from 7.35 to 11.46 mol dm^{-3} for L–alanyl-l-glutamine. With the increase in temperature, k_{obs} were found to increase.
The temperature variation data are represented in **Table 1**.

Test of free radical

The absence of polymerization in the reaction mixture in presence of acrylonitrile indicated the absence of free radical formation in the redox reactions of both the substrates.

Mechanism of the reaction

The mechanism for the oxidation of amino acid and peptide in sulfuric acid medium has been proposed by considering that the manganese(III) and the substrate molecule interacts with each other to yield the product as given in Scheme-I.

$$S + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} SH^+ \quad (1)$$

$$S + Mn(III) \overset{K_2}{\rightleftharpoons} X \quad (2)$$

Where, $K_1 = [SH^+]_e / ([S]_e[H^+]_e)$ and $K_2 = [X]_e / [S]_e[Mn(III)]_e$

$$X + Mn(III) \xrightarrow{k_3} .S' + H_2O \quad (3)$$

Where S = Substrate, SH^+ = Protonated substrate.

Scheme – 1

Amino acid and peptide in the solution in presence of acid can have protonated and unprotonated form. The total concentration of the amino acid and peptide can be given as

$[S]_T = [S]_e + [SH^+]_e$ (4)
$= [S]_e + K_1[S]_e[H_+]_e$
$[S]_T = [S]_e\{ 1 + K_1[H^+]_e\}$
$[S]_e = [S]_T / \{1 + K_1[H^+]_e\}$ (5)
$Rate = k_3 [X]_e[Mn(III)]_T$
$= k_3K_2[S]_e[Mn(III)]^2$
$Rate = k_3K_2[S]_T[Mn(III)]^2 / \{1 + K_1[H^+]_e \}$ (6)
$Rate = k_{obs} [Mn(III)]_T$ (7)
Where $k_{obs} = k_3K_2[S]_T[Mn(III)]_T / \{1 + K_1[H^+]\}$ (8)
$k_{obs} / [S]_T = k_2' = k_3K_2[Mn(III)]_T / \{1 + K_1[H^+]\}$ (9)
Let $K = k_3 K_2[Mn(III)]_T$ (10)
$k_2' = K / \{1 + K_1[H^+] \}$ (11)
$1 / k_2' = \{1 + K_1[H^+]\} / K$ (12)
$1 / k_2' = 1 / K + \{K_1 / K\} [H^+]$ (13)
$1 / k_2' = 1 / k_3 K_2[Mn(III)]_T + \{K_1 / k_3 K_2[Mn(III)]_T\} [H^+]$ (14)

The rate law eq. (6) was consistent with the experimental data. The reaction was first order with respect to [substrate], second order with respect to Mn(III) and observed kinetics are similar to reported earlier [20,21].

The equilibrium constant K_1 of the fast step of Scheme I were obtained from the slopes and intercepts of the plots of $[S]_T/ k_{obs}$ *versus* $[H^+]$ from eq. 13 for different temperatures and the composite rate constant $K_2k_3 = k'$ can be obtained from the intercepts of the plot. From the equilibrium constants (K_1) and composite rate constants (k') the thermodynamic parameters and activation parameters were calculated (**Table 2**).

Table 2 Equilibrium constant (K_1) and composite rate constants ($K_2k_3 = k'$) for the reaction of $Mn(OAc)_3$ with DL-alanine and L-alanyl-l-glutamine at different temperatures and their thermodynamic parameters and activation parameters

Temp(K)	K_1(mol dm^{-3} s^{-1})		10^3 k′/mol dm^{-3} s^{-1}	
	DL-alanine	L-alanyl-l-glutamine	DL-alanine	L-alanyl-l-glutamine
295	1.73	0.323	780.77	15.76
300	1.87	0.351	1200.16	18.20
305	2.26	0.358	1764.92	20.87
310	2.78	0.374	2421.43	26.51
Thermodynamic parameters from equilibrium constants				
	DL-alanine		L-alanyl-l-glutamine	
ΔH^0 (kJ mol^{-1})	24.5 ± 5.0		6.9 ± 1.76	
ΔS^0 (J K^{-1} mol^{-1})	87.5 ± 17.2		14.6 ± 5.20	
Activation parameters from composite rate constant				
	DL-alanine		L-alanyl-l-glutamine	
$\Delta H^{\#}$ (kJ mol^{-1})	55.10 ± 3.0		23.27 ± 3.90	
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	- 24.5 ± 9.94		- 143.22 ± 12.38	

Conclusion

The kinetics of oxidation of free amino acid, DL-alanine and dipeptide L-alanyl-l-glutamine by Mn(III) in aqueous H_2SO_4 medium is first order dependence with respect to free amino acid and dipeptide but inverse order dependence with respect to H_2SO_4. The rate of oxidation of dipeptide was much slower than the free amino acid. This is due to increase difference between the functional groups and consequently weaker electrostatic effects and hydrophobicity of dipeptide. Activation parameters for oxidation of DL-alanine was $H^{\#}$ = 55.10 ± 3.0 kJ mol^{-1} and $S^{\#}$ = - 24.5 ± 9.94 J K^{-1} mole^{-1} and for dipeptide L-alanyl-l-glutamine was $H^{\#}$ = 23.27 ± 3.9 kJ mol^{-1} and $S^{\#}$ = - 143.22 ± 12.38 J K^{-1} mole^{-1}. These moderate values of activation parameter favor the electron transfer process. The $H^{\#}$ values were due to release of energy of solution changes in the transition state. Negative value of $S^{\#}$ is due to loss of degree of freedom and formation of a rigid transition state. The above mechanism shows the way of transformation of free amino acid and peptide in biological systems.

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References

[1] L. J. Boucher, *Coord. Chem. Rev.*, **1972**, **7**, 289.
[2] M. Calvin, *Rev. Pure. Appl. Chem.*, **1965**, 15, 1.
[3] G. Davies, *Coord. Chem. Rev.*, **1969**, 4, 199.

[4] K.S. Rangappa, S. Chandraju and N.M. Made Gowda, *Int. J. Chem. Kinet.*, **1998**, 30, 7.
[5] I. Pinto, B.S. Sherigara and H.V.K. Udupa, *Bull. Chem. Soc*. Japan, **1990**, 63, 3625.
[6] R. Singh, D.K. Tamta, S.K. Joshi, N. Chandra and N.D. Candpal, J. Chem. Pharm. Res., **2011**, 3(1), 529-533.
[7] I. Pinto, B.S. Sherigara and H.V.K. Udupa, *Analyst*, 1991, 116(3), 285-289.
[8] K. Ramakrishan, K.R. Shankaran and V.S. Srinivasan, Indian *J. Chem.,* **1990**, 29A, 843.
[9] K. Ishwarbhat and B.S. Sherigara, *Trans. Met. Chem.,* **1994**, 19(2), 178-182.
[10] R. Varadarajan and M. Joseph, *Indian J. Chem.,* **1980**, 19A, 1977.
[11] Kamaluddin, *Indian J. Chem.* **1980**, 19A, 491.
[12] B.S. Sherigara, K. Ishwarabhat and I. Pinto, *Amino acids*,**1995**, 8(3), 291-303.
[13] B. S. Sherigara, K. Ishwar Bhat, I. Pinto and N.M. Made Gowda, *Int. J. Chem. Kinet.*, **1995**, 27(7), 675-690.
[14] M.S. Ramachandran, T.S. Vivekanandan and S.S. Khadar, *Indian J. Chem.* **1984**, 23A, 379.
[15] S. Chandraju, B. S. Sherigara and N.M. Made Gowda, *Int. J.* Chem. *Kinet.*, **1994**, 26(11), 1105.
[16] R.R. Babu, P. Vani and L.S.A. Dikshitulu, *Indian J. Chem.*, **1975**, **13**, 1167.
[17] T.J. Kemp and W.A. Water, *J. Chem. Soc.*, **1966**, 339.
[18] B. Mohanty, J. Behera, S. Acharya, P. Mohanty and A.K. Patnaik, Int. J. of Adv. Chemistry, **2014**, 2(1), 39-43.
[19] K. Nakamato, *Infrared and Raman spectra of Inorg. and Coord. complexes*, Fifth Edn., John Willey and Sons Inc. Publication.
[20] M. A. Beg and Kamaluddin, *Indian J. Chem.*, **1975**, 13, 1167.
[21] I. Pinto, B.S. Sherigara and H.V.K. Udupa, *Analyst*, 1991, 116(3), 285-289.

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