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Kinetics of Oxidative Deamination and Decarboxylation of DL-Leucine by Acidic Permanganate in Presence of Silver Ion

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The title reaction has been carried out in moderately concentrated sulphuric acid medium. The reaction is found to be a two stage process. In both the stages the reaction follows first order behaviour with respect to each of dL-leucine and permanganate and fractional with respect to silver ion. Applicability of Zücker Hammett's and Bünnett's hypotheses exhibits that a water molecule acts as a proton abstracting agent in the rate determining stage. The activation parameters have been evaluated and a probable mechanism consistent with the observed results has been proposed.

INTRODUCTION

The study on the kinetics of oxidation of amino acids has received considerable interest by a number of workers.[1–6] However, no attempts have been made to study the oxidation reactions of permanganate ion in the presence of silver ion. Therefore, it was worthwhile to initiate the study in this regard.

EXPERIMENTAL

All the chemicals used were of BDH, AnalaR or SM 'GR' specifications. Crystalline DL-leucine (Renal, Hungary) was biochemically pure sample. Potassium permanganate and silver nitrate solutions were prepared as given by Vogel[7] and were kept covered with black paper to avoid any photochemical decomposition. Redistilled water was used to prepare all the solutions.

The progress of reaction was followed by iodometric estimations of the reaction mixture at various time intervals.

RESULTS AND DISCUSSIONS

The kinetics of oxidation of DL-leucine by permanganate in the presence of silver ion under pseudo first order conditions was investigated in the moderately concentrated sulphuric acid medium.

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It has been observed that the oxidation of DL-leucine is two stages process and both the stages are linear, indicating the first order dependency of the rate on permanganate ion concentration (Fig. 1A). It has been observed that first fast stage process follows second slower stage process.

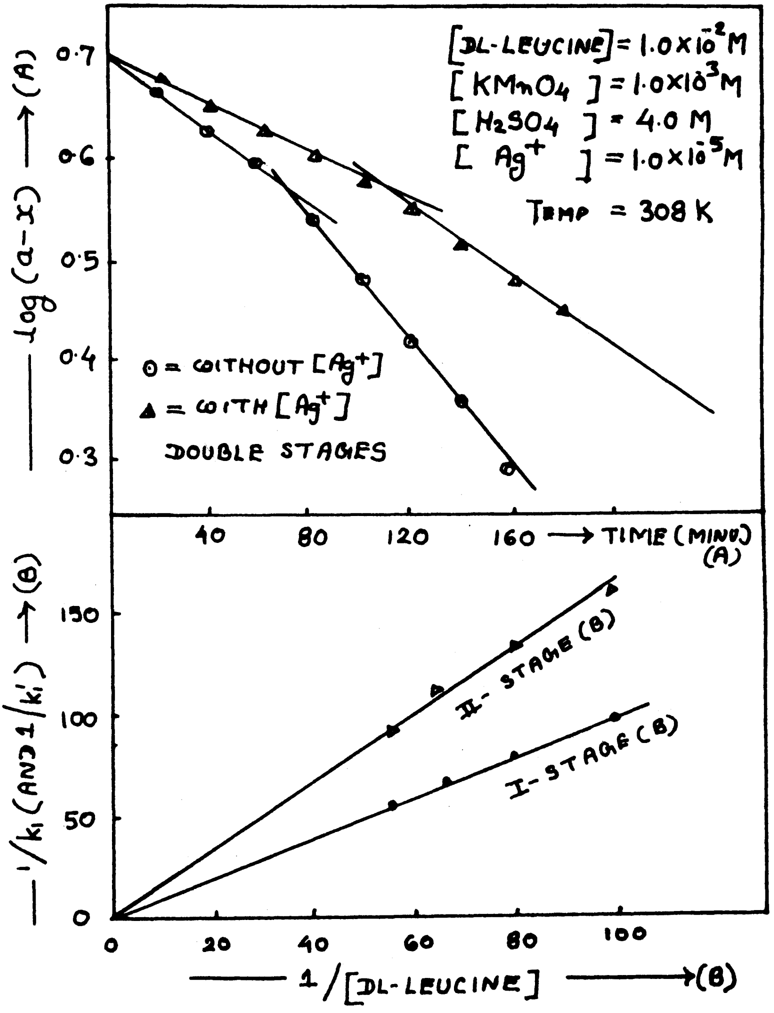

Fig. 1 (A) log (a–x) against time (B) $1/k_1$ (and $1/k_1'$) against 1/[DL-leucine]

The pseudo first order rate constants (k_1 for first stage and k_1' for second stage) increase with DL-leucine concentration. (Table1). The plots of log k_1 (and k_1') against DL-leucine concentration have been found linear with a slope value of unity. This shows that the order of the reaction is one with respect to DL-leucine for both the stages. Similarly the graphs between $1/k_1$ (and $1/k_1'$) and 1/[DL-leucine] (Fig. 1 B) give straight lines passing through the origin for both the stages thus confirming that no intermediate complex is formed[8] and if any complex is formed, its formation constant would be extremely small.[9]

TABLE-1
SUBSTRATE VARIATION

Temperature = 308 K $[KMnO_4] = 1.0 \times 10^{-3}$ M
$[H_2SO_4] = 4.0$ M $[Ag^+] = 1.0 \times 10^{-5}$ M

DL-leucine (M)	$k_1 \times 10^{-3}$ min^{-1} I stage	$k_1' \times 10^{-3}$ min^{-1} II stage	$k_s' \times 10^4$ L mol^{-1} min^{-1}	$k_s'' \times 10^4$ L mol^{-1} min^{-1}
0.0100	10.4107	6.3425	10.41	6.34
0.0125	13.1011	7.5691	10.48	6.05
0.0150	15.3155	9.2590	10.21	6.17
0.0175	18.6542	11.1411	10.65	6.36

Ave. $K_s' = 10.43 \pm 0.15$ L. mol^{-1} min^{-1}, $k_s'' = 6.23 \pm 0.12$ L mol^{-1} min^{-1}

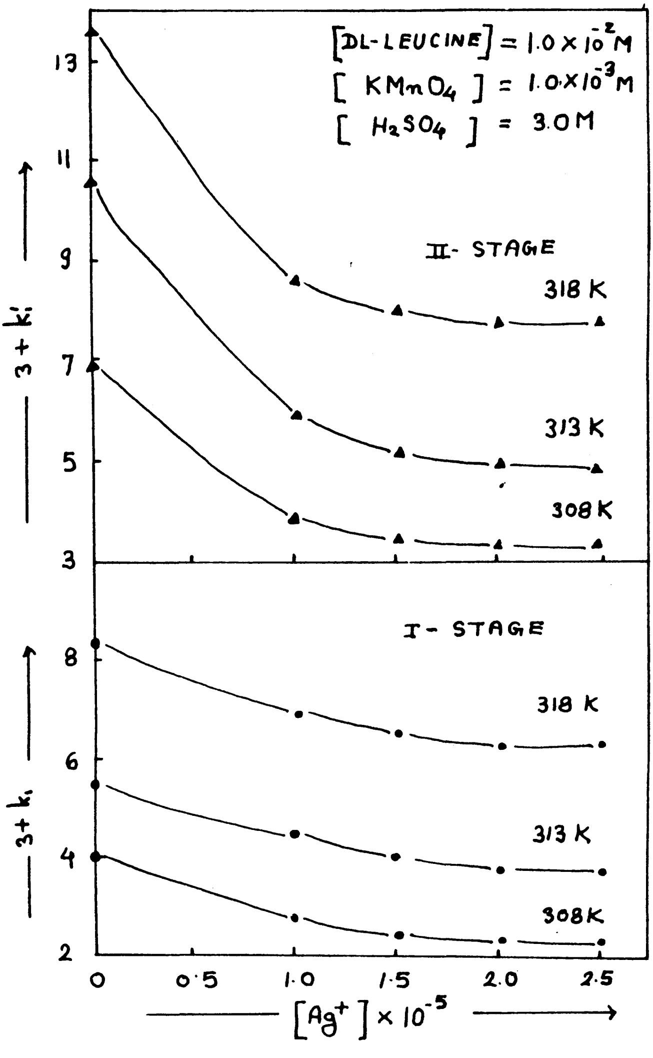

Fig. 2. k_1(and k_1') against $[Ag^+]$ at different temperatures

The Ag(I) concentration was varied at different temperatures. It was found that the reaction velocity retarts with increase in silver ion concentration and at and beyond 2.0×10^{-5} M concentration of silver ion, rate of reaction becomes constant *i.e.* no further retardation has been observed. The plots of k_1 and k_1' against silver ion concentration are not found to be straight lines (Fig. 2) suggesting that the order of reaction with respect to silver ion should be fractional.

Reaction velocities of both the stages get enhanced with H^+ concentration (Table-2). It is most probaly due to the protonation of the oxidant in accordance with the equilibrium $MnO_4^- + H^+ \rightleftarrows HMnO_4$ supported by spectral studies[10]. Similar observation in the present case lead us to suggest that $HMnO_4$ is the one of the active oxidizing species.

TABLE-2

VARIATION OF [H_2SO_4]

[DL-leucine] = 0.01 M Temperature = 308 K

[Ag^+] = 1.0×10^{-5} M [$KMnO_4$] = 1.0×10^{-3} M

H_2SO_4(M)	$k_1 \times 10^{-3}$ min^{-1}	$k_1' \times 10^{-3}$ min^{-1}	$-H_0$	$-\log {}^aH_2O$
3.5	5.7979	4.0263	1.62	0.111
4.0	10.4107	6.3425	1.85	0.142
4.5	21.0108	12.1579	2.06	0.176
5.0	45.9480	24.8378	2.28	0.219

The two Zücker-Hammett[11] plots log k against H_0 and log k against log [H^+] were found linear. This shows that the reaction is acid catalysed. However, non of the plots produces the ideal slope value of unity (Table-3). In view of these departures from ideal slope values Bünnett[12] hypothesis was tested. The slope values indicate that the water molecule should act as a proton abstracting agent in the rate determining step[12a]. The values of $-H_0$ and log ${}^aH_2O$ corresponding to given acid concentration have been taken from Paul and Long[13] and Bünnett[12b] respectively.

TABLE-3

CORRELATION OF RATE WITH ACID CONCENTRATION *i.e.* [H^+]

[DL-leucine] = 0.01 M [$KMnO_4$] = 1.0×10^{-3} M

[Ag^+] = 1.0×10^{-5} M Temperature 308 = K

Correlation	Parameters	Slope Values	
		I stage	II stage
(A) Zücker-Hammett plot	—	1.64	1.35
(i) H_0 against log k_1	—	6.73	6.00
(ii) log [acid] against log k_1			
(B) Bünnett plots			
(i) log k_1 + H_0 against log ${}^aH_2O$	W	−2.88	−2.10
(ii) log k_1 − log [acid] against log ${}^aH_2O$	W*	7.33	6.58

The specific rate increases with rise in temperature. The reaction was studied at 303, 308, 313 and at 318 K to evaluate various kinetic and activation parameters. It has been observed that oxidation reaction follows the Arrhenius relationship. Results have been summarised in Table-4.

TABLE-4
ACTIVATION PARAMETERS IN ABSENCE AND PRESENCE OF OF SILVER (I) ION

[DL-leucine] = 0.01 M $[H_2SO_4] = 3.5$ M
$[KMnO_4] = 1.0 \times 10^{-3}$ M   Temperature = 308 K

	$\Delta E^{\#}$ kcal $mole^{-1}$	$\Delta H^{\#}$ kcal $mole^{-1}$	$\Delta S^{\#}$ cal $mole^{-1}$ K^{-1}	PZ L $mole^{-1}$ min^{-1}
$[Ag^+]$ = NIL	15.39	14.78	–19.73	3.11×10^{8}
I Stage				
II Stage	13.52	12.89	–24.64	2.64×10^{7}
$[Ag^+] = 1.0 \times 10^{-5}$ M				
I Stage	18.75	17.40	–9.54	5.27×10^{10}
II Stage	16.09	15.18	–17.50	9.92×10^{8}

In this oxidation reaction presence of silver ion exerts retardation effect and reaction slow down than the reaction absence in silver ion. In such reactions higher energy of activation is expected in negatively catalysed reaction than in uncatalysed one. It is true in the present case. It may be due to the fact that the activated complex so formed has higher number of degrees of freedom and is more bulky than simple uncatalysed one. The values of entropy of activation are less and negative; hence both the stages come under the category of slow reaction as pointed out by Glasstone[14]. The negative values of entropy also suggest a bimolecular reaction in the rate determining step in the presence of water molecule as a solvent and the involvement of a proton transfer during the rate determining step.[15] Under the conditions employed the products of oxidation were identified as CO_2, iso-valeraldehyde[16] and ammonia as ammonium ions in the reaction solutions. The presence of free radicals as reaction intermediate has been confirmed by the reduction of mercuric chloride.[17] The values of energy of activation are fairly within the range of activation energy for the reactions involving free radicals.[18]

The stoichiometry of the reaction was determined by analytical method. It has been found that the five molecules of substrate require two molecules of permanganate for complete oxidation as given below.

$$5\,CH_2CH(CH_3)_2CHNH_2COOH + 2\,MnO_4^- + 11\,H^+ \xrightarrow{[Ag^+]}$$

$$5\,CH_2CH(CH_3)_2CHO + 3\,H_2O + 2\,Mn^{2+} + 5\,CO_2 + 5\,NH_4^+$$

On the basis of the kinetic results, and the discussion presented above, the following scheme of mechanism is being proposed.

$$S + H^+ \underset{\text{Acidic}}{\overset{K_1}{\rightleftharpoons}} SH^+$$

$$Ag^+ + MnO_4^- \overset{K_2}{\rightleftharpoons} AgMnO_4$$

$$AgMnO_4 + SH^+ \xrightarrow[\text{Slow Reduction}]{H_2O\ k_1} AgS' + CO_2 + H_2MnO_4$$

$$H^+ + MnO_4^- \overset{K_3}{\rightleftharpoons} HMnO_4$$

$$AgS' + HMnO_4 \xrightarrow[\text{Slow}]{H_2O\ k_2} \text{Products} + Ag^+ \ldots$$

The rate of reaction is

$$V = k_1[AgMnO_4][SH^+][H_2O] + k_2[AgS'][HMnO_4^-][H_2O]$$

$$= \left\{\frac{k_1K_1K_2[Ag^+][S][H^+]}{1 + K_1[Ag^+]} + \frac{k_2K_2K_3[Ag^+][S][H^+]}{1 + K_3[Ag^+]}\right\} [MnO_4^-] \times [{}^1H_2O]$$

So the first order rate constant is

$$k_{1st} = \left\{\frac{k_1K_1K_2[Ag^+][S][H^+]}{1 + K_1[Ag^+]} + \frac{k_2K_2K_3[Ag^+][S][H^+]}{1 + K_3[Ag^+]}\right\} {}^aH_2O$$

Therefore, overall second order rate constant is

$$k_{2nd} = \left\{\frac{k_1K_1K_2[Ag^+][H^+]}{1 + K_2[Ag^+]} + \frac{k_2K_2K_3[Ag^+][H^+]}{1 + K_3[Ag^+]}\right\} {}^aH_2O$$

$$\frac{k_{1st\ Stage}\,[Ag^+]}{1 + K_2[Ag^+]} + \frac{k_{2nd\ stage}\,[Ag']}{1 + K_2\,[Ag^+]}$$

where $k_{1st\ stage} = k_1K_1K_2[H^+]$

$k_{2nd\ stage} = k_2K_2K_3[H^+]$

It shows fractional order of silver ion in the reaction in both the stages and there is no complex formation prior to the slow step. S is for DL-leucine i.e. $CH_2CH(CH_3)_2CHNH_2COOH$.

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