



Kinetics and mechanistic study of oxidation of α -amino acid leucine by TCICA in aqueous acetic acid medium

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The kinetics of oxidation of an α -amino acid-Leucine [LEU] by trichloroisocyanuric acid [TCICA] in 50% acetic acid-50% water (v/v) solvent medium in the presence of chloride ion have been investigated. It was noted that the oxidation is first order in each [LEU], [TCICA] and fractional order with negative slope with respect to $[H^+]$. The main product of the oxidation is 2-methyl butanal. The increase of water content of the solvent medium increases the rate of the reaction indicates the reaction to be of dipole-dipole type. HOCl has been postulated as the reactive oxidizing species. A suitable mechanism has been proposed.

Keywords: Amino acid, trichloroisocyanuric acid, oxidation, kinetics, acidic medium.

Introduction

N-Halo compounds have been extensively employed as halogenating and oxidizing agent for organic substrates. Also the widespread use of variety of N-halo compounds arises from the fact that they are good sources of positive halogen¹⁻³. Trichloroisocyanuric acid [TCICA]-1,3,5-trichloro-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione is found to be more versatile oxidizing and halogenating reagent among the large variety of N-halo compounds and its kinetic and mechanistic aspects of many reactions are well documented⁴⁻⁶. The kinetics of oxidation of α -amino acid Alanine [ALA] by trichloroisocyanuric acid [TCICA] in aqueous acetic acid medium have been investigated kinetically⁷. To extend our studies on branched α -amino acid, Leucine [LEU] has been investigated in the identical conditions. Here the results of the kinetics of oxidation of a α -amino acid, Leucine [LEU] by trichloroisocyanuric acid [TCICA] in aqueous acetic acid medium in the presence of chloride ion have been reported.

Experimental

Leucine (E. Merck/AR) and trichloroisocyanuric acid (Aldrich, USA) were used as supplied. Doubly distilled water and purified acetic acid were used. Potassium chloride (AnalaR) was used as source of chloride ions. Sulphuric acid

(BDH/AR) was standardized using sodium hydroxide solution with phenolphthalein as an indicator.

Kinetic procedure:

Most of the reactions were carried out under pseudo-first order condition with large excess of [LEU] while compared with [TCICA]. The course of the reaction was followed by pipetting out 5 mL aliquot of the reaction mixture at various time intervals (as read by an accurate stop-watch) and analyzing the TCICA concentration iodometrically^{4,8}. The pseudo-first order rate constants computed from the plots of $\log(b-x)$ against time were reproducible within $\pm 3\%$ (Fig. 1).

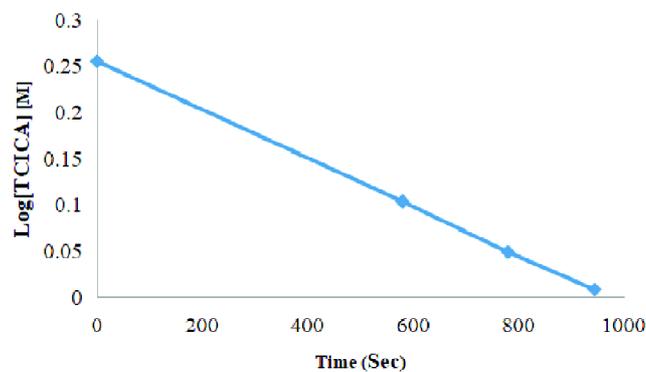


Fig. 1. First order plot: $\log [TCICA]$ vs time .

Reaction products:

0.05 M of Leucine and 0.05 M trichloroisocyanuric acid were dissolved in 50% water, 50% acetic acid (v/v) containing 0.05 M KCl. The reaction mixture as allowed to stand at room temperature for a day to completion of reaction and then the reaction mixture was poured into 25 mL of a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl with stirring. The solution was kept at low temperature for overnight to form hydrazones. The product was identified as 2-methyl butanal by the 2,4-DNP derivative.

Results and discussion

Effect of dependence of reactants concentration:

The variation of concentration of substrate [LEU] with keeping others constant. From the slope of double logarithmic plots, the reaction orders were determined. The plot of $\log k_{obs}$ against $\log [LEU]$ is linear ($r = 0.9933$) with a slope value of 0.9754 in the presence of mineral acid (Fig. 2) and a plot of k_{obs} versus [LEU] is also linear passing through the origin indicating a first order dependence on [LEU] (Fig. 3). The linearity of the plots of $\log [TCICA]$ versus time shows that the first order with respect to [TCICA] (Table 1).

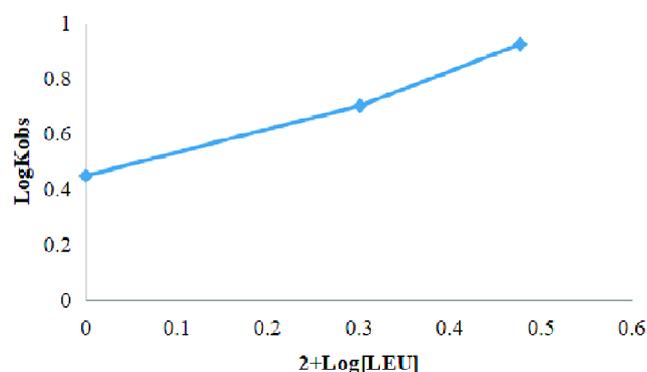


Fig. 2. Dependence of substrate: $\log k_{obs}$ vs $\log [LEU]$.

Effect of added mineral acid:

The change of concentration of mineral acid $[H^+]$ in the range of 0.1 M to 0.2 M observed that decreasing rate constants (Table 1). Also showed that inverse fractional order from linear negative slope of the plot of $\log k_{obs}$ vs $\log [H^+]$ (Fig. 4).

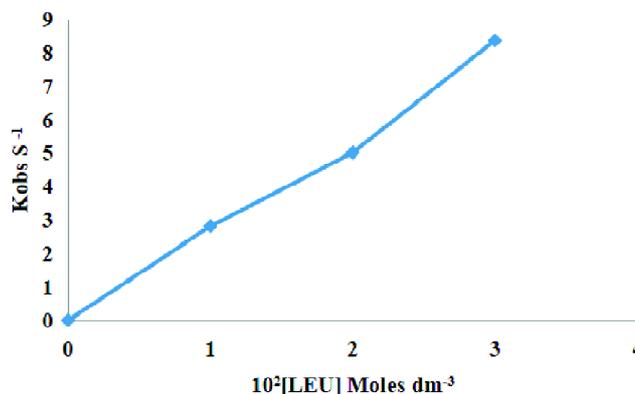


Fig. 3. k_{obs} vs [LEU].

Table 1. Rate constant for the oxidation of Leucine by TCICA in aqueous acetic acid medium at 300 K

$10^2[LEU]$ (mol dm ³)	$10^3[TCICA]$ (mol dm ³)	$[H_2SO_4]$ (mol dm ³)	$10^2[KCl]$ (mol dm ³)	CH_3COOH- $H_2O\%$ (v/v)	$10^4 k_{obs}$ (s ⁻¹)
1.0	2.0	0.1	1.0	50-50	2.81
2.0	2.0	0.1	1.0	50-50	5.01
3.0	2.0	0.1	1.0	50-50	8.36
2.0	2.0	0.1	1.0	50-50	5.01
2.0	2.0	0.15	1.0	50-50	3.89
2.0	2.0	0.2	1.0	50-50	2.98
2.0	1.0	0.1	1.0	50-50	2.32
2.0	1.5	0.1	1.0	50-50	3.80
2.0	2.0	0.1	1.0	50-50	5.01
2.0	2.0	0.1	1.0	75-25	1.55
2.0	2.0	0.1	1.0	50-50	5.01
2.0	2.0	0.1	1.0	25-75	8.54

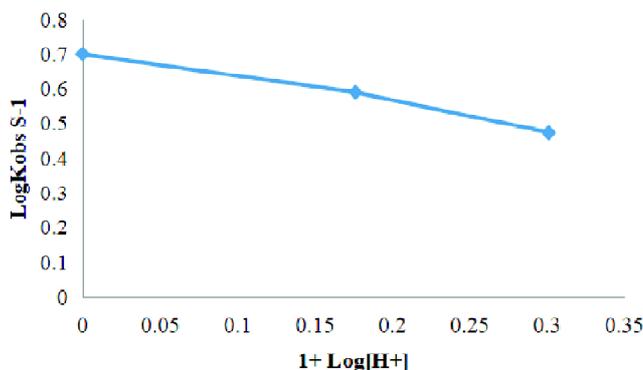


Fig. 4. Effect of added mineral acid: $\log k_{obs}$ vs $\log [H^+]$.

Effect of solvent composition:

In order to study the effect of solvent composition, the concentration of acetic acid were varied in the range of 25–75% (v/v) composition. It was observed that the rate constants are increases with decrease of acetic acid content in solvent mixture. It is attributing the rate constants are increases by increasing the dielectric constant and decreasing acidity of the medium. It is noted that a positive slope with linear curve of a plot of $\log k_{obs}$ versus $\log [H_2O]$ (Fig. 5). This is provide the evidence of the role of HOCl in oxidation reaction.

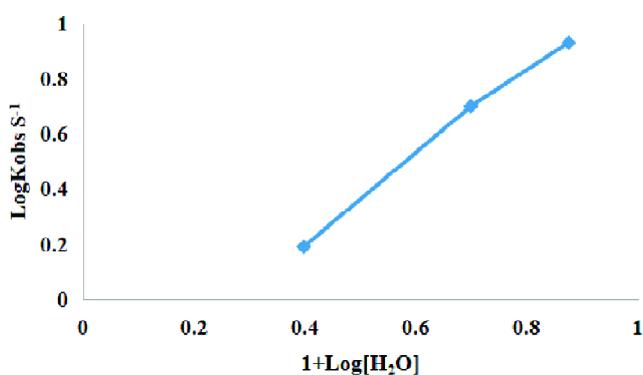
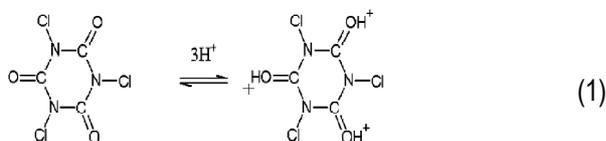


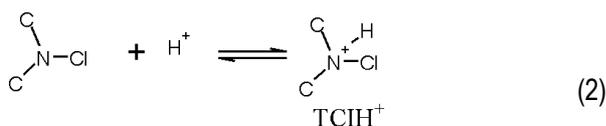
Fig. 5. Effect of solvent composition: $\log k_{obs}$ vs $\log [H_2O]$.

Mechanism:

A perusal of literature^{6,9} and from the observed kinetic results, the possible oxidizing species of TCICA is HOCl in aqueous acidic medium. The order of the reaction dependence on [TCICA] and [LEU] are unity and a negative fractional order in $[H^+]$. The TCICA exists in the following equilibrium¹⁰.

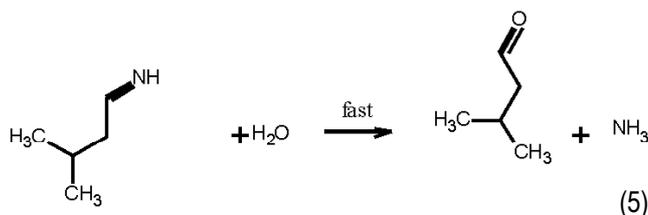
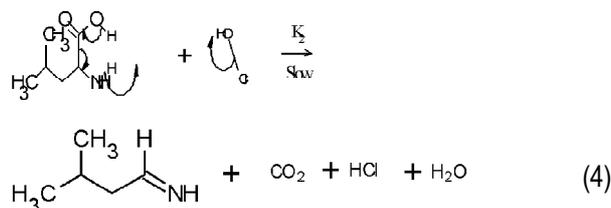
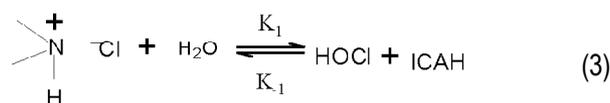


TCICA may be represented as N-chloro reagent, N-Cl. The protonated form TCIH^+ may be represented as



The hydrolysis constants of various species of TCICA are

reported by Pati Subas and Chintamani Sarangi¹¹. According to the earlier investigation on oxidation of N-halo compounds¹². The slow reactions can be traced as an interaction of HOCl and Leucine molecule, in which the amino N-H bond cleaves with the hydrogen moving away as a hydride ion. The mechanism can be proposed for the oxidation as follows in which rate law can be derived.



$$\text{Rate} = k_2 [\text{HOCl}] [\text{LEU}] \quad (6)$$

Scheme 1

The concentration of the HOCl in the above rate expression may be calculated as follows: On the assumption that all the TCICA is reacting as TCIH^+ one can find an expression for [HOCl] as follows:

$$\begin{aligned} [\text{HOCl}] &= K_1 [\text{TCIH}^+] [H_2O] / K_{-1} [\text{ICAH}] \\ &= K_1 [\text{TCIH}^+] [H_2O] / K_{-1} [\text{ICA}] [H^+] \\ \text{Rate} &= k_2 [\text{LEU}] K_1 [\text{TCIH}^+] [H_2O] / K_{-1} [\text{ICA}] [H^+] \quad (7) \end{aligned}$$

The rate law shows that reaction follows first order kinetics with respect to [TCICA], [LEU] and inverse fractional order with respect to $[H^+]$ and dielectric constant of the medium increases the rate of oxidation. The proposed mechanism is consistent with all the experimental data obtained in the present investigation.

Conclusions

In the present investigation optimum conditions for the easy oxidation of α -amino acid Leucine with TCICA in aqueous

ous acetic acid medium have been obtained. It can be concluded that the reaction between TCICA and α -amino acid proceeds by HOCl generated by TCIH^+ and unprotonated amino acid which then reacts in slow step with the abstraction of the hydrogen atom from N-H bond of the amino acid moiety as a hydride ion.

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