Kinetics of oxidation of amino acid by Trichloroisocyanuric acid in aqueous acetic acid medium

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Abstract — The kinetics of oxidation of an amino acid namely, Alanine(ALA) by Trichloroisocyanuric acid (TCICA) in aqueous acetic acid medium in the presence of added chloride ions have been investigated. The observed rate of oxidation is first order in [ALA],[TCICA] and of inverse fractional order in[H^+]. No effect on added Cl^- ions. The main product of the oxidation is acetaldehyde. The effect of changing the dielectric constant of the medium on the rate indicates the reaction to be of dipole-dipole type. Hypochlorous acid has been postulated as the reactive oxidizing species. The rate increases with electron releasing group in the amino acid moiety has been observed. A suitable mechanism consistent with the experimental results has been proposed.

Keywords: amino acid, acetic acid, trichloroisocyanuric acid, acetaldehyde, kinetics

I. INTRODUCTION

N-halogeno compounds have been extensively employed as halogenating [1] and oxidizing [2] agents for substrates. The widespread use of a variety of N-halo compounds arises from the fact that they are good source of positive halogen [3]-[4]. The nature of active oxidizing species and mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. A lot of work has been reported on the oxidation of organic compounds by N-halo compounds [5]-[10]. It is to be noted that very few systematic kinetic investigation on the oxidation of alpha amino acids by Trichloroisocyanuric acid has been reported in the literature. Here, the results of the kinetics of the oxidation of Alanine (ALA) with Trichloroisocyanuric acid (TCICA) in aqueous acetic acid medium in the presence of chloride ion have been reported.

II. EXPERIMENTAL

Alanine (Analar), Phenylalanine (Analar) 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. Most of the reactions were carried out under pseudo-first order condition [ALA] >> [TCICA]. The course of the reaction was followed by pipetting out 5mL aliquot of the reaction mixture at various time intervals (as read by an accurate stop-watch) and analyzing the TCICA concentration idometrically [11]-[12]. The initial rates were evaluated from the plots of log [oxidant] versus time and were reproducible within ± 3 %(Fig.1).

III. RESULTS AND DISCUSSION

A Reaction products

0.05M of Alanine and 0.05M trichloroisocyanuric acid were dissolved in 50% water, 50% acetic acid(v/v) containing 0.05M NaCl. The reaction mixture was allowed at 30^oC for 24h to completion and then the reaction mixture was poured into 25mL of a saturated solution of 2, 4-dinitrophenylhydrazine in 2M HCl with stirring. The solution was kept at low temperature and left overnight to ensure completion of the hydrazones formation. The product was identified as acetaldehyde by a 2,4-DNP derivative.

B. Reaction Order

The reaction orders were determined from the slope of the double logarithmic plots by varying the concentration of substrate [ALA] in turn, while keeping others constant. The plot of log kobs against log [ALA] is linear (r = 0.995) with a slope value of 0.9716 in the presence of chloride ion (Fig.2) and a plot of kobs versus [ALA] is also linear passing through the origin indicating a first order dependence on [ALA] (Fig.3). The linearity of the plots of log [TCICA] versus time indicates that the order with respect to [TCICA] is unity, which is also confirmed by the constant k_{obs} values at varying [TCICA] (Table 1).

C. Effect of added KCl

The effect of addition of KCl on the rate of oxidation of Alanine by TCICA was studied by varying the concentration of KCl in the range of 0.01M to 0.03M.(Table 1). It was observed that the negligible fractional negative dependence.

D. Effect of solvent composition

The effect of changing solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 25 – 75%. The pseudo first order increase with decrease acetic acid content of the solvent mixture. The enhancement of the reaction rate with decrease in the amount of acetic acid may generally be attributed to two factors viz (i) decrease in acidity at constant $[H^+]$ and (ii) increase in dielectric constant with increase in water content. A plot of $\log k_{obs}$ against composition of H_2O is linear with positive slope (Fig. 4). This supports the postulation of HOCl as the reactive species.

Table 1. Rate constant for the oxidation of Alanine by TCICA in aqueous acetic acid medium at 30^0C

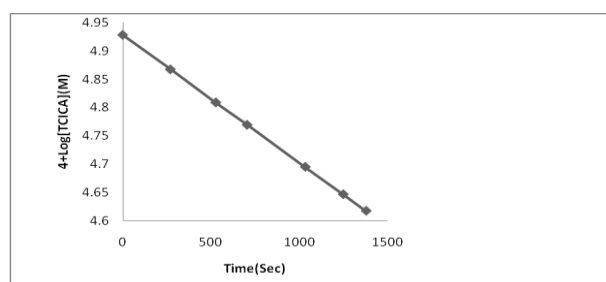| $10^2[ALA]$ Mol dm^{-3}	$10^3[TCICA]$ Mol dm^{-3}	$[H^+]$ mol dm^{-3}	$10^2[KCl]$mol dm^{-3}	CH$_3$COOH- H$_2$O% (v/v)	$10^2[PLA]$ Mol dm^{-3}	10^4K_{obs} s^{-1}
1.0	1.0	0.1	1.0	50-50	-	5.15
1.5	1.0	0.1	1.0	50-50	-	7.53
2.0	1.0	0.1	1.0	50-50	-	10.11
2.5	1.0	0.1	1.0	50-50	-	12.62
1.0	1.0	0.1	1.0	50-50	-	5.15
1.0	1.0	0.15	1.0	50-50	-	3.64
1.0	1.0	0.2	1.0	50-50	-	3.33
1.0	1.0	0.1	1.0	50-50	-	5.15
1.0	2.0	0.1	1.0	50-50	-	4.91
1.0	3.0	0.1	1.0	50-50	-	5.06
1.0	1.0	0.1	1.0	50-50	-	5.15
1.0	1.0	0.1	2.0	50-50	-	4.94
1.0	1.0	0.1	3.0	50-50	-	4.76
1.0	1.0	0.1	1.0	75-25	-	1.69
1.0	1.0	0.1	1.0	50-50	-	5.15
1.0	1.0	0.1	1.0	25-75	-	8.68
1.0	1.0	0.1	1.0	50-50		5.15
	1.0	0.1	1.0	50-50	1.0	4.86

Fig.1 Log[TCICA] Vs time

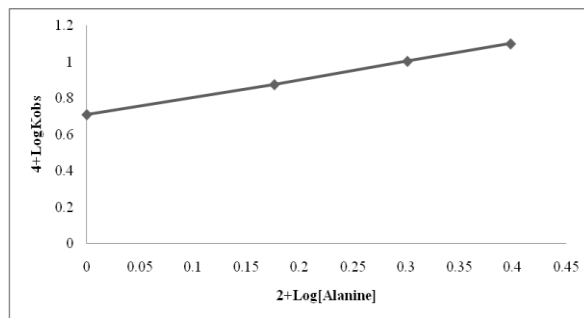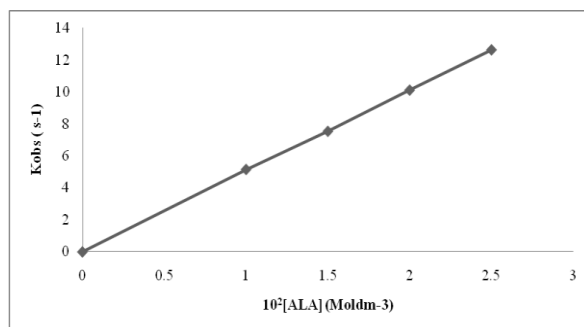Fig.2 Log K_{obs} Vs Log [ALA]
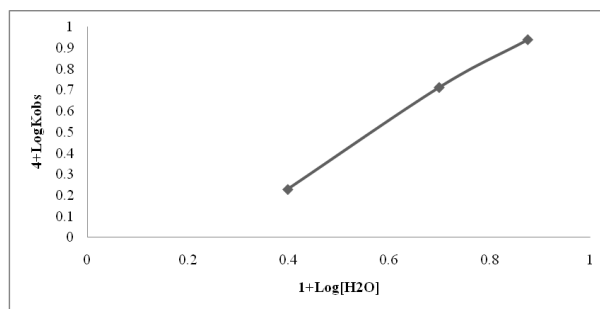

Fig. 3 Kobs Vs [ALA]

Fig.4 Log Kobs Vs Log [H$_2$O]

E. Effect of mineral acid

The pseudo first order rate constant decrease with increase in $[H^+]$ in the range 0.1M to 0.2M (Table 1). The plot of $\log k_{obs}$ versus log $[H^+]$ is linear with negative slope indicating inverse fractional order dependence on $[H^+]$ (Fig. 5).
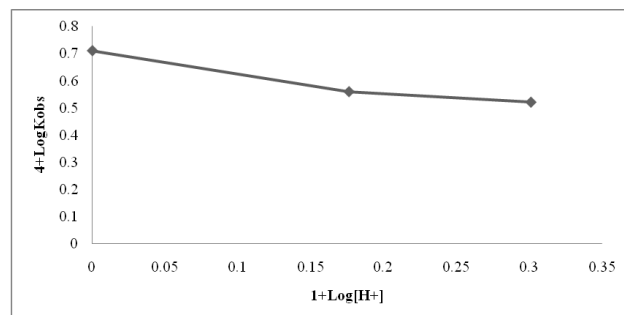

Fig. 5 Log Kobs Vs Log $[H^+]$

F. Effect of substituent

The oxidation of Alanine and phenylalanine were carried out in the identical conditions. The values of

reaction constants are shown in Table1. It is interesting to note that the reactivity for substituent in the order: Methyl > Phenyl.

It is clear from the data that electron releasing group increases the rate and vice versa. The polar effects of the substituent are more important than the resonance effects.

G. Mechanism

It is clear from the literature [5] & [13] that the probable reactive species of TCICA in acid solution is HOCl. The reaction is first order in [TCICA] and [ALA] and inverse fractional order in [H$^+$]. It is quiet likely that under the condition of solvent medium employed the TCICA exists in the following equilibrium [14].


(1)
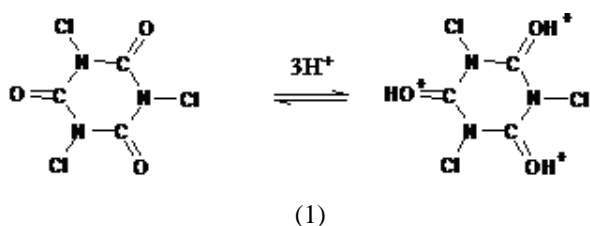
Although TCICA has three such potentially reactive centers, it may be represented as N-Chloro reagent, N-Cl. The protonated form TCIH$^+$ may be represented as

(2)
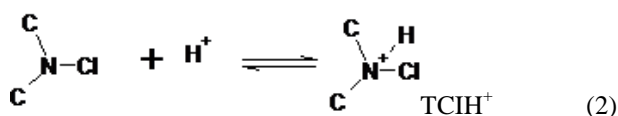
The hydrolysis constants of various species of TCICA are reported by Subas C Pati and Chintamani Sarangi [15]. According to them the first stage of hydrolysis seems to be kinetically important one. Therefore the predominant reactive species is assumed to be HOCl.

Among the four probable oxidizing species in the reaction, viz TCICA, TCIH$^+$, HOCl and H$_2$OCl$^+$, the HOCl is considered as the active oxidizing species since the rate is an inverse function of [H$^+$]. The solvent effect does point out that the reaction with unprotonated alanine should be more predominant.

Based on the earlier kinetic work on oxidation of N-halo compounds [16]-[18], one can reasonably suggest that the most likely oxidizing species is HOCl under acidic condition. If the slow reactions can be traced as an interaction of HOCl and alanine molecule, in which the amino N-H bond of the amino acid moiety is involved and that this N-H bond breaks with the hydrogen going away as a hydride ion. More specifically in the present case, one can suggest a slow step involving a cyclic transition state. The following mechanism can be proposed for the oxidation for which the rate law can be derived

(3)

[Complex]

(4)

(5)
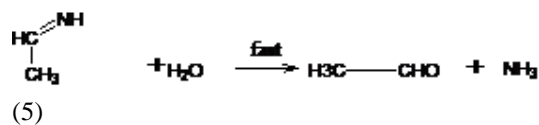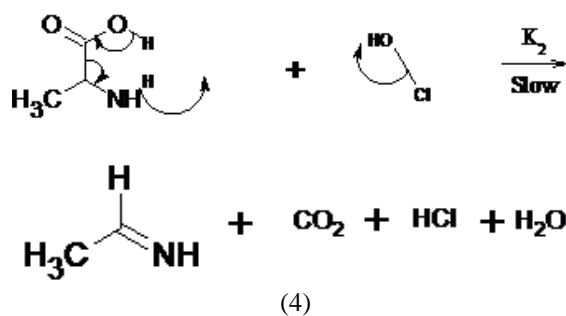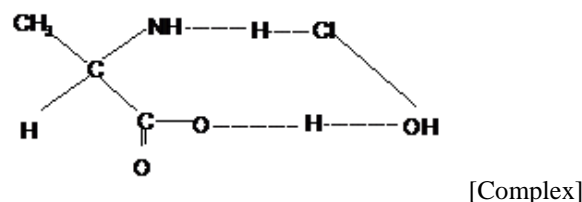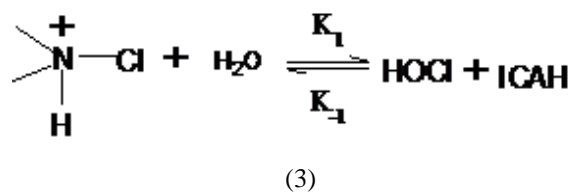
Rate = K_2 [HOCl] [ALA]   (6)

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.

$$[HOCl] = K_1[TCIH^+][H_2O] / K_{-1} [ICAH]$$
$$= K_1[TCIH^+][H_2O] / K_{-1}[ICA][H^+]$$
$$Rate = K_2[ALA] K_1[TCIH^+][H_2O] / K_{-1}[ICA][H^+]   (7)$$

The rate law shows that reaction follows first order kinetics with respect to [TCICA], [ALA] and inverse fractional order kinetics with respect to [H$^+$] negligible influence of changes in [Cl$^-$] and the effect of dielectric constant of the medium on the rate of oxidation. The proposed mechanism is consistent with all the experimental data obtained in the present study.

IV CONCLUSION

Thus, it may be concluded that the reaction between TCICA and amino acid proceeds by a rapid formation of a cyclic transition state between 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.

V. ACKNOWLEDGEMENT

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