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β-Cyclodextrin catalyzed oxidation of some α-amino acids with chloramine-T in alkaline medium: Kinetics and mechanistic studies

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ABSTRACT

The kinetics of oxidation of α-amino acids (AAs) by chloramine-T (CAT) using β-cyclodextrin (BCD) as catalyst was studied in aqueous sodium hydroxide medium at 313 K. The kinetics of reactions was fractional-order with respect to [amino acids] and [β-cyclodextrin]. First-order with respect to [chloramine-T] and inverse fractional-order with respect to [OH^-] have been found. Effect of ionic strength, added salt and reaction product (PTS) had no effect on reaction rate. The dependence of the reaction rate on temperature was studied and activation parameters were computed from Arrhenius–Eyring plots. The reaction mechanism and the derived rate law are consistent with the observed experimental results.

1. Introduction

Aromatic *N*-halosulfonamides, a group of mild oxidizing agents, have been extensively used for the oxidation of a variety of organic compounds, including aldehydes, amines, and amino acids [1–3]. These oxidants contain strongly polarized *n*-linked halogens which are in +1 state. They undergo two electron changes to form prominent member of this class of oxidants that is *N*-chloro-*p*-toluene sulfonamide (chloramines-T, abbreviated as CAT or RNClNa).

Previously, kinetics and mechanism of oxidation of neutral L-amino acids by sodium *N*-chloro-*p*-toulene sulfonamide in acid medium have been reported [4]. Oxidations of α-amino acids by CAT in aqueous acid medium were investigated by Quine et al. [5].

Pyridine catalyzed oxidative decarboxylation of aminoacids by chloramine-T in aqueous acid medium has been reported by Quine and Gowda [6]. Recently Gowda and Geetha [7] reported the role of chloride and sulfate ions in kinetics of oxidative decarboxylation of amino acids. OsO_4 catalyzed oxidation of aspartic acid by chloramine-T in alkaline medium was investigated by Suryanarayana and Ramam [8]. It was found to be first order with respect to [CAT], [ASP] and [Os (VIII)].

The kinetics of OsO_4 catalyzed oxidation of glycine by CAT in alkaline medium has been studied by Lakshmi and Ramam [9]. The oxidation follows first-order kinetics with respect to [CAT] and [AA] and inversely proportional to [OH^-]. The kinetic results were consistent with a mechanism involving the formation of adduct between Os (VIII) and amino acids. Neutral salts such as NaCl, KCl and $NaNO_3$ were found to have negligible effects on the rate of the reaction.

However, β-cyclodextrin catalyzed oxidation of α-amino acids with chloramine-T in alkaline medium has not been reported. Therefore, we investigated β-cyclodextrin catalyzed oxidation of α-amino acids by chloramine-T in alkaline medium. In the present studies, the oxidation behavior of chloramine-T towards AAs in alkaline medium has been studied extensively.

2. Experimental

2.1. Materials

α-Amino acids Glycine, Valine, Leucine, and Alanine were purchased from Sigma Chemicals (St. Louis, MO). Chloramine-T and

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Table 1
Effect of varying reactant concentration on the reaction rate with $[OH^-] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[BCD] = 3.0 \times 10^{-3}$ mol dm^{-3}; $T = 313$ K.

$[CAT] \times 10^4$ mol dm^{-3}	$[AA] \times 10^4$ mol dm^{-3}	$k_{obs} \times 10^4$ (s^{-1})			
		Glycine	Valine	Leucine	Alanine
3.0	0.5	2.52	13.78	18.46	28.28
4.0	0.5	2.47	13.69	18.50	28.25
5.0	0.5	2.55	13.77	18.48	28.28
6.0	0.5	2.58	13.75	18.52	28.31
0.5	2.5	2.50	13.79	18.43	28.26
0.5	3.5	1.68	9.02	18.20	11.11
0.5	5.0	–	10.93	22.80	–
0.5	7.5	3.22	15.83	–	20.05
0.5	8.0	–	–	36.08	–
0.5	10.0	4.06	17.50	–	24.94
0.5	15.0	4.79	19.85	–	18.83

β-cyclodextrin were purchased from E-Merck. All other reagents were of analytical grade.

2.2. Preparation of chloramine-T

Chloramine-T was purified by the method of Morris et al. [10]. The aqueous solution of CAT was prepared afresh each day and its strength was checked iodometrically [11] and stored in amber-colored, stoppered bottles until further use. Aqueous solutions of AAs of known concentrations were prepared. A solution of BCD in 0.05 mol dm^{-3} in NaOH was used as the catalyst. The reaction product (*p*-toluene sulfonamide) was also prepared in alkali medium. All other reagents were of analytical grade. Double distilled water was used throughout the investigation.

2.3. Kinetic measurements

The kinetics was carried out under pseudo-first-order conditions by taking a known excess of $[substrate]_0$ over $[oxidant]_0$ at 313 K. The reactions were carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. For each run, requisite amounts of solutions of substrate, NaOH, catalyst and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 313 K until thermal equilibrium was attained. A measured amount of CAT solution, which was also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The course of the reaction was monitored by the iodometric determination of unreacted CAT in 5 ml of aliquots of the reaction mixture withdrawn at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudo-first-order rate constant (k_{obs}) calculated from the linear plots of log [CAT] versus time was reproducible within ±3% error. Regression analysis of experimental data to obtain regression coefficient, *r*, was performed using an EC-72 statistical calculator.

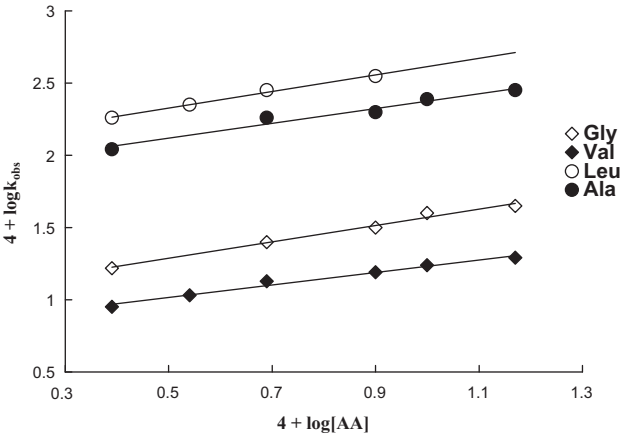


Fig. 1. Effect of [AA] on the reaction rate.

3. Results

3.1. Dependence of rate on [CAT], [AA]

All kinetic runs were performed under pseudo-first-order conditions with $[AA]_0 \gg [CAT]_0$. Plots of log [CAT] versus time ($r = 0.997$), which were linear with slopes 0.99, 1.03, 1.05 and 0.98 for over 75% of the reaction, showing a first-order dependence of the rate on $[CAT]_0$ (Table 1). At constant $[CAT]_0$, $[Product]_0$, $[NaOH]_0$, $[BCD]_0$ and temperature, the rate increased with increase in $[AA]_0$ (Table 1). Plots of log k_{obs} versus log $[AA]_0$ (Fig. 1) were linear with slopes 0.57, 0.45, 0.52, and 0.54 for Glycine, Valine, Leucine and Alanine respectively, indicating fractional order dependence on the substrate.

3.2. Dependence of the rate on [NaOH]

At constant [AA], [CAT] and [BCD], the values of k_{obs} decreased with an increase in $[OH^-]$ (Table 2]. The order of reaction in hydroxide ion was calculated from the slope of plots of k_{obs} versus

Table 2
Effect of varying base concentration on the reaction rate with $[AA] = 0.5 \times 10^{-4}$ mol dm^{-3}; $[CAT] = 5.0 \times 10^{-4}$ mol dm^{-3}; $[BCD] = 3.0 \times 10^{-3}$ mol dm^{-3}; $T = 313$ K.

$[HO^-] \times 10^3$ mol dm^{-3}	$k_{obs} \times 10^4$ (s^{-1})			
	Glycine	Valine	Leucine	Alanine
0.25	5.32	19.26	–	29.57
0.50	3.56	15.99	39.43	22.84
0.75	2.94	14.60	33.46	20.11
1.00	2.55	13.77	28.28	18.48
1.50	1.99	11.73	24.10	14.54
2.00	1.45	10.73	20.86	13.60

Table 3
Effect of varying catalyst concentration [BCD] on the reaction rate with [AA] = 0.5×10^{-4} mol dm^{-3}; [CAT] = 5.0×10^{-4} mol dm^{-3}; [OH$^-$] = 1.0×10^{-3} mol dm^{-3}; T = 313 K.

[BCD] $\times 10^3$ mol dm^{-3}	$k_{obs} \times 10^4$ (s^{-1})			
	Glycine	Valine	Leucine	Alanine
1.0	1.23	9.13	16.35	11.00
2.0	2.03	11.93	24.00	15.36
3.0	2.55	13.77	28.28	18.48
4.0	3.00	15.59	32.96	21.31
5.0	3.51	16.73	35.72	23.58

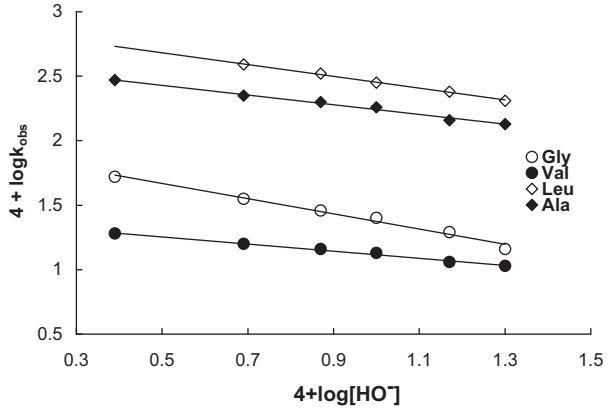


Fig. 2. Effect of [OH$^-$] on the rate of reaction.

log [OH$^-$] (Fig. 2). The data reveal that the reaction follows an inverse fractional order dependence on [OH$^-$].

3.3. Dependence of the rate on catalyst [BCD]

The rate of a reaction increased with increase in [BCD] (Table 3). Plot log k_{obs} versus log [BCD] was linear with slope less than unit, indicating fractional order dependence on catalyst (Fig. 3).

3.4. Dependence of the rate on ionic strength, added salt, reduction product

Ionic strength of the reaction mixture was varied by adding $NaClO_4$ solution (0.1–0.5 mol dm^{-3}). It was seen that, variation of the ionic strength had no effect on the rate of reaction. Addition of Cl^- ion in the form of NaCl (0.02–0.1 mol dm^{-3}) on the rate was insignificant. The effect on the rate of varying concentration of *p*-toluene sulfonamide (which is the reduction product of the oxidant, CAT) was investigated. An increase in [*p*-toluene sulfonamide] (from 0.01 to 0.08 mol dm^{-3}), had no effect on the rate, indicating that the product is not involved in a pre-equilibrium to the rate limiting step.

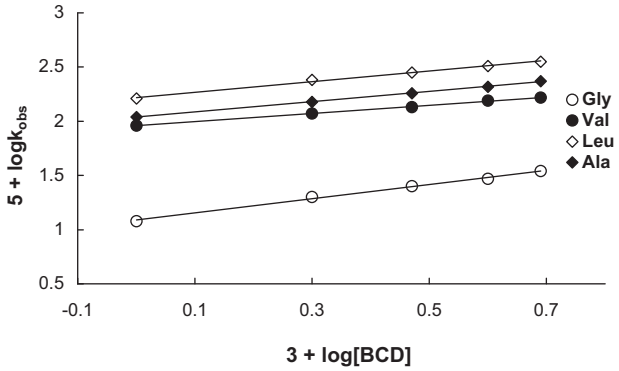


Fig. 3. Effect of [BCD] on the rate of reaction.

3.5. Effect of solvent composition on reaction rate

The dielectric constant of the medium was varied by adding methanol (0.0–40%) to the reaction mixture. It is observed that rate decreased with increasing proportion of methanol in case of Glycine and Leucine, while straight line was noticed with Valine and Alanine. In the present investigations, plots of log k_{obs} versus $1/D$ (D is dielectric constant of the medium) were linear (Table 4, Fig. 4) with a negative slope for Glycine. This observation indicates the dipole–dipole interactions. Blank experiments (without adding substrate) performed showed that methanol is not oxidized by CAT under experimental conditions.

3.6. Activation parameters

To determine the activation parameters, the reactions were carried out at different temperature (303–323 K, Table 5). Arrhenius plots log k_{obs} versus $1/T$ (Fig. 5) which were linear with slopes 0.99, 1.04, 1.03 and 0.97 used to calculate activation energies (E_a). Based on these values, the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ along with the frequency factor (log A) were evaluated (Table 6). The moderate values of $\Delta H^{\ddagger}$ and the firmly high value of $\Delta G^{\ddagger}$ support the mechanism. The near constancy of $\Delta G^{\ddagger}$ values indicates a solvated AA operation of similar mechanism for the oxidation of all AAs.

3.7. Test for free radical

Addition of reaction mixture to aqueous acrylamide monomer solutions did not initiate polymerization, showing the absence of *in situ* formation of free radical species in the reaction.

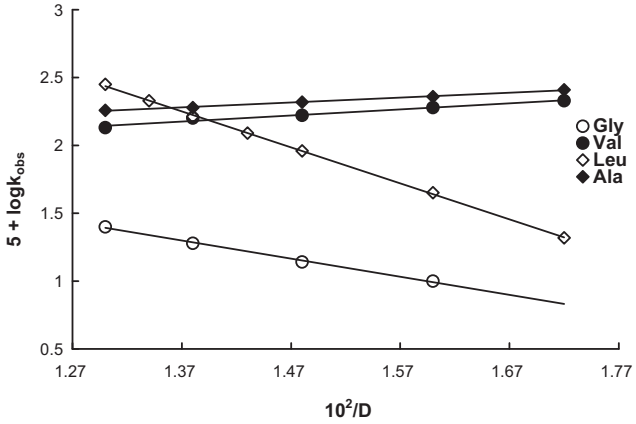


Fig. 4. Effect of varying dielectric constant (D) on the rate reaction.

Table 4
Effect of varying solvent composition (0.0–40%) on the reaction rate with [AA] = 0.5×10^{-4} mol dm^{-3}; [CAT] = 5.0×10^{-4} mol dm^{-3}; [BCD] = 3.0×10^{-3} mol dm^{-3}; [OH^-] = 1.0×10^{-3} mol dm^{-3}; T = 313 K.

Methanol (% v/v)	Dielectric constant $1/D \times 10^2$	$k_{obs} \times 10^4$ (s^{-1})			
		Glycine	Valine	Leucine	Alanine
00	1.30	2.55	13.77	28.28	18.48
05	1.34	–	–	21.60	–
10	1.38	1.94	15.93	16.22	19.25
15	1.43	–	–	12.52	–
20	1.48	1.39	–	12.52	–
30	1.60	1.02	19.19	4.51	23.03
40	1.72	–	21.80	2.11	25.73

Table 5
Temperature dependence of the oxidation of AA with [CAT] = 5.0×10^{-4} mol dm^{-3}; [AA] = 0.5×10^{-4} mol dm^{-3}; [BCD] = 3.0×10^{-3} mol dm^{-3}; [OH^-] = 1.0×10^{-3} mol dm^{-3}.

Temperature (K)	$(1/T) \times 10^3$ (K^{-1})	$k_{obs} \times 10^4$ (s^{-1})			
		Glycine	Valine	Leucine	Alanine
303	3.30	0.805	4.094	7.96	5.32
308	3.24	1.535	7.276	13.59	9.07
310	3.22	–	–	18.025	11.37
313	3.19	2.558	13.778	28.28	18.48
316	3.16	4.138	21.938	–	–
323	3.09	7.194	36.516	–	–

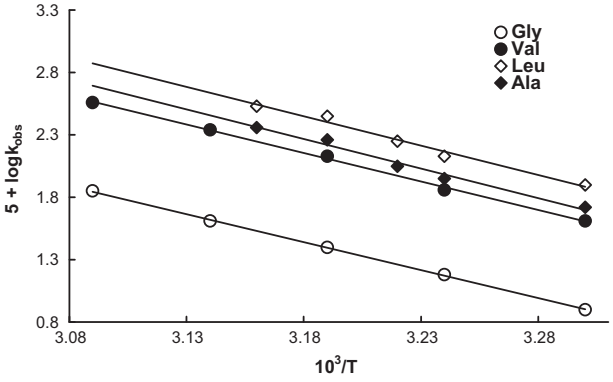


Fig. 5. Effect of temperature on the rate of reaction.

3.8. Stoichiometry

Reaction mixtures containing AA (0.5×10^{-4} mol dm^{-3}), sodium hydroxide (0.1×10^{-2} mol dm^{-3}), BCD (0.3×10^{-2} mol dm^{-3}) and excess CAT (5.0×10^{-4} mol dm^{-3}) were kept at 313 K for 48 h. Estimation of unreacted CAT showed that one mole of oxidant was sufficient to oxidize 1 mole of amino acid leading to products aldehydes, ammonia, carbon dioxide and *p*-toluene sulfonamide (oxidation product).

Based on these results, the following stoichiometry equations were suggested.

A general stoichiometry equation for AA:

$$R'CH(NH_2)COOH + RNHClN_a + H_2O \rightarrow R'CHO + RNH_2 + NH_3 + CO_2 + NaCl. \quad (1.1)$$

where R' = –H for Glycine; $(CH_3)_2CH$– for Valine; $(CH_3)_2CHCH_2$– for Leucine and $-CH_3$ for Alanine. R represents the aromatic moiety $CH_3C_6H_5SO_2$. Stoichiometry experiments were also carried out under experimental conditions where (amino acid) > (CAT).

3.9. Product analysis

By micro Kjeldal procedure, the ammonia which is present in the reaction mixture was estimated quantitatively. In a typical experiment 2.5×10^{-5} mol dm^{-3} of [CAT] were mixed with 2×10^{-3} mol dm^{-3} of AA in a total volume of 20 ml under experimental conditions. The ammonia formed was distilled and absorbed in 2% boric acid solution. It was then titrated against 0.01 mol dm^{-3} HCl using a mixed indicator (methyl red bromocresol green). The solution consumed 2.5 ml of 0.01 mol dm^{-3} HCl corresponding to the formation of 2.5×10^{-5} mol dm^{-3} of NH_3. The liberated CO_2 was identified by the conventional limewater test. The aldehydes were characterized by their 2,4-dinitrophenyl hydrazine (2,4-DNP) derivatives. The *p*-toluene sulfonamide (PTS) reaction product was detected by paper chromatography using benzyl alcohol saturated with water as the solvent and 0.5% vanillin in 1% HCl solution in ethanol as spray reagent (R_f = 0.905).

4. Discussion

From the above results the rate shows first-order dependence on [CAT] and fractional order in substrate, catalyst and inverse fractional in [OH^-]. The experimental rate law is thus given by Eq. (1.2).

$$\frac{-d[CAT]}{dt} = k'[CAT][BCD]^x[S]^y[OH^-]^{-z} \quad (1.2)$$

where *x*, *y* and *z* are fractions (<1.0).

Table 6
Activation parameters for the oxidation of AA by [CAT] = 5.0×10^{-4} mol dm^{-3}; [AA] = 0.5×10^{-4} mol dm^{-3}; [BCD] = 3.0×10^{-3} mol dm^{-3}; [OH^-] = 1.0×10^{-3} mol dm^{-3}.

Substrate	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J k^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	Log *A*
Glycine	91.92	89.32 ± 0.3	−28.93 ± 0.4	98.38 ± 0.5	11.69
Valine	90.96	88.35 ± 0.5	−18.35 ± 0.2	94.09 ± 0.3	12.88
Leucine	79.79	77.21 ± 0.2	−48.74 ± 0.6	92.32 ± 0.2	10.69
Alanine	86.17	83.59 ± 0.1	−31.62 ± 0.7	93.40 ± 0.3	11.62

The oxidation potential of chloramine-T–sulfonamide system is pH dependent and decrease with increase in pH of the medium (1.14 V at pH 0.65 and 0.5 V at pH 12). It has been reported by Pryde and Soper [12], Morris et al. [13] and Bishop and Jennings [14] that chloramine-T behaves as strong electrolyte in aqueous solution forming different species whose equilibria [14–17] are represented by Eqs. (1.3)–(1.7).

$$TsNClNa \rightleftharpoons TsNCl^- + Na^+ \quad (1.3)$$

$$TsNCl^- + H^+ \rightleftharpoons TsNHCl \quad (1.4)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \quad (1.5)$$

$$2TsNHCl \rightleftharpoons TsNH_2 + TsNCl_2 \quad (1.6)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \quad (1.7)$$

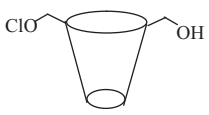
In acidic medium the probable oxidizing species are T_SNHCl^-, dichloramine-T (T_SNCl_2), HOCl and H_2OCl^+. However in alkaline solution T_SNCl_2 and H_2OCl^+ do not exist. The species T_SNHCl^-, HOCl and T_SNCl^- can be considered to be reactive species. In addition to OCl^- formed in the equilibrium given by Eq. (1.8). Other equilibrium of T_SNCl^- is given in Eqs. (1.9) and (1.10).

$$TsNCl^- + H_2O \rightleftharpoons TsNH_2 + OCl^- \quad (1.8)$$

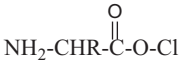
$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad (1.9)$$

$$TsNCl^- + H_2O \rightleftharpoons TsNHCl + OH^- \quad (2.0)$$

If HOCl were to be considered as oxidizing species, a first-order retardation, of rate on added T_SNH_2 (reaction product toluene sulfonamide) was expected. However, there was no such effect is seen, since no effect on reaction rate. A retarding influence of $[OH^-]$ on the reaction rate has been observed in many reactions. This can be explained by the equilibrium given by Eq. (2.0) where in the free acid TsHCl is formed from TsHCl in aqueous solution. Thus in the present investigation the inverse fractional order in $[OH^-]$ suggests T_SNHCl as the most likely oxidizing species [15–19]. The fractional order of the catalyst (BCD) and substrate indicates that the oxidizing species form a complex (X) with the catalyst (BCD) which



(X)



(X')

(The tumbler shape denotes the catalyst BCD)

Scheme 1.

interacts with the substrate (S) to form an intermediate (X') that rearranges in aqueous solution, in a slow step to give the products. These sequences are summarized in the eqs. (2.1)–(2.4) and Scheme 1

$$TsNCl^- + H_2O \overset{K_1}{\rightleftharpoons} TsNHCl^- \quad (2.1)$$

$$TsNHCl^- + BCD \overset{K_2}{\rightleftharpoons} X \quad (2.2)$$

$$X + S \overset{K_3}{\rightleftharpoons} X' \quad (2.3)$$

$$X' + OH^- \xrightarrow{k_4} \text{Products (slow and rds)} \quad (2.4)$$

If the intermediate complex X and X' can be represented in Scheme 1

$[CAT]_t$ represents total effective concentration of CAT; then from the above eqs. (2.1)–(2.4), it can be written as

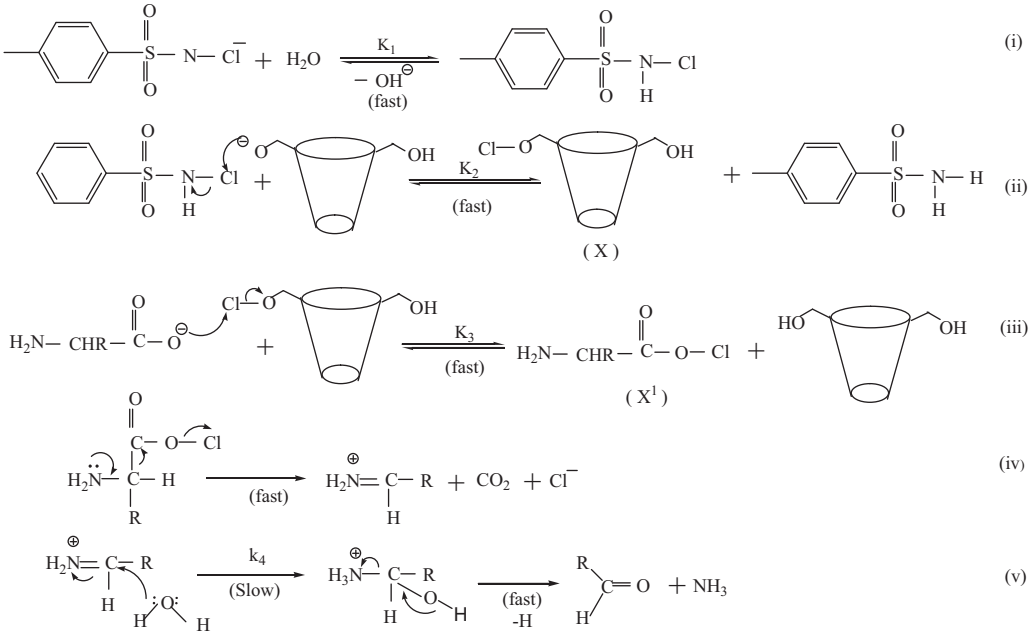
$$[CAT]_t = TsNCl + X + X' \quad (2.5)$$

$$\text{Sincerate} = k_4[H_2O][X'] \quad (2.6)$$

But

$$X = \frac{X'}{K_3[S]} \quad \text{and}$$

$$X' = \frac{K_3 K_2 K_1[BCD][H_2O][S][CAT]_t}{[OH^-] + K_1[H_2O]K_2K_1[BCD][H_2O] + K_3K_2K_1[BCD][H_2O][S]}$$



Scheme 2.

Substituting for X' in Eq. (2.5) we have

$$\frac{-d[CAT]}{dt} = \frac{k_4K_3K_2K_1[BCD][H_2O]^2[S][CAT]_t}{[OH-] + K_1[H_2O]K_2K_1[BCD][H_2O] + K_3K_2K_1[BCD][H_2O][S]} \quad (2.7)$$

But the observed rate is given by

$$\text{Rate} = k'[CAT]_t \quad (2.8)$$

Hence we can write

$$k' = \frac{k_4K_3K_2K_1[BCD][H_2O]^2[S]}{[OH-] + K_1[H_2O]K_2K_1[BCD][H_2O] + K_3K_2K_1[BCD][H_2O][S]} \quad (2.9)$$

Eq. (2.7) is identical with the experimental rate law (2.7) and thus explains the observed kinetic behavior (**S_1**); it also thus supports the proposed Scheme 2.

Plots of 1/k' versus [OH^-], 1/k' versus 1/[BCD] and 1/k' versus 1/[S] gives straight line (**S_3**). From the slope and intercept, the values of k_4, K_1, K_2 and K_3 have been evaluated (**S_2**). It can be seen that k_4 has a low value supporting eqs. (2.1)–(2.4) and step V in Scheme 2 where step V has been proposed as rate limiting step. In the light of the experimental results, a suitable β-cyclodextrin (BCD) catalyzed mechanism for AA in Scheme 2 has been proposed.

A negative $\Delta S^{\#}$ value also supports the proposed mechanism and indicates the formation of transition state fairly rapidly with lower degree of freedom. This is also supported by large values of K_2 and K_3. Further the other thermodynamic parameters also support the proposed Schemes 1 and 2 and the high value of free energy of activation suggests a solvated activated complex.

5. Conclusion

Kinetics and mechanism of the oxidation of α-amino acids viz., glycine, valine, leucine, alanine by CAT in aqueous alkaline medium in presence of β-cyclodextrin as catalyst at 313 K were discussed. It shows first-order dependence on $[CAT]_0$, fractional order on $[AA]_0$, catalyst $[BCD]_0$ and inverse fractional order on [OH^-]. The thermodynamic parameters have been evaluated. Aldehydes are the main products of the reaction and suitable kinetic mechanism has been proposed.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.11.013.

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