

## $\beta$ -Cyclodextrin catalyzed oxidation of some $\alpha$ -amino acids with chloramine-T in alkaline medium: Kinetics and mechanistic studies

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### ABSTRACT

The kinetics of oxidation of  $\alpha$ -amino acids (AAs) by chloramine-T (CAT) using  $\beta$ -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 [ $\beta$ -cyclodextrin]. First-order with respect to [chloramine-T] and inverse fractional-order with respect to [ $\text{OH}^-$ ] 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.

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## 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 RNCINA).

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

Pyridine catalyzed oxidative decarboxylation of amino acids 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.  $\text{OsO}_4$  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  $\text{OsO}_4$  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 [ $\text{OH}^-$ ]. 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  $\text{NaNO}_3$  were found to have negligible effects on the rate of the reaction.

However,  $\beta$ -cyclodextrin catalyzed oxidation of  $\alpha$ -amino acids with chloramine-T in alkaline medium has not been reported. Therefore, we investigated  $\beta$ -cyclodextrin catalyzed oxidation of  $\alpha$ -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

$\alpha$ -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  $[\text{OH}^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BCD}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $T = 313 \text{ K}$ .

$[\text{CAT}] \times 10^4 \text{ mol dm}^{-3}$	$[\text{AA}] \times 10^4 \text{ mol dm}^{-3}$	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$			
		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

$\beta$ -cyclodextrin were purchased from E-Merck. All other reagents were of analytical grade.

## 2.2. Preparation of chloramine-T

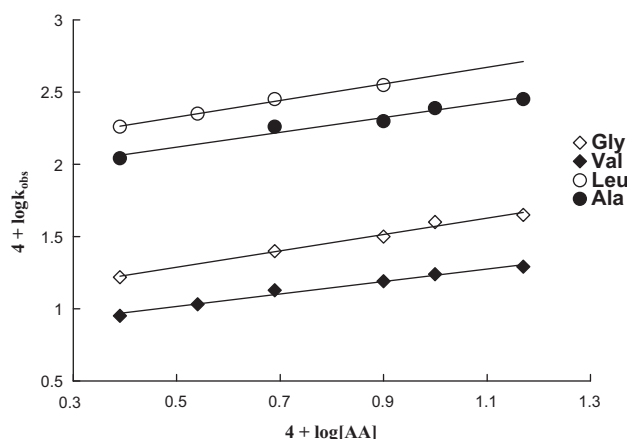
Chloramine-T was purified by the method of Morris et al. [10]. The aqueous solution of CAT was prepared afresh each day and its strength was checked iodometrically [11] and stored in amber-colored, stoppered bottles until further use. Aqueous solutions of AAs of known concentrations were prepared. A solution of BCD in  $0.05 \text{ mol dm}^{-3}$  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  $[\text{substrate}]_0$  over  $[\text{oxidant}]_0$  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 ( $k_{\text{obs}}$ ) calculated from the linear plots of  $\log[\text{CAT}]$  versus time was reproducible within  $\pm 3\%$  error. Regression analysis of experimental data to obtain regression coefficient,  $r$ , was performed using an EC-72 statistical calculator.

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

$[\text{HO}^-] \times 10^3 \text{ mol dm}^{-3}$	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$			
	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



**Fig. 1.** Effect of  $[\text{AA}]$  on the reaction rate.

## 3. Results

### 3.1. Dependence of rate on $[\text{CAT}]$ , $[\text{AA}]$

All kinetic runs were performed under pseudo-first-order conditions with  $[\text{AA}]_0 \gg [\text{CAT}]_0$ . Plots of  $\log[\text{CAT}]$  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  $[\text{CAT}]_0$  (Table 1). At constant  $[\text{CAT}]_0$ ,  $[\text{Product}]_0$ ,  $[\text{NaOH}]_0$ ,  $[\text{BCD}]_0$  and temperature, the rate increased with increase in  $[\text{AA}]_0$  (Table 1). Plots of  $\log k_{\text{obs}}$  versus  $\log[\text{AA}]_0$  (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 $[\text{NaOH}]$

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

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