Kinetics of Oxidation and Mechanism of Glycine by Tributylammonium Chlorochromate in Acid Medium

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ABSTRACT

Kinetics of oxidation of glycine by tributylammonium chlorochromate has been studied spectrophotometrically at 445 nm in acid medium. The reaction was first order dependence on TriBACC, glycine and fractional order with respect to H^+. No significant effect was observed by added salt. The main oxidation product of glycine has been identified as corresponding carbonyl compound. The reaction does not induce the polymerization of acrylonitrile. The reaction has been investigated at different temperature and activation parameters were calculated and the suitable mechanism has been proposed.

INTRODUCTION

The oxidation of glycine has received much attention because it is useful in the inhibitory neurotransmitter in the central nervous system, especially in the brainstem, spinal cord, and retina. When glycine receptors are activated chloride enters the neuron via ionotropic receptors causing an inhibitory postsynaptic potential [1]. In addition to being the building block of protein synthesis, glycine is a building block to numerous other chemical compounds [2]. Every cell function involving the formation of DNA and RNA is glycine dependant because it's role in purine biosynthesis and improves the sleep [3-4]. Amino acid residues are the main constituents of proteins and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modification [5].

Chromium compounds have been used in aqueous and nonaqueous medium for the oxidation of various organic substrates. Chromium (VI) reagents have been versatile and capable of oxidizing all the oxidizable organic moieties [6]. The development of Chromium (VI) reagents for the oxidation of organic substrates continues to be of interest.

Many such Cr (VI) reagents have been developed in recent years [7-13]. Tributylammonium chlorochromate is also one such oxidant developed recently. It is a more efficient and mild oxidizing agent [14-15]. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. Many kinetic studies have been carried out on the oxidation of glycines such as using metal catalyzed oxidation [16-23] and many other wells are known oxidizing agents. Literature survey reveals that no report is available on kinetics and mechanism of oxidation of glycine by TriBeCC. Hence we have considered it to study the kinetics and mechanism of oxidation of glycine by TriBeCC.

MATERIALS AND METHODS

Tributylamine, chromium trioxide and L-Alanine reagents used were of analytical grade. Acetic acid was purified by distillation over CrO_3 followed by fractionation in the presence of acetic anhydride. The pure acetic acid fraction was collected over 118ºC. Stock Solution of glycine was prepared in double distilled water and acetic acid, this solution was employed for kinetic studies. All other reagent was of analytical grade. The reaction was carried out by

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UV–vis spectrophotometer with a 1 cm quartz cell at 445 nm. Kinetics of reaction was followed by the temperature range 303-323 K.

Preparation of tributylammonium chlorochromate [$(C_4H_9)_3NHCrO_3Cl$]

Chromium (VI) oxide (CrO_3; 15 g, 0.15mol) was dissolved in water in a beaker and 6 M hydrochloric acid (25 mL, 0.30 mol) was added with stirring at 0ºC. To the resultant clear orange solution, tributylamine (71.29 mL, 0.3 mol) was carefully added over a period of 30 min and stirring was continued for 30 min at 0ºC. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3×60 mL) and dried under vacuum for 2h at room temperature [14], (Yield 45.81 gm. (95%); m.p. 165ºC). A solution of the compound was prepared in acetic acid and stored in the brown bottle to prevent its photochemical degradation.

 Product Analysis:

Product analysis was carried under kinetic conditions. In a typical experiment, a mixture of glycine (0.1 mol dm^{-3}) and TriBACC (0.01 mol dm^{-3}) was made up to 50 ml with acetic acid in presence of HCl (0.8 mol dm^{-3}). The mixture was kept in the dark for twelve hours until completion of oxidation. It was then treated overnight with an excess (125 ml) of a freshly filtered saturated solution of 2, 4-dinitrophenylhydrazine in 2M HCl. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was collected by filtration, dried, recrystallized from ethanol and weighed. The product was found identical m.p with an authentic sample of DNP of Acetaldehyde. The yield was 80%. Ammonia was identified by Nessler's reagent [24]. The presence of corresponding aldehyde and ammonium ions were also confirmed by the spot tests [25], with chromotropic acid and p-nitrobenzene diazonium chloride respectively.

Stoichiometry:

The stoichiometry of the reaction was determined by carrying out several sets of experiment with the varying amount of (TriBACC) largely in excess over glycine in acetic acid by using 1M H_2SO_4. The remaining (TriBACC) was then analyzed spectrophotometrically. The result indicated that 1 mole of glycine reacts with 1 mole (TriBACC).

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Kinetic procedure:

The reactions were followed under pseudo first-order conditions by keeping large excess (x 10 or greater) of the glycine over TriBACC. The reactions were followed at constant temperatures (303K), by monitoring the decrease in [TriBACC] spectrophotometrically at 445 nm the pseudo first-order rate constant k_{obs}, was evaluated from the linear (r = 0.990-0.999) plots of log [TriBACC] against time for up to 80% completion of the reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%.

RESULTS AND DISCUSSION:

The results of oxidation of Glycine by TriBACC are represented in table 1-6.

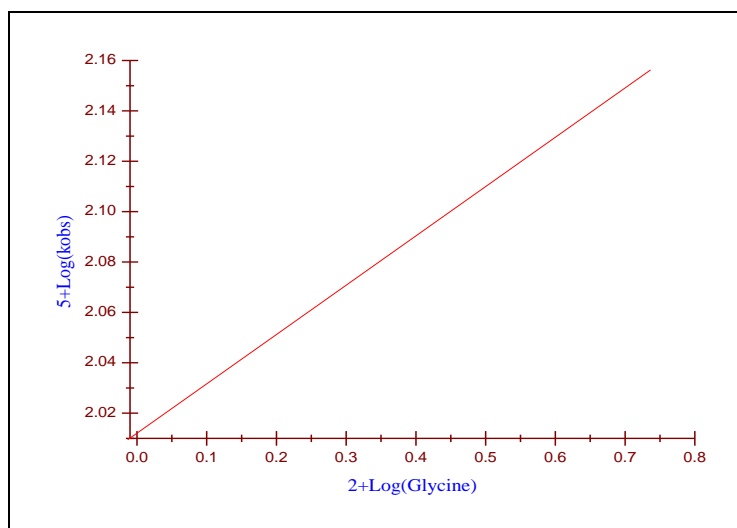**Effect of variation of concentration of Glycine on the rate of reaction:**

The oxidation of glycine with TriBACC in acetic acid in presence of sulphuric acid yields Acetaldehyde, by keeping constant [TriBACC] and [H_2SO_4], the increase in [Glycine] increases the rate of reaction (Table-1). The plot of the log of k_{obs} versus log [Glycine] for the different initial concentration of glycine is linear demonstrates that first order dependence of rate on glycine (Fig. 1).
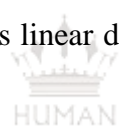
TABLE – 1: Effect of varying [Glycine] on the rate of oxidation by TriBACC

[TriBACC] = 1 x10^{-3} mol dm^{-3}; [H_2SO_4] = 1mol dm^{-3}, Temperaturer. = 303K

Gly (mol dm^{-3})	k_{obs} S^{-1}
0.01	0.00107
0.02	0.00122
0.03	0.00125
0.04	0.00137
0.05	0.00141

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Fig.1: 5+log [Kobs] Verses 2+log [Glycine]

Effect of varying [TriBACC] on the rate of oxidation of glycine:-

At constant [glycine] and [H_2SO_4] by varying the concentration of [TriBACC] from 2 x 10^{-3} to 6 x 10^{-3} mol dm^{-3} rate of reaction is increases Table-2. The plot of log k_{obs} versus log [TriBACC] for the different initial concentration of TriBACC is linear with positive slope presents the first order dependence of rate on TriBACC (Fig. 2).

TABLE – 2: Effect of varying [TriBACC] on the rate of oxidation of [Glycine]

[Glycine] = 1 x10^{-2} mol dm^{-3}; [H_2SO_4] = 1mol dm^{-3}, Temperature. = 303K.

TriBACC (mol dm^{-3})	k_{obs} S^{-1}
0.002	0.00120
0.003	0.00130
0.004	0.00135
0.005	0.00135
0.006	0.00148

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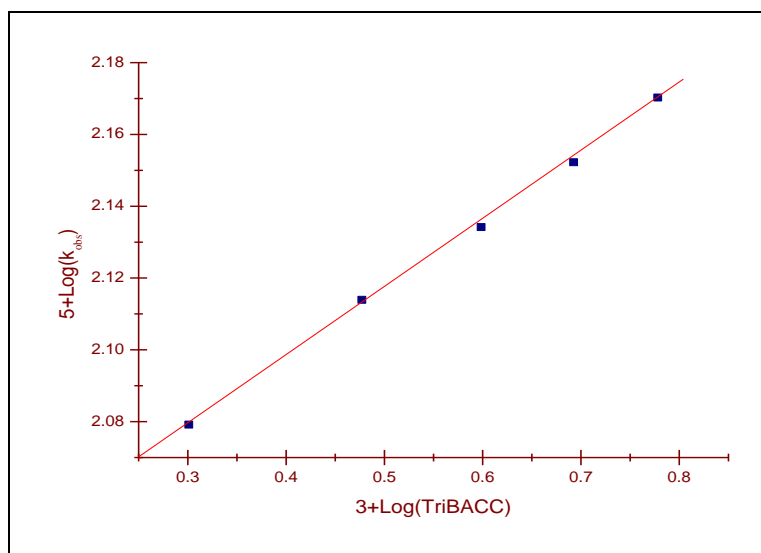
Fig.2: 5+ Logs (Kobs) Verses 3+Log [TriBACC]

**Effect of varying [H$_2$SO$_4$] on reaction rate:**

The rate of reaction was studied by varying sulphuric acid concentration. The rate of reaction increased with increasing the concentration of sulphuric acid and a plot of log conc. vs. Log (K$_{obs}$) was linear with a less than unit slope indicate the fractional order dependence of rate on [H$^+$] Table-3, (Fig. 3).

Table – 3: Effect of varying [H$_2$SO$_4$] on the rate of oxidation of [Glycine]

[Glycine] = 1 x10^{-2} mol dm^{-3}, [TriBACC] = 1 x10^{-3} mol dm^{-3}, Temperature. = 303K.

[H$^+$] mol dm^{-3}	k$_{obs}$ S^{-1}
2	0.00129
3	0.00139
4	0.00144
5	0.00160
6	0.00181

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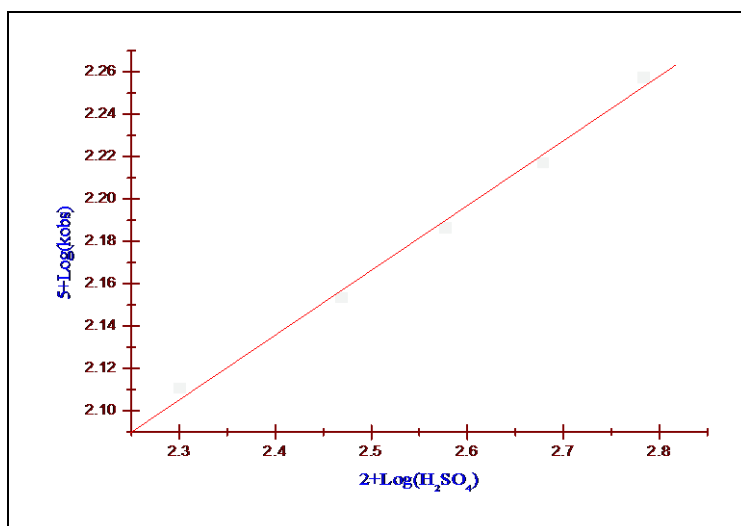
Fig.3: 5+Log (Kobs) Verses 2+Log [H_2SO_4]

Effect of Salts:

The effect of added salts on the reaction rate was studied by adding 0.001 mol dm^{-3} of the salts, by keeping the concentrations of glycine, H_2SO_4 and TriBACC constant. It was observed that the rate of oxidation does not alter by the addition of salts Table-4.

Table 4: Effect of variation of [salts] on reaction rate

Glycine 1x10^{-2} mol dm^{-3}; [TriBACC] = 1 x10^{-3} mol dm^{-3}; [H_2SO_4] = 1 mol dm^{-3}, Temperature. = 303K

| Salts 10^{-3} mol dm^{-3}	k_{obs} S^{-1}
KCl	0.00146
NaCl	0.00155
CaCl$_2$	0.00146
MgSO$_4$	0.00149
Ag(NO$_3$)$_2$	0.00147

Effect of Temperature:

To study the effect of temperature on the rate of oxidation of glycine by TriBACC has been investigated at 303-323K by keeping the concentration of glycine, TriBACC & H_2SO_4 constant. Rate constants are given in Table-5. The Arrhenius plots of log k vs. 1/T were

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found to be linear (Fig. 4).The activation energy (Ea) was calculated from the slope of the plots. From this value, the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ was evaluated Tabel-6.

Table-5: Effect of variation of Temperatures on reaction rate

Glycine 1×10^{-2} mol dm^{-3}; [TriBACC] = 1 $\times 10^{-3}$ mol dm^{-3}; [H$_2$SO$_4$] = 1mol dm^{-3}.

Temperature	k_{obs} S^{-1}
303 K	0.00200
308 K	0.00231
313 K	0.00251
318 K	0.00288
323 K	0.00311
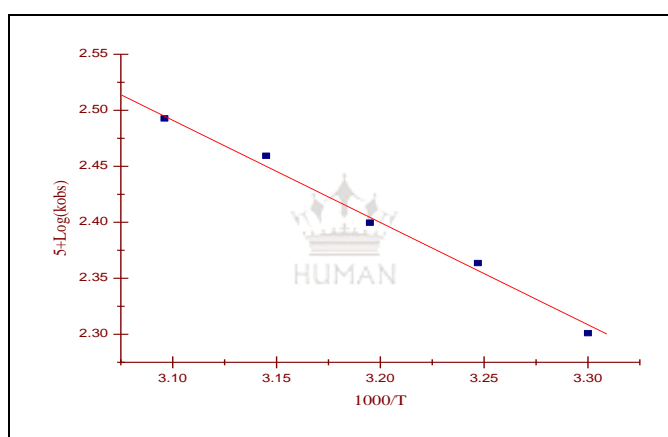
Fig.4: 5+log k$_{obs}$ VS 1000/T

Table-6: Activation Parameters

Glycine 1×10^{-2} mol dm^{-3}; [TriBACC] = 1 $\times 10^{-3}$ mol dm^{-3}; [H$_2$SO$_4$] = 1 mol dm^{-3}, Temperature. = 303K

Activation Parameters	
Ea KJ mol^{-1}	18.021
$\Delta H^{\#}$ KJ mol^{-1}	15.336
$\Delta S^{\#}$ JK^{-1} mol^{-1}	-247.96
$\Delta G^{\#}$ KJ mol^{-1}	95.426

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Effect of acrylonitrile as free radical detector

The addition of acrylonitrile to the reaction mixture at 35 and 45^{0}C did not alter the reaction rate and there was absolutely no polymer or change in the viscosity was detected, showing the absence of free radicals in the reaction mechanism.

CONCLUSION:

Sulphuric acid catalyzed the oxidation of glycine by Tributylammonium chlorochromate was studied in an acid medium at 303 K. It shows the first-order dependence of rate with respect to TriBACC, glycine and fractional order on sulphuric acid. Glycine was oxidized into corresponding carbonyl compound. An added salt does not alter the rate of reaction and also the addition of acrylonitrile did not polymerize the reaction. The thermodynamic parameters have been evaluated. The aldehyde is the main products of the reaction and the suitable kinetic mechanism has been proposed (Scheme-1).

Mechanism of oxidation of Glycine by TriBACC:

Scheme-1

Where, R = H for Glycine
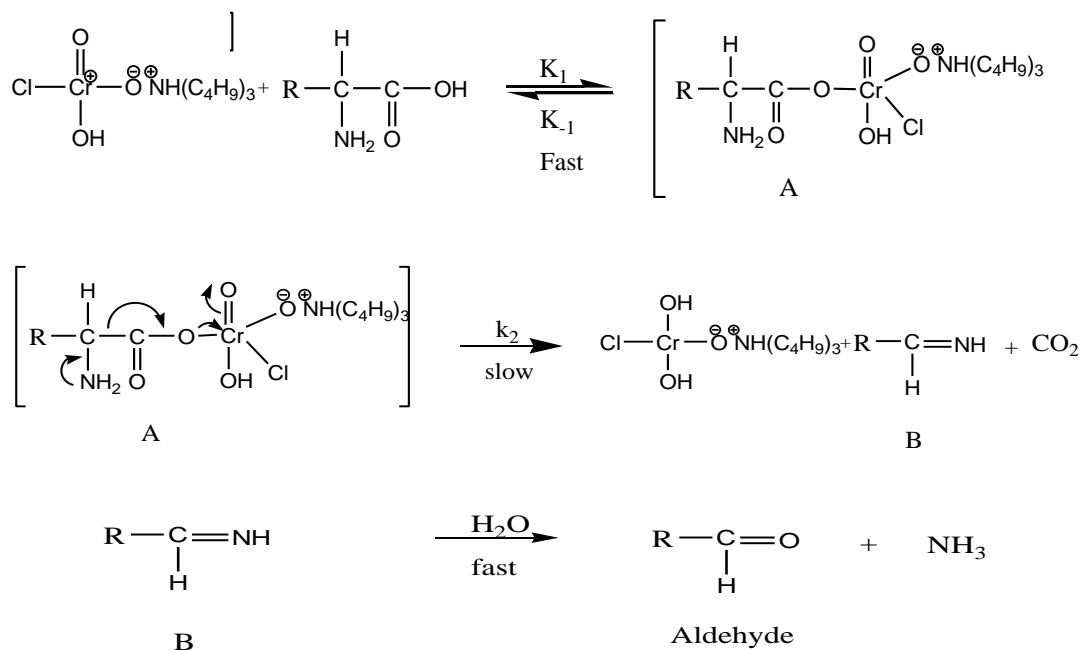
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