



A KINETICS AND THERMODYNAMICS OF OXIDATION OF DL-ORNITHINE BY TRIBUTYLAMMONIUM CHLOROCHROMATE IN ACID MEDIUM

Prabhakar Kute¹, Ganesh Andhale² and Nandkishor Choudhari^{*}

¹Department of Chemistry, Pratishthan Mahavidyalaya Paithan, Aurangabad (M.S)

²Department of Chemistry, Shri Shivaji Arts, Commerce and Science College, Akot, District Akola (M.S.)

^{*}Department of Physics, Pratishthan Mahavidyalaya Paithan, Aurangabad (M.S).

Corresponding Author- E-mail: nk.dchoudhari@gmail.com.

ABSTRACT :

The kinetics of acid catalysed oxidation of DL-Ornithine by Tributylammonium Chlorochromate (TriBACC) was studied spectrophotometrically at 445 nm in the temperature range 303-323 K. The observed rate of oxidation is first order with respect to oxidant and DL-Ornithine, dependence with a fractional order in $[H^+]$. The stoichiometry is i.e. (TriBACC): (Ornithine) =1:1. The main product of the oxidation of Ornithine is corresponding carbonyl compound. It failed to induce polymerization of acrylonitrile and also on addition of salts has no significant effect on the rate of oxidation. The activation parameters with respect to slow step of the mechanism of Ornithine have been calculated. A suitable mechanism has been proposed.

KEYWORDS : Kinetics, Oxidation, Amino acids, Tributylammonium Chlorochromate.

1: INTRODUCTION

Study of amino acid oxidation and kinetics is an important due to it is not only acts as building blocks of protein synthesis but also plays an important role in metabolism. Ornithine is also one of them, during the citric acid cycle, arginine, aprotic amino acid is broken down to Ornithine, which is a non protein amino acid [1]. It helps to build muscles and reduce body fat, especially in combination with Arginine and Ornithine. It is one of the key reactants in the urea cycle that is responsible for 80% of the nitrogen excretion from the liver and reduces the effect of cirrhosis, of the liver and other disorder accompanying with to malfunctioning the liver. It is also of use in healing and repairing skin and tissue. Ornithine has the ability to regenerate the thymus gland, liver, and heart tissue, enhance muscle growth, and increase immune system function [2]. Very few reports are available in the literature regarding the kinetics and oxidation of Ornithine by different oxidant [3-9]. Tributylammonium chlorochromate is also one of the oxidizing agent it is mild, stable and efficient oxidising reagent in synthetic organic chemistry [10]. In recent years, (TriBACC) have been used for oxidation of various organic compounds [11]. Literature survey reveals that no report is available on kinetics and mechanism of oxidation of Ornithine by TriBACC. Hence we have considered it to study the kinetics and mechanism of oxidation of Ornithine by TriBACC.

2: MATERIALS AND METHODS

All reagents used were of AR grade and doubled distilled water was used throughout the kinetic study. Acetic acid was purified by distillation over CrO_3 followed by fractionation in the presence of acetic anhydride. Pure acetic acid fraction was collected over 118 °C. A solution of Ornithine (Merck) was prepared by dissolving an appropriate amount of recrystallized sample in doubled distilled water and acetic acid 1:1. The purity of Ornithine was checked by comparing its melting point 232-234 °C with literature data [MP-233 °C] and TLC. The required molar concentration of Ornithine was obtained from its stock solution. Tributyl

Ammonium Chlorochromate was prepared by reported method [12]. The stock solution of TriBACC was prepared in acetic acid and distilled water 3:1 and stored in brown bottle to prevent its photochemical degradation. All other reagents were of AR grade. The reaction progress was carried out by UV-vis Spectrophotometer with 1 cm quartz cell at 445 nm in the temperature range 303-323 K.

3: KINETIC MEASUREMENTS

The kinetic measurements were performed on UV-vis Spectrophotometer. The kinetics were followed under pseudo-first order condition, where Ornithine \gg TriBACC at 303 K. unless specified. The reaction was initiated by mixing TriBACC with the Ornithine solution, which also contained the required concentration of sulphuric acid as a catalyst. The progress of the reaction was followed spectrophotometrically at 445 nm by monitoring the decrease in absorbance due to TriBACC. It was observed that there is no interference from other species present in the reaction mixture at this wavelength. The reaction was followed to more than 80 % completion. Plots of $\log(\text{TriBACC})$ versus time lead to the pseudo-first order rate constant were evaluated from the linear ($r=0.990-0.999$) regression coefficient. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$.

4: RESULTS AND DISCUSSION

4.1: Stoichiometry and product analysis:-

Different sets of reaction mixtures containing varying ratios of TriBACC to Ornithine in the presence of constant amount of sulphuric acid in acetic acid medium were kept for 6 h in a closed vessel under nitrogen atmosphere. The remaining (TriBACC) was then analyzed spectrophotometrically at 445 nm the result indicated that 1 mole of Ornithine react with 1 mole of oxidant.

Product analysis was carried under kinetic conditions. In a typical experiment, a mixture of Ornithine (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 and mixed m.p with an authentic sample of DNP of 4-aminobutanal. The yield was 78%. Ammonia was identified by Nessler's reagent [13]. The presence of corresponding aldehyde and ammonium ions were also confirmed by the spot tests [14], with chromotropic acid and p-nitrobenzene diazonium chloride respectively.

4.2: Reaction orders

The oxidation of DL-Ornithine Monohydrochloride by Tributylammonium Chlorochromate has been investigated in acetic acid medium. The reaction orders have been determined from the slopes of $\log(\text{Concentration})$ versus $\log k_{\text{obs}}$ plots by varying the concentration of TriBACC, DL-Ornithine, Sulphuric Acid, in turns while keeping others constant. The reaction was followed under the condition, $[\text{TriBACC}] = 1 \times 10^{-3}$, $[\text{OMH}] = 1 \times 10^{-2}$, Sulphuric Acid 1 N, mol dm^{-3} . The rate constant was obtained by plotting $\log(\text{absorbance})$ versus time by following the progress of the reaction spectrophotometrically at 445 nm.

4.3: Effect of Tributylammonium Chlorochromate:-

The concentration of TriBACC was varied in the range 2×10^{-3} to $6 \times 10^{-3} \text{ mol dm}^{-3}$ at constant concentration of $[\text{OMH}] 1 \times 10^{-2}$, Sulphuric acid 1 N mol dm^{-3} . The rate of reaction increases with increase in the concentration of TriBACC (**Table-1**). This is also confirmed by plotting different initial concentration of TriBACC versus rate constant is linear with unit slope indicates the pseudo-first order dependence of rate on TriBACC (**Figure-1**).

4.4: Effect of [DL-Ornithine Monohydrochloride]

The DL-Ornithine monohydrochloride concentration was varied from 1×10^{-2} to 5×10^{-2} mol dm⁻³ at 303 K while keeping other reaction concentrations and conditions constant. The k_{obs} values increase with the increase in the concentration of DL-Ornithine Monohydrochloride (**Table-1**) indicating first order dependence of rate on [OMH] this is also confirmed by plotting log [Ornithine] versus log [k_{obs}] is a straight line with unit slope (**Figure-2**).

4.5: Effect of Sulphuric Acid

The effect of sulphuric acid on k_{obs} was studied in the range 1 N to 6 N at constant concentration of TriBACC, OMH, Salts and temperature. It was observed that rate of reaction increases with increase in the concentration of sulphuric acid (**Table-1**). The plot of log [sulphuric acid] versus log [k_{obs}] is a straight line with positive slope but less than unity indicates that fractional order dependence of rate on [H⁺] (**Figure-3**).

Table-1
Effect of varying concentration of [TriBACC], [OMH], [H⁺] on the reaction rate at 303 K.

TriBACC 10^{-3} (mol dm ⁻³)	DL-[OMH] 10^{-2} (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	$10^{-4} k_{obs}$ sec. ⁻¹
1	1	1	20.4
1	2	1	22.2
1	3	1	23
1	4	1	24
1	5	1	28
2	1	1	20.5
3	1	1	21.8
4	1	1	24.8
5	1	1	26.0
6	1	1	28.1
1	1	2	20.5
1	1	3	21.3
1	1	4	24.1
1	1	5	25.8
1	1	6	27.8

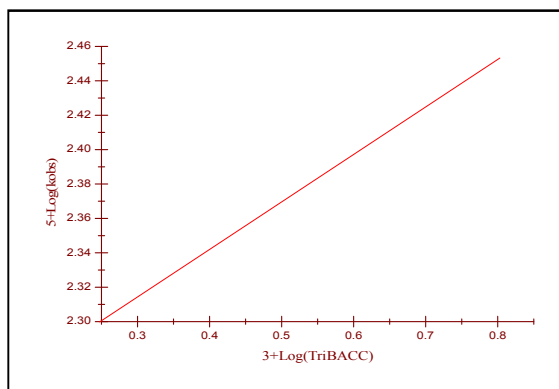


Figure-1 Effect of varying concentration of (TriBACC) on the k_{obs} values at 303K. Plot of $3+\log(\text{TriBACC})$ vs. $5+\log(K_{obs})$, [Ornithine] 1×10^{-2} mol dm⁻³, [H⁺] 1N.

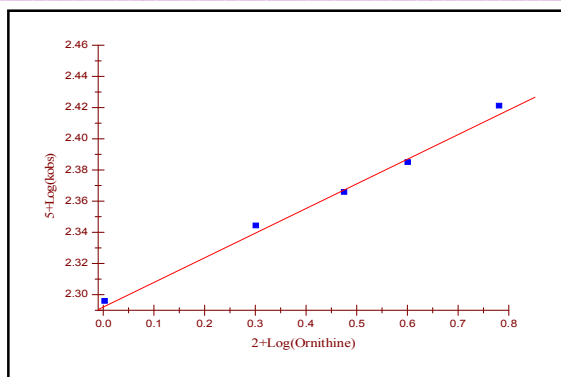


Figure 2: Effect of varying concentration of [OMH] on the k_{obs} values at 303K. Plot of $2+\log(\text{Ornithine})$ vs. $5+\log(k_{obs})$, TriBACC $1 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] 1\text{N}$.

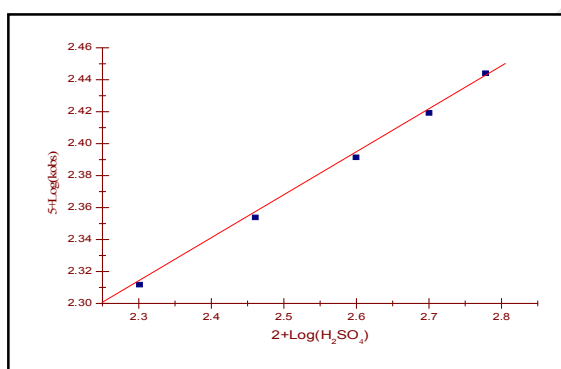


Figure 3: Effect of varying concentration of $[\text{H}_2\text{SO}_4]$ on the k_{obs} values at 303K. Plot of $2+\log(\text{H}_2\text{SO}_4)$ vs. $5+\log(k_{obs})$, TriBACC $1 \times 10^{-3} \text{ mol dm}^{-3}$, [Ornithine] $1 \times 10^{-2} \text{ mol dm}^{-3}$

4.6: Effect of Salts on k_{obs}

The effect of added salts on the rate of oxidation of Ornithine was investigated by adding $0.001 \text{ mol dm}^{-3}$ of the salts (KCl, NaCl, CaCl_2 , MgSO_4 , AgNO_3) by keeping the concentration of [Ornithine], TriBACC, and sulphuric acid constant it was observed that rate of oxidation does not change by the addition of salts **Table-2**.

Table -2:-Effect of variation of [salts] on reaction rate

Sr. No.	Name of Salt $10^{-3} \text{ mol dm}^{-3}$	$k_{obs} 10^{-4} \text{ sec}^{-1}$
1	KCl	12.4
2	NaCl	12.6
3	CaCl_2	12.3
4	MgSO_4	12.5
5	AgNO_3	12.5

4.7: Test for Free Radical Intermediates

The oxidation of Ornithine with TriBACC catalysed by sulphuric acid in the presence of acrylonitrile has been studied. The reaction mixture neither fails to induce the polymerisation nor retards the rate. From the results it reveals that the reaction takes place through the formation of intermediate complex.

4.8: Effect of Temperature on k_{obs}

The reaction was investigated at five different temperatures, viz, 303, 308, 313, 318, 323 K, by keeping constant amount of TriBACC- 1×10^{-3} , [Ornithine] $\times 10^{-2}$, sulphuric acid- 1 N mol dm^{-3} . The k_{obs} increases with the increase in temperature and the plot of $1/T$ versus $\log k_{obs}$ was a straight line (Arrhenius plot) **Figure-4**. From the slope and intercept of the straight line, the thermodynamic parameters were calculated **Table -3**. The positive value of free energy of activation (ΔG) and enthalpy of activation (ΔH) suggested that transition state was highly solvated. While negative value of entropy of activation (ΔS) suggested that formation of rigid transition state with deflation of degree of freedom of molecule.

Table-3:- A- Effect of temperature and B- activation parameters.

A-Temperature	$k \times 10^{-4} \text{ sec.}^{-1}$
303	23.1
308	26
313	28.8
318	32.2
323	35.8
B- activation parameters	
$E_a \text{ KJ moles}^{-1}$	18.293
$\Delta H^\ddagger \text{ KJ moles}^{-1}$	15.606
$\Delta S^\ddagger \text{ KJ moles}^{-1}$	-246.0
$\Delta G^\ddagger \text{ KJ moles}^{-1}$	95.057

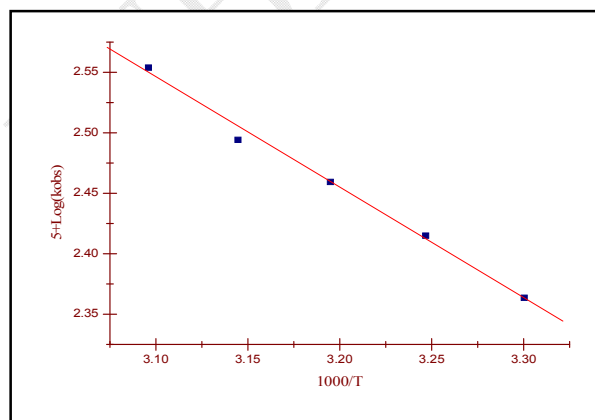


Figure-4: Arrhenius plot of oxidation of Ornithine, plot of $1000/T$ vs. $4+\log k_{obs}$

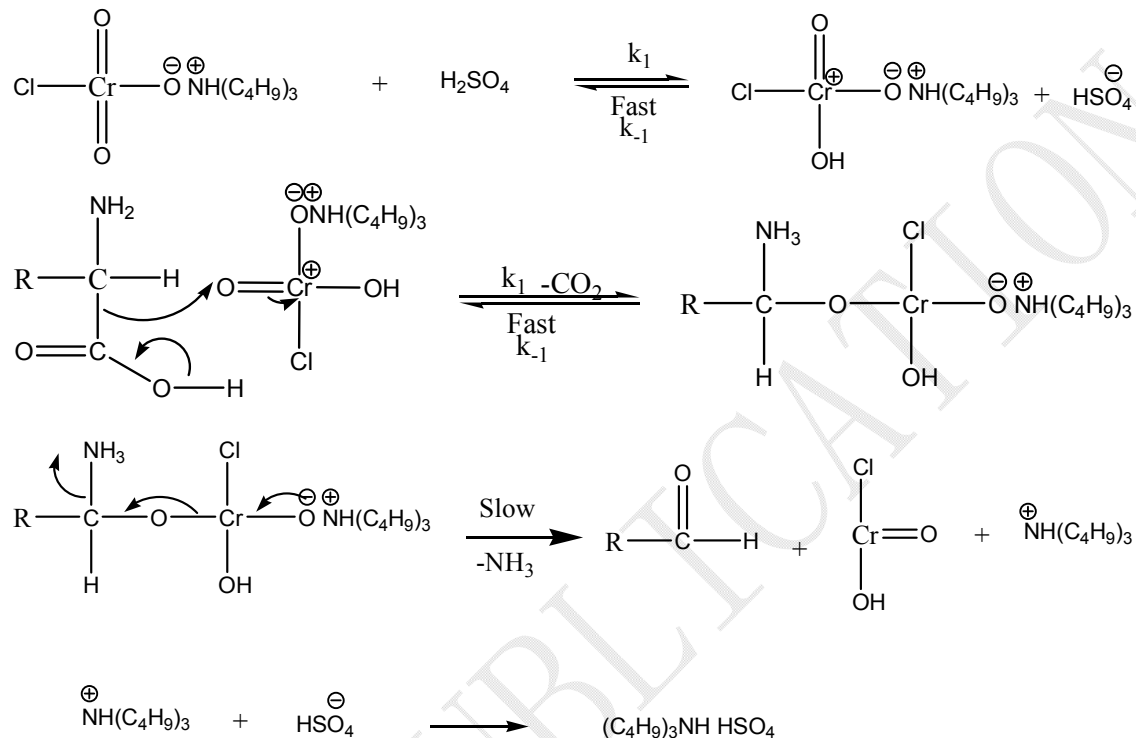
5: CONCLUSION

The oxidation of [OMH] by TriBACC has been investigated in acid medium spectrophotometrically at 445 nm at 303 K. From the results of kinetic study it is concluded that the rate of reaction follows pseudo-first order dependence with respect to TriBACC and OMH and fractional order dependence with respect to sulphuric acid. Oxidation products were identified as 4-amino butanal. No significant change was observed on the rate by changing bivalent and trivalent salts. The reaction does not show polymerisation which is

indicates that absence of free radical. The kinetic study was carried out at 303-323 K and the activation and thermodynamic parameters were calculated. A suitable reaction mechanism was proposed to explain experimental observation (Scheme-1).

Mechanism of oxidation of Ornithine by TriBACC:

Scheme-1



Where - R = -CH₂-CH₂-CH₂-CH₂-NH₂

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