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Kinetics and Mechanism of Oxidation of L-Valine by Tributyl Ammonium Chlorochromate in Acid Medium



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ABSTRACT

The kinetics of the oxidation of L-valine by Tributyl ammonium chlorochromate (TriBACC) in acid medium was studied spectrophotometrically at 445 nm. Analysis of the kinetic result revealed that the rate of oxidation was first order in TriBACC and inverse first order in both L-Valine and sulphuric acid. The reaction between oxidant and L-Valine in acid medium exhibit 1:1 stoichiometry. Variation of ionic strength had no significant effect on the rate. The reaction was investigated at different temperatures and the activation parameters were calculated. The main product was identified as the carbonyl compound by spot test. A plausible mechanism was proposed to explain the results of kinetic studies, reaction stoichiometry and product analysis.



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INTRODUCTION

L-Valine was first isolated from casein in 1901. It is one of the essential basic amino acid classified as non-polar and forms active sites of enzymes and helps in maintaining proper conformation by keeping them in proper ionic states. It is essential in the nutrition of mammals. Its role is crucial in the development of organs, especially in children. It also finds applications in medicine and pharmaceuticals [1]. Hence oxidation of L-valine may help in understanding some aspect of enzyme kinetics.

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, Cr(VI) as chromate is highly soluble in water, and is reported to be highly toxic[2-3]. There is continued interest in the development of new chromium (VI) reagents for the effective and selective oxidation of organic substrates in mild conditions. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. Many such Cr (VI) reagents have been developed in recent years [4-12]. Tributylammonium chlorochromate is also one such oxidant developed recently. It is a more efficient and mild oxidizing agent [13-14]. 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. The kinetics of oxidation of L-Valine have been studied by many reagents such as potassium permanganate[15], ruthenium(III) catalyzed oxidation of L-valine by potassium permanganate in alkaline medium [16], silver (I) catalysed oxidation of valine by cerium (IV) [17], Cr (III) catalysed oxidation of L-valine by permanganate in alkaline medium [18], Mn (II)-catalyzed oxidation of α -amino acids by peroxomonosulfate in alkaline medium [19], Ruthenium(III) chloride catalyzed oxidation of valine by N-Bromo phthalimide [20a], Pd(II) catalyzed oxidation of valine by N-Bromo phthalimide [20b], and many other well-known oxidizing agents. Literature survey reveals that no report is available on kinetics and mechanism of oxidation of L-valine by TriBACC. Hence we have considered it to study the kinetics and mechanism of oxidation of L-Alanine by TriBACC.

MATERIALS AND METHODS

Tributylamine, chromium trioxide and L-valine reagents used were of analytical grade. 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 . Stock Solution of L-

valine was prepared in doubly distilled water and acetic acid, this solution were employed for kinetic studies. All other reagent was of analytical grade. The reaction was carried out by UV-visible spectrophotometer with a 1 cm quartz cell at 445 nm. Kinetics of reaction was followed by temperature range 303-323 K.

Preparation of tributylammonium chlorochromate [(C₄H₉)₃NHCrO₃Cl]

Chromium (VI) oxide (CrO₃; 15 g, 0.15 mol) was dissolved in water in a beaker and 6 M hydrochloric acid (25 mL, 0.30 mol) was added with stirring at 0⁰C. 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 0⁰C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 mL) and dried under vacuum for 2h at room temperature [21] (Yield 45.81 gm. (95%); m.p. 165⁰C). A solution of the compound was prepared in acetic acid and stored in brown bottle to prevent its photochemical degradation.

Product Analysis:

Product analysis was carried under kinetic conditions. In a typical experiment, a mixture of L-valine (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 Isobutyraldehyde. The yield was 81%. Ammonia was identified by Nessler's reagent [22]. The presence of corresponding aldehyde and ammonium ions were also confirmed by the spot tests [23], 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 varying amount of (TriBACC) largely in excess over L-valine in acetic acid by using

1M H₂SO₄. The remaining (TriBACC) was then analyzed spectrophotometrically. The result indicated that 1 mole of L-valine reacts with 1 mole (TriBACC).

Kinetic procedure:

The reactions were followed under pseudo-first-order conditions by keeping large excess (x 10 or greater) of the L-valine 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 reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$.

RESULTS

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

Effect of variation of concentration of L-valine on rate of reaction:

The oxidation of L-valine with TriBACC in acetic acid in presence of sulphuric acid yields Isobutyraldehyde, by keeping constant [TriBACC] and [H₂SO₄], the increase in [L-valine] decreases the rate of reaction (Table-1). The plot of \log of k_{obs} versus $\log [L\text{-valine}]$ for different initial concentration of L-valine is linear with negative unit slope demonstrates that inverse first order dependence of rate on L-valine (Figure: 1).

Table – 1: Effect of varying [L-valine] on the rate of oxidation by TriBACC $R^2=0.996$
 [TriBACC] = $1 \times 10^{-3} \text{ mol dm}^{-3}$; [H₂SO₄] = 1 mol dm^{-3} , Temperaturer. = 303K

L-valine (mol dm ⁻³)	0.001	0.002	0.003	0.004	0.005
$K \times 10^{-4} \text{ S}^{-1}$	17.7	16.7	16.6	16.2	15.6

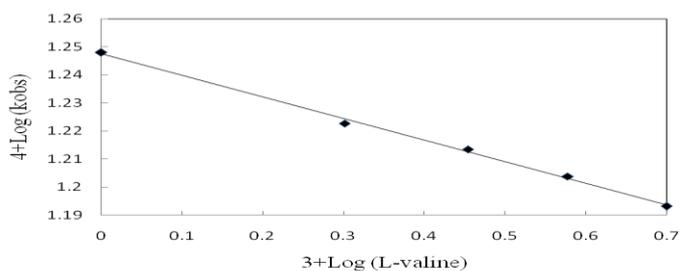


Figure-1: 4+log [Kobs] VS 3+log [L-valine]

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

At constant [L-valine] and [H₂SO₄] by varying the concentration of [TriBACC] from 2.0 x 10⁻³ to 6.0 x 10⁻³ mol dm⁻³ rate of reaction increases Table-2. The plot of log k_{obs} verses log [TriBACC] for different initial concentration of TriBACC is linear with positive unit slope presents the first order dependence of rate on TriBACC.

Table – 2: Effect of varying [TriBACC] on the rate of oxidation of [L-valine]

[L-valine] = 1 x 10⁻² mol dm⁻³; [H₂SO₄] = 1 mol dm⁻³, Temperature. = 303K.

TriBACC (mol dm ⁻³)	0.002	0.003	0.004	0.005	0.006
K x 10 ⁻⁴ S ⁻¹	15.0	18.9	21.6	22.6	24.6

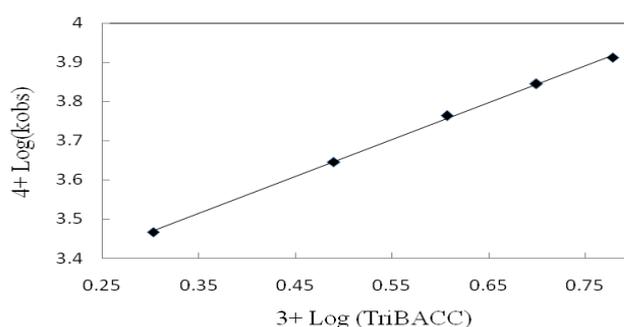


Figure-2: 4+Log (Kobs) VS 3+Log [TriBACC]

Effect of H₂SO₄ on reaction rate:

The rate of reaction was studied by varying sulphuric acid concentration. The rate of reaction decreased with increasing the concentration of sulphuric acid and a plot of log conc. vs. Log (Kobs) was linear with a unit slope indicating first order on [H⁺] table-3.

TABLE – 3: Effect of varying [H₂SO₄] on the rate of oxidation of [L-valine]

[L-valine] = 1 x10⁻² mol dm⁻³, [TriBACC] = 1 x10⁻³ mol dm⁻³, Temperature. = 303K.

[H ⁺] mol dm ⁻³	2	3	4	5	6
K _{obs} x10 ⁻⁴ S ⁻¹	21.6	21.0	20.3	19.8	19.1

Effect of ionic strength:

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 L-valine, H₂SO₄ and TriBACC constant. It was observed that the rate of oxidation does not alter by the addition of salts.



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

L-valine 1x10⁻² mol dm⁻³; [TriBACC] = 1 x10⁻³ mol dm⁻³; [H₂SO₄] = 1 mol dm⁻³, Temperature. = 303K

Salts 0.001 mol dm ⁻³	KCl	NaCl	CaCl ₂	MgSO ₄	Al(NO ₃) ₂
k _{obs} X 10 ⁻⁴ S ⁻¹	12.1	12.4	12.3	12.3	12.4

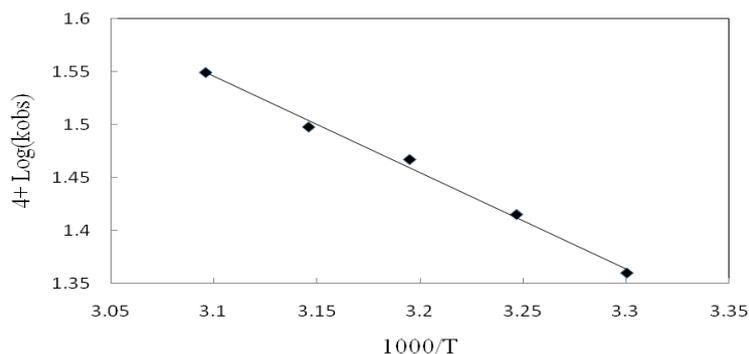
Effect of Temperature:

The study of effect of temperature on rate of oxidation of L-valine by TriBACC has been investigated at 303-323K by keeping the concentration of L-valine, TriBACC& H₂SO₄ constant. Rate constants are given in Table 5. The Arrhenius plots of log k vs. 1/T were found to be linear (**Fig.3**). The activation energy (Ea) was calculated from the slope of the plots. From this value, the thermodynamic parameters ΔH[#], ΔS[#], ΔG[#] was evaluated (**Tabel-6**).

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

L-leucine $1 \times 10^{-2} \text{ mol dm}^{-3}$; [TriBACC] = $1 \times 10^{-3} \text{ mol dm}^{-3}$; [H₂SO₄] = 1 mol dm^{-3} ,

Temp.	303 K	308 K	313 K	318 K	323 K
$K \times 10^{-4} \text{ S}^{-1}$	22.9	26.0	29.3	31.0	35.4



4+log k_{obs} VS 1000/T

Figure: 3: Arrhenius plot of oxidation of L-valine

Activation parameters are presented in (Table 6). The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ΔG value indicates that similar mechanism is operative for the oxidation of L-valine.

Table-6: Activation Parameters

L-valine $1 \times 10^{-2} \text{ mol dm}^{-3}$; [TriBACC] = $1 \times 10^{-3} \text{ mol dm}^{-3}$; [H₂SO₄] = 1 mol dm^{-3} ,
Temperature. = 303K

Activation parameters	E _a KJ mol ⁻¹	ΔH^\ddagger KJ mol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	ΔG^\ddagger KJ mol ⁻¹
	19.438	16.835	-242.15	92.628

Effect of acrylonitrile as free radical detector

The addition of acrylonitrile to the reaction mixture at 35 and 45°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.

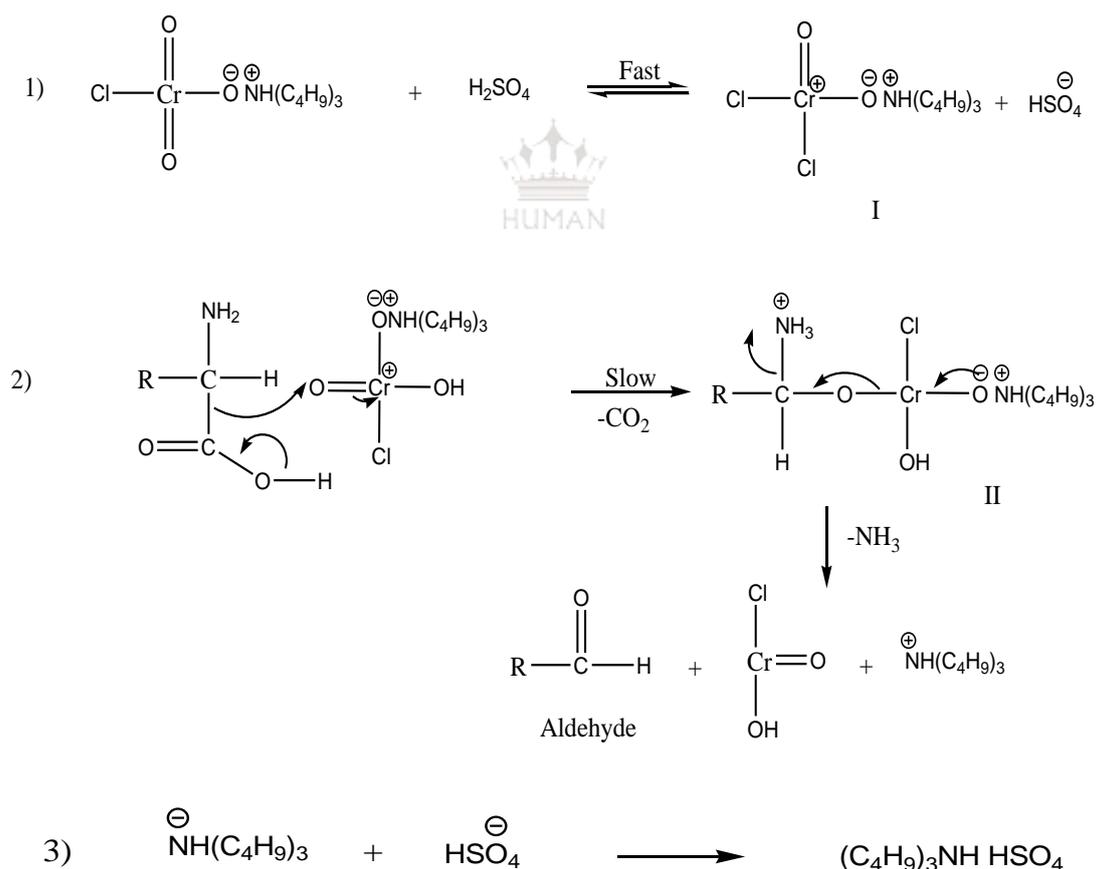
CONCLUSION

Sulphuric acid catalyzed oxidation of L-valine by Tributylammonium chlorochromate was studied in acid medium at 303 K. It shows first-order dependence on TriBACC, Inverse first order on L-valine and sulphuric acid, L-valine was oxidized into corresponding carbonyl compound. Ionic strength does not alter the rate of reaction and also addition of acrylonitrile did not polymerize the reaction. The thermodynamic parameters have been evaluated. Aldehyde is the main products of the reaction and suitable kinetic mechanism has been proposed (scheme-1).

Mechanism of oxidation of L-valine by TriBACC:

Scheme-1

Where, R = (CH₃)₂CH- for L-valine



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