OXIDATION OF LYSINE BY CHROMIUM (VI) IN ACID PERCHLORATE MEDIUM : A KINETIC STUDY

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ABSTRACT

The kinetics of oxidation of lysine with chromium (VI) has been studied in perchloric acid medium. The oxidation product was identified as chromium (III) and 5-aminopentanaldehyde. The reaction is first order with respect to chromium (VI) and less than unit order in lysine concentration. Increase in acid concentration accelerates the reaction rate. Ionic strength and added products did not have any significant effect on the reaction. A suitable mechanism is proposed and reaction constants have been evaluated. Activation parameters have also been calculated.

Keywords: Kinetics, Mechanism, Oxidation, Lysine, Chromium (VI).

INTRODUCTION

Chromium (VI) is considered as an important reagent in organic and inorganic synthesis and has been employed widely as an oxidant in perchloric acid, chloride and acetate media[1-3]. Chromic acid, aqueous dichromate, chromyl chloride and other substituted chromates have been employed in oxidation of organic as well as inorganic compounds in aqueous acid and alkaline media[4-8]. The mechanistic propositions in these reactions are based mainly upon identification of products and the role of intermediate chromium (IV) and chromium (V).

Lysine, an essential amino acid is a necessary building block for all types of proteins in the body. It plays a major role in calcium absorption, building muscle protein, recovering from surgery or sports injuries and the body's production of hormones, enzymes and antibodies. In biological events, the effect of oxidants on biological targets is a very significant process[9,10] because studies emphasize the mechanism involved in the conversion

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of target molecules in the biological systems. Since amino acid residues are the main constituents of proteins, the study of its oxidation open up a new area to understand the mechanism and oxidative behaviour of amino acid with metal ions. Hence, we have investigated the kinetics of oxidation of lysine by chromium (VI) in perchloric acid medium in order to identify the chromium (VI) intermediates and to derive a suitable mechanism.

EXPERIMENTAL

Materials

The solutions were prepared in doubly distilled water, the second distillation was done in presence of potassium permanganate. The stock solution of chromium (VI) was obtained by dissolving a known weight of potassium dichromate (AR) in water and solution was standardized by known method[11,12]. All other reagents employed in this study were either of AnalaR or guaranteed reagent grade.

Kinetic measurements

Kinetics were followed at $45 \pm 0.1°C$ and ionic strength 1.5 mol dm^{-3}. The reaction was initiated by adding previously thermostated reactant solution of chromium (VI) in lysine, which also contained required volume of perchloric acid and sodium perchlorate. The progress of the reaction was followed by measuring the absorbance of chromium (VI) in the reaction mixture at 360 nm in different time intervals on UV visible spectrophotometer (UV win 2000^+). The kinetics were studied under pseudo first order conditions, lys $\geq$ 10 chromium (VI). Other experimental details were same as described elsewhere[13].

RESULTS AND DISCUSSION

Stoichiometry and product analysis

The different sets of concentration of reactants with fixed concentration of other reaction ingredients were allowed to occur in thermostatic water bath at $45 \pm 1°C$. The oxidant chromium (VI) was analysed by measuring absorbance. The results indicate that two moles of chromium (VI) react with three moles of lysine as represented by equation (1).

$$3 \text{ RCHNH}_2\text{COOH} + 2 \text{ Cr(VI)} + 3 \text{ H}_2\text{O} \rightarrow 3 \text{ RCHO} + 2 \text{ Cr(III)} + 3 \text{ NH}_3 + 3 \text{ CO}_2 + 6 \text{ H}^+ \text{ ...(1)}$$

$$R = (CH_2)_4 \text{ NH}_2$$
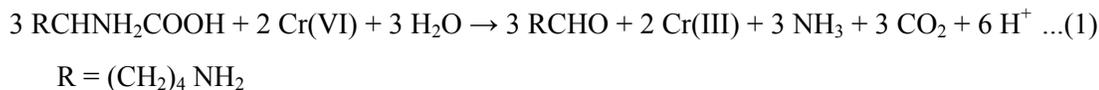
The oxidation products were identified as chromium (III) and 5-aminopentanaldehyde, ammonia and carbondioxide. Chromium (III) was identified by recording its absorbance at

575 nm and aldehyde was detected quantitatively by 2,4 DNP test[11]. The yellow ppt. of 2,4-dinitrophenylhydrazone of aldehyde product was obtained. The other products ammonia was detected by Nesseler's reagent test[14] and CO_2 was qualitatively detected by passing the liberated gas through a tube containing lime water.

Reaction orders

The concentration of chromium (VI) was varied from 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} at fixed concentration of other reaction ingredients at 45°C. Pseudo first order plots were made (Fig. 1). The pseudo first order rate constant (k_0) found to be independent of the initial chromium (VI) concentration, commensurate with a first order process with respect to oxidant (Table 1).
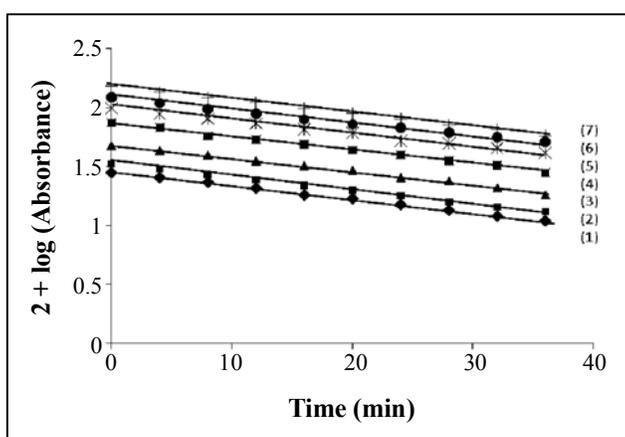

Fig. 1: Pseudo first order plots for the variation of Cr (VI)

[Lys] = 2×10^{-2} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3}; [I] = 1.5 mol dm^{-3}; Temp. = 45°C,
[Cr(VI)] = (1) 5.0×10^{-5} mol dm^{-3} (2) 7.5×10^{-5} mol dm^{-3}; (3) 1.0×10^{-4} mol dm^{-3};
(4) 2.0×10^{-4} mol dm^{-3}; (5) 3.0×10^{-4} mol dm^{-3}; (6) 4.0×10^{-4} mol dm^{-3}; (7) 5.0×10^{-4} mol dm^{-3}

The concentration of lysine was varied from 5×10^{-3} to 5×10^{-2} mol dm^{-3} at fixed concentration of chromium (VI) = 2×10^{-4}, [H$^+$] = 1.0 mol dm^{-3} and ionic strength 1.5 mol dm^{-3} at three temperature 40, 45 and 50°C, respectively. The rate constant (k_0) increases with increasing concentration of lysine (Table 1). The order with respect to lysine concentration was found to be less than unity (0.82). In order to check the effect of H$^+$, at fixed concentration of chromium (VI), lysine and at constant ionic strength, the perchloric acid concentration was found to increase with increasing perchloric concentration (Table 1). The order with respect to perchloric acid concentration calculated from plot of log k_0 versus log [H$^+$] was found to be 0.78.

Table 1: Effect of variation of chromium (VI), lysine and perchloric acid in the reaction of chromium (VI) and lysine in acid medium at I = 1.5 mol dm^{-3} at 45°C

10^4 [Cr(VI)] mol dm^{-3}	10^2 [Lys] mol dm^{-3}	[HClO$_4$] mol dm^{-3}	10^4 [k$_0$] (sec^{-1})
0.5	2.0	1.0	4.13
0.75	2.0	1.0	4.10
1.0	2.0	1.0	4.08
2.0	2.0	1.0	4.14
3.0	2.0	1.0	4.16
4.0	2.0	1.0	4.13
5.0	2.0	1.0	4.12
2.0	0.5	1.0	1.30
2.0	0.75	1.0	1.75
2.0	1.0	1.0	2.25
2.0	2.0	1.0	4.13
2.0	3.0	1.0	5.55
2.0	4.0	1.0	7.25
2.0	5.0	1.0	8.65
2.0	2.0	0.5	3.27
2.0	2.0	0.75	3.63
2.0	2.0	1.0	4.13
2.0	2.0	1.25	4.41
2.0	2.0	1.50	4.67

The ionic strength was varied with concentration of sodium perchlorate from 1.5 to 3.0 mol dm^{-3} at fixed concentration of reactants and other conditions. The result indicates no significant effect of the ionic strength on the rate of reaction. The effect of initially added product chromium (III) was studied in the concentration 1×10^{-4} to 5×10^{-4} mol dm^{-3} keeping the other conditions constant. It was observed chromium (III) did not have any effect on the reaction rate. When reactant concentration and other conditions were kept constant, ion such as Na$^+$, NO$_3^-$, CH$_3$COO$^-$ did not have any effect on the rate of reaction whereas Mn^{2+} decreases the reaction rate.

The effect of temperature on the reaction was studied at 40, 45 and 50°C by varying concentration of lysine and H^+ ion concentration. The rate constants were found to increase with increasing temp. The rate constant (k) was determined from the intercept of $1/k_0$ versus $1/[Lys]$ plot at three different temperature (Fig. 2) The energy of activation was calculated by the plot of log k versus $1/T$ and activation parameters were calculated (Table 2).

Table 2: Activation parameters and thermodynamic quantities of the reaction of chromium (VI)-lysine reaction in acid medium

(a) Activation parameters with respect to slow step of Scheme 1

Temperature (K)	10^3 (k) s^{-1}	Activation parameters
313	1.53	E_a = 47.85 KJ mol^{-1}
318	2.00	$\Delta H^{\neq}$ = 45.20 KJ mol^{-1}
323	2.85	$\Delta S^{\neq}$ = -296 JK^{-1} mol^{-1}
		$\Delta G^{\neq}$ = 94.45 KJ mol^{-1}

(b) Thermodynamic quantities with respect to first step (K_1) and second step (K_2) of Scheme 1

ΔH (KJ mol^{-1})	-31.0	-39.7
ΔS (JK^{-1} mol^{-1})	-267	-193
ΔG (KJ mol^{-1})	84.99	61.5

Fig. 1 shows the first order dependence of the reaction rate on chromium (VI) in perchloric acid. Chromium (VI) is known to participate in acid-base equilibria and exist in aqueous acid solution in a variety of forms such as CrO_4^{2-}, $HCrO_4^-$, $HCrO_3^+$ and dimeric species $Cr_2O_7^{2-}$[15]. The most probable and relevant equilibria involving chromium (VI) species are reported[16] as follows –

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,HCrO_4^-$$

$$CrO_4^- \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} HCrO_4^- \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2CrO_4 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} HCrO_3^+ + H_2O$$
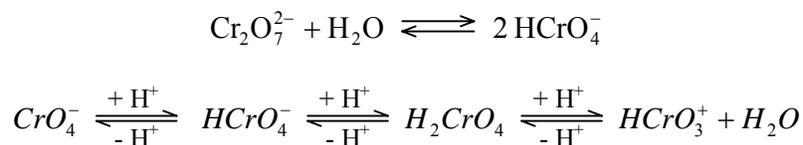
Under the present experimental conditions, the chromium (VI) species involved in the reaction seems to be H_2CrO_4. The results suggest that H_2CrO_4 react with lysine

forming a complex, which decomposes in the rate determining step to give an intermediate chromium (IV) species and product, further acid chromate H_2CrO_4 react with lysine and form another mole of an intermediate chromium (IV) and product. In the next step, two molecule of chromium (IV) react with one molecule of lysine giving final product 5-amino pentanaldehyde and chromium (III). On the basis above results the following mechanism is proposed (**Scheme 1**).

$$HCrO_4^- + \left[H^+\right] \underset{}{\overset{K_1}{\rightleftharpoons}} H_2CrO_4$$

$$H_2CrO_4 + RCHNH_2COOH \underset{}{\overset{K_2}{\rightleftharpoons}} Complex(C)$$

$$Complex(C) \xrightarrow[k]{slow} RCHO + H_3CrO_4^- + CO_2 + NH_3 + H^+$$

$$H_2CrO_4 + RCHNH_2COOH \xrightarrow{fast} RCHO + H_3CrO_4^- + CO_2 + NH_3 + H^+$$

$$2H_3CrO_4^- + RCHNH_2COOH \xrightarrow{fast} RCHO + CrO_2^- + CO_2 + NH_3$$
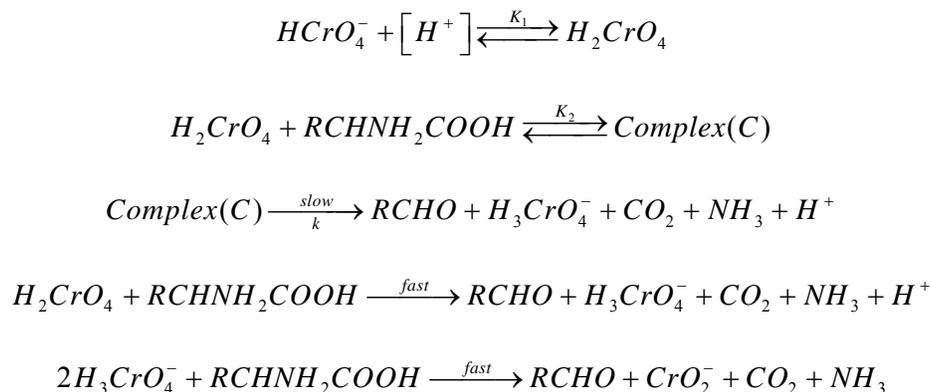
Scheme 1

The results indicate that the formation of complex between lysine and chromium (VI) is in acid perchlorate medium. The formation of this complex was proved kinetically by Michaelis-Menten plot, a non-zero intercept of the plot $1/k_0$ versus $1/[Lys]$ (Fig. 2). The complex formation between oxidant and substrate was also reported[17]. The intervention of chromium (IV) is evident from the rate decrease in the presence of increasing concentration of Mn (II). From the above mechanism (**Scheme 1**), the following rate law is derived.

$$k_{obs} = \frac{kK_1K_2[Lys][H^+]}{1 + K_1[H^+] + K_1K_2[Lys][H^+]} \qquad \ldots(2)$$

The rate law (2) can be rearranged to equation (3).

$$\frac{1}{k_{obs}} = \frac{1}{kK_1K_2[Lys][H^+]} + \frac{1}{kK_2[Lys]} + \frac{1}{k} \qquad \ldots(3)$$

According to equation (3), the plot of $1/k_o$ versus $1/[H^+]$ should be linear (Fig. 3) at 40, 45 and 50°C. The slow step rate constant (k) of the **Scheme 1** were calculated from the intercept of $1/k_o$ versus $1/[Lys]$. The value of equilibrium constants K_1 and K_2 at 40, 45 and

50°C were calculated from the slopes and intercepts of Fig. 3. The calculated values of $K_1 \times 10^{-2}$ dm^3 mol^{-1} and $K_2 \times 10^2$ dm^3 mol^{-1} are 6.21, 7.20, 8.99 and 6.69, 5.14, 3.63, respectively at 40, 45 and 50°C. Van't Hoff plots were made for the variation of K_1 and K_2 with temperature (i.e. log K_1 vs 1/T and log K_2 vs 1/T). The values of ΔH, ΔS and ΔG were calculated for the first and second equilibrium steps of **Scheme 1** (Table 2).
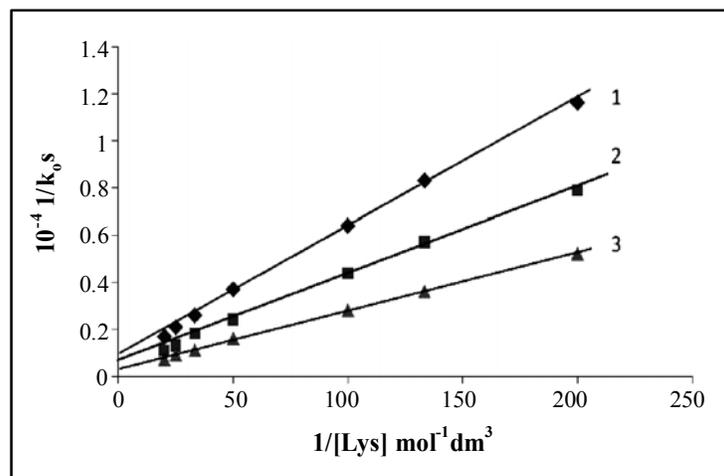

Fig. 2: A plot of k_o^{-1} versus [Lys^{-1}]: [Cr(VI)] = 2 × 10^{-4} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3}; [I] = 1.5 mol dm^{-3}; Temp. = (1) 40°C, (2) 45°C, (3) 50°C
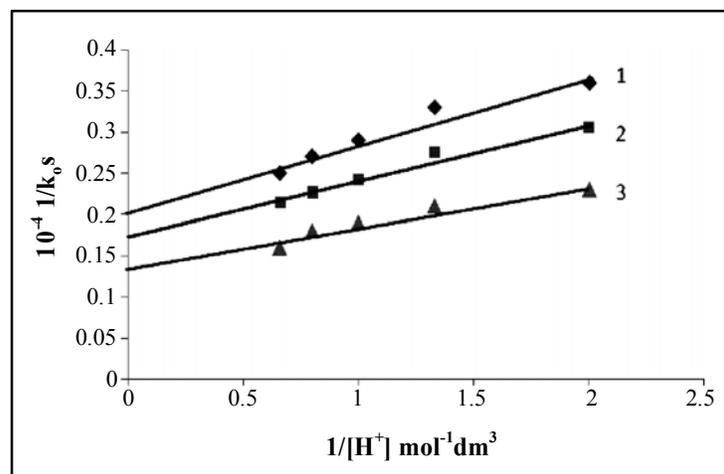
Fig. 3: A plot of k_o^{-1} versus [H$^+$]$^{-1}$: [Cr(VI)] = 2 × 10^{-4} mol dm^{-3}; [Lys] = 2 × 10^{-2} mol dm^{-3}; [I] = 1.5 mol dm^{-3}; Temp. = (1) 40°C, (2) 45°C, (3) 50°C

Comparison of these values with those obtained for the slow step (k) of the reaction shows that these values mainly refers to the rate determining step, supporting the effect the reaction before rate determining step is fairly fast. Moderate values of ΔH, ΔS are favourable for electron transfer process. The negative value of ΔS indicate that complex is more ordered than reactant[18].

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