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KINETICS AND MECHANISM OF IRIDIUM (III) CATALYZED OXIDATION OF SOME AMINO ACIDS BY HEXACYANOFERRATE (III) IONS IN AQUEOUS ALKALINE MEDIUM

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ABSTRACT

The kinetics of oxidation of some amino acids like – alanine, valine and leucine by hexacyanoferrate (III) ions catalyzed by iridium (III) in aqueous alkaline medium at constant ionic strength and temperature has been studied spectrophotometrically. The results show that the reaction rates follow first order kinetics with respect to hexacyanoferrate (III), iridium (III) and hydroxide ions concentration in the oxidation of all the three amino acids. The dependence of rate on substrate concentration has been found first order at lower concentration, which tends to be zero order at higher concentration in the oxidation of all the three amino acids. The linear plots between log (-dc/dt) and $\sqrt{\mu}$ suggest positive salt effect. Thermodynamic parameters were evaluated by studying the reactions at four different temperatures between 35^0C to 50^0C under pseudo first order conditions. 2 : 1 Stoichiometry was observed between hexacyanoferrate (III) and amino acids. From the results, it has been concluded that all the three amino acids show same kinetic behavior. Therefore, a common mechanism involving the formation of complex between catalyst and substrate has been suggested.

Key words : Hexacyanoferrate (III) ions, Iridium (III), Oxidation.

INTRODUCTION

Amino acids represent for organism, forerunners of essential biomolecules such as proteins, hormones, enzymes, etc. They may also serve as energy source, losing their amino group by two path ways : transamination or oxidative deamination. Oxidation of α-amino acids has been studied in both alkaline and acidic medium by variety of oxidants[1-4]. Lambert and Jones[5] have shown that uncatalyzed oxidation of α-amino acids by alkaline hexacyanoferrate (III) (abbreviated as HCF (III)) is extremely slow even at very high ionic

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strength (4.5 M KNO_3). Some metal ions like Os (VIII). Ru (III) and Ag(I) are known to catalyze the oxidation of amino acids by alkaline HCF (III)[6-9] but the catalytic effect of iridium (III) in the oxidation of α-amino acids by HCF (III) is still unknown. The catalytic effect of Ir (III) in hexacyanoferrate (III) oxidation in alkaline medium is well documented[10-13]. In the present work, the kinetics and mechanism of Ir (III) catalyzed oxidation of alanine, valine and leucine by HCF (III) is reported. It has been observed that the presence of a trace amount of Ir (III) is sufficient to catalyze the oxidation of α-amino acids by alkaline HCF (III) to significant rate.

EXPERIMENTAL

Aqueous solutions of alanine, valine and leucine (AnalaR) were always prepared afresh. Solution of Ir (III) chloride (SRL) was prepared in very dilute solution of HCl. The final strength of iridium trichloride was kept 3.35 x 10^{-3} M. NaOH, HCF (III) and KCl of (AnalaR) grade were used. All solutions were made in double distilled water. The kinetic experiments were carried out by mixing the required quantity of amino acid solution maintained at constant temperature with solution of HCF (III), NaOH, KCl and iridium (III) chloride kept at the same temperature. The concentration of HCF (III) was not kept more than 5 x 10^{-4}M. All experiments were carried out in thermostatic water bath at constant temp. 35 ± 0.1ºC and ionic strength 0.5 M. KCl was used to keep the ionic strength constant.

The progress of the reaction was measured spectrophotometrically at λ_{max} 420 mm. Plane mirror and Guggenheim methods were used for evaluation of initial rates [(dA/dt)] and pseudo-first order rate constant k_1, respectively. Spot test and TLC[14, 15] were used to identify the oxidation products of amino acids, using the solvent ethanol and NH_3 and $FeCl_3$ as locating agent.

The stoichiometry of the reaction was studied by estimating the amount of HCF (III) ions produced after definite interval of time with standard solution of ceric (IV) sulphate using ferroin as redox indicator. 2 : 1 stoichiometry was observed between HCF (III) and amino acids. The reaction may be represented by the following equation –

$$RCHNH_2COOH + 2\,[Fe(CN)_6]^{3-} + 2\,OH^- \longrightarrow RCOOH + NH_3 + 2\,[Fe(CN)_6]^{4-} + H_2O$$

R represents CH_3, $(CH_3)_2CH$ and $(CH_3)_2CHCH_2$ for alanine, valine and leucine, respectively.

RESULTS AND DISCUSSION

The iridium (III) catalyzed oxidation of alanine, valine and leucine has been studied in aqueous alkaline medium using conditions where the uncatalysed reaction is negligible. Kinetic experiments were made at different concentrations of one reactant keeping the concentrations of others constant.

Table 1.Effect of [HCF (III)] on reaction rate

[Substrate] = 1.00 x 10^{-5} M μ = 0.5 M [OH^-] = 0.4 M

[Ir (III)] = 6.7 x 10^{-5} M Temp. = 35ºC ± 0.1ºC

[HCF (III)] x 10^4 M	**k_1 x 10^4 sec^{-1}**		
	Alanine	**Valine**	**Leucine**
1.00	-	-	1.15
2.00	2.87	2.11	2.11
3.00	3.65	2.49	2.88
4.00	4.20	2.88	3.65
5.00	4.60	3.07	4.22
6.00	4.99	3.26	5.18
7.00	5.18	-	5.76

Table 2.Effect of [OH^-] on reaction

[Substrate] = 3.0 x 10^{-3} M [HCF (III)]=3.0 x 10^{-4} M [Ir (III)] = 6.7 x 10^{-5} M

μ = 0.5 M Temp. = 35ºC ± 0.1ºC

[OH^- x 10 M]	**k_1 x 10^4 sec^{-1}**		
	Alanine	**Valine**	**Leucine**
0.50	0.768	2.111	1.727
1.00	1.343	3.263	3.262
2.00	2.495	4.989	5.758
3.00	3.455	5.758	6.717
4.00	4.414	6.141	7.677

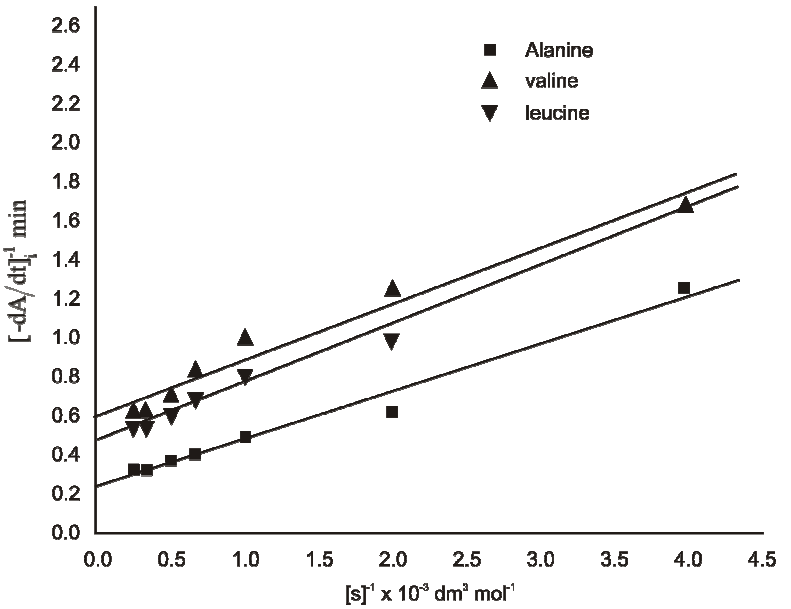
Alanine
valine
leucine
[-dA/dt]$_t^{-1}$ min
[s]$^{-1}$ x 10^{-3} dm^3 mol^{-1}

Fig. 1

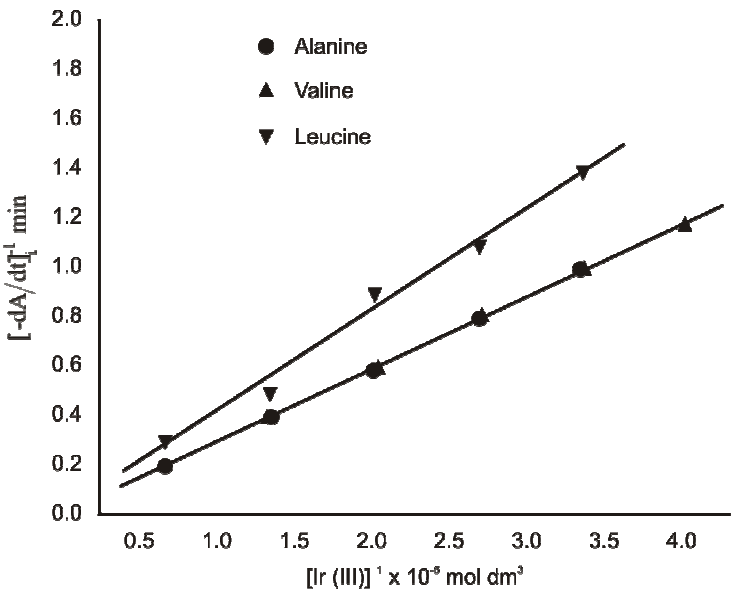
Alanine
Valine
Leucine
[-dA/dt]$_t^{-1}$ min
[Ir (III)] ^{1} x 10^{-6} mol dm^3

Fig. 2

The kinetic results given in Table 1 reveal that oxidation of all the above said amino acids follow first order kinetics with respect to HCF (III). The concentration of HCF (III) was varied from 1 x 10^{-4} M to 7 x 10^{-4} M. the initial rates were calculated by plotting absorbance vs time plots. The straight line plots plotted between initial rates in terms of $[(dA/dt)_i]$ vs concentration of HCF (III) confirms the first order kinetics with respect to HCF (III). A gradual increase in rate with hydroxide concentration reveals first order kinetics with respect to hydroxide concentration (Table 2).

Table 3.Effect of [Substrate] on reaction rate

[HCF (III)] = 3.0 x 10^{-4} M [OH^-] = 0.4 M [Ir (III)] = 6.7 x 10^{-5} M

μ = 0.5 M Temp. = 35ºC ± 0.1ºC

Substrate x 10^3 M	**k_1 x 10^4 sec^{-1}**		
	Alanine	**Valine**	**Leucine**
0.25	--	0.959	0.960
0.50	2.60	1.535	1.343
1.00	2.90	2.303	1.920
2.00	3.07	2.878	2.303
4.00	3.20	3.454	2.495
6.00	3.60	3.838	2.687
8.00	3.99	4.414	-

To study the effect of substrate concentration on reaction rate, the substrate concentration has been varied from 0.25 x 10^{-3} to 8.0 x 10^{-3} M. The data presented in Table 3 show nearly first order dependence of rate on lower concentrations of substrate which tends to be zero order at its higher concentrations. The linear plots of $rate^{-1}$ vs $[Substrate]^{-1}$ (Fig. 1) suggest Michaelis – Menten type of kinetics. The straight line plot (Fig. 2) between rate and catalyst concentration indicates a direct dependence of rate on catalyst concentration in case of all the three amino acids. The plots show that the rates for alanine and valine are nearly same. The concentration of iridium was varied from 0.67 x 10^{-5} M to 9.35 x 10^{-5} M (Fig. 2).

Effect of ionic strength was also studied by using neutral salt as KCl (Table 4). The linear increase in log(-dc/dt) with $\sqrt{\mu}$ suggest a positive salt effect i. e. the involvement of two similarly charged reacting species in the reaction. To evaluate the thermodynamic

parameters, the reaction was studied at four different temperatures between 35ºC to 50ºC under pseudo first order conditions. Activation parameters were evaluated from linear Arrhenius plots. The values of energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta F^{\#}$) evaluated are given in Table 5. The entropy of activation in each case was found negative suggesting the formation of a solvated and charged transition state. Nearly same value of $\Delta F^{\#}$ also suggests a common mechanism in case of all the three amino acids.

Table 4.Effect of ionic strength on reaction rate

[HCF (III)] = 3.0 x 10^{-4} M [Substrate] = 3.0 x 10^{-3} M

[Ir (III)] = 6.7 x 10^{-5} M Temp. = 35ºC ± 0.1ºC

Substrate μ x 10^2 M	**4+log [-dc/dt]**		
	Alanine	**Valine**	**Leucine**
38	0.7781	0.9031	0.6021
44	0.9031	1.0000	0.7781
50	1.0000	1.1461	0.8451
54	1.0790	1.2553	1.0000
63	1.2041	1.3010	1.0792
67	1.2553	-	1.1139

Table 5.Activation parameters

[Substrate] = 3.0 x 10^{-3} M [HCF (III)] = 3.0 x 10^{-4} M

[Ir (III)] = 6.7 x 10^{-5} M μ = 0.5 M

Substrate	**Ea (k cal/mol)**	**$-\Delta S^{\#}$ (E. U.)**	**$\Delta H^{\#}$ (kcal/mol)**	**$\Delta F^{\#}$ (kcal/mol)**
Alanine	14.50	20.02	13.87	20.19
Valine	14.58	18.43	13.85	19.67
Leucine	13.73	21.25	13.06	19.77

MECHANISM

Before proposing the probable oxidation mechanism, it is necessary to know the

probable reacting species of iridium (III) in alkaline medium. It is reported that Ir (I) and Ir (II) are the stable species of iridium[3, 4]. But in alkaline medium it is reported that $[IrCl_6]^{3-}$ is the only reacting species of iridium[11, 12].

Based upon the above results, the following reaction mechanism has been proposed-

$$S + OH^- \underset{}{\overset{K}{\rightleftharpoons}} S^- + H_2O \quad ...(1)$$

$$S^- + [IrCl_6]^{3-} \overset{K_1}{\rightleftharpoons} \text{Complex } (C_1) \quad ...(2)$$

$$\text{Complex } (C_1) + [Fe(CN)_6]^{3-} \overset{K_2}{\rightleftharpoons} \text{Complex } (C_2) \quad ...(3)$$

$$\text{Complex } (C_2) \xrightarrow[\text{slow}]{k} [IrCl_5]^{4-} + [Fe(CN)_6]^{4-} + \text{Product} + H^+ \quad ...(4)$$

$$[IrCl_5]^{4-} + 2\,[Fe(CN)_6]^{3-} + H_2O \xrightarrow{\text{fast}} [IrCl_5(H_2O)]^{2-} + 2\,[Fe(CN)_6]^{4-} \quad ...(5)$$

$$[IrCl_5(H_2O)]^{2-} + Cl^- \xrightarrow{\text{fast}} [IrCl_6]^{3-} + H_2O \quad ...(6)$$

where S represents the substrate (Amino acid).

In the above mechanism, it is assumed that organic substrate and $[IrCl_3]^{3-}$ form a loosely bonded complex C_1, which combines with HCF (III) to give another complex C_2[10]. This complex C_2 slowely disproportionates into Ir (I) and HCF (II) alongwith oxidation products (acid). Ir (I) is reoxidised to Ir (III) by two molecules of HCF (III).

The rate of reaction can be given as-

$$\text{rate} = -\frac{d[\text{HCF (III)}]}{dt} = k\,[C_2]$$

According to above mechanism, the rate of disappearance of HCF (III) can be given as-

$$-\frac{d[\text{HCF (III)}]}{dt} = \frac{kKK_1K_2\,[\text{HCF (III)}]\,[Ir^{3+}]_t\,[S]\,[OH^-]}{1 + KK_1\,[S]\,[OH^-] + KK_1K_2\,[S]\,[OH^-] + KK_1K_2\,[S]\,[OH^-]\,[\text{HCF (III)}]} \quad ...(7)$$

At very low concentrations of OH^- , amino acids and HCF (III), $1 >>> 1 + KK_1$ [Substrate] $[OH^-] + KK_1K_2$[Substrate] $[OH^-]$ [(HCF (III)] and equation (7) reduces to –

$$\text{Rate} = kKK_1K_2[\text{HCF (III)}]\,[Ir^{3+}]_t\,[S]\,[OH^-] \qquad ...(8)$$

This equation is in agreement with experimental results at low concentration of HCF (III), Ir (III), substrate and hydroxide ions.

The validity of rate law might be ensured by rewriting the equation (7) as follows –

$$\frac{1}{\text{Rate}} = \frac{1}{kKK_1K_2[\text{HCF (III)}]\,[S]\,[OH^-]} + \frac{1}{kK_2[\text{HCF (III)}]\,[Ir^{3+}]_t} + \frac{1}{k[Ir^{3+}]_t} \qquad ...(9)$$

The straight line plots between 1/r vs 1/[Substrate], 1/r vs 1/$[OH^-]$ and 1/r and vs $1/\{[Ir^{3+}]_t$ proves the validity of above rate law. The value of k has been calculated from the intercept of 1/r a vs $1/\{[Ir^{3+}]_t$ plots. The values are 1.24 L mol^{-1} sec^{-1} for alanine and valine and 1.66 1 mol^{-1} sec^{-1} for leucine. The constancy in the values of k clearly confirms the validity of above rate law and proposed mechanism.

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