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Full Length Research Paper

A kinetic and mechanistic study on the oxidation of arginine and lysine by hexacyanoferrate (III) catalysed by iridium (III) in aqueous alkaline medium

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The kinetics of Ir (III) catalysed oxidation of some amino acids like arginine and lysine by hexacyanoferrate (abbreviated as HCF) (III) ions in aqueous alkaline medium at constant ionic strength 0.5 mol dm^{-3} and temperature 35ºC has been studied spectrophotometrically. The reactions exhibit 2:1 stoichiometry and follow first order kinetics in [HCF (III)] and [alkali]. The dependence of the rate on substrate concentration has been found to be of Michaelis-Menten type. The ionic strength of the reaction mixture shows positive salt effect on the reaction rate. To calculate thermodynamic parameters, the reactions have been studied at four different temperatures between 35 to 50ºC. A complex mechanism involving the complex formation between catalyst and the substrate has been proposed. Keto acids; ε-guanidino-α-oxo valeric acid and 6 – amino-α-oxo caproic acid have been identified chromatographically and spectroscopically as the final product of oxidation of arginine and lysine, respectively. Based on the kinetic data and product analysis a reaction mechanism is proposed.

Key words: HCF (III), iridium (III), oxidation, arginine, lysine.

INTRODUCTION

Oxidation reactions are of fundamental importance in nature, and are key transformations in organic synthesis. Oxidation of α- amino acids is of great importance both from chemical point of view and its bearing on the mechanism of amino acids metabolism (Devra Vijay, 2005). Amino acids have been oxidised by a variety of reagents under different experimental conditions (Goel and Sharma, 2010; Goel et al*.,* 2002; Gupta et al., 1986; Harihar et al., 1999; Hemmige et al., 2003; Jeffery et al., 1996; Jose et al., 2006).

It was shown by the previous workers that the oxidation of α - amino acids by hexacyanoferrate (III) poceeds very slowly in the absence of any catalyst while it follows a complex kinetics in the presence of a catalyst (Kapoor et al., 1991). The oxidation rate was improved by the use of some metal ions: Os, Ru and Ag (Mahadevappa et al., 1982; Mahanti and Laloo, 1990). These reactions follow a complex kinetics in the presence of catalyst (Naik et al*.,* 2008; Patil et al., 2009).

Thus to understand about the catalysis of Ir (III) in oxidation of amino acids by HCF (III) and to explore the mechanism of these oxidations in aqueous alkaline medium, two amino acids like arginine and lysine have been selected as substrate for oxidation.

EXPERIMENTAL

All chemicals and reagents used were of AR grade. All solutions and reaction mixture were prepared in double distilled water. Absorbance was recorded on Systronic UV-vis spectrophotometer. λ_{max} for the reaction mixture was 420 nm at which the absorbance was noted only in the period in which the λ_{max} did not change and no precipitate/turbidity appeared. $IrCl_3$ $10H_2O$ (SRL) was prepared by dissolving the sample in dil. HCl. The final strength of iridium trichloride was kept 3.35×10^{-3} mol dm^{-3}. The kinetic experiments

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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 mixture and stock solution of amino acid was then clamped in a thermostate at 35 ± 0.1ºC. After 0.5 h, a required amount of amino acid solution was added to the mixture and stirred to start the reaction. Aliquots were withdrawn from the reaction mixture after repeated intervals of 5 min and the absorbance was recorded. Initial rates $(dA/dt)_i$ were evaluated after 5 min from the start of the reaction by plane mirror method and pseudo first order rate constant 'k_1' were calculated by Guggenheim's method.

The stoichiometry of the reaction was studied by estimating the amount of HCF (II) ions produced after definite interval of time with standard solution of ceric (IV) sulphate using ferroin as redox indicator. Estimation of the residual oxidant showed that one mole of substrate consumed two moles of hexacyanoferrate (III), corresponding to the stoichiometry.

$$RCH(NH_2)COOH + 2[Fe(CN)_6]^{-3} + 2OH^- \rightarrow RCOCOOH + NH_3 + 2[Fe(CN)_6]^{-4} + H_2O$$

Using the same experimental conditions that were used for the kinetic determinations, solutions of substrate and oxidant, and NaOH (ionic strength adjusted by the addition of the requistic amount of KCl) were mixed and kept at atmospheric conditions for about 24 h. The main reaction products were identified as keto acid and ammonia. Ammonia was identified by Nessler's reagent (Patil et al., 2009) and keto acid by the following methods. The reaction mixture was extracted with diethyl ether and then concentrated. The concentrated extract was subject to TLC which shows the presence of single white product, keto acid (Puttaswamy and Vaz, 2001; Salem 2006). The concentrated extract was evaporated at room temperature. A solid residue was left. It was analysed by melting point determination, spot test analysis and I. R. spectroscopy. The melting point of the two ketoacids- ε - guanidino - α -oxo valeric acid and 6 – amino - α -oxo caproic acid separated are 214 and 211°C, respectively (Literature value 216 and 212°C, respectively. The I R bands at frequency 1644 cm^{-1}(carbonyl group) and 1632 cm^{-1} (acid group) for arginine and 1635 cm^{-1}(carbonyl group) and 1614 cm^{-1} (acid group) for lysine shows the presence of keto acid group in the final products extracted.

RESULTS AND DISCUSSION

Kinetic experiments were made at different concentration of one reactant keeping the concentration of others constant.

The concentration of substrate (lysine and arginine, abbreviated as S) was varied in the range of 1×10^{-3} – 10×10^{-3} mol dm^{-3} at 35ºC keeping all other reactants concentration constant (Table 1). The data presented in Table 1 shows first order dependence on lower concentration of substrate which tends to be zero order at its higher concentration. The effect of $[OH^-]$ on the rate of reaction was studied at constant [S], [HCF (III)] and ionic strength at 0.5 mol dm^{-3} at 35ºC (Table 1). A perusal of data reveals first order kinetics with respect to OH^- concentration. The [HCF (III)] was varied in the range 2×10^{-4} – 7×10^{-4} mol dm^{-3} at fixed [S], $[OH^-]$ and ionic strength. The k_1 values indicate that the order in [HCF(III)] is unity (Table 1). The effect of iridium (III) concentration on the oxidation of amino acids was also studied. The results presented in Table 1 clearly reveal first order kinetics with respect to Ir (III) concentration in the concentration range of 0.67×10^{-5} – 3.01×10^{-5} mol dm^{-3}.

The effect of ionic strength was studied by varying the [KCl] in the reaction mixture. The ionic strength of the reaction medium was varied from 0.5 to 0.7 mol dm^{-3} at constant [HCF (III)], [S], and $[OH^-]$. The positive salt effect was found (Table 2).

To calculate the thermodynamic parameters, the effect of temperature on the rate of the oxidation was studied by carrying out the reaction at four temperatures 35, 40, 45 and 50ºC. Linear plots of log k_1 vs 1/T indicate that the reaction obeys Arrhenius equation. The values of energy of activation Ea, enthalpy of activation $\Delta H^{\#}$, entropy of activation $\Delta S^{\#}$ and free energy of activation $\Delta F^{\#}$ were evaluated as given in Table 3. The value of $\Delta F^{\#}$ are approximately the same for both the reactions studied, indicating that common mechanism is followed in these amino acids oxidation. Large negative values of entropy of activation suggest the formation of a solvated and charged transition state.

Mechanism

Keeping in view of the above experimental results, the following mechanistic path has been suggested for the oxidation of arginine and lysine by hexacyanoferrate (III) in aqueous alkaline medium in presence of Ir (III)

$$RCHNH_2COOH + OH^- \overset{K}{\rightleftharpoons} RCHNH_2COO^- + H_2O \quad (1)$$

$$RCHNH_2COO^- + IrCl_6^{3-} \overset{K_1}{\rightleftharpoons} \underset{C_1}{[RCHNH_2COO\ldots IrCl_6]^{4-}} \quad (2)$$

$$[RCHNH_2COO\ldots,IrCl_6]^{4-} + Fe(CN)_6^{3-} \overset{K_2}{\rightleftharpoons} \underset{C_2}{[RCHNH_2COO^-\ldots IrCl_6\ldots Fe^{3+}]} \quad (3)$$

$$[RCHNH_2COO^-\ldots.IrCl_6\ldots Fe^{3+}] \xrightarrow[slow]{k} Cl^- + IrCl_5^{4-} + Fe^{2+} + product \quad (4)$$

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

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

Table 1. Effect of [S] [NaOH] [HCF (III)] on reaction rate at Temperature = 35 ± 0.1ºC, μ=0.5 mol dm^{-3}.

[S] $x10^3$ (mol dm^{-3})	[NaOH] (mol dm^{-3})	[HCF(III)]$x10^4$ (mol dm^{-3})	[Ir(III)] $x10^5$ (mol dm^{-3})	k_1 x 10^4(sec^{-1}) Lysine	Arginine
1.0	0.40	3.00	3.35	2.68	2.68
2.0	0.40	3.00	3.35	3.83	3.07
3.0	0.40	3.00	3.35	4.66	4.20
4.0	0.40	3.00	3.35	5.75	4.60
5.0	0.40	3.00	3.35	6.90	5.37
6.0	0.40	3.00	3.35	7.67	6.14
7.0	0.40	3.00	3.35	8.06	6.52
8.0	0.40	3.00	3.35	8.44	6.90
9.0	0.40	3.00	3.35	8.82	7.29
10.0	0.40	3.00	3.35	9.21	7.67
3.0	0.10	3.00	3.35	1.92	2.67
3.0	0.20	3.00	3.35	3.07	3.83
3.0	0.30	3.00	3.35	3.83	4.60
3.0	0.40	3.00	3.35	4.98	6.14
3.0	0.50	3.00	3.35	5.75	6.52
3.0	0.40	2.00	3.35	3.07	3.83
3.0	0.40	3.00	3.35	4.20	4.66
3.0	0.40	4.00	3.35	4.70	5.75
3.0	0.40	5.00	3.35	5.37	5.75
3.0	0.40	6.00	3.35	6.14	6.14
3.0	0.40	7.00	3.35	6.52	6.52
3.0	0.40	3.00	0.67	6.14	10.74
3.0	0.40	3.00	1.01	6.90	3.83
3.0	0.40	3.00	1.34	7.29	4.60
3.0	0.40	3.00	1.67	7.67	5.75
3.0	0.40	3.00	2.09	8.44	6.52
3.0	0.40	3.00	2.34	9.21	8.06
3.0	0.40	3.00	2.67	9.59	8.82
3.0	0.40	3.00	3.01	9.97	9.59

Table 2. Effect of ionic strength on reaction rate**,** [HCF(III)] = 3.0 × 10^{-4} mol dm^{-3}, [S] =3.0 × 10^{-3} mol dm^{-3}, [Ir (III)] = 3.35 × 10^{-5} mol dm^{-3}, Temperature = 35 ± 0.1ºC.

Parameter	k_1 x 10^4(sec^{-1})	
μ x 10^1 mol dm^{-3}	Lysine	Arginine
0.5	3.07	2.30
0.55	4.22	3.07
0.60	5.76	4.22
0.65	7.29	5.37
0.70	9.60	5.75

as catalyst.

It is reported that Ir (I) and Ir (II) are the stable species of iridium, but in alkaline medium $[IrCl_6]^{3-}$ is the only reacting species of iridium (Singh et al., 1994; Srivastava et al., 1980). It is reported that the oxidation of amino acids involves the cleavage of N-H and C-H bond in the rate determining step (Shukla and Upadhyay, 2008). Based on the above facts it is assumed in the present study that substrate anion forms a loose bonded complex 'C_1' with iridium trichloride. The carbonyl oxygen of acid is most likely involved in the formation of complex C_1. In

Table 3. Activation parameters, [S] = 3.0 × 10^{-3} mol dm^{-3}, [HCF (III)] = 3.0 × 10^{-4} mol dm^{-3}, [Ir(III)] = 3.35 × 10^{-5} mol dm^{-3}, μ = 0.5 mol dm^{-3}.

T/K (± 0.1°)C	k_1 x 10^{-4} Lysine	Arginine
308	2.30	3.07
313	3.07	4.22
318	4.60	5.75
323	6.14	7.67
Ea kcal mol^{-1}	11.5	12.1
$\Delta H^{\#}$ kcal mol^{-1}	10.7	11.5
$\Delta S^{\#}$ e.u.	-28.3	- 25.9
$\Delta F^{\#}$ kcal mol^{-1}	18.3	19.6
A x10^7 l $mol^{-1}sec^{-1}$	1.16	3.21

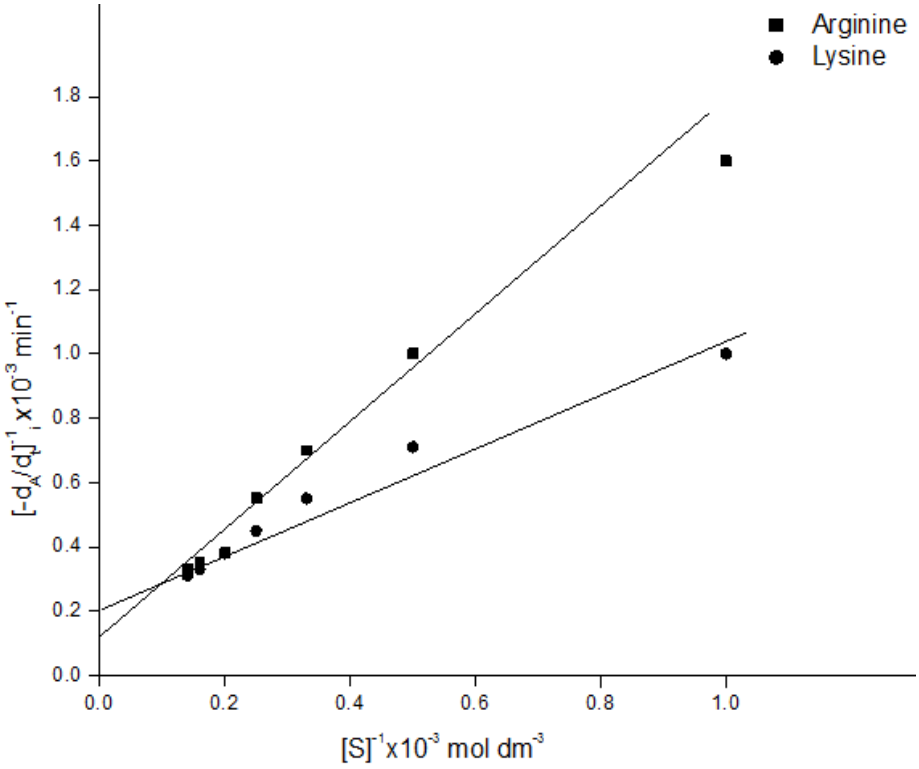

Figure 2. Plot between $rate^{-1}$ Vs $[S]^{-1}$

the next step the complex 'C_1' then combines with HCF (III) through electron abstraction to form complex (C_2). The complex (C_2) then slowly disproportionates into Ir^{1+} and HCF (II) along with final product. Ir^{1+} is reoxidized to Ir^{3+} by two moles of HCF (III) via one electron transfer process. The metal ion complexes with organic substrate to make the electron transfer easier (Shukla and Upadhyay, 2008).

The formation of the complex was proved kinetically by Michaelis – Menten plot that is, a non - zero intercept of the plot of 1/rate vs. 1/ [S] (Figure 1). The complex formation between oxidant and substrate was also reported in literature (Richard and Emmett, 1958).

The reaction rate(r) is measured in terms of rate of disappearance of HCF (III). According to step (III) the rate of disappearance of HCF (III) would be

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

Now the total concentration of Ir^{3+} will be

$$[Ir^{3+}]_t = [Ir^{3+}] + [C_1] + [C_2] \qquad \text{(ii)}$$

Substituting the values of $[Ir^{3+}]$, (C_1) and (C_2) in Equation (i)

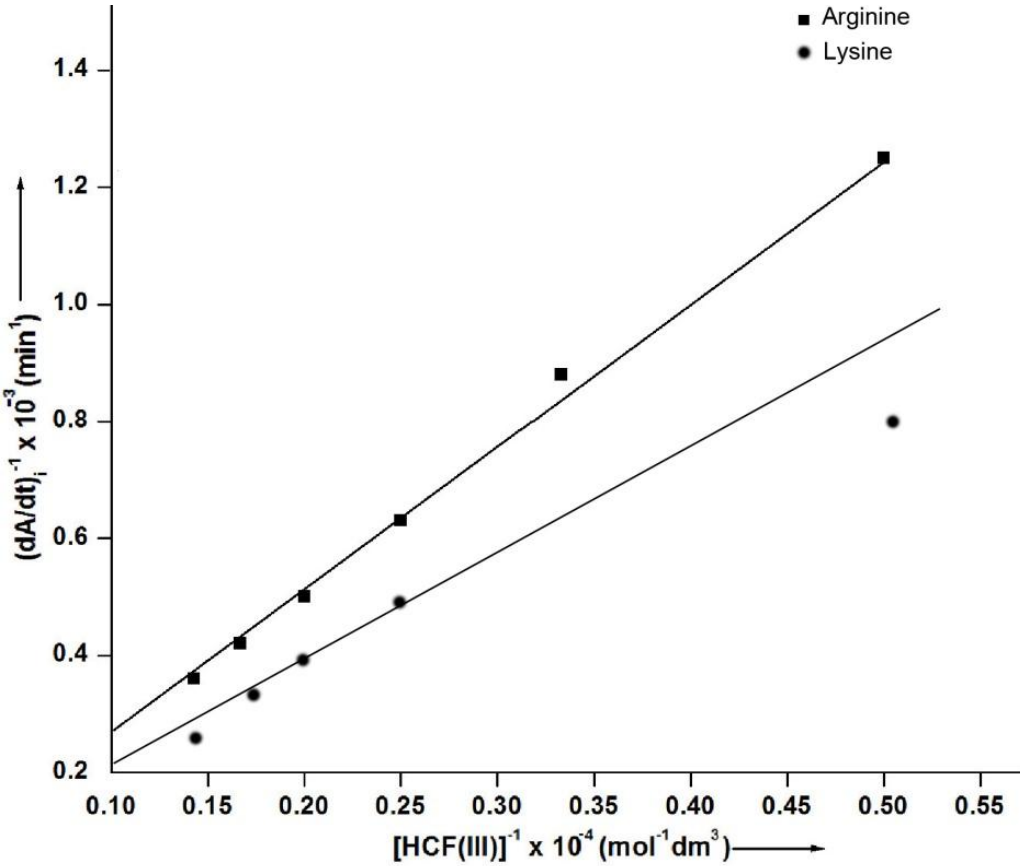

Figure 1. Plot between rate^{-1} Vs [HCF(111)]$^{-1}$

$$rate = \frac{kK_1'K_2\,[HCF(III)][Ir^{3+}]_t\,[S][OH^-]}{1 + K_1'[S][OH^-] + K_1'K_2[S][OH^-][HCF(III)]} \quad \text{(iii)}$$

Where $K_1' = KK_1$

At low concentration of HCF (III), S and OH^-, eq. (iii) reduces to

$$r = k K_1' K_2 [HCF(III)] [Ir^{3+}]_t [S] [OH^-] \quad \text{(iv)}$$

The rate law (iv) clearly accounts for the first order kinetics with respect to HCF (III), organic substrate, hydroxide ion and catalyst at their lower concentrations. In order to verify this law (iii) at higher concentration of above said reactants it could be re-written as-

$$\frac{1}{r} = \frac{1}{kK_1'K_2\,[HCF(III)][Ir^{3+}]_t\,[S][OH^-]} + \frac{1}{kK_2\,[HCF(III)][Ir^{3+}]_t} + \frac{1}{k\,[Ir^{3+}]_t} \quad \text{(v)}$$

This Equation (v) indicates that the plot of 1/rate vs. 1/[HCF(III)] & 1/rate vs. 1/[S] should give a straight line with positive intercept at 1/rate axis. Such plots are presented in Figures 1 and 2 for arginine and lysine, respectively. A close examination of these figures clearly indicate that these are evidently straight lines with positive intercept at 1/rate axis. The rate constant of slow step k, the ionization constant K_1' of the first step and the formation constant of the complex 'K_2' of the second step of all organic substrate at four different temperatures (35, 40, 45 and 50°C) were calculated from intercept and slope of the straight line plots between rate^{-1} vs. [HCF(III)]$^{-1}$ and rate^{-1} vs. [S]$^{-1}$ for both the organic substrate (arginine and lysine). Data are presented in Tables 4a and b for equilibrium constants and thermodynamic parameters, respectively. The constancy in K_1', K and K_2 values clearly validates the derived rate law equation on the basis of proposed mechanism. A comparison of the later values with those obtained for the slow step of the raection shows that these values mainly refer to the rate limiting step.value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.

The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction. The observed modest enthalpy of activation and a relatively low value of entropy of activation indicate that the oxidation presumably occurs via an inner – sphere mechanism.

Table 4a. Effect of temperature on equilibrium constants.

Temperature ± 0.1	Arginine		Lysine	
(°K)	K_1'	K_2	K_1'	K_2
308	24.0	520.8	124.6	2.69
313	58.3	666.6	144.3	2.74
318	70.8	793.5	180.8	2.94
323	78.6	1235.0	196.7	2.99

Table 4b. Thermodynamic parameters

Parameter	Arginine		Lysine	
	value from K_1'	value fromK_2	value from K_1'	value from K_2
Ea (kcal mol^{-1})	8.01	9.81	33.55	10.2
$\Delta S^{\#}$ (e.u.)	-27.92	-16.36	56.22	-15.32
$\Delta H^{\#}$ (kcal mol^{-1})	7.36	9.17	32.91	9.573
$\Delta F^{\#}$ (kcal mol^{-1})	16.18	14.33	15.17	14.40

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