Research Paper

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Kinetics and Mechanism of Ruthenium(Iii) Catalysed Oxidation of L-Arginine by Hexacyanoferrate(Iii) in Alkaline Medium

Chemistry

KEYWORDS : Oxidation of L-arginine, hexacynoferrate (III), ruthenium(III).

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ABSTRACT

The kinetics of the ruthenium(III) catalysed oxidation of L-arginine by hexacyanoferrate(III) [HCF(III)] was studied spectrophotometrically in alkaline medium at 420 nm. It was found that the reaction is first order with respect to [catalyst] and [hexacyanoferrate(III)]. The reaction showed fractional order dependence on [substrate] and [alkali]. The oxidation product of the reaction was found to be α- keto acid. The anionic species of arginine (Arg-) is considered to be the reactive species.A suitable mechanism involving complexation between Arg- and [Ru(H2O)5OH]2+ was proposed leading to the rate law

$$\frac{-d[HCF(III)]}{dt} = \frac{k K_1 K_2 [Arg]_t [OH^-][Ru(III)]_t}{1 + K_1[OH^-] + K_1 K_2 [Arg]_t [OH^-]}$$

The activation parameters of the rate determining step Ea, and ΔS#, were computed to be 38.03 ± 0.72kJ mol-1 and -202.80± 2.16 JK-1mol-1 respectively.

1. Introduction

Oxidation of amino acids has received considerable attention so far. Arginine, an essential amino acid, is needed to remove toxic ammonia from the body and also plays an important role in cell division, immune function and in the release of hormones. There have been only few investigations on the oxidation of arginine(arg) using oxidants like Chloramine-T[1,2], Bromamine-T[3], hexacyanoferrate(III)[4], diperiodato nickelate(IV) (DPN)[5], N-bromo succinimide[6], Mn(III)[7,8], quinquevalentvanadium[19,10], Ru(III) catalysed alkaline permanganate[11], N-chloronicotinamide[12] and N-chlorosaccharin[13], hydroxopentaaquarhodium(III) ion[14].

Hexacynoferrate(III) (HCF(III)) has been widely used to oxidize numerous organic and inorganic compounds in alkaline medium. The kinetics of uncatalysed oxidation of arginine by HCF(III) was studied at higher temperature in the range 318-338K since there is no direct reaction between arginine by HCF(III) at 303K.Ruthenium(III) acts as an efficient catalyst in many redox reactions involving different complexities due to the formation of different intermediate complexes, free radicals and multiple oxidation states of ruthenium. A microscopic amount of ruthenium(III) is sufficient to catalyse the reaction between L-arginine and hehacyanoferrate(III) in the alkaline medium. Herein we describe the results of the title reaction in order to understand the active species of oxidant, reductant and catalyst and to arrive at a plausible mechanism.

2. Experimental

The standard solution of L-arginine was prepared by using double distilled water. The other chemicals used were HCF(III), sodium hydroxide, ruthenium(III) and $NaClO_4$. All chemicals used were of AR grade.

About 0.5 g of ruthenium(III) chloride is continuously fumed with concentrated sulfuric acid till all the chloride is completely expelled and finally diluted to 500 ml. The solution thus prepared is standardized by the method suggested by Beamish and Valnoon[15]. Solution of desired concentration is prepared from this stock by suitable dilution.

The reaction was initiated by mixing a calculated amount of HCF(III) to a mixture of L-arginine, sodium hydroxide, ruthenium(III) and sodium perchlorate at a constant temperature of 30 ± 0.1°C. The progress of the reaction was followed by measuring the absorbance of HCF(III) at 420 nm using Milton Roy 1201 UV-Visible spectrophotometer with 1cm glass cells. The temperature is kept constant using a SISKIN JULABO V constant temperature liquid circulatory bath.

3. Results and Discussion

Known amounts of L-arginine were allowed to react completely with a known excess of HCF(III) in presence of ruthenium(III) at 30°C in 0.4mol dm^{-3} NaOH at an ionic strength of 0.5 mol dm^{-3}. The remaining HCF(III) was then analyzed spectrophotometrically. As per these results the stoichiometry was found to correspond to the equation

$$RCH(NH_2)COO^- + 2HCF(III) + OH^- \xrightarrow{Ru(III)} RCOCOOH + 2HCF(II) + NH_3$$

where $R = NH_2—\underset{\underset{NH}{||}}{CH}—NH_2—(CH_2)_3$

The test for free radicals was carried out by taking L-arginine, NaOH, Ru(III) in a thumberg tube and acrylonitrile and HCF(III) in a bent tube. After evacuating the system the solutions were mixed by tilting the tube. The reaction mixture was kept aside and even after 24 hrs no precipitate was observed, indicating the absence of free radicals.

The product analysis has been carried out under the experimental conditions employing [arginine] excess over [HCF (III)] and the product has been identified to be arginine keto acid by neutral $FeCl_3$ that gives reddish brown precipitate indicating the presence of a keto acid. Further the product was extracted into ether and the isolated compound was analysed by IR spectrum (Fig.3.1) which revealed the presence of keto acid υ at 1725.72cm^{-1}. Ammonia is identified by Nessler's reagent.

The reaction orders were determined from the slopes of log k' versus log (concentration) plots by varying the concentrations of the oxidant, reductant, alkali or catalyst, while keeping the concentrations of the other reacting species constant.

The [arginine] was varied in the range of 1.0-6.0 x 10^{-2} mol dm^{-3} at different temperatures 25, 30, 35, and 40°C, by keeping all other reactant concentrations and conditions constant. The rate constant values increased with increase in [arginine] and the order with respect to [arginine] as given in Table 1 was found to be fractional. Further the plots of 1/k′ versus 1/[argi-

nine](Fig. 1) were found to be good straight lines with positive intercepts on the rate axis indicating that the reaction obeys Michaelis-Menten behaviour. But no spectrophotometric evidence for complexation was obtained between ruthenium(III) and arginine.

The effect of alkali on the rate of the reaction was studied at constant concentrations of arginine and HCF(III) and at a constant ionic strength of 0.8 mol dm^{-3} at 30^0C.The rate constants obtained were found to increase with the increase in [alkali] as given in theTable 1.When a plot log $k^/$ versus log $[OH^-]$ was plotted, a straight line with a slope of 0.73 is obtained indicating fraction order dependence on [alkali].

The effect of [HCF(III)] was studied by varying the [HCF(III)] in the reaction medium from 2.0 – 12.0 x 10^{-4} mol dm^{-3} at constant arginine, alkali, and ruthenium(III) concentrations. The rate constant were found to decrease with increase in [HCF(III)] .

The catalyst, [ruthenium(III)] was varied in the range 2.0-6.5.0 X 10^{-6} mol dm^{-3} keeping the concentration of all other reactants constant. When the pseudo first order rate constants obtained from the absorbance versus time plots were plotted against [ruthenium(III)] a straight line passing through origin is obtained indicating the order with respect to [ruthenium(III)] to be unity.

The effect of ionic strength was studied by varying the [$NaClO_4$] in the reaction medium from 0.5–1.2 mol dm^{-3} at constant [HCF(III)], [arginine], [alkali], and [ruthenium(III)]. The rate constant was found to increase with increase in the ionic strength of the medium which were given in table 1.

Arginine contains strongly basic guanidinium group in its side chain and has three different pK_a values, pK_1 = 2.17, pK_2 = 9.04 and pK_3 = 12.48 corresponding to the carboxylic group, amino and guanidinium groups respectively.

Under the present experimental conditions, at a $[OH^-]$ 0.4 mol dm^{-3} arginine exists in the form of anionic species, Arg^- (IV) to the extent of 98.5% and as neutral species, Arg_z (III) to the extent of 1.5%. HCF(III) is a low spin octahedral complex. In alkaline medium[15], ruthenium(III) exists as

$$[Ru(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Ru(H_2O)_5OH]^{2+} + H_2O$$

Since the rate of the reaction increases with increase in $[OH^-]$ the active form of ruthenium(III) is considered to be $[Ru(H_2O)_5OH]^{2+}$.Basing on these observations the following mechanism is proposed involving complexation between arginine and ruthenium(III).

3.1 Mechanism

$$[Ru(H_2O)_6] + OH^- \overset{K_1}{\rightleftharpoons} [Ru(H_2O)_5OH]^{2+} + H_2O \quad ----- (1)$$

$$[Ru(H_2O)_5OH]^{2+} + Arg^- \overset{K_2}{\rightleftharpoons} Complex\,(C) \quad ----- (2)$$

$$C + [Fe(CN)_6^{3-}] \xrightarrow[slow]{k} Intermediate\,(I) \quad ----- (3)$$

$$I + [Fe(CN)_6^{3-}] \xrightarrow{fast} products \quad ----- (4)$$

$$Rate = \frac{-d[Fe(CN)_6^{3-}]}{dt} = k[C][Fe(CN)_6^{3-}]$$

$$= kK_2[Ru(H_2O)_5OH^{2+}]_e[Arg^-]_e \quad ----- (5)$$

$$since\ [Ru(H_2O)_5OH^{2+}]_e = \frac{K_1[OH^-]_e[Ru(III)_t]}{1+K_1[OH^-]_e + K_1K_2[Arg^-]_e[OH^-]_e} \quad ----- (6)$$

$$Rate = \frac{kK_1K_2[Arg^-]_e[OH^-]_e[Ru(III)_t][Fe(CN)_6^{3-}]}{1+K_1[OH^-]_e + K_1K_2[Arg^-]_e[OH^-]_e} \quad ---- (7)$$

Substituting for $[Ru(H_2O)_5OH^{2+}]_e$ from equation(6) in equation(5) leads to

But $[Arg]_e = [Arg]_t$ and $[OH]_e = [OH]_t$

$$Rate = \frac{kK_1K_2[Arg^-]_e[OH^-]_e[Ru(III)_t][Fe(CN)_6^{3-}]}{1+K_1[OH^-]_e + K_1K_2[Arg^-]_e[OH^-]_e} \quad ----- (8)$$

$$since\ \frac{rate}{[Fe(CN)_6^{3-}]} = k^/ \text{ and hence equation (8) becomes}$$

$$k^/ = \frac{kK_1K_2[Arg]_t[OH^-][Ru(III)]_t[Fe(CN)_6^{3-}]}{1+K_1[OH^-] + K_1K_2[Arg]_t[OH^-]} \quad ----- (9)$$

The rate equation explains first order dependence on $[Fe(CN)_6^{3-}]$ and $[Ru^{III}]$ and fractional order with respect to [Arg] and $[OH^-]$.

Taking reciprocals on both sides it leads to

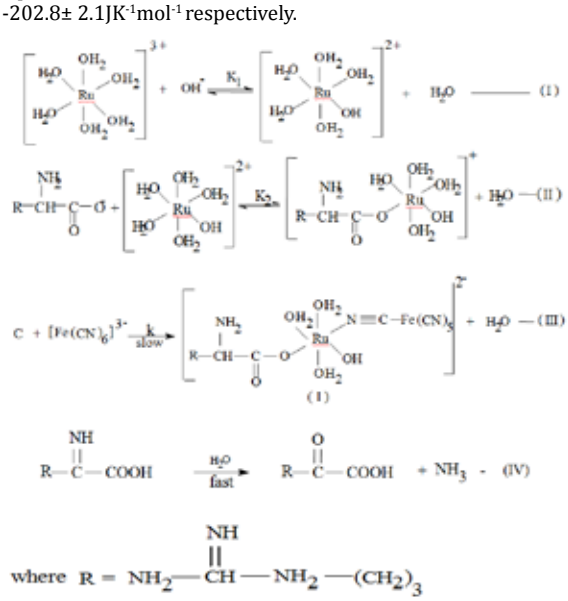
$$\frac{1}{kK_1K_2[Arg][OH^-][Ru(III)]} + \frac{1}{kK_2[Arg][Ru(III)]} + \frac{1}{k[Ru(III)]} \quad ----- (10)$$

The above equation predicts the plots of $1/k^/$ vs $1/[OH^-]$ and $1/k^/$ vs 1/ [Arginine] to be straight lines with positive intercepts on y-axis. Similar plots were obtained experimentally (Fig.1and 2) thus supporting the proposed mechanism.

From the intercepts of $1/k^/$ vs $1/[Arginine^-]$ the rate constants, k of the slow step were determined at four different temperatures 25, 30, 35and 40ºC (Fig. 1) are incorporated in (Table. 6).

Further, from the slope of $1/k^/$ vs $1/[Arginine^-]$,at 30ºC K_1 was determined and found to be 4.23X10^{-2} mol dm^{-3} respectively. From the slope and intercept of the plot $1/k^/$ vs $1/[OH^-]$, K_1 and K_2 are determined and were found to be 5.93X10^{-2} mol dm^{-3} and 8.50 X 10^2 mol dm^{-3}. The K_1 values obtained from these two plots are in good agreement with each other thus substantiating the proposed mechanism.

Further the energy of activation, E_a and entropy of activation $\Delta S^{\#}$ for the rate determining step were computed using linear least squares method and were found to be 38.0 ± 0.7 kJ mol^{-1} and -202.8± 2.1$JK^{-1}mol^{-1}$ respectively.



where $R = NH_2—CH(NH)—NH_2—(CH_2)_3$

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4. Intimate Mechanism

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Fig. 1: Plot of 1/k/ versus 1/arginine at four different temperatures

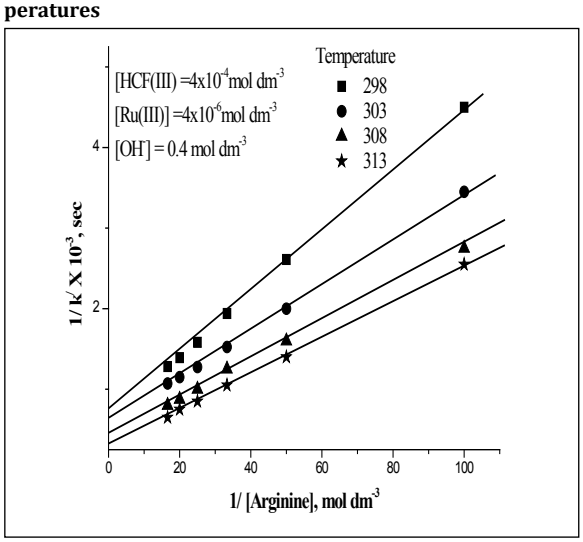

Fig. 2: Plot of 1/k/ versus1/[OH-]

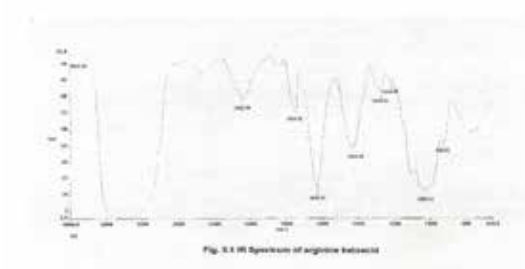

Table 1: Effect of [arginine], [HCF(III)],[Ru(III)],[OH-],μ and temperature on the pseudo-first order rate constant, k/.

Temp K	[Arg] X 10^2 (mol dm^{-3})	[HCF(III)] $X10^4$ (mol dm^{-3})	[Ru(III)] $X10^6$ (mol dm^{-3})	[OH] $X10^1$ (mol dm^{-3})	μ $X1\ 0^1$ (mol dm^{-3})	k¢x 10^4 (sec^{-1})
303	2.0	2.0	4.0	4.0	5.0	5.2
303	2.0	4.0	4.0	4.0	5.0	4.9
303	2.0	6.0	4.0	4.0	5.0	3.1
303	2.0	8.0	4.0	4.0	5.0	2.4
303	2.0	10.0	4.0	4.0	5.0	1.7
303	2.0	12.0	4.0	4.0	5.0	1.7
298	1.0	4.0	4.0	4.0	5.0	2.2
298	2.0	4.0	4.0	4.0	5.0	3.8
298	3.0	4.0	4.0	4.0	5.0	5.1
298	4.0	4.0	4.0	4.0	5.0	6.3
298	5.0	4.0	4.0	4.0	5.0	7.1
298	6.0	4.0	4.0	4.0	5.0	7.8
303	1.0	4.0	4.0	4.0	5.0	3.2
303	2.0	4.0	4.0	4.0	5.0	5.1
303	3.0	4.0	4.0	4.0	5.0	6.0
303	4.0	4.0	4.0	4.0	5.0	7.9
303	5.0	4.0	4.0	4.0	5.0	8.7
303	6.0	4.0	4.0	4.0	5.0	9.3
308	1.0	4.0	4.0	4.0	5.0	3.6
308	2.0	4.0	4.0	4.0	5.0	6.2
308	3.0	4.0	4.0	4.0	5.0	8.1
308	4.0	4.0	4.0	4.0	5.0	10.0
308	5.0	4.0	4.0	4.0	5.0	11.4
308	6.0	4.0	4.0	4.0	5.0	12.5
313	1.0	4.0	4.0	4.0	5.0	3.9
313	2.0	4.0	4.0	4.0	5.0	7.1
313	3.0	4.0	4.0	4.0	5.0	9.5
313	4.0	4.0	4.0	4.0	5.0	11.7
313	5.0	4.0	4.0	4.0	5.0	13.3
313	6.0	4.0	4.0	4.0	5.0	15.4
303	2.0	4.0	2.0	4.0	5.0	2.0
303	2.0	4.0	3.0	4.0	5.0	3.6
303	2.0	4.0	4.0	4.0	5.0	5.1
303	2.0	4.0	5.0	4.0	5.0	6.2
303	2.0	4.0	6.0	4.0	5.0	7.6
303	2.0	4.0	6.5	4.0	5.0	8.3
303	2.0	4.0	4.0	3.0	5.0	5.4
303	2.0	4.0	4.0	4.0	5.0	6.6
303	2.0	4.0	4.0	5.0	5.0	7.7
303	2.0	4.0	4.0	6.0	5.0	8,7
303	2.0	4.0	4.0	7.0	5.0	9.8
303	2.0	4.0	4.0	8.0	5.0	10.5
303	2.0	4.0	4.0	4.0	6.0	5.4
303	2.0	4.0	4.0	4.0	7.0	6.1
303	2.0	4.0	4.0	4.0	8.0	6.6
303	2.0	4.0	4.0	4.0	10.0	7.5
303	2.0	4.0	4.0	4.0	12.0	8.3

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