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Kinetics and Mechanism of Uncatalyzed and Ag (I) Catalyzed Oxidation of Hydroxylysine by Cerium (IV) in Acid Medium

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Abstract

The kinetics of the uncatalyzed and silver (I) catalyzed oxidation of Hydroxylysine with cerium (IV), has been studied in perchloric acid medium. The reaction is second order, which is first order with respect to each reactant. The mode of electron transfer has been indicated through an adduct between Ag^I and hydroxylysine, *via* oxygen atom of the carboxyl group rather than the amino group. Uncatalyzed reaction simultaneously occurs with silver (I) catalyzed reaction and the rate law (1) conforms to all experimental data observed in the reaction.

$$k = \frac{k_1[H^+]}{K_h + [H^+]} + \frac{k_2[Ag^I][H^+]}{K_h + [H^+]}$$

where k is an observed second order rate constant. A reaction mechanism accounting for all these experimental observations has been suggested.

Keywords: Hydroxylysine; Cerium (IV); Silver (I); Oxidation; Mechanism

Introduction

The oxidative decarboxylation of amino acids is one of the well-known biochemical processes and has importance both from chemical view point, and also from the view point of mechanism of amino acid metabolism. Specific metabolic role of amino acids includes biosynthesis of polypeptides and proteins and synthesis of nucleotides [1,2]. Their studies related to oxidative decarboxylation are important to understand more complicated enzyme catalyzed reactions and their mechanism.

Kinetics of oxidation of amino acids by a variety of oxidants like Mn III [3], Co (III) [4], Fe (CN)$_6$ [4,5], Chloramine-T [6,7], 1-Chlorobenzotriazole [8], N-bromo succinamide [9,10] and N-bromo-benzenesulphonamide [11], in both acid and alkaline media have been studied. Although, various types of the reaction models have been suggested by different researchers [12-16], the specific details are yet to be discovered. Also, there are still controversies regarding the mechanistic pathway of chemical processes of oxidative decarboxylation of amino acids [12,13]. In most of the reactions, the end products are aldehydes [14,15]. The intermediate $R\text{-}CH = \overset{+}{N}H_2$, if undergoes hydrolysis yields aldehyde, whereas its interaction with the oxidant yields nitrile [16]. However, evidence for the presence of such an imine intermediate is difficult to get in oxidation system. It has also been reported that the products vary with the variation of pH of the reaction mixture [9].

The oxidizing potentialities of cerium (IV) in H_2SO_4 medium have conclusively been established [17-19], and the oxidant exists in the form of sulphato species. Nevertheless, the oxidant has scantly been employed in per chloric acid medium, probably owing to the presence of dimers and polymers of Ce(IV) [20-22]. Although, the concentration of such dimers and polymers are significantly less, their contribution to the overall rate of reaction cannot be neglected in higher concentration of Ce(IV).

The observations, which prompted us to undertake the title study, are as follows:

(i)   Contradictory reports regarding dependence of Ce(IV) on the rate in its various reactions.

(ii)   The identification of the oxidation products of amino acid, and

(iii)   The optimization of kinetic parameters for determining the oxidation of Hydroxylysine by Ce(IV) in acid perchlorate medium.

Experimental Procedure

The kinetic studies of oxidation of Hydroxylysine by Ce(IV) in acid medium, has been studied by monitoring Ce(IV). The solution of ceric perchlorate was prepared by dissolving ceric ammonium nitrate (B.D.H.AnalaR) in perchloric acid (E. Merck) and solution was standardized by titrating aliquot of the test solution against standard ferrous ammonium sulphate (E. Merck) solution, employing ferroin as indicator. However, all other reagents were of AnalaR or guaranteed reagent grade, and were used as supplied without any further treatment. Corning glass vessels were employed for kinetic study. Doubly-distilled water was employed throughout the work for dilution.

Kinetic measurements

The reaction was carried out in stoppered Erlenmeyer flasks

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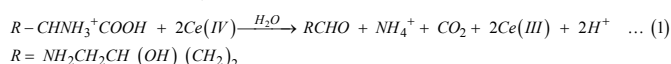
immersed in a water bath thermostated at 45 ± 0.1°C. All the ingredients of the reaction mixture except ceric perchlorate were taken in the flasks, and the reaction was initiated by adding a known volume of temperature pre-equilibrated solution of ceric perchlorate. Since the reaction is slow, the initial time was recorded when the pipette was half emptied. However, order of mixing was without any effect on the kinetics. An aliquot sample (5 cm³) from the reaction mixture was withdrawn periodically, and was added into dil. H_2SO_4 (~ 1.0 mol dm³), and Ce(IV) was titrated against the standard solution of ferrous ammonium sulphate using ferroin as an indicator.

The kinetics of the reaction was studied under pseudo first order conditions and rate measurements are reproducible within ± 6%. Initial rates are also calculated employing plane mirror method [23].

Stoichiometry and product analysis

The reaction mixtures with amino acid in excess over Ce(IV), were allowed to stand in thermostated water bath at 45 ± 0.1°C for 24 hr. After Ce(IV) was completely utilized, the solutions were concentrated and tested for the presence of both nitrile and aldehyde, the products usually reported in the oxidation of amino acids [9,24]. Nitrile tests were negative and qualitative tests of aldehyde were positive. Therefore, the stoichiometry of the reaction based on the formation of an aldehyde can be represented by Equation (1).

$$R - CHNH_3^+COOH + 2Ce(IV) \xrightarrow{H_2O} RCHO + NH_4^+ + CO_2 + 2Ce(III) + 2H^+ \quad \dots (1)$$
$$R = NH_2CH_2CH(OH)(CH_2)_2$$

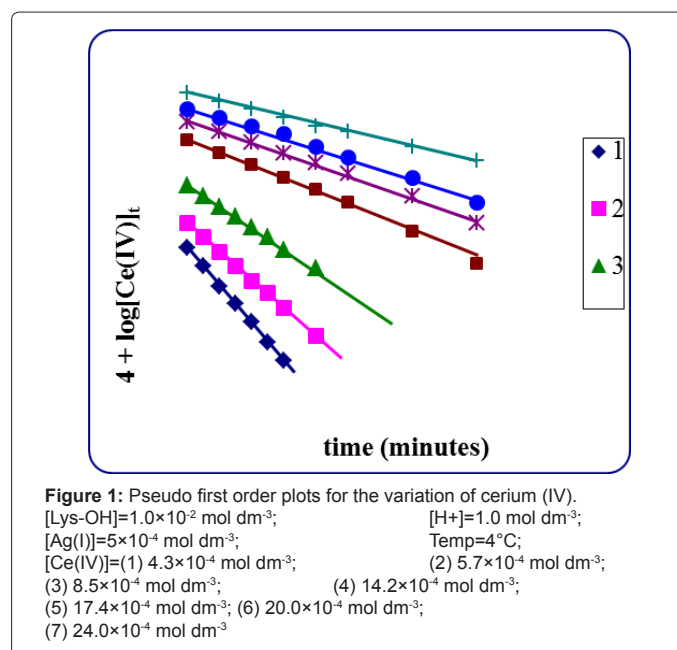The liberated CO_2 was detected by the lime water test.

Results

Cerium (IV) dependence

The concentration of cerium (IV) was varied from 4.3×10^{-4} to 2.4×10^{-3} mol dm³ at fixed concentration of Hydroxylysine (Lys-OH)=1.0×10^{-2} mol dm³ and [H⁺]=1.0 mol dm³ for uncatalyzed reaction. Pseudo first order plots were made, and pseudo first order rate constant (k′) were found to be independent of concentration of Ce(IV). For catalyzed reaction, the concentration of cerium (IV) was varied from 4.3×10^{-4} to 2.4×10^{-3} mol dm-3 at different concentration of Hydroxylysine, viz 1.0×10^{-2}, 2.0×10^{-2}, 3.0×10^{-2} mol dm³, respectively, [H⁺]=1.0 mol dm³ and [Ag(I)]=5.0×10^{-4} mol dm³ at temp=45°C. Pseudo first order plots of log $[Ce(IV)]_t$ versus time (t) (Figure 1) were made and the value of pseudo first order rate constants (k′) were calculated. The first order rate constant in silver (I) catalyzed were also independent of initial concentration of cerium (IV) (Table 1).

Lysine dependence

The concentration of Hydroxylysine was varied from 5.0×10^{-3} to 5.0×10^{-2} mol dm³ at [Ce(IV)]=5.7×10^{-4} mol dm³ and [H⁺]=1.0 mol dm³ for uncatalyzed reaction. The plot of pseudo first order rate constant (k′) vs [Lys-OH] yielded a straight line passing through the origin, indicating first order dependence with respect to amino acid.

The concentration of Hydroxylysine in silver (I) catalyzed reaction was varied from 5.0×10^{-3} to 5.0×10^{-2} mol dm³ at fixed concentration of [H⁺]=1.0 mol dm³, [Ag(I)]=5.0×10^{-4} mol dm³, C and at three concentration of cerium (IV), viz 5.7×10^{-4}, 1.42×10^{-3} and 2.0×10^{-3} mol dm³, respectively at 45°C. The pseudo first order rate constants (k′) calculated in these reactions also exhibit proportionate increase with increasing Hydroxylysine concentration, further confirming first order dependence with respect to Hydroxylysine (Table 1).

Figure 1: Pseudo first order plots for the variation of cerium (IV).
[Lys-OH]=1.0×10^{-2} mol dm³;   [H+]=1.0 mol dm³;
[Ag(I)]=5×10^{-4} mol dm³;   Temp=4°C;
[Ce(IV)]=(1) 4.3×10^{-4} mol dm³;   (2) 5.7×10^{-4} mol dm³;
(3) 8.5×10^{-4} mol dm³;   (4) 14.2×10^{-4} mol dm³;
(5) 17.4×10^{-4} mol dm³; (6) 20.0×10^{-4} mol dm³;
(7) 24.0×10^{-4} mol dm³

Silver(I) dependence

The concentration of silver (I) was varied from 1.0×10^{-4} to 1.0×10^{-3} mol dm³ at [Ce(IV)]= 5.7×10^{-4} mol dm³, [Lys-OH]=1.0×10^{-2} mol dm³ and [H+]=1.0 mol dm³ at 45°C. Pseudo first order plots were made and pseudo first order rate constants (k′) on plotting against the concentration of silver (I) yielded straight line with non-zero intercept. Such a rate behavior conforms to first order dependence with respect to silver (I). However, a straight line with non-zero intercept also indicates a simultaneous uncatalyzed reaction of cerium (IV) with amino acid. Thus, the empirical rate equation (2) accounts for an uncatalyzed and silver (I) catalyzed reactions-

$$-d[Ce(1V)]/dt = (k_\alpha + k_\beta)[Ag(I)][Ce(1V)][Lys-OH] \quad (2)$$

Where, k_α and k_β are the second order rate constants in absence and presence of silver (I) catalyst.

Hydrogen ion dependence

The hydrogen ion concentration was varied by employing perchloric acid from 0.5 to 2.0 mol dm³ at fixed ionic strength [I]=2.0 mol dm³ (Ionic strength was adjusted employing sodium perchlorate), [Ce(IV)]=5.7×10^{-4} mol dm³ and [Lys-OH]=1.0×10^{-2} mol dm³ at 45°C. The rate initially increases, and then tends towards a limiting value with increasing hydrogen ion concentration in uncatalyzed reaction.

Similarly, in case of silver (I) catalyzed reaction, the hydrogen ion concentration was varied from 0.5-2.5 mol dm³, employing perchloric acid at fixed concentration of [Ce(IV)]=5.7×10^{-4} mol dm³, [Lys-OH]=1.0×10^{-2} mol dm³ [Ag(I)]=5.0×10^{-4} mol dm³ and I=2.5 mol dm³ at three different temperatures, viz 40°C, 45°C and 50°C, respectively. First order rate constant increases with increasing concentration of hydrogen ion.

Effect of ionic strength

The effect of ionic strength on the rate in uncatalyzed reaction was studied by varying the concentration of sodium perchlorate (0.25 to 1.5 mol dm³), at fixed concentration of [Ce(IV)]=5.7×10^{-4} mol dm³, [Lys-OH]=1.0×10^{-2} mol dm³ and [H+]=1.0 mol dm³. The rate of reaction

slightly increases with increasing concentration of sodium perchlorate, without exhibiting much change in rates by this inert electrolyte.

In case of silver (I) catalyzed reaction, effect of ionic strength was studied by employing sodium perchlorate (0.5 to 2.0 mol dm-3), at fixed concentration of $[Ce(IV)] = 5.7 \times 10^{-4}$ mol dm^{-3}, $[Lys\text{-}OH] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[H+] = 1.0$ mol dm^{-3} and $[Ag(I)] = 5.0 \times 10^{-4}$ mol dm^{-3}. The rate was independent of ionic strength in this reaction.

Effect of Cerium (III)

The effect of cerium (III) was also studied, and the rate of reaction remains unchanged with the variation of concentration of Ce(III). This shows that any fast equilibrium involving Ce(III) and preceded by the rate limiting step in the reaction mechanism can be eliminated.

Discussion

The reactions of cerium (IV) in $HClO_4$ medium proceeds much faster than the reaction in sulphate medium [25]. Kinetic investigations of oxidation by cerium (IV) have been carried out extensively in sulphuric acid medium and sulphato complexes, such as $CeSO_4^{2+}$, $Ce(SO_4)^2$ and $Ce(SO_4)3^{2-}$ have been established and quantified [26]. However, cerium (IV) in perchloric acid medium does not indicate complex formation, although Ce^{4+}, $Ce(OH)^{3+}$, $(Ce\text{-}O\text{-}Ce)^{6+}$ and $(HOCe\text{-}O\text{-}CeOH)4+$ species of cerium (IV) are well established [27].

Cerium (IV) in acid perchlorate medium exists predominantly in the monomeric form, such as $Ce4+$ and its hydrolyzed forms, $[CeOH^{3+}]$ and $[Ce(OH)_2^{2+}]$, apart from the dimeric and polymeric forms [28-31]. The polymeric species are significantly less than the dimeric species in acidic solution of cerium (IV) concentration. However, numbers of difficulties are encountered in proper and precise proposition of the reaction mechanism. Infact, if the concentration of the monomeric cerium (IV) species is calculated only on the basis of dimerization constant neglecting polymeric forms, a quantitative approach to analyze the kinetic data is more successful. It is with this view; the oxidation kinetics of amino acids was undertaken. Since the dimerization constant is known to be ~ 20, the same is employed to calculate the monomeric cerium(IV) concentrations using equation (3) [32].

$$[Ce(IV)]_m = \left[(1+8K_d[Ce(IV)])^{1/2} -1 \right] / 4K_d \qquad (3)$$

These $[Ce(IV)]_m$ concentrations were used, instead of $[Ce(IV)]$ in kinetic analysis.

However, several values of hydrolysis constant (K_h) of cerium (IV) are available in the literature. McAuley and Amzad [33] determined K_h to be 0.2 ± 0.02 mol dm^{-3} at 25°C, which is compared well with the values of 0.18 (25°C) and 0.11 (5°C), reported by Offner and Skoog [34]. However, the value of K_h determined kinetically in this work is 0.5 mol dm^{-3}, which agreed well with these values. Since the rate increases with increasing hydrogen ion concentration, $Ce4+$ should be more reactive species than its hydrolyzed form.
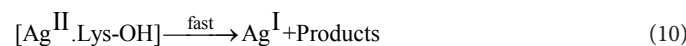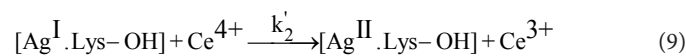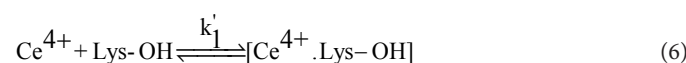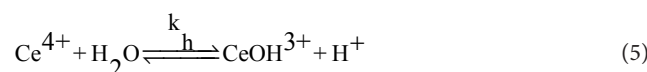
Further, the amino acids are known to exist in zwitter ionic form in equilibrium with anionic and cationic forms depending upon the pH of the solution. The concentration of the hydrogen ion employed in the reaction is sufficiently high; therefore, Hydroxylysine in view of its pK's, should predominantly be in the cationic forms.

$$RCHNH_3^+COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_3^+COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_2COO^- \qquad (4)$$

Cation   Zwitter ion Anion

Where $R = NH_2CH_2CH(OH)(CH_2)_2$

Amino acids are reported to form an adduct with Ag^I, owing to availability of electron pair on oxygen atom [35]. Therefore, an adduct between Ag^I and Hydroxylysine is initially formed, that on further interaction with Ce(IV) yields another adduct of higher valent silver. Thus considering first order with respect to cerium (IV) and Hydroxylysine each and also simultaneous uncatalyzed reaction in presence of silver(I), the following reaction mechanism consisting of steps (5) to (10) can be proposed.

$$Ce^{4+} + H_2O \overset{k_h}{\rightleftharpoons} CeOH^{3+} + H^+ \qquad (5)$$

$$Ce^{4+} + Lys\text{-}OH \overset{k_1'}{\rightleftharpoons} [Ce^{4+}.Lys\text{-}OH] \qquad (6)$$

$$[Ce^{4+}.Lys\text{-}OH] \overset{k_1'}{\longrightarrow} Products \qquad (7)$$

$$Ag^I + Lys\text{-}OH \overset{k_2'}{\rightleftharpoons} [Ag^I.Lys\text{-}OH] \qquad (8)$$

$$[Ag^I.Lys\text{-}OH] + Ce^{4+} \overset{k_2'}{\longrightarrow} [Ag^{II}.Lys\text{-}OH] + Ce^{3+} \qquad (9)$$

$$[Ag^{II}.Lys\text{-}OH] \overset{fast}{\longrightarrow} Ag^I + Products \qquad (10)$$

The proposed mechanism leads to the rate law (11) accounting for an experimental observation

$$\frac{-d[Ce(IV)]}{dt} = \left[\frac{k_1'K_1'[H^+]}{(K_h+[H^+])(1+K_1'[Lys-OH])} + \frac{k_2'K_2'[Ag^I][H^+]}{(K_h+[H^+])(1+K_2'[Lys-OH])} \right][Ce^{4+}][Lys-OH]$$

$$(11)$$

Since the order with respect to lysine is one, the inequality in terms, viz $1 \gg K_1'$ [Lys], $1 \gg K_2'$ [Lys] in the denominator of the equation (11) is valid. This reduces the rate law (11) to (12).

$$\frac{-d[Ce(IV)]}{dt} = \left[\frac{k_1'K_1'[H^+]}{(K_h+[H^+])} + \frac{k_2'K_2'[Ag^I][H^+]}{(K_h+[H^+])} \right][Ce^{4+}][Lys-OH] \quad (12)$$

$$k = \left[\frac{k_1'K_1'[H^+]}{(K_h+[H^+])} + \frac{k_2'K_2'[Ag^I][H^+]}{(K_h+[H^+])} \right] \qquad (13)$$

Where k is the observed second order rate constant, and it has been calculated to be 1.59 (average value) dm^3 mol^{-1} s^{-1}, from pseudo first order rate constants (Table 1). The equation (13) can be further re-arranged to equation (14).

$$k(K_h+[H^+]) = k_1'K_1'[H^+] + k_2'K_2'[Ag^I][H^+] \qquad (14)$$

Since equilibrium constants in the rate equation (14) are small, equation (14) can be further reduced to equation (15).
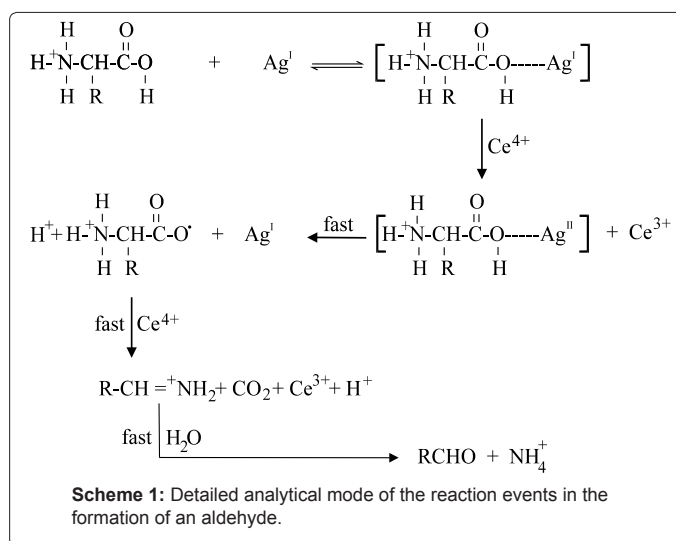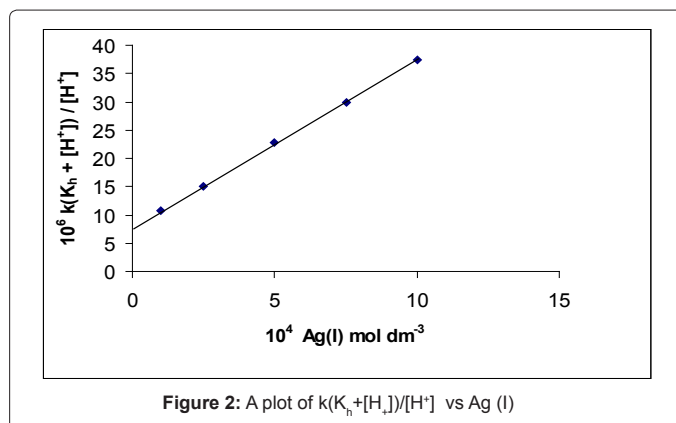
10^4 [Ce(IV)], mol dm^{-3}	10^2 [Lys-OH], mol dm^{-3}	104 (k'), sec^{-1}	10^5 (k), dm^3 mol^{-1} s^{-1}
4.3	1.0	3.85	1.62
5.7	1.0	2.90	1.61
8.5	1.0	1.96	1.61
14.2	1.0	1.15	1.62
17.5	1.0	0.92	1.61
20.0	1.0	0.81	1.62
24.0	1.0	0.68	1.61
4.3	2.0	7.60	1.60
5.7	2.0	5.60	1.56
8.5	2.0	3.80	1.56
14.2	2.0	2.30	1.62
17.5	2.0	1.85	1.61
20.0	2.0	1.62	1.60
24.0	2.0	1.35	1.60
4.3	3.0	11.5	1.61
5.7	3.0	8.40	1.56
8.5	3.0	5.70	1.56
14.2	3.0	3.45	1.62
17.5	3.0	2.80	1.61
20.0	3.0	2.40	1.58
24.0	3.0	2.00	1.58
5.7	0.50	1.40	1.56
5.7	0.75	2.20	1.63
5.7	1.0	2.90	1.61
5.7	1.5	4.20	1.56
5.7	2.0	5.60	1.56
5.7	3.0	8.40	1.56
5.7	4.0	11.2	1.56
5.7	5.0	14.0	1.56
14.2	0.50	0.58	1.63
14.2	0.75	0.86	1.61
14.2	1.0	1.15	1.62
14.2	1.5	1.73	1.62
14.2	2.0	2.30	1.62
14.2	3.0	3.45	1.62
14.2	4.0	4.60	1.62
14.2	5.0	5.75	1.62
20.0	0.50	0.40	1.60
20.0	0.75	0.61	1.61
20.0	1.0	0.81	1.60
20.0	1.5	1.20	1.58
20.0	2.0	1.62	1.60
20.0	3.0	2.40	1.58
20.0	4.0	3.25	1.60
20.0	5.0	4.00	1.58

Table 1: Pseudo-first order and second order rate constant for the reaction of [Lys-OH] and [Ce(IV)] in HClO$_4$ medium.
[Ag(I)]=5×10-4 mol dm-3, [H+]=1.0 mol dm-3, Temp.=45°C.

$$k(K_h + [H^+]) = k_1[H^+] + k_2[Ag^I][H^+] \qquad (15)$$

Where $k_1 = k_1' K_1'$ $k_2 = k_2' K_2'$

A plot of k (K$_{h+}$[H$^+$])/[H$^+$] versus [Ag^I] was made from the equation (15), a straight line with non-zero intercept was obtained (Figure 2). k$_1$ and k$_2$ were calculated to be 7.5×10^{-6} dm^3 mol^{-1} s^{-1} and 3.0×10^{-2} dm^3 mol^{-1} s^{-1}, respectively from the intercept and slope. The values of such constants are comparable to previously reported values for oxidation of other amino acids in similar experimental conditions [36,37].

Figure 2: A plot of k(K$_h$+[H$_+$])/[H$^+$] vs Ag (I)

Scheme 1: Detailed analytical mode of the reaction events in the formation of an aldehyde.

So far as the transfer of electron from the substrate to the oxidant is concerned, the detailed analytical mode of the reaction events can be given as Scheme 1. The imine can interact with other molecules of Ce(IV) to form nitrile or can undergo hydrolysis. Since nitrile was not observed in the reaction, the intermediate R-CH=$\overset{+}{N}$H$_2$ hydrolysis compete its interaction with the oxidant. It is probably this reason of formation of an aldehyde to be the oxidation product of Hydroxylysine instead of nitrile.

Conclusion

The reaction between Hydroxylysine and Cerium (IV) is very slow at room temperature. The reaction occurs in measurable quantities at 45°C and 1M HClO$_4$ concentration in the presence of silver (I) catalyst. The order respect to oxidant, substrate and catalyst are found to be unity. The mode of electron transfer has been indicated through an adduct between Ag^I and hydroxylysine *via* oxygen atom of the carboxyl group rather than the amino group. The overall mechanistic sequence described here is consistent with product, kinetic and mechanistic study.

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