Kinetics and Mechanism of Electron Transfer Reactions in Aqueous Solutions: Silver(I) Catalyzed Oxidation of Aspartic Acid by Cerium(IV) in Acid Perchlorate Medium

INDU SHARMA, VIJAI DEVRA, DIVYA GUPTA,
C.M. GANGWAL, and P.D. SHARMA
Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Abstract

Silver(I) catalyzed oxidation of aspartic acid by cerium(IV) was studied in acid perchlorate medium. The stoichiometry of the reaction is represented by the eq. (i)

$$\text{(i)}\qquad R\text{-}CHNH_3^+COOH + 2CE(IV) \xrightarrow{H_2O} R\text{-}CHO + NH_4^+ + CO_2 + 2Ce(III) + 2H^+$$

Dimeric cerium(IV) species has been indicated and employed in calculations of monomeric cerium(IV) species concentrations. The reaction is second-order and uncatalyzed reaction also simultaneously occurs along with the silver(I) catalyzed reaction conforming to the rate law (ii)

$$\text{(ii)}\qquad k = \frac{k_1[H^+]}{(K_h + [H^+])} + \frac{k_2[H^+][Ag^I]}{(K_h + [H^+])} + \frac{k_3K[Ag^I][bipy][H^+]^2}{(1 + K[bipy])(K_h + [H^+])}$$

where k is an observed second-order rate constant. A probable reaction mechanism is suggested. © 1995 John Wiley & Sons, Inc.

Introduction

The oxidative decarboxylation of amino acids is important both from a pure photochemical viewpoint and also from the viewpoint of mechanism of amino acid metabolism. Specific metabolic role of amino acids includes biosyntheses of polypeptides and proteins, and syntheses of nucleotides [1]. However, metallic ions play a significant role in the oxidative decarboxylation of amino acids. Kinetics of oxidation of amino acids by a variety of oxidants such as Mn(III) [2], Co(III) [3], Os(VIII)—$Fe(CN)_6^{3-}$ [4], chloramine-*T* [5], 1-chlorobenzotriazole [6], and *N*-bromosuccinamide [7,8] in both acid and alkaline media have been reported. There had been controversial reports regarding the oxidation products of amino acids in these reactions more particularly from the viewpoint of either hydrolysis of intermediate imine or an interaction of imine with the oxidant [9]. The hydrolysis of imine yields either aldehyde [9] or α-keto acids [4] if carboxylate imine is an intermediate [10]. However, the interaction of imine with two-equivalent oxidants yields only nitriles [5–7].

So far as cerium(IV) chemistry in perchloric acid is concerned [11], cerium (IV) exists mainly as a mixture of several species such as Ce^{4+}, $CeOH^{3+}$, $Ce(OH)_2^{2+}$, $(CeOCe)^{6+}$, and $(HOCeOCeOH)^{4+}$ in perchloric acid. There are reports that the polymeric species of significantly high molecular weights have also been identified [12]. However, such

International Journal of Chemical Kinetics, Vol. 27, 311–319 (1995)

CCC 0538-8066/95/040311-09

polymeric species create problems in analysis of the kinetic data in perchloric acid medium.

Thus in view of these problems arising out of cerium(IV) mechanistic propositions in perchloric acid and the importance of amino acid oxidative decarboxylation in biochemistry, the title study tempted us from two viewpoints, viz.,

Firstly, no quantitative approach has, yet, been made in identifying the reactive species of cerium(IV) in perchloric acid despite the known dimerization constant of cerium(IV) species in perchloric acid. Since the concentrations of cerium(IV) polymeric species are negligible as compared to dimeric species in solutions of $[\mathrm{Ce(IV)}] \leq 1.0 \times 10^{-2}$ mol dm^{-3}, these are the ideal conditions to quantify the monomeric cerium(IV) species in perchloric acid.

Secondly, the role of silver(I) as a catalyst in such reactions can help in fragmentizing such reaction events which in absence of the catalyst can escape detection.

Experimental

The ceric perchlorate solution was prepared by dissolving ceric ammonium nitrate (BDH AnalaR) in perchloric acid (E. Merck) and the solution was standardized by titrating against standard ferrous ammonium sulphate solution employing ferroin as an indicator. Since the aspartic acid solubility in water is low, the solution was therefore prepared in the presence of 0.5 mol dm^{-3} perchloric acid for the higher amino acid concentrations. All other chemicals were either of AnalaR or G. R. Merck quality and were used as received without any further treatment.

Doubly distilled water was employed throughout the study, the second distillation was from alkaline permanganate solution in an all glass assembly.

The reactions were carried out in stoppered Erlenmeyer flasks immersed in a water bath thermostated at 50 ± 0.1°C unless stated otherwise. All but cerium(IV) reaction components were taken in these flasks and then allowed to attain the bath temperature. The reactions were initiated by adding a known volume of temperature pre-equilibrated ceric perchlorate solution. However, the order of mixing of the reagents was without any effect on the kinetics. The kinetics were monitored by estimating cerium(IV) in an aliquot (5 cm^3) withdrawn at different intervals of time by titrating against ferrous ammonium sulphate solution employing ferroin indicator [13].

No precautions were taken to exclude the diffused light entering into the reaction mixture [14]. The cerium(IV) solution is thermally quite stable [15] in the visible region and undergoes photochemical decomposition [16] only in the ultra-violet region. Since the oxidation [17] of water even at 60°C by cerium(IV) is immeasurably slow and insignificant, no further precautions were taken to account for this.

Initial rates were measured employing plane-mirror method [18] and the pseudo-first-order plots were constructed wherever reaction conditions permitted.

Stoichiometry

Since most of the reaction kinetics were studied under pseudo-first-order conditions, the stoichiometry of the reaction was determined only in such reactions where amino acid was in excess over cerium(IV). These reactions were allowed to occur in a thermostatted water-bath at 50 ± 0.1°C for 24 h. When the cerium(IV) was completely utilized, the solutions were concentrated and tested for both nitrile and aldehyde, the products usually reported in the oxidation of amino acids. Nitrile tests were negative. However, aldehyde was also not clearly identified, the qualitative tests were positive. Further no 2,4-dinitrophenyl hydrazone derivative of aldehyde was obtained. However, this does not seem to be a reason of rejecting aldehyde as a product. Since ammonia is formed in the reaction, its interaction with aldehyde may yield an adduct to check the formation of the hydrozone derivative in the acidic medium as has been earlier confirmed in a number of reactions. Therefore, the stoichiometry of the reaction with positive test of an aldehyde can be represented by the eq. (1).

$$\text{(1)} \qquad \text{R-CHNH}_3^+\text{COOH} + 2\text{Ce(IV)} \xrightarrow{\text{H}_2\text{O}} \text{R-CHO} + \text{NH}_4^+ + \text{CO}_2 + 2\text{Ce(III)} + 2\text{H}^+$$

Results

Cerium(IV) Dependence

The concentration of cerium(IV) was varied from 4.6×10^{-4} to 4.9×10^{-3} mol dm^{-3} at $[\text{H}^+] = 1.0$, 1.5, and 2.5 mol dm^{-3}, respectively, $[\text{Asp}] = 5.0 \times 10^{-2}$ mol dm^{-3} and $I = 3.0$ mol dm^{-3}. Pseudo-first-order plots were made and the pseudo-first-order rate constants (k') were found to be independent of initial concentrations of cerium(IV) (Table I). The concentration of cerium(IV) was varied from 5.0×10^{-4} to 5.0×10^{-3} mol dm^{-3} in silver(I) catalyzed reaction at $[\text{Asp}] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[\text{H}^+] = 1.0$ mol dm^{-3}, and $[\text{Ag(I)}] = 5.0 \times 10^{-4}$ mol dm^{-3}. The pseudo-first-order rate constant (k') in silver(I) catalyzed reaction were also independent of the initial cerium(IV) concentrations (Table I).

Aspartic Acid Dependence

The concentration of aspartic acid was varied from 2.0×10^{-2} to 9.0×10^{-2} mol dm^{-3} at $[\text{Ce(IV)}] = 8.8 \times 10^{-4}$ mol dm^{-3}, $[\text{H}^+] = 1.0$ mol dm^{-3} and $I = 3.0$ mol dm^{-3}. The plot of pseudo-first-order rate constants vs. [Asp] yielded a straight line passing through the origin indicating first-order dependence with respect to amino acid. Aspartic acid concentration in silver(I) catalyzed reaction was varied from 2.0×10^{-2} to 10.0×10^{-2} mol dm^{-3} at $[\text{Ce(IV)}] = 9.9 \times 10^{-4}$ mol dm^{-3}. $[\text{H}^+] = 1.0$ mol dm^{-3} and $[\text{Ag(I)}] = 5.0 \times 10^{-4}$ mol dm^{-3}. The order with respect to amino acid is also one in the catalyzed reaction (Table I).

Hydrogen Ion Dependence

Hydrogen ion concentration was varied from 0.5 to 2.5 mol dm^{-3} at $[\text{Ce(IV)}] = 8.8 \times 10^{-4}$ mol dm^{-3}, $[\text{Asp}] = 5.0 \times 10^{-2}$ mol dm^{-3}, and $I = 3.0$ mol dm^{-3}. The rate initially increases and then tends towards a limiting value with increasing hydrogen ion concentration. Similarly in case of silver(I) catalyzed oxidation of aspartic acid, hydrogen ion concentration was varied employing perchloric acid from 1.0 to 3.0 mol dm^{-3} at $[\text{Ce(IV)}] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[\text{Asp}] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[\text{Ag(I)}] = 5.0 \times 10^{-4}$ mol dm^{-3}, and $I = 3.0$ mol dm^{-3} (Ionic strength(I) was adjusted employing lithium perchlorate). The rate of the reaction increases with increasing hydrogen ion concentration. Also, the variation in hydrogen ion concentration was made in the similar range in presence of $[\text{Ag(I)}] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[\text{bipy}] = 5.0 \times 10^{-6}$ mol dm^{-3}, and $I = 3.0$ mol dm^{-3}. The rate increases with increasing

TABLE I. Pseudo-first-order and second-order rate constants for the reaction of aspartic acid and cerium(IV) in $HClO_4$ medium. $I = 3.0$ mol dm^{-3}, [Ag(I)] $= 2.0 \times 10^{-4}$ mol dm^{-3}, 50°C.

10^3 [Ce(IV)], mol dm^{-3}	10^2 [Asp], mol dm^{-3}	[H$^+$] mol dm^{-3}	10^5 (k') s^{-1}	10^6 (k) dm^3 mol^{-1} s^{-1}
0.46	5.0	1.0	40.90	3.70
0.79	5.0	1.0	25.30	3.80
0.88	5.0	1.0	21.10	3.60
1.90	5.0	1.0	10.80	3.80
0.46	5.0	1.5	40.90	3.70
0.79	5.0	1.5	25.00	3.80
0.88	5.0	1.5	21.50	3.70
1.90	5.0	1.5	11.00	3.80
2.90	5.0	1.5	7.67	3.9
3.90	5.0	1.5	5.88	3.9
4.90	5.0	1.5	4.60	3.80
0.46	5.0	2.5	41.5	3.8
0.88	5.0	2.5	21.00	3.60
1.90	5.0	2.5	10.80	3.80
2.90	5.0	2.5	7.67	4.00
3.90	5.0	2.5	5.63	3.90
4.90	5.0	2.5	4.79	3.90
0.88	2.0	1.0	8.40	3.60
0.88	3.0	1.0	13.10	3.70
0.88	4.0	1.0	17.50	3.70
0.88	5.0	1.0	21.30	3.60
0.88	6.0	1.0	25.00	3.60
0.88	7.0	1.0	30.00	3.70
0.88	8.0	1.0	34.70	3.70
0.88	9.0	1.0	40.20	3.80

hydrogen ion concentration and the increase in rate in presence of 2.2′-bipyridyl (bipy) is larger than that in the presence of silver(I).

Effect of Ionic Strength

The effect of ionic strength was studied by varying the concentration of lithium perchlorate at [Ce(IV)] $= 9.0 \times 10^{-4}$ mol dm^{-3}, [Asp] $= 5.0 \times 10^{-2}$ mol dm^{-3}, and [H$^+$] $= 1.0$ mol dm^{-3}. The rate of the reaction increases with increasing ionic strength. However, the rate was independent of ionic strength in silver(I) catalyzed reaction.

Silver(I) Dependence

The concentration of silver(I) was varied from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at [Ce(IV)] $= 1.0 \times 10^{-3}$ mol dm^{-3}, [Asp] $= 5.0 \times 10^{-2}$ mol dm^{-3}, and [H$^+$] $= 1.0$ mol dm^{-3}, and also at 45, 50, and 55°C respectively. A plot of rate against [Ag(I)] yields a straight line with nonzero intercept that conforms to a simultaneous uncatalyzed reaction.

Effect of 2,2′-Bipyridyl

The concentration of 2,2′-bipyridyl was varied from 5.0×10^{-6} to 5.0×10^{-5} mol dm^{-3} at $[Ce(IV)] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[Asp] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0$ mol dm^{-3}, and $[Ag(I)] = 5.0 \times 10^{-4}$ mol dm^{-3}, and also at 45, 50, and 55°C, respectively. The rate increases with increasing bipyridyl concentration.

Effect of Cerium(III)

The effect of cerium(III) on the rate was also studied and was found to be independent of cerium(III) concentration ruling out any possibility of the rate limiting step preceded by the reversible equilibrium involving cerium(III).

Discussion

The reactions of cerium(IV) in $HC10_4$ medium proceed much faster than the reactions in sulphate medium. However, number of difficulties are encountered in proper and precise proposition of the reaction mechanism in perchloric acid medium. Infact, if the concentration of the monomeric cerium(IV) species is calculated only employing dimerization constant negating the presence of polymeric forms, a quantitative approach to analyze the kinetic data is more successful. Since the dimerization constant is know [12], the same can be employed to calculate the concentration of monomeric cerium(IV) species.

However, there are available in the literature several values of hydrolysis constants (K_h) of cerium(IV). McAuley et al. [19] determined K_h to be 0.2 ± 0.02 mol dm^{-3} at 25°C which compared well with the values of 0.18 (25°C) and 0.11 (5°C) reported by Offner and Skoog [20]. These values of K_h are reported to be closer to the values determined for other M^{4+} aqua-ions [21]. However, the values of K_h determined kinetically to be 0.5 mol dm^{-3} agreed well with these values provided the effects of ionic strength and temperature are accounted for. Since the rate increases with increasing hydrogen ion concentration, Ce^{4+} 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 [1]. The concentration of hydrogen ion employed in the reaction is sufficiently high, aspartic acid in view of its pK_a [22] should be exclusively be in the cationic form.

$$(3) \qquad R\text{-}CHNH_3^+COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} R\text{-}CHNH_3^+COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} R\text{-}CHNH_2COO^-$$

where $R = \text{-}CH_2.COOH$

Amino acids are reported [3] to form an adduct with Ag^I owing to availability of electron pair on oxygen atom [23]. Therefore, an adduct between Ag^I and aspartic acid is initially formed that on further interaction with cerium(IV) yields another adduct of higher valent silver. Thus considering first-order with respect to cerium(IV) and aspartic acid each and also simultaneous uncatalyzed reaction in presence of silver(I) and bipyridyl, the following reaction mechanism consisting of steps (4) to (14) can be proposed.

(4) $$\mathrm{Ce^{4+} + H_2O \xrightleftharpoons{K_h} CeOH^{3+} + H^+}$$

(5) $$\mathrm{Ce^{4+} + Asp \xrightleftharpoons{K_1'} [Ce^{4+}_{.}Asp]}$$

(6) $$\mathrm{[Ce.^{4+}Asp] \xrightleftharpoons{K_1'} Products}$$

(7) $$\mathrm{Ag^I + Asp \xrightleftharpoons{K_2'} [Ag^I_{.}Asp]}$$

(8) $$\mathrm{[Ag^I_{.}Asp] + Ce^{++} \xrightleftharpoons{K_2'} [Ag^{II}_{.}Asp] + Ce^{3+}}$$

(9) $$\mathrm{[Ag^{II}_{.}Asp] \xrightleftharpoons{Fast} Ag^I + products}$$

(10) $$\mathrm{bipy + H^+ \xrightleftharpoons{K'} [bipy, H^+]}$$

(11) $$\mathrm{Ag^I + [bipy.H^+] \xrightleftharpoons{K_3'} [Ag^I_{.}bipy.H^+]}$$

(12) $$\mathrm{[Ag^I_{.}bipy.H^+] + Asp \xrightleftharpoons{K_4'} [Ag^I_{.}bipy.H.^+Asp]}$$

(13) $$\mathrm{[Ag^I_{.}bipy.H.^+Asp] + Ce^4 \xrightarrow{k_3} [Ag^{II}_{.}bipy.Asp] + Ce^{3+} + H^+}$$

(14) $$\mathrm{[Ag^{II}bipy.Asp] \xrightarrow{Fast} Ag^I + bipy + products}$$

The loss of cerium(IV) leads to the rate law (15).

(15) $$-\frac{d[\mathrm{Ce(IV)}]}{dt} = \left\{ \frac{k_1'K_1'[\mathrm{H^+}]}{(k_h + [\mathrm{H^+}](1 + K_1'[\mathrm{Asp}]))} + \frac{k_2'K_2'[\mathrm{Ag^I}][\mathrm{H^+}]}{(K_h + [\mathrm{H^+}])(1 + K_2'[\mathrm{Asp}])} + \frac{k_3'K_3'K_4'K[\mathrm{Ag^I}][\mathrm{H^+}]^2[\mathrm{bipy}]}{(k_h + [\mathrm{H^+}])(1 + K[\mathrm{bipy}] + K_3'K_4'[\mathrm{Asp}])} \right\} [\mathrm{Ce^{4+}}][\mathrm{Asp}]$$

Since the order with respect to aspartic acid is one; the inequality in terms, viz., $1 \gg K_1'[\mathrm{Asp}]$, $1 \gg K_2'[\mathrm{Asp}]$, and $(1 + K[\mathrm{bipy}]) \gg K_3'K_4'[\mathrm{Asp}]$ in the denominator of the eq. (15) is valid. This reduces the rate law (15) to (16) or (17).

(16) $$-\frac{d[\mathrm{Ce(IV)}]}{dt} = \left\{ \frac{k_1'K_1'[\mathrm{H^+}]}{(K_h + [\mathrm{H^+}])} + \frac{k_2'K_2'[\mathrm{Ag^I}][\mathrm{H^+}]}{(K_h + [\mathrm{H^+}])} + \frac{k_3'K_3'K_4'K[\mathrm{Ag^I}][\mathrm{H^+}]^2[\mathrm{bipy}]}{(1 + K[\mathrm{Asp}])(K_h + [\mathrm{H^+}])} \right\} [\mathrm{Ce(IV)}][\mathrm{Asp}]$$

(17) $$k'(K_h[\mathrm{H^+}]) = k_1'K_1'[\mathrm{H^+}] + k_2'K_2'[\mathrm{Ag^I}][\mathrm{H^+}] + \frac{k_3'K_3'K_4'K[\mathrm{Ag^I}][\mathrm{bipy}][\mathrm{H^+}]^2}{(1 + K[\mathrm{bipy}])}$$

Since the equilibrium constants in the rate eq. (17) are small, eq. (17) can be further reduced to eq. (18).

(18) $$(K_h + [\mathrm{H^+}])k = k_1[\mathrm{H^+}] + k_2[\mathrm{Ag^I}][\mathrm{H^+}] + \frac{k_3'K[\mathrm{Ag^I}][\mathrm{bipy}][\mathrm{H^+}]^2}{(1 + K[\mathrm{bipy}])}$$

where $k_1 = k_1'K_1'$, $k_2 = k_2'K_3'$. $k_3 = k_3'K_3'K_4'$, and k is an observed second-order rate constant.

A plot of $k(K_h + [\mathrm{H^+}])/[\mathrm{H^+}]$ versus $[\mathrm{Ag^I}]$ was made from the eq. (18) when the reactions were carried out in absence of 2,2′-bipyridyl, a straight line with nonzero

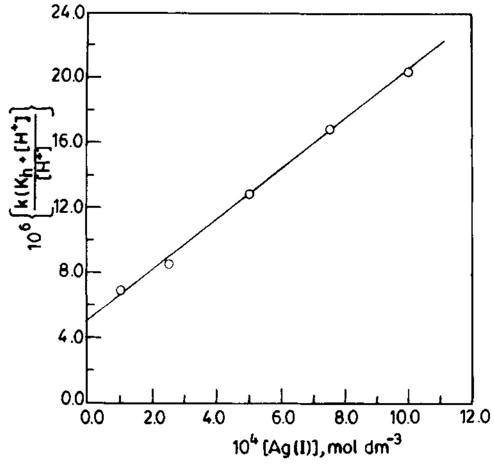


Figure 1.

intercept was obtained (Fig. 1), k_1 and k_2 were calculated from the intercept and slope to be 5.0×10^{-6} dm^3 mol^{-1} s^{-1}, and 15.6×10^{-3} dm^3 mol^{-1} s^{-1}, respectively. Further, a plot of $k(K_h + [H^+])/[Ag^I][H^+]$ vs. $[H^+]$ was also made from the eq. (18) in the presence of 2,2′-bipyridyl. Under conditions where 1 : 1 Ag^I-bipy complex is only formed, a straight line with nonzero intercept was obtained (Fig. 2). The intercept of this latter plot yielded the value of k_2 to be 15.0×10^{-3} dm^3 mol^{-1} s^{-1} in agreement with the value calculated from the kinetic data of the Figure 1. Since a significant catalytic role of Ag^I-bipy is exhibited in the reaction, this can be accounted for the fact that Ag^I-bipy complex is a better catalyst than base Ag^I. This is also thermodynamically reasonable in view of the reduced redox potential of Ag^I-Ag^{II} couple in presence of 2,2′-bipyridyl and this makes Ag^I-bipy complex easily amenable to oxidation by cerium(IV).

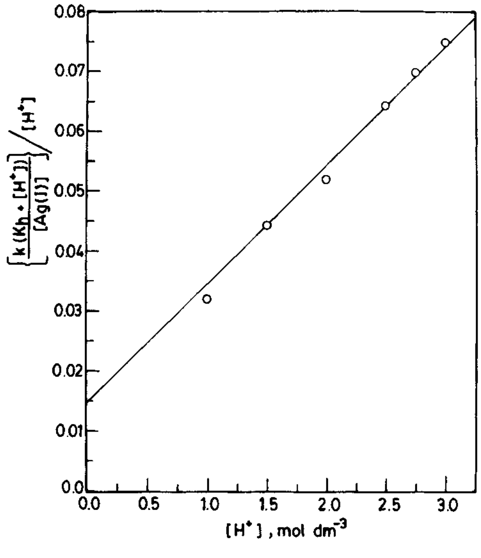
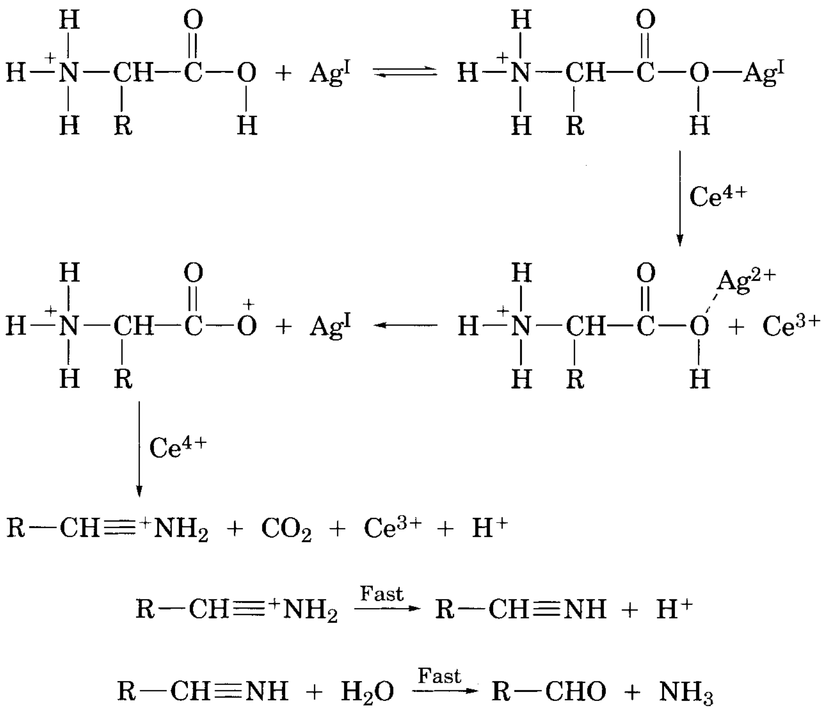


Figure 2.



$$R{-}CH{\equiv}{}^{+}NH_2 + CO_2 + Ce^{3+} + H^+$$

$$R{-}CH{\equiv}{}^{+}NH_2 \xrightarrow{\text{Fast}} R{-}CH{\equiv}NH + H^+$$

$$R{-}CH{\equiv}NH + H_2O \xrightarrow{\text{Fast}} R{-}CHO + NH_3$$

Scheme I

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 in Scheme I. Since the p*K*'s of amino acids generally vary from 2.1 ± 0.3 to 9.6 ± 0.7, the presence of alkyl group at the α-carbon hardly influences either amino or carboxyl groups. The hydrocarbon portion of the amino acid does not undergo any chemical reaction obviously owing to the highly reactive functional groups.

The imine intermediate involves the cleavage of the bond between the α-carbon and the carboxylic carbon. However, there are two distinct possibilities of the intermediate imine undergoing reactions to the final products, either by reacting with water or by an interaction of imine with the oxidizing species taking place. Of these, the reaction with water is an acid catalyzed reaction. Since the acid catalysis has been observed in the title reaction, the hydrolysis of imine appears to be the most predominant path. Imines of the type $RCH = NH$ with hydrogen attached to the nitrogen have been identified spectrophotometrically [24]; these cannot be isolated owing to their fast decomposition [25].

Since the transformations develop the partial (+)ve charge on the α-carbon in the transition state, this may be attributed to the (+)ve charge on the nitrogen that allows the cleavage of the carbon—carbon bond to precede carbon—nitrogen bond formation. Therefore, cerium(IV) attacks carboxyl group bonded to Ag^I instead of amino group bonded to Ag^I. Moreover, the reaction has been carried out in sufficiently high hydrogen ion concentrations, the interaction of electron deficient metal ion with the protonated amino group cannot be considered to be a sound proposition. The color reaction [26] for the presence of nitrile in the reaction mixture was done by adding hydroxylamine and ferric chloride; this test, however, confirmed its absence and ruled out any further interaction of the imine R– CH = NH with cerium(IV). Thus the hydrolytic decomposition of imine rather than interaction of cerium(IV) becomes important reaction events yielding aldehyde to be the oxidation product of the amino acid.

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Received March 11, 1994
Accepted July 26, 1994