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Silver(I) catalysis of oxidative deamination and decarboxylation of L-asparagine and L-histidine by platinum(IV) in perchloric acid solutions: A comparative kinetics study

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ABSTRACT

Silver(I)-catalyzed oxidation of two amino acids (AA), namely L-asparagine and L-histidine, with platinum(IV) as hexachloroplatinate(IV) ion (HCP) has been investigated in perchloric acid solutions at constant ionic strength of 2.5 mol dm^{-3} and at 25 °C. The courses of the oxidation reactions were followed spectrophotometrically. The kinetics of oxidation of both amino acids by HCP are identical, being first order in [HCP] and fractional-first orders with respect to [AA], $[H^+]$ and [Ag(I)]. The rates of both reactions decrease with increasing ionic strength and dielectric constant of the media. Addition of small amounts of Cu(II) and Al(III) increases the rates of reactions. Raising temperature enhances the rates. Amino acids are oxidized to form the corresponding aldehydes, ammonium ion and carbon dioxide. The rate law associated with the reaction mechanism is deduced. Activation parameters of the catalyzed oxidation reactions have been evaluated and discussed.

1. Introduction

Biologically active platinum(IV) complexes have attracted many researchers in the last decades due to their anticancer properties [1–3]. They are usually substitution-inert and require reduction to Pt(II) species to act as potential anticancer drugs. Hexachloroplatinate(IV) ion (HCP) is considered as one of the most important platinum(IV) complexes which has been applicable to oxidize a number of organic [4–12] and inorganic [13–16] compounds in different media. The mechanism of antitumor activity of platinum (IV) compounds [12,13] can be understood by studying the reactivity of such compounds toward their reduction by potential bio-reductants such as amino acids.

Amino acids play a significant role in the metabolism and the specific metabolic role of them includes the biosynthesis of polypeptides and proteins, as well as the synthesis of nucleotides [17]. Amino acids oxidation is vital because of its bearing on the mechanism of amino acid metabolism. Kinetics of oxidation of amino acids by various oxidants in different media has been studied earlier [5–9,18–29], and they often undergo oxidative decarboxylation and deamination. L-Asparagine (Asn) occurs in relatively high concentrations in plant tissues. Its role in the metabolism is crucial. It is highly applicable in the production of pharmaceuticals and medicine. Oxidation of L-asparagine has previously been studied in both acidic [5,6,21] and alkaline [7,18–20] media, and the final oxidation products of L-asparagine were identified as α-formyl acetamide, ammonia and carbon dioxide. L-Histidine (His) is an essential amino acid that finds application as a reducing agent in chemical and biochemical systems. Kinetics of oxidation of L-histidine by several oxidants have also been studied previously [8,9,22–26]. In some of its oxidations, 2-imidazole acetaldehyde was identified to be the main oxidation product. Kinetics and mechanism of the homogeneous catalyzed oxidation of amino acids in the liquid phase is considered as an important field of chemistry due to the role played by metals in biological systems, but such studies are limited [5–9,12,19].

An extensive literature survey reveals that there are no reports on the oxidation of L-asparagine or L-histidine by platinum(IV) in perchloric acid solution. In view of the above mentioned arguments, we have carried out a detailed study on the kinetics and mechanism of oxidation of L-asparagine and L-histidine amino acids by biologically active hexachloroplatinate(IV) complex in perchloric acid in the presence of silver(I) catalyst. This work aims to study the selectivity of the studied amino acids towards

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hexachloroplatinate(IV) in perchloric acid solutions, to check the catalytic activity of Ag(I) catalyst on such reactions, to understand the active species of the reductants, oxidant and catalyst in such medium and to elucidate a plausible reaction mechanism.

2. Experimental

2.1. Materials

Solutions of L-asparagine and L-histidine were prepared afresh by dissolving amino acids samples (E. Merck, UK) in doubly distilled water. A solution of the oxidant, chloroplatinic acid, (Johnson Matthey, UK) was freshly prepared before each experiment by proper dilution of its original solution and was standardized spectrophotometrically [30]. The solution was stored in a dark bottle away from light and was re-standardized periodically. All other chemicals were of analytical reagent grade and doubly distilled water was used throughout the work.

2.2. Kinetic measurements

Kinetic runs were performed under pseudo-first order conditions where the amino acids were in large excess over that of HCP at constant ionic strength of 2.5 mol dm^{-3} (adjusting by addition of sodium perchlorate as an inert electrolyte) and at constant temperature of 25 ± 0.1 °C unless stated otherwise. The courses of the reactions were followed spectrophotometrically by monitoring the decrease in the absorbance of HCP at λ = 262 nm, its absorption maximum, as a function of time using Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer (Japan) with a cell compartment kept at constant temperature. The reactions were followed for more than three half-lives. Values of the pseudo-first order rate constants of the catalyzed reactions (k_C) were obtained as gradients of the linear ln(absorbance) versus time plots, which were the average of at least three independent kinetic runs and were reproducible to within ±4%. Double logarithmic plots were used to determine the order with respect to each reactant.

3. Results

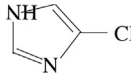
3.1. Spectral changes

Fig. 1(a,b) shows spectral changes during silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. The absorption spectrum of HCP at λ_{max} = 262 nm decreased gradually as the reactions proceeded, suggesting reduction of Pt(IV) to Pt(II) by the amino acids.

3.2. Stoichiometry and products identification

Different reaction mixtures containing various amounts of HCP and amino acids at constant [H^+] and ionic strength were allowed to react for 24 h. After completion of the reactions, the unreacted [HCP] was assayed spectrophotometrically. The results indicate that the reaction stoichiometry was 1:1, as represented by the following equation

$$RCH(NH_2)COOH + [Pt^{IV}Cl_6]^{2-} + H_2O \xrightarrow{Ag(I)} RCHO + NH_4^+ + CO_2 + [Pt^{II}Cl_4]^{2-} + 2Cl^- + H^+$$

where $R = H_2N(CO)CH_2$— for L-asparagine and R =  for L-histidine, and RCHO is the corresponding aldehyde (α-formyl acetamide for L-asparagine and 2-imidazole acetaldehyde for L-histidine), which were identified using spot tests [31]. The other oxidation products of the amino acids were identified as ammonium ion by Nessler's reagent [32] and carbon dioxide by lime water. The corresponding aldehydes were also estimated quantitatively as their 2,4-dinitrophenylhydrazone derivatives [32]. Similar oxidation products with different experimental conditions have also been reported earlier [5–9,18,26]. On the other hand, formation of $[Pt^{II}Cl_4]^{2-}$ was confirmed [10] by the observed black precipitate of platinum(II) hydroxide on addition of alkali to the reaction mixture according to the reaction: $[PtCl_4]^{2-} + 2OH^- = Pt(OH)_2 + 4Cl^-$.

3.3. Effect of [HCP] oxidant

The effect of HCP on the rates of reactions was studied by varying its concentration in the range of 4.0×10^{-5} to 12.0×10^{-5} mol dm^{-3}, keeping other concentrations constant. The first order plots were found to be linear and showed no variation in k_C values at various [HCP] (Table 1), confirming the first order kinetics with respect to [HCP].

3.4. Effect of [amino acid] reductants

Kinetic measurements were performed with various initial concentrations of the reductants, L-asparagine and L-histidine, while the concentrations of HCP, H^+, Ag(I) and $NaClO_4$ were kept constant. Plots of k_C values versus [AA] at constant pH are linear with positive intercepts (figure not shown) suggesting that the orders with respect to the amino acids are less than unity.

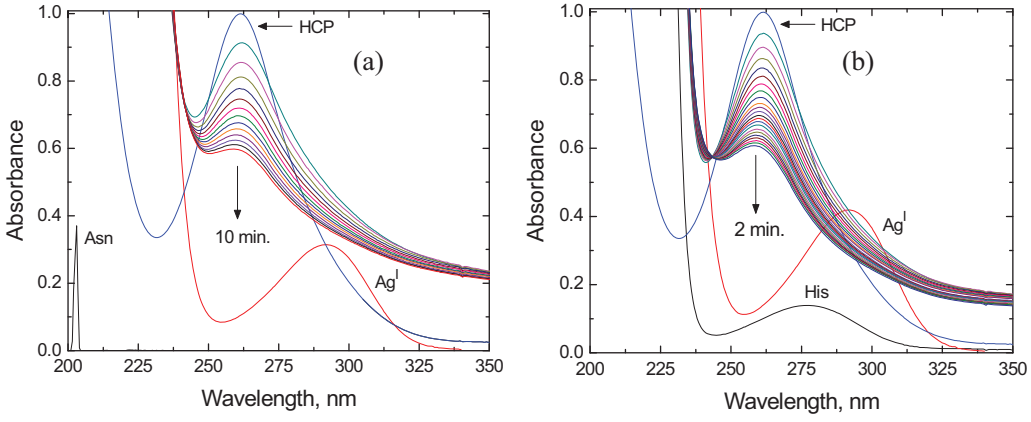


Fig. 1. Spectral changes during silver(I)-catalyzed oxidation of: (a) L-asparagine, and (b) L-histidine, by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5, [Ag(I)] = 6.0×10^{-5}, and I = 2.5 mol dm^{-3} at 25 °C.

Table 1
Effect of variation of [HCP], [AA], [H^+], [Ag(I)], and ionic strength, *I*, on the oxidation rates of L-asparagine and L-histidine by HCP in perchloric acid solutions at 25 °C.

10^5 [HCP] (mol dm^{-3})	10^2 [AA] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^5 [Ag(I)] (mol dm^{-3})	*I*(mol dm^{-3})	10^5 k_C (s^{-1})	
					Asn	His
4.0	3.0	1.5	6.0	2.5	7.3	39.8
6.0	3.0	1.5	6.0	2.5	7.2	41.1
7.6	3.0	1.5	6.0	2.5	7.6	40.2
10.0	3.0	1.5	6.0	2.5	7.9	39.5
12.0	3.0	1.5	6.0	2.5	8.1	40.6
7.6	1.0	1.5	6.0	2.5	2.7	16.1
7.6	2.0	1.5	6.0	2.5	4.5	27.3
7.6	3.0	1.5	6.0	2.5	7.6	40.2
7.6	4.0	1.5	6.0	2.5	9.8	51.0
7.6	5.0	1.5	6.0	2.5	12.9	60.2
7.6	3.0	0.5	6.0	2.5	3.9	19.2
7.6	3.0	1.0	6.0	2.5	6.1	31.3
7.6	3.0	1.5	6.0	2.5	7.6	40.2
7.6	3.0	2.0	6.0	2.5	10.2	53.1
7.6	3.0	2.5	6.0	2.5	13.1	66.4
7.6	3.0	1.5	2.0	2.5	3.7	28.2
7.6	3.0	1.5	4.0	2.5	5.1	35.1
7.6	3.0	1.5	6.0	2.5	7.6	40.2
7.6	3.0	1.5	8.0	2.5	9.1	47.5
7.6	3.0	1.5	10.0	2.5	11.0	52.3
7.6	3.0	1.5	6.0	2.5	7.6	40.2
7.6	3.0	1.5	6.0	2.7	7.3	38.5
7.6	3.0	1.5	6.0	3.0	6.9	36.5
7.6	3.0	1.5	6.0	3.5	6.5	33.0
7.6	3.0	1.5	6.0	4.0	6.1	30.1

Experimental error ±4%.

3.5. Effect of [H^+]

The reaction rates were measured at constant [AA], [HCP], [Ag (I)], ionic strength and temperature but with various [H^+] (0.5–2.5 mol dm^{-3}). The rates of reactions were found to increase with increasing [H^+]. Plots of k_C versus [H^+] were linear with positive intercepts (figure not shown) confirming the less than unit order in [H^+].

3.6. Effect of ionic strength and dielectric constant

To study the effect of ionic strength on the oxidation reactions, sodium perchlorate was added to the reactions media at constant other variables. The results show that the rate constants decrease with increasing ionic strength of the medium and the Debye–Hückel plots are linear with negative slopes (Fig. 2).

The effect of dielectric constant (*D*) of the media on the rates was studied as follow: the oxidation reactions were carried out at different solvent compositions (v/v) of acetic acid and water. The results indicate that the rate constants increase with the decrease in dielectric constant of the solvent mixture, i.e., increase in acetic acid content. The plots of log k_C versus $1/D$ were linear with positive slopes as shown in Fig. 3.

3.7. Effect of [Ag(I)] catalyst

The reaction rates were measured with various [Ag(I)], (2.0–10.0) × 10^{-5} mol dm^{-3} at constant other variables. The rates were found to increase with the increase [Ag(I)] (Table 1). The orders with respect to [Ag(I)] were 0.42 and 0.69 for L-asparagine and L-histidine, respectively, as found from the plots of ln k_C versus ln [Ag(I)] as shown in Fig. 4.

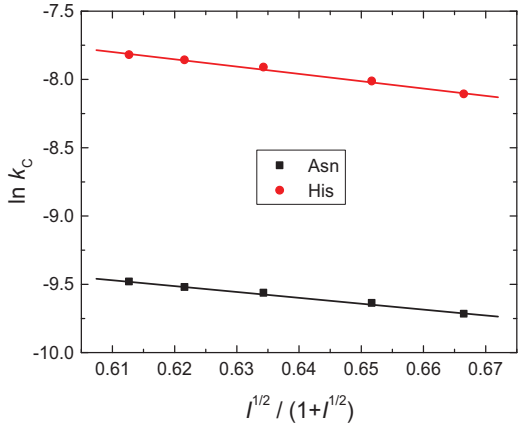


Fig. 2. Debye–Hückel plots in the silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0 × 10^{-2}, [HCP] = 7.6 × 10^{-5}, [H^+] = 1.5 and [Ag(I)] = 6.0 × 10^{-5} mol dm^{-3} at 25 °C.

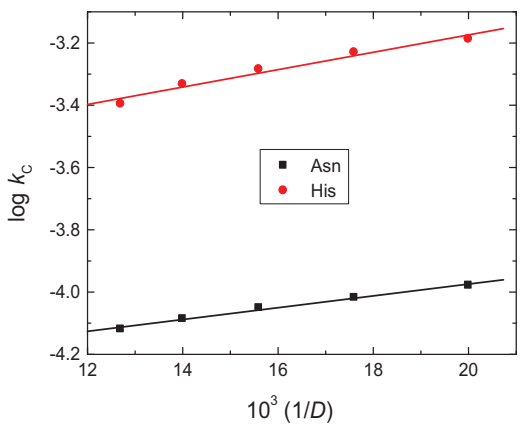


Fig. 3. Plots of log k_C versus $1/D$ for the silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0 × 10^{-2}, [HCP] = 7.6 × 10^{-5}, [H^+] = 1.5, [Ag(I)] = 6.0 × 10^{-5} and 2.5 mol dm^{-3} at 25 °C.

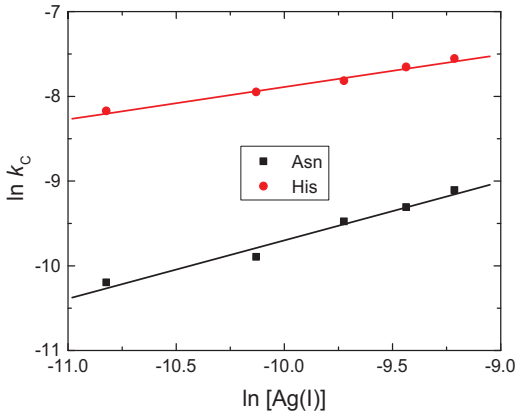


Fig. 4. Plots of ln k_C versus ln [Ag(I)] in the silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5 and I = 2.5 mol dm^{-3} at 25 °C.

3.8. Effect of added salts

Reaction rates were studied with different concentrations of added Cu(II) and Al(III) salts but at constant concentrations of the reactants. Values of k_C were found to increase with increase in [Cu (II)] and [Al(III)], and the order of effectiveness is Cu(II) > Al(III), as shown in Fig. 5(a,b).

3.9. Polymerization test

To study the possible intervention of free radicals during the oxidation reactions, the reaction mixtures to which known amounts of acrylonitrile were initially added and were kept for about 2 h in inert atmosphere. On diluting the mixtures with methanol, no white precipitates were formed confirming the absence of free radical intervention in such reactions.

3.10. Effect of temperature

The oxidation rates were investigated at moderate temperatures range (15–35) °C (to avoid any probability of temperature effect on the stability of the reactants, intermediates or products). The obtained results indicate that the reaction rates increase with raising the temperature. The activation parameters of the second-order rate constants k_2 ($k_2 = k_C/[AA]$) are calculated using Arrhenius, Fig. 6(a), and Eyring, Fig. 6(b), plots and are listed in Table 2.

4. Discussion

Martell and Smith [33] reported that in acid solutions, amino acids predominantly tend to protonate at higher acid concentration as represented in Eq. (2). The high concentration of hydrogen ion employed in the present reactions as well as the observed enhancement of the reaction rates upon increasing acid concentration suggest protonation of the amino acids in a pre-equilibrium step and their protonated forms (AA^+) appear to be the reactive species in the rate-determining step.

It is also reported [34] that platinum(IV) species in acid solutions is present as $[PtCl_6]^{2-}$, which is assumed to be the principal reactive oxidant. Reduction of platinum(IV) complexes by different reagents generally proceeds via a free radical one-electron transfer mechanism [16]. The second path, whereby platinum(IV) undergoes a two-electron reduction, has also been shown to occur [15]. This depends on the reductant and experimental conditions. Therefore, two alternative reaction mechanisms for the oxidation of amino acids by HCP may be considered, a simultaneous two-electron transfer in a single step or two successive one-electron transfer steps. In the present study, addition of acrylonitrile monomer to the reactions mixtures failed to give polymerized products, i.e. absence of free radicals intervention, suggesting that the two-electron transfer mechanism seems plausible. On the other hand, because platinum (IV) complexes are generally substitution-inert [35], initial complex formation between platinum(IV) and amino acid prior to electron transfer can be excluded.

5. Reaction mechanism

The reactions between HCP and the studied amino acids in the presence of small amounts of silver(I) catalyst have a stoichiometry of 1:1 with first order dependence on [HCP] and less than unit orders with respect to amino acids and silver(I) catalyst concentrations. The rates of reduction of HCP increase with increasing [H^+] with less than unit order, suggesting that amino acid substrates are first protonate, Eq. (2), in a pre-equilibrium step. The rates of the reactions decrease on increasing the ionic strength and dielectric constant of the media, suggesting that the reactions occur between two ions with opposite charge [36a,b,c]. The observed less than unit order for both [AA] and [Ag(I)] suggests formation of complexes between silver(I) catalyst and amino acid substrates prior to the reaction with the oxidant. Complex formation was also proved kinetically by a non-zero intercept of the plot of [Ag(I)]/k_C versus 1/[AA] (Fig. 7). Such complexes have been reported earlier [6]. It was reported [5–9] that transition metal ions have been

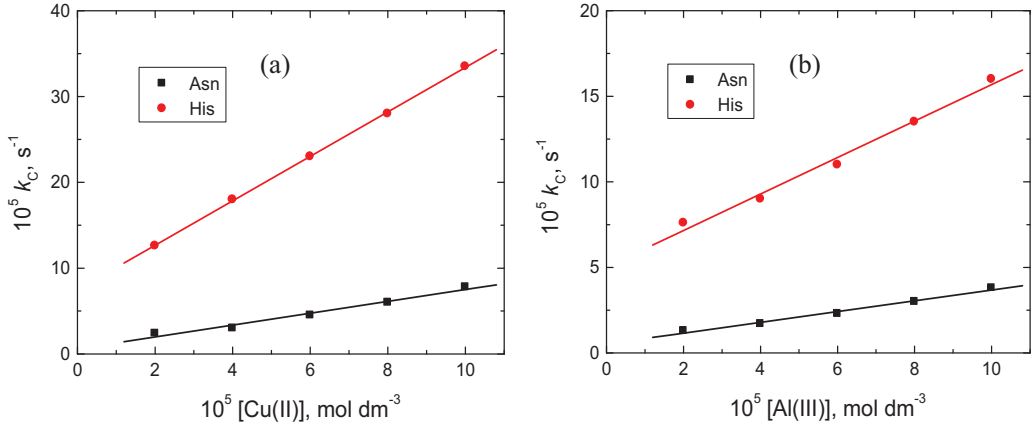


Fig. 5. Effect of: (a) Cu(II) and (b) Al(III) on the oxidation rates of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5 and I = 2.5 mol dm^{-3} at 25 °C.

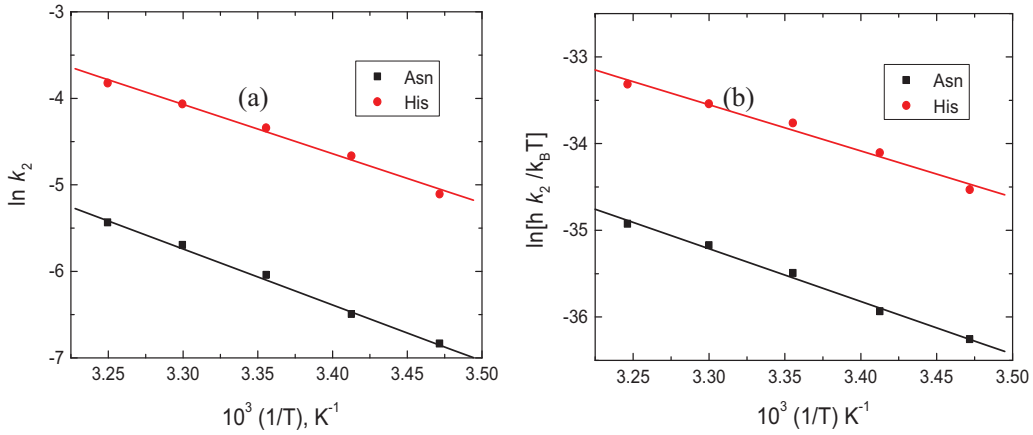


Fig. 6. (a) Arrhenius plots and (b) Eyring plots in the silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5, [Ag(I)] = 6.0×10^{-5} and I = 2.5 mol dm^{-3}.

Table 2
Activation parameters of the second-order rate constants, k_2, in the silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5, [Ag(I)] = 6.0×10^{-5} and I = 2.5 mol dm^{-3}.

Amino acid	Parameter			
	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}	$E_a^{\neq}$, kJ mol^{-1}
L-asparagine	−125.54	50.57	87.99	56.04
L-histidine	−132.44	44.31	83.78	47.39

Experimental error ±4%.

widely employed as homogeneous catalysts for oxidation of organic and inorganic substrates. This was interpreted by either formation of complexes with the reactants, oxidation of the substrate itself or through the formation of free radicals.

In view of the above arguments, the reactions mechanism was suggested as shown in Scheme 1. It is proposed that the protonated species of amino acid combines with Ag(I) to form an intermediate complex (C), $[AA–Ag]^{2+}$, which then reacts in a slow step with one mole of HCP to yield the oxidation products with regeneration of the catalyst Ag(I) as illustrated by the following sequence:

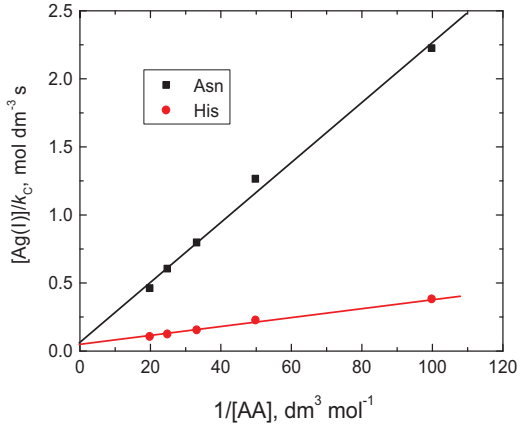
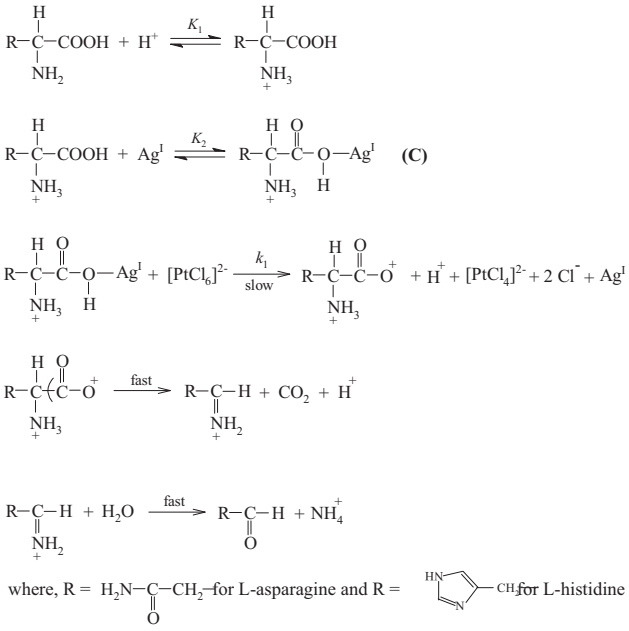


Fig. 7. Plots of [Ag(I)]/k_C versus 1/[AA] in silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions. [HCP] = 7.6×10^{-5}, [H^+] = 1.5 and I = 2.5 mol dm^{-3} at 25 °C.



Scheme 1. Mechanism of silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid solutions.

The proposed mechanism leads to the following rate law,

$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = k_1[\text{C}][\text{HCP}] \quad (7)$$

The relationship between reaction rate and substrate, hydrogen ion, catalyst and oxidant concentrations has been deduced (see Appendix A) to give the following rate-law expression,

$$\text{Rate} = \frac{k_1K_1K_2[\text{AA}][\text{H}^+][\text{Ag(I)}][\text{HCP}]}{(1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+][\text{Ag(I)}])(1 + K_1K_2[\text{AA}][\text{H}^+])} \quad (8)$$

In view of low [Ag(I)] used, the term K_1K_2[H^+][Ag(I)] in the denominator can be neglected. Therefore, Eq. (8) becomes,

$$\text{Rate} = \frac{k_1K_1K_2[\text{AA}][\text{H}^+\text{Ag(I)}][\text{HCP}]}{(1 + K_1[\text{H}^+])(1 + K_1K_2[\text{AA}][\text{H}^+])} \quad (9)$$

Under pseudo-first order conditions,

$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = k_C[\text{HCP}] \quad (10)$$

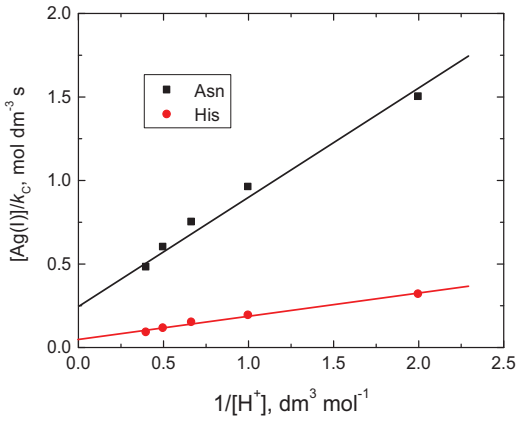


Fig. 8. Plots of $[Ag(I)]/k_C$ versus $1/[H^+]$ in silver(I)-catalyzed oxidation of L-asparagine and L-histidine by HCP in perchloric acid medium. $[HCP] = 7.6 \times 10^{-5}$, $[AA] = 3.0 \times 10^{-2}$ and $I = 2.5$ mol dm^{-3} at 25 °C.

Comparing Eqs. (9) and (10) and rearranging, Eq. (11) is obtained,

$$\frac{[Ag(I)]}{k_C} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 [H^+]}\right)\frac{1}{[AA]} + K' \quad (11)$$

where $K' = (1 + K_1[H^+])/k_1$.

According to Eq. (11), plots of $[Ag(I)]/k_C$ against $1/[AA]$, at constant $[H^+]$, and $[Ag(I)]/k_C$ against $1/[H^+]$, at constant [AA], should be linear with positive intercepts on the $[Ag(I)]/k_C$ axes as were obtained experimentally as shown in Figs. 7 and 8, respectively.

Unfortunately, the values of the rate constants of the slow step (k_1) along with their activation parameters could not be evaluated because of the unavailability of the protonation constants (K_1) of the investigated amino acids and/or the formation constants (K_2) of silver(I)–asparagine and silver(I)–histidine complexes under the present experimental conditions and at different temperatures.

The activation parameters listed in Table 2 may be interpreted as follows: the observed large negative values of $\Delta S^{\neq}$ confirm the compactness of the silver(I)–substrate complexes formed and such activated complexes are more ordered than the reactants [37]. The positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate the endothermic formation of the intermediate and its nonspontaneity, respectively.

6. Conclusion

The oxidation reactions of L-asparagine and L-histidine with hexachloroplatinate(IV) in perchloric acid solutions do not proceed in the absence of silver(I) catalyst. The reactions occur in measurable quantities in the presence of low concentration of Ag(I). Addition of other metal cations, such as Cu(II) and Al(III) also enhanced the rates and the order of catalytic efficiency is: Ag(I) > Cu(II) > Al(III). In the presence of Ag(I) catalyst, the rate of oxidation of L-histidine is significantly higher than that of L-asparagine.

Appendix A.

According to the suggested mechanism for silver(I)-catalyzed oxidation reactions, and regarding to reaction (4)

$$\text{Rate}_{(C)} = \frac{-d[HCP]}{dt} = k_1[C][HCP] \quad (A.1)$$

From reaction (2),

$$K_1 = \frac{[AA^+]}{[AA][H^+]}, \quad (A.2)$$

Therefore,

$$[AA^+] = K_1[AA][H^+] \quad (A.3)$$

From reaction (3) and Eq. (A.3),

$$K_2 = \frac{[C]}{[AA^+][Ag(I)]} = \frac{[C]}{K_1[AA][H^+][Ag(I)]}. \quad (A.4)$$

Therefore,

$$[C] = K_1K_2[AA][H^+][Ag(I)] \quad (A.5)$$

Substituting Eq. (A.5) into Eq. (A.1) yields,

$$\text{Rate}_{(C)} = k_1K_1K_2[AA][H^+][Ag(I)][HCP] \quad (A.6)$$

The total concentration of amino acid is given by,

$$[AA]_T = [AA]_F + [AA^+] + [C], \quad (A.7)$$

where $[AA]_T$ and $[AA]_F$ stand for total and free concentrations of amino acid, respectively.

Substituting Eqs. (A.3) and (A.5) into Eq. (A.7) gives,

$$[AA]_T = [AA]_F + K_1[AA]_F[H^+] + K_1K_2[AA]_F[H^+][Ag(I)] \quad (A.8)$$

$$[AA]_T = [AA]_F\,(1 + K_1[H^+] + K_1K_2[H^+][Ag(I)]). \quad (A.9)$$

Therefore,

$$[AA]_F = \frac{[AA]_T}{1 + K_1[H^+] + K_1K_2[H^2][Ag(I)]} \quad (A.10)$$

Similarly,

$$[Ag(I)]_T = [Ag(I)]_F + [C] \quad (A.11)$$

Substituting Eq. (A.5) into Eq. (A.11) and rearranging gives,

$$[Ag(I)]_F = \frac{[Ag(I)]_T}{1 + K_1K_2[AA][H^+]}. \quad (A.12)$$

In view of high $[H^+]$,

$$[H^+]_T = [H^+]_F. \quad (A.13)$$

In addition,

$$[HCP]_T = [HCP]_F. \quad (A.14)$$

Substituting Eqs. (A.10),(A.12)–(A.14) into Eq. (A.6) (and omitting 'T' and 'F' subscripts) gives,

$$\text{Rate}_{(C)} = \frac{k_1K_1K_2[AA][H^+][Ag(I)][HCP]}{(1 + K_1[H^+] + K_1K_2[H^+][Ag(I)])(1 + K_1K_2[AA][H^+])} \quad (A.15)$$

In view of low [Ag(I)] used, the term $K_1K_2[H^+][Ag(I)]$ in the denominator of Eq. (A.15) can be neglected. Therefore, Eq. (A.15) becomes,

$$\text{Rate}_{(C)} = \frac{k_1K_1K_2[AA][H^+][Ag(I)][HCP]}{(1 + K_1[H^+])(1 + K_1K_2[AA][H^+])} \quad (A.16)$$

Under pseudo-first-order conditions, the rate law can be expressed as,

$$\text{Rate}_{(C)} = \frac{-d[HCP]}{dt} = k_C[HCP] \quad (A.17)$$

Comparing Eqs. (A.16) and (A.17), the following relationship is obtained,

$$k_C = \frac{k_1 K_1 K_2 [AA][H^+][Ag(I)]}{(1 + K_1[H^+])(1 + K_1 K_2 [AA][H^+])} \quad (A.18)$$

and with rearrangement it becomes,

$$\frac{[Ag(I)]}{k_C} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 [H^+]}\right)\frac{1}{[AA]} + \frac{1 + K_1[H^+]}{k_1}. \quad (A.19)$$

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