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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

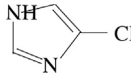
3.1. Spectral changes

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.

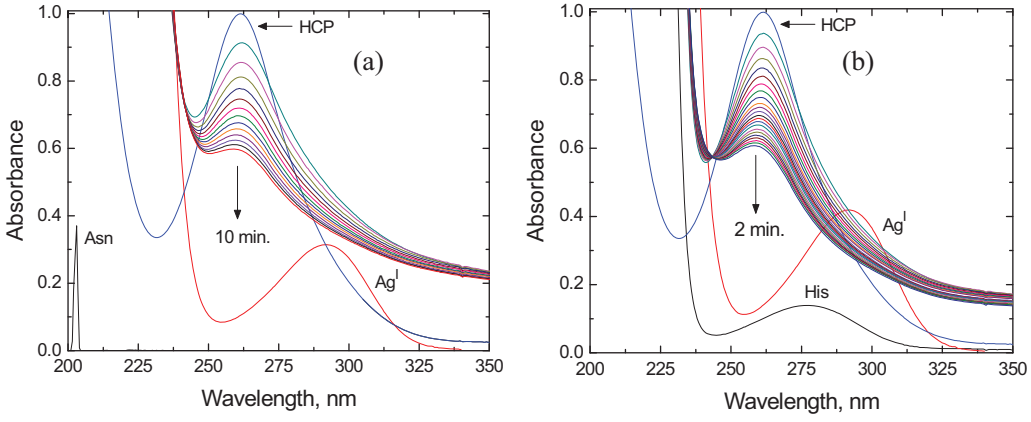


Fig. 1. Spectral changes during silver(I)-catalyzed oxidation of: (a) L-asparagine, and (b) L-histidine, by HCP in perchloric acid solutions. [AA] = 3.0×10^{-2}, [HCP] = 7.6×10^{-5}, [H^+] = 1.5, [Ag(I)] = 6.0×10^{-5}, and I = 2.5 mol dm^{-3} at 25 °C.