Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 3159-0040
Vol. 2 Issue 5, May - 2015

Mechanistic Investigation of Copper(II)-Catalyzed Oxidation of L-Asparagine by Hexachloroplatinate(IV) in Aqueous Alkaline Medium: A Kinetic Approach

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***Abstract*—Kinetics and mechanistic investigations of copper(II)-catalyzed oxidation of L-asparagine (Asn) by hexachloroplatinate(IV) (HCP) was performed in alkaline medium at a constant ionic strength of 0.2 mol dm^{-3} and at 25 ^{o}C using a conventional spectrophotometric technique. A first order dependence in both [HCP] and [Cu^{II}] and fractional-first order kinetics with respect to both [Asn] and [OH^-] were observed. Increasing ionic strength and dielectric constant increases the oxidation rate. The proposed mechanism indicated that the reaction proceeds *via* formation of copper(II)–asparagine intermediate complex, which reacts with the oxidant in the rate-determining step to give rise to the oxidation products which were identified as α-formyl acetamide, ammonia and carbon dioxide. In this context, platinum(IV) is reduced to platinum(II) by the substrate in a one-step two-electron transfer process. The rate law associated with the reaction mechanism is deduced. Activation parameters of the reaction have been evaluated and discussed.**

Keywords—Kinetics, mechanism, copper(II) catalysis, oxidation, L-asparagine, hexachloroplatinate(IV)

Introduction

In the last decades, some metal ions in their complex forms act as good oxidants in acidic, basic and neutral media. One significant category of them is biologically active platinum(IV) complexes which have become of fundamental importance due to their anticancer properties [1]. Hexachloroplatinate(IV), HCP, oxidation studies of organic [2-8] and inorganic [9-12] substrates have been reported in which $[PtCl_6]^{2-}$ may behave as one- or two-electron oxidant, depending upon the substrate and experimental conditions [13-16]. However, the reduction of some platinum(IV) complexes by different substrates generally proceeds via a free radical mechanism, i.e, one-electron transfer process [17-19]. The alternative path, where by platinum(IV) undergoes a two-electron reduction, has also been shown to occur [20]. This is depending upon the reductant and experimental conditions.

The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidants to yield different products [21-24]. L-asparagine (Asn) is considered to be the first amino acid to be isolated from *asparagus juice* and creates in the liver to help feed the nervous system. Its role in the metabolism is crucial. It finds extensive applications in the production of pharmaceuticals and medicine and as a reducing agent in chemical and biochemical systems. The oxidation of L-asparagine in alkaline medium has been previously studied by sodium N-chloro-*p*-toluene sulphonamide catalyzed by copper(II) [25] and by diperiodatonickelate(IV) complex [26]. In most the cases, the final oxidation products of L-asparagine were α-formyl acetamide, ammonia and carbon dioxide.

Kinetic studies of the oxidation reactions of amino acids catalyzed by different metal ions are an important field of chemistry due to the role played by metals in biological systems. Copper(II) ion acts as a catalyst in the oxidation of some amino acids [27]. Copper(II) complexes of amino acids present important pharmacological interest as several of them show a wide spectrum of effects, including anti-inflammatory, antiulcer, anticonvulsant and even anti-tumoral activity [28-30]. The pharmacological activity of certain copper complexes when compared with that of the free ligands, the complexes are usually more active than the parent ligands. Some copper(II) complexes with L-asparagine have been reported in earlier studies [31-33]. The mechanism of catalyzed reaction can be quite complicated due to formation of different intermediate complexes. Although, the mechanism of catalysis depends on the nature of the substrate, oxidant and on the experimental conditions, it has been shown [34] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactant or oxidation of the substrate itself or through the formation of free

radicals. Fawzy [3] reported the kinetics of oxidation of L-asparagine by hexachloroplatinate(IV) in sulfuric acid medium in the absence and presence of copper(II) catalyst. L-asparagine is suggested to combine with Cu^{II} species to form an intermediate complex which then reacts in a slow step with another $[PtCl_6]^{2-}$ species to give rise to the products with regenerating the catalyst.

No work, however, has been reported on the oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium in either absence or presence of a catalyst. The present report deals with the title reaction in order to understand the active species of oxidant and catalyst, to examine the catalytic activity of the catalyst and to propose the appropriate reaction mechanism.

EXPERIMENTAL

Materials

All chemicals employed in the present work were of reagent grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. A stock solution of L-asparagine (E. Merck) was prepared afresh by dissolving the amino acid sample in bidistilled water. Chloroplatinic acid solution (Johnson Matthey) was used without further purification. Required solution of the oxidant was freshly prepared before each experiment by proper dilution of its original solution which is standardized spectrophotometrically [35]. The solution was stored in a bottle away from light and re-standardized periodically.

Kinetic Measurements

The kinetic runs were followed under pseudo-first order conditions with L-asparagine in at least a 10-fold excess over that of hexachloroplatinate(IV) at a constant ionic strength, *I*, of the reaction medium of 0.2 mol dm^{-3} (using $NaClO_4$ as an inert electrolyte) and at a constant temperature of 25±0.1 ^{o}C, unless stated otherwise. The rate of disappearance of HCP was followed spectrophotometrically by monitoring the decrease in its absorbance at λ_{max} = 262 nm, its absorption maximum. The spectrophotometer, Shimadzu UV-1800 PC automatic scanning double-beam, had a cell compartment kept at constant temperature by circulating water from a thermostat. Solutions of the oxidant and the mixture containing L-asparagine substrate, alkali and copper(II) catalyst were separately thermostated for nearly 1 h. Platinum(IV) oxidant was then added to the mixture, the overall reaction mixture was transferred to the cell of path length 1 cm, and 3-4 experimental readings were taken in each run. It was observed that the oxidation reaction do not proceed in the absence of copper(II) catalyst. Good straight lines for ln(absorbance) versus time plots were obtained for at least three half-lives and the pseudo-first order rate constant values of the catalyzed reaction (k_C) were calculated as the gradients of such plots. The rate constants were reproducible to within 4%.

The effect of dissolved oxygen on the reaction rates was checked by preparing the reaction mixtures and following the reactions under a nitrogen atmosphere. There are no significant changes in the results obtained in the presence of nitrogen from those in the presence of air.

RESULTS

Spectroscopic Changes

The spectroscopic changes associated with the L-asparagine oxidation by hexachloroplatinate(IV) in alkaline medium in the presence of copper(II) catalyst are shown in Fig. 1(a,b). The scanned spectra shown in Fig. 1(a) indicate gradual disappearance of HCP band with time located at λ = 262 nm as a result of reduction of HCP. A careful examination of the spectral scans, Fig. 1(b), manifests a simultaneous growing of an absorption band located in the region *ca*. 318-380 nm with an isosbestic point centered at λ = 318 nm. These spectroscopic features are consistent with the formation of a copper(II)-asparagine intermediate complex.

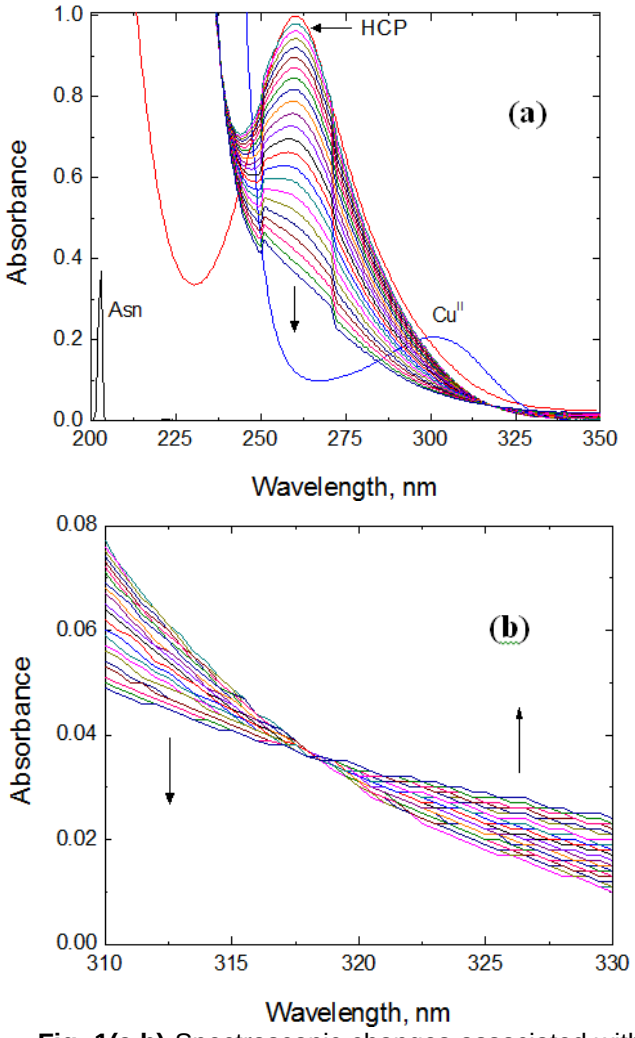
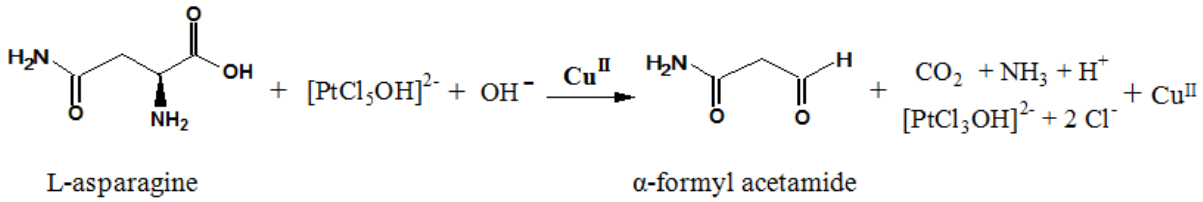


Fig. 1(a,b) Spectroscopic changes associated with copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08, [Cu^{II}] = $2x10^{-5}$ and *I* = 0.2 mol dm^{-3} at 25 ^{o}C. Scanning time intervals = 1 min.

Stoichiometry and Product Analysis

Reaction mixtures containing various amounts of hexachloroplatinate(IV) and L-asparagine at constant pH, ionic strength and temperature were allowed to react for 24 h in an inert atmosphere. The remaining [HCP] was assayed spectrophotometrically by measuring the absorbance at 262 nm. The results showed that one mole of HCP consumed one mole of Asn in accordance with the following stoichiometric equation:



L-asparagine α-formyl acetamide (1)

The above stoichiometric equation is consistent with the results of product analysis. The product, α-formyl acetamide was estimated quantitatively as its 2,4-DNP derivative [36]. The byproducts were identified as ammonia by Nessler's reagent [37] and the carbon dioxide was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing limewater. Similar oxidation products with different experimental conditions have been also reported earlier [25,26]. On the other hand, formation of platinum(II) was confirmed by the black precipitate obtained after standing of the reaction mixture for several hours. Such black precipitate is formed as a result of transformation of $[PtCl_4]^{2-}$ in alkaline medium into hydrated PtO as indicated by thermogravimetric and IR spectral analysis [38]

$$[PtCl_4]^{2-} + 2OH^- \longrightarrow Pt(OH)_2 + 4\,Cl^- \qquad (2)$$

There is also an literature evidence [39] to indicate that platinum(II) oxide exists as $Pt(OH)_2$. Furthermore, similar product was reported [38,40] for the reaction between platinum(IV) and different reductants.

Reaction Order

The reaction orders with respect to the reactants were determined from the slopes of the log k_C versus log (concentration) plots by varying the concentrations of substrate, alkali and catalyst, in turn, while keeping other conditions constant.

Effect of [HCP]

The pseudo-first order rate constant (k_C) were determined at different [HCP] in the region: (4–12) $x10^{-5}$ mol dm^{-3} but at constant other variables such as [Asn], [OH^-], ionic strength, temperature and [Cu^{II}]. Plots of ln (absorbance) versus time were linear up to about 85% of the reaction completion with no variation in the slope of such plots (k_C) for different [HCP], Table 1, suggesting that the reaction order in [HCP] as unity.

Effect of [Asn]

The observed rate constant was determined at different initial concentrations of the reductant asparagine keeping all other reactant concentrations constant including copper(II) catalyst. It was found that the rate of reaction increased with increasing the concentration of asparagine substrate as listed in Table 1. The observation that when log k_C was plotted against log [Asn], Figure not shown, straight line with a slope of 0.93 was obtained suggesting that oxidation reaction is fractional-first order in the amino acid.

Effect of [Alkali]

The reaction rate was measured at constant [Asn], [HCP], [Cu^{II}], ionic strength and temperature but with various [OH^-] (0.02 – 0.16 mol dm^{-3}). The rate of reaction was found to increase with increase in [OH^-], Table 1, and the order with respect to the alkali was less than unity.

Effect of Ionic Strength and Dielectric Constant

At constant concentrations of HCP, Asn, Cu^{II} and OH^-, and at constant temperature, the addition of $NaClO_4$ to the reaction medium was found to accelerate the reaction rate. The results are presented in Table 1. These results show that the pseudo-first order rate constant k_C increases with increase in the ionic strength of the medium, and the Debye-Hückel plot was found to be linear with a positive slope (Fig. 2).

In order to determine the effect of dielectric constant (D) of the medium on the rate, the oxidation of L-asparagine by HCP were studied at different solvent compositions (v/v) of *t*-butyl alcohol and water. The dielectric constant of the medium at different compositions was calculated using dielectric constants of water and *t*-butyl alcohol. The data clearly reveals that the rate constant decreases with the decrease in dielectric constant of the solvent mixture; i.e. increase in *t*-butyl alcohol content. The plot of log k_C versus $1/D$ was linear with a negative slope as shown in Fig. 3.

Effect of [Cu^{II}]

The copper(II) catalyst concentration was varied from $1x10^{-5}$ to $5x10^{-5}$ mol dm^{-3} at constant [Asn], [HCP], [OH^-] and at constant ionic strength and temperature. Reaction rate was directly proportional to [Cu^{II}] (Table 1) suggesting that the order in [Cu^{II}] is one. This was also confirmed from the linearity of the plot of log k_C versus log[Cu^{II}] with a slope ≈ 1 as shown in Fig. 4.

Effect of Added Salts

The effect of added salts on the first order rate constant was studied at constant concentrations of the reactants but at different concentrations of added salts such as silver(I) nitrate and chromium(III) sulfate. The value of k_C was found to increase with increase in [Ag^{I}] and [Cr^{III}] and the order of effectiveness is Ag^{I} > Cr^{III} (Fig. 5).

Effect of [Cl^-]

The effect of chloride ions on the reaction rates was investigated by the addition of different concentrations of NaCl solution ranging from $1x10^{-3}$ to $1x10^{-2}$ mol dm^{-3} at constant other variables. The values of the rate constants were found to be independent of sodium chloride concentrations.

Test for Free Radicals

The intervention of free radicals was examined as follows; the reaction mixture, to which a known quantity of acrylonitrile monomer had been added initially, was kept in an inert atmosphere for 6 hours. On diluting the reaction mixture with methanol, no white precipitate was formed, indicating the absence of free radicals in the reactions.

Table 1 Effect of variation of [HCP], [Asn], [OH^-], [Cu^{II}] and ionic strength, *I*, on the pseudo-first order rate constant value in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium at 25 ^oC.

10^5 [HCP] (mol dm^{-3})	10^2 [Asn] (mol dm^{-3})	10^2 [OH^-] (mol dm^{-3})	10^5 [Cu^{II}] (mol dm^{-3})	*I* (mol dm^{-3})	10^5 k_C (s^{-1})
4.0	4.0	8.0	2.0	0.2	21.3
6.0	4.0	8.0	2.0	0.2	23.3
8.0	4.0	8.0	2.0	0.2	22.8
10.0	4.0	8.0	2.0	0.2	21.9
12.0	4.0	8.0	2.0	0.2	23.5
8.0	2.0	8.0	2.0	0.2	12.2
8.0	3.0	8.0	2.0	0.2	18.0
8.0	4.0	8.0	2.0	0.2	22.8
8.0	6.0	8.0	2.0	0.2	34.5
8.0	8.0	8.0	2.0	0.2	43.2
8.0	4.0	2.0	2.0	0.2	9.3
8.0	4.0	4.0	2.0	0.2	14.3
8.0	4.0	8.0	2.0	0.2	22.8
8.0	4.0	12.0	2.0	0.2	28.7
8.0	4.0	16.0	2.0	0.2	35.6
8.0	4.0	8.0	1.0	0.2	10.9
8.0	4.0	8.0	2.0	0.2	22.8
8.0	4.0	8.0	3.0	0.2	31.2
8.0	4.0	8.0	4.0	0.2	41.5
8.0	4.0	8.0	5.0	0.2	54.3
8.0	4.0	8.0	2.0	0.2	22.8
8.0	4.0	8.0	2.0	0.3	26.2
8.0	4.0	8.0	2.0	0.4	30.1
8.0	4.0	8.0	2.0	0.5	33.4
8.0	4.0	8.0	2.0	0.6	37.2

Experimental error ± 3%

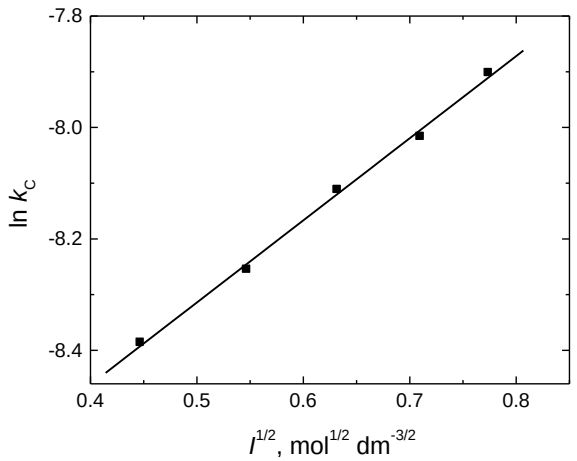


Fig. 2. Debye-Hückel plot in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08 and [Cu^{II}] = $2x10^{-5}$ mol dm^{-3} at 25 ^oC.

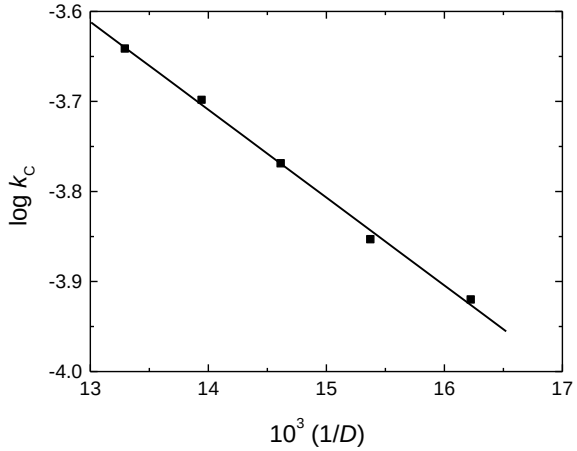


Fig. 3 Plot of log k_C versus 1/*D* in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08 and [Cu^{II}] = $2x10^{-5}$ mol dm^{-3} at 25 ^oC.

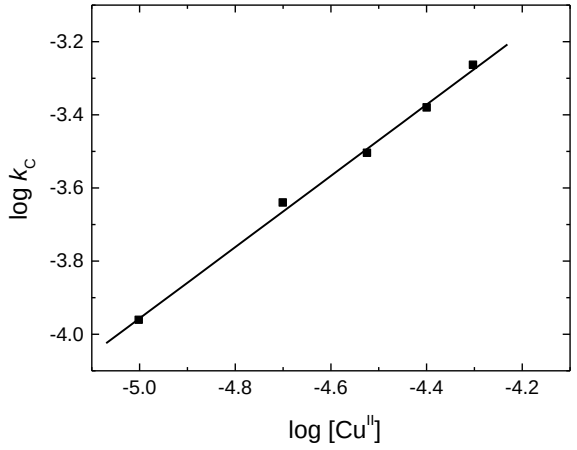


Fig. 4 Plot of log k_C versus log [Cu^{II}] in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$ and [OH^-] = 0.08 mol dm^{-3} at 25 ^oC.

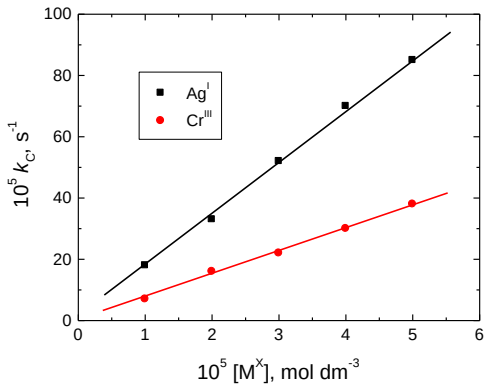


Fig. 5 Effect of Ag^{I} and Cr^{III} on the pseudo-first order rate constant in the oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08 and [Cu^{II}] = $2x10^{-5}$ mol dm^{-3} at 25 ^{o}C.

Effect of Temperature

The kinetics was studied at different temperatures, 15, 20, 25, 30 and 35 ^{o}C, at constant concentrations of the reactants and other conditions being constant. The obtained results indicate that the pseudo-first order rate constant values were increased with an increase in temperature. The activation parameters of the second order rate constants, k_2 ($k_2 = k_C / [Asn]$), are calculated using Arrhenius, Fig. 6(a), and Eyring, Fig. 6(b), plots and are listed in Table 2.

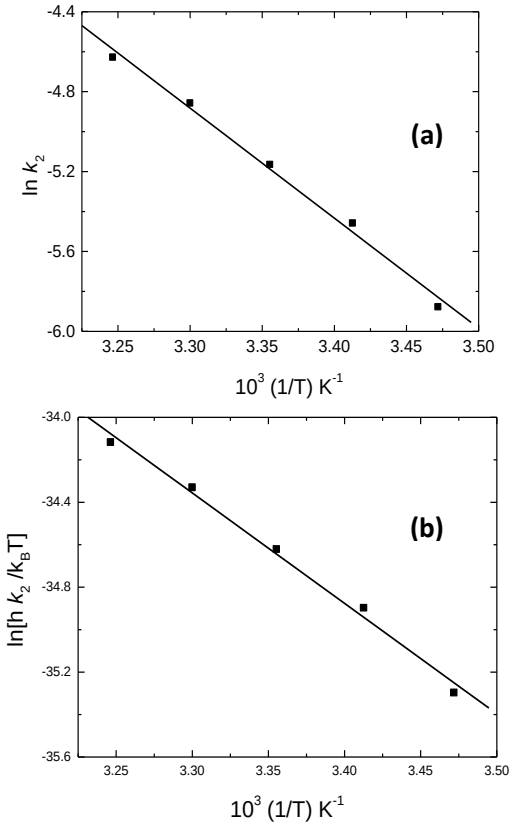


Fig. 6(a,b) Arrhenius (a) and Eyring (b) plots in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08 and [Cu^{II}] = $2x10^{-5}$ mol dm^{-3}.

Table 2 Activation parameters of the second order rate constants k_2 in the copper(II)-catalyzed oxidation of L-asparagine hexachloroplatinate(IV) in alkaline medium. [Asn] = 0.04, [HCP] = $8x10^{-5}$, [OH^-] = 0.08 and [Cu^{II}] = $2x10^{-5}$ mol dm^{-3}.

$\Delta S^{\neq}$, J $mol^{-1}K^{-1}$	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}	$E_a^{\neq}$, kJ mol^{-1}
-141.33	43.23	85.45	45.27

Experimental error ±5%

DISCUSSION

Reductions of hexachloroplatinate(IV) by different reductants have been shown to proceed via a free-radical mechanism in two successive one-electron transfer steps [20,41]. Also, the path by which platinum(IV) is reduced by different reductants has been the subject of much discussion [13,19], which was mainly concerned with the possibility of platinum(III) as an intermediate. However, the alternative mechanistic paths whereby platinum(IV) undergoes a simultaneous two-electron transfer reduction have also been reported [10,16]. In the present study, the absence of free radical intervention in the reactions suggests the possibility of the two-electron transfer mechanism.

It was reported [42] that hexachloroplatinate(IV) ion hydrolyzes in aqueous solutions according to the following equation

$$[PtCl_6]^{2-} + H_2O \longrightarrow [PtCl_5H_2O]^{-} + Cl^{-} \quad (3)$$

followed by rapid deprotonation of the aquo-complex upon increasing pH to form $[PtCl_5OH]^{2-}$

$$[PtCl_5H_2O]^{-} \overset{K_a}{\rightleftharpoons} [PtCl_5OH]^{2-} + H^{+} \quad (4)$$

where K_a is the acid dissociation constant (K_a = 3.5) [43]

Also, there is a literature evidence [44] to indicate that, in alkaline medium (pH > 8), $[PtCl_6]^{2-}$ changes to $[PtCl_5OH[^{2-}$ in a fast step as follows:

$$[PtCl_6]^{2-} + OH^{-} \longrightarrow [PtCl_5OH]^{2-} + Cl^{-} \quad (5)$$

In the present work, addition of Cl^- to the reaction mixture failed to inhibit the rate indicating that the above step is not reversible. The ligand replacement reaction between $[PtCl_5OH]^{2-}$ and OH^- to give $[PtCl_4(OH)_2]^{2-}$ and Cl^-, followed by the oxidation of asparagine by $[PtCl_4(OH)_2]^{2-}$ can be ruled out since the dihydroxy platinum(IV) complex is unstable in aqueous solution and readily disproportionate [45] according to the following equation:

$$2\,[PtCl_4(OH)_2]^{2-} \longrightarrow [PtCl_2(OH)_4]^{2-} + [PtCl_6]^{2-} \quad (6)$$

Consequently, under the present experimental conditions $[PtCl_5OH]^{2-}$ may act as the sole oxidizing species.

It was suggested [46] that amino acid in aqueous solutions is known to exist as zwitterion, whereas in

aqueous alkaline media it exists in anionic form according to the following equilibria,

$$\underset{\text{Amino acid}}{RCH(NH_2)COOH} \overset{\text{Aq.}}{\rightleftharpoons} \underset{\text{Zwitterion}}{RCH(\overset{+}{N}H_3)COO^-} \overset{OH^-}{\rightleftharpoons} \underset{\text{Anionic form}}{RCH(NH_2)COO^-} + H_2O \quad (7)$$

The increase in the reaction rate with increasing pH of the medium suggests deprotonation of asparagine prior to the rate-determining step, i.e. the deprotonated form is proposed to be the principal reactive species.

Reaction Mechanism

It is reported [27] that copper(II) acts as an efficient catalyst in some redox reactions involving amino acids, particularly in an alkaline medium. However, in aqueous alkaline media [47] Cu^{II} ions form a tetrahydroxycuprate(II) complex, $[Cu(OH)_4]^{2-}$.

The reaction between $[PtCl_5OH]^{2-}$ and asparagine in the presence of small amounts of copper(II) catalyst exhibits a stoichiometry of 1:1 with a first order dependence on both [HCP] and $[Cu^{II}]$ and with apparent less than unit order with respect to each [Asn] and $[OH^-]$. Based on the experimental results and product analysis, a mechanism is proposed (Scheme I) for which all the observed orders in each constituent such as [oxidant], [reductant], [alkali] and [catalyst] may be well accommodated. These results imply that the amino acid substrate first deprotonate by the alkali followed by combination of the deprotonated asparagine with Cu^{II} species, $[Cu(OH)_4]^{2-}$, to form an intermediate complex, $[Asn - Cu(OH)_4]^{3-}$, prior to the rate-limiting step. The observed less than unit order in [Asn] presumably results from such complex formation. The formation of the complex was also proved kinetically by a non-zero intercept of the plot of $[Cu^{II}]/k_C$ versus 1/[Asn] (Fig. 7). Such complexes between asparagine and copper(II) catalyst have been reported in earlier studies [31-33]. Then, the active species of the oxidant, $[PtCl_5OH]^{2-}$, attack the formed intermediate in the slow step to give rise to the initial products with regeneration of the catalyst Cu^{II}. This is followed by other fast steps to yield the final oxidation products. The results are accommodated in the following sequence,

$$Asn + OH^- \overset{K_1}{\rightleftharpoons} Asn^- + H_2O \quad (8)$$

$$Asn^- + [Cu(OH)_4]^{2-} \overset{K_2}{\rightleftharpoons} [Asn - Cu(OH)_4]^{3-} (C) \quad (9)$$

$$[Asn - Cu(OH)_4]^{3-} + [PtCl_5OH]^{2-} \xrightarrow[\text{slow}]{k_1} \text{Products} + [Cu(OH)_4]^{2-} \quad (10)$$

According to the proposed mechanism, the rate of disappearance of HCP or formation of the intermediate complex (C) can be expressed by the following rate-law equation,

$$\text{Rate} = \frac{-d[HCP]}{dt} = \frac{+d[C]}{dt} = k_1[C][HCP] \quad (11)$$

The relationship between the rate of complex formation and the substrate, hydroxyl ion, catalyst and oxidant concentrations has been deduced to give the following rate-law equation,

$$Rate = \frac{k_1K_1K_2[Asn][OH^-][Cu^{II}][HCP]}{(1+K_1[OH^-]+K_1K_2[OH^-][Cu^{II}])(1+K_1K_2[Asn][OH^-])} \quad (12)$$

In view of low concentration of both $[Cu^{II}]$ and $[OH^-]$ used, the term $K_1K_2[OH^-][Cu^{II}]$ in the denominator can be neglected. Therefore, Eq. (12) becomes,

$$Rate = \frac{k_1K_1K_2[Asn][OH^-][Cu^{II}][HCP]}{(1+K_1[OH^-])(1+K_1K_2[Asn][OH^-])} \quad (13)$$

$$Rate = \frac{k_1K_1K_2[Asn][OH^-][Cu^{II}][HCP]}{1+K_1K_2[Asn][OH^-]+K_1[OH^-]+K_1^2K_2[Asn][OH^-]^2} \quad (14)$$

The term $K_1^2K_2[Asn][OH^-]^2$ in the denominator of Eq. (14) is negligibly small compared to unity in view of the low concentration of Asn and OH^- used. Therefore Eq. (14) can be written as:

$$\text{Rate} = \frac{k_1K_1K_2[Asn][OH^-][Cu^{II}][HCP]}{1+K_1K_2[Asn][OH^-]+K_1[OH^-]} \quad (15)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[HCP]}{dt} = k_C[HCP] \quad (16)$$

Comparing Eqs. (15) and (16) we obtain,

$$k_C = \frac{\text{Rate}}{[HCP]} = \frac{k_1K_1K_2[Asn][OH^-][Cu^{II}]}{1+K_1K_2[Asn][OH^-]+K_1[OH^-]} \quad (17)$$

Equation (17) can be rearranged to the following forms, which is suitable for verification:

$$\frac{[Cu^{II}]}{k_C} = \left(\frac{1}{k_1K_1K_2[OH^-]} + \frac{1}{k_1K_2}\right)\frac{1}{[Asn]} + \frac{1}{k_1} \quad (18)$$

$$\frac{[Cu^{II}]}{k_C} = \left(\frac{1}{k_1K_1K_2[Asn]}\right)\frac{1}{[OH^-]} + \frac{1}{k_1K_2[Asn]} + \frac{1}{k_1} \quad (19)$$

According to Eqs. (18) and (19), plots of $[Cu^{II}]/k_C$ versus 1/[Asn] at constant $[OH^-]$ and $[Cu^{II}]/k_C$ versus $1/[OH^-]$ at constant [Asn] should be linear with positive intercepts and are found to be so as shown in Fig. 7 suggesting the validity of the proposed mechanism.

Activation parameters listed in Table 2 may be discussed as follows, the observed large negative values of $\Delta S^{\neq}$ confirms the compactness of the intermediate complex formed and such activated complex is more ordered than the reactants due to loss of degree of freedom [48]. The experimental values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were both favorable for electron transfer process. Again, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate the endothermic formation of the intermediate and its non-spontaneity, respectively. This evidence accords with the suggested transition states which may confirm the formation of the intermediate complex via the inner-sphere electron transfer mechanism. This mechanism is supported by the proposition made by Stewart and co-workers [49,50]. They reported that the entropy of activation tends to be more positive for reactions of outer-sphere mechanisms, whereas it is more negative for reactions of inner-sphere type. Therefore, such agreement may be considered as evidence to support the formation of intermediate complexes of inner-sphere nature for electron transfer mechanism with respect to the present redox reaction.

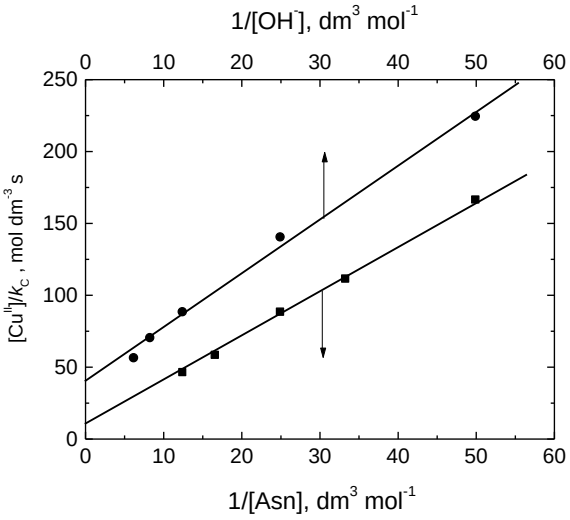
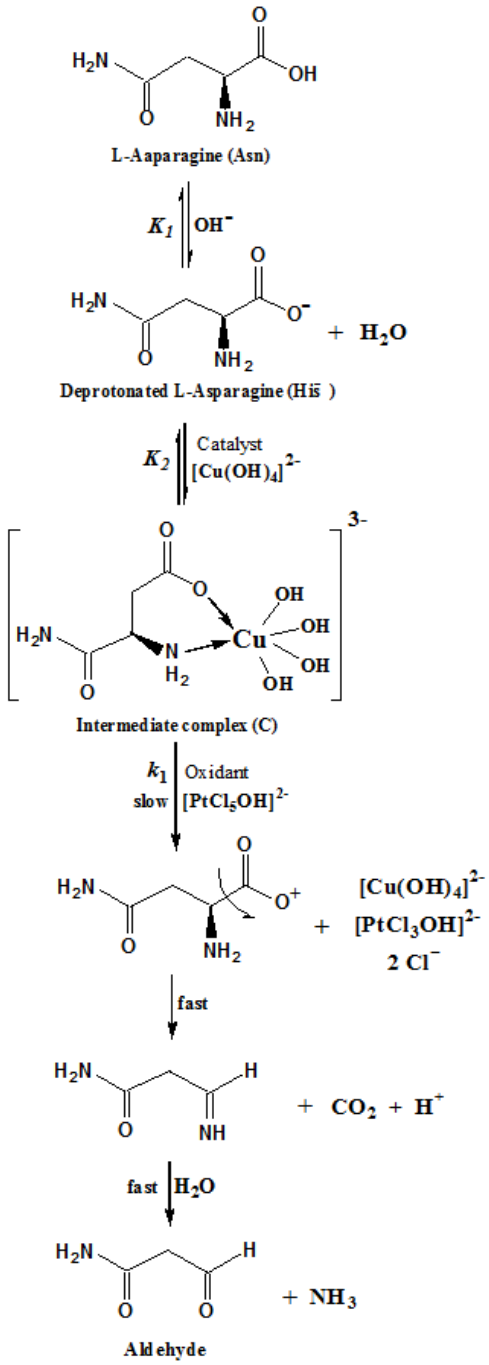


Fig. 7 Verification of the rate law (15) in the form of Eqs. (18) and (19) in the copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium. [HCP] = $8x10^{-5}$ and I = 0.2 mol dm^{-3} at 25 ^{o}C.



Scheme I. Mechanism of copper(II)-catalyzed oxidation of L-asparagine by hexachloroplatinate(IV) in alkaline medium.

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