

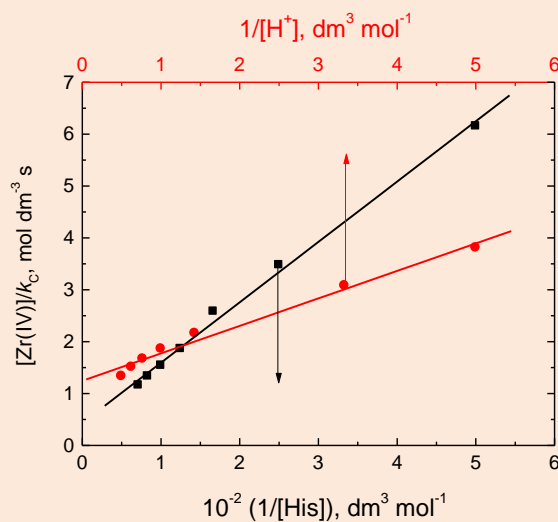
Research Article

Kinetic and Mechanistic Investigation on the Zirconium(IV)-Catalyzed Oxidation of L-Histidine by Hexachloroplatinate(IV) in Acid Medium

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Kinetic investigation on the hexachloroplatinate(IV) (HCP) oxidation of L-histidine (His) catalyzed by zirconium(IV) has been performed in sulfuric acid medium at constant ionic strength and temperature. The reaction has been followed spectrophotometrically. A first order dependence on [HCP] and fractional-first order dependences with respect to [His], [acid] and [Zr(IV)] are obtained. Increasing ionic strength and dielectric constant decreases the oxidation rate. On the basis of the experimental results, a suitable mechanism has been proposed. The reaction is suggested to proceed via formation of zirconium(IV)-histidine intermediate complex, which reacts with the oxidant by an inner-sphere mechanism leading to decomposition of the complex in the rate-determining step to give rise to the oxidation products which are identified as the corresponding aldehyde (2-imidazole acetaldehyde), ammonium ion and carbon dioxide. The appropriate rate law is deduced and the activation parameters are evaluated and discussed.

Keywords: Hexachloroplatinate(IV), oxidation, L-histidine, zirconium(IV) catalyst, kinetics, mechanism

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Introduction

L-Histidine (His), an α -amino acid, is an essential component of almost all the proteins, found abundantly in hemoglobin and has been used in the treatment of rheumatoid arthritis, allergic diseases, ulcers and anemia. Its deficiency can cause poor hearing. The importance of the amino acid, L-histidine lies in the fact that the body uses it to manufacture histamine which is responsible for a wide range of physiological processes. It finds extensive applications as a reducing agent in chemical and biochemical systems. Rate of reduction by L-histidine depends on the oxidant nature and pH of the medium. The oxidation of L-histidine has been previously studied by few reagents in different media [1-9]. In most cases, the final oxidation products of it were 2-imidazole acetaldehyde, ammonia and carbon dioxide. It also provides metal binding sites in many enzymes. Due to the high reactivity of its imidazole group, L-histidine residue is often found at the active site of enzymes and involved directly in catalysis. It controls the transmission of metals in biological bases [10]. The formation and structure of L-histidine complexes with some transition metal ions have been studied in aqueous medium [9, 11-13]. Such metal complexes are usually more active than the parent ligands.

In the last decades, the chemistry of biologically active platinum(IV) complexes has become of fundamental importance for their remarkable anticancer properties [14-16]. The anticancer activity of such complexes is likely to be due to effective Pt(IV) transport into the cell followed by reduction to the more reactive platinum(II) compounds. Studies of oxidation of inorganic and organic substrates using platinum(IV) complexes in the form of

hexachloroplatinate(IV), $[\text{PtCl}_6]^{2-}$, as an oxidant are scarce and limited to a few cases [8,9,17-24], in which $[\text{PtCl}_6]^{2-}$ may behave as one or two electron oxidant, depending upon the substrate and experimental conditions. The knowledge of the reactivity of platinum(IV) compounds towards their reduction by potential bioreductant like L-histidine may be important for understanding the mechanism of where antitumor activity as well as for designing new compounds with the least side effect.

Studies of the oxidation reactions of amino acids catalyzed by metal ions are an important field of chemistry due to the role played by metals in biological systems. Kinetics and mechanism of oxidation of L-histidine by hexachloroplatinate(IV) in acid medium in the absence and presence of silver(I) catalyst has been reported earlier by Fawzy and Asghar [8]. They found that the oxidation reaction proceeds with a measurable rate in the absence of silver(I) catalyst and with a significantly faster one in the presence of the catalyst. The present study deals with the title reaction in attempt to understand the catalytic activity of zirconium(IV) towards the oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium.

Experimental

Materials

Reagent grade chemicals and doubly distilled water were used throughout the work. A stock solution of L-histidine (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 [25]. The solution was stored in a bottle away from light and re-standardized periodically. Zirconium(IV) nitrate (Robert Johnson) was used as received. All other reagents used were of analytical grade and their solutions were prepared by dissolving requisite amounts of the samples in doubly distilled water.

Kinetic Measurements

All kinetic runs were followed under pseudo-first order conditions with L-histidine in a large excess over that of HCP. The reaction was performed at constant ionic strength, I , of 2.0 mol dm^{-3} and at constant temperature of $25 \pm 0.1 \text{ }^\circ\text{C}$. The reaction was initiated by mixing the previously thermostatted solutions of HCP and His that also contained the required amounts of H_2SO_4 and Na_2SO_4 to maintain the required acidity and ionic strength, respectively, and Zr(IV) catalyst. The progress of the reaction was followed by measuring the decrease in absorbance of HCP, as a function of time, at its absorption maximum, 262 nm, where HCP absorbs to a considerably greater extent than any of the other reactants and products. It was verified that there is no interference from other reagents at this wavelength. The absorption measurements were made in a thermostatted quartz cell on a Shimadzu UV-1800 PC automatic scanning double-beam spectrophotometer. The applicability of Beer's law was verified at 262 nm under the reaction conditions that molar extinction coefficient was determined ($\epsilon = 13117 \pm 273 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and was found to be in a good agreement with that reported previously [25].

As the reduction of hexachloroplatinate(IV) by L-histidine in acid medium proceeds with a measurable rate in the absence of the catalyst, the catalyzed reaction is understood to occur in parallel paths, with contributions from both the catalyzed and uncatalyzed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions ($k_C = k_T - k_U$). Hence, during a calculation of k_C , the uncatalyzed rate constant k_U must be taken into account. So, kinetic runs under similar conditions in the absence of a catalyst were also carried out. The reaction was followed for more than three half-lives. The values of k_C were obtained from the slopes of $\log(\text{absorbance})$ versus time plots. The average of at least three independent kinetic runs was calculated. The runs were reproducible to within $\pm 4\%$. The orders of the various reactants were determined from the plots of $\ln k_C$ versus $\ln(\text{conc.})$ except in [HCP] by varying the concentrations of reductant, catalyst and acid in turn, while keeping others constant in the variation of each reactant.

The effect of dissolved oxygen on the reaction rate was also checked by preparing another batch of reaction mixtures then conducting the same set of reactions under a nitrogen atmosphere. No significant differences in the results were seen with and without oxygen.

Results

Time-Resolved Spectra

The spectral changes during the oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium in the presence of zirconium(IV) catalyst are shown in **Figure 1**. Gradual decrease of HCP absorbance at its absorption maximum with time was observed.

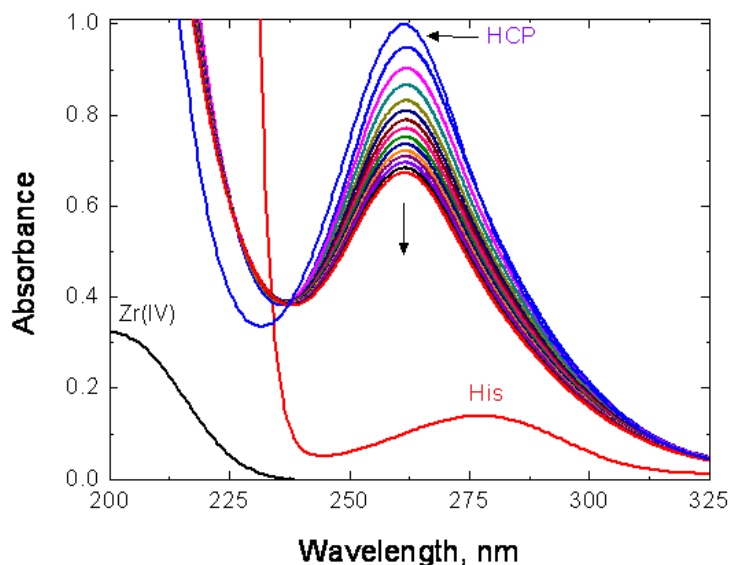
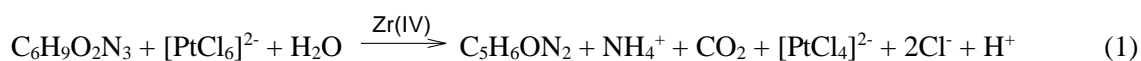


Figure 1 Time-resolved spectra in the oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[\text{His}] = 8.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$, $[\text{Zr(IV)}] = 8.0 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C . Scanning time intervals = 2 min

Stoichiometry and Product Analysis

Reaction mixtures containing various ratios of the amino acid to HCP were mixed at constant acidity, ionic strength and temperature, and then equilibrated for 24 h in an inert atmosphere. Estimation of the unreacted [HCP] was performed spectrophotometrically by measuring the absorbance at 262 nm. The results showed that one mole of HCP consumed one mole of L-histidine according to the following stoichiometric equation,



Where, $\text{C}_6\text{H}_9\text{O}_2\text{N}_3$ and $\text{C}_5\text{H}_6\text{ON}_2$ are L-histidine and its corresponding aldehyde (2-imidazole acetaldehyde), respectively. The above stoichiometric equation is consistent with the results of product analysis. The product, aldehyde was estimated quantitatively as its 2,4-DNP derivative [26]. Other products were identified as discussed earlier [27, 28]. Similar oxidation products with different experimental conditions have been also reported earlier [1-9]. On the other hand, formation of $[\text{PtCl}_4]^{2-}$ was confirmed by the observed black precipitate of platinum(II) hydroxide on addition of alkali to the reaction mixture.

Effect of [HCP] on the Reaction Rate

The oxidant, hexachloroplatinate(IV), concentration was varied in the range of 2.0×10^{-5} to 14.0×10^{-5} mol dm⁻³ at fixed [His], [Zr(IV)], [H⁺], ionic strength and temperature. The non-variation in the pseudo-first order rate constant at various concentrations of HCP (**Table 1**) indicates that the order with respect to the oxidant is confirmed to be one.

Table 1 Effect of variation of [HCP], [His], [H⁺], [Zr(IV)] and ionic strength, *I*, on the pseudo-first order rate constant *k_C* in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium at 25°C.

10⁵ [HCP] (mol dm ⁻³)	10³ [His] (mol dm ⁻³)	[H⁺] (mol dm ⁻³)	10⁴ [Zr(IV)] (mol dm ⁻³)	<i>I</i> (mol dm ⁻³)	10⁵ <i>k_C</i> (s ⁻¹)
2.0	8.0	1.0	8.0	2.0	42.5
4.0	8.0	1.0	8.0	2.0	44.2
6.0	8.0	1.0	8.0	2.0	43.3
8.0	8.0	1.0	8.0	2.0	43.1
10.0	8.0	1.0	8.0	2.0	43.2
12.0	8.0	1.0	8.0	2.0	42.7
14.0	8.0	1.0	8.0	2.0	42.9
8.0	2.0	1.0	8.0	2.0	13.9
8.0	4.0	1.0	8.0	2.0	22.8
8.0	6.0	1.0	8.0	2.0	31.2
8.0	8.0	1.0	8.0	2.0	43.1
8.0	10.0	1.0	8.0	2.0	51.7
8.0	12.0	1.0	8.0	2.0	60.3
8.0	14.0	1.0	8.0	2.0	69.2
8.0	8.0	0.2	8.0	2.0	21.2
8.0	8.0	0.4	8.0	2.0	26.1
8.0	8.0	0.7	8.0	2.0	37.0
8.0	8.0	1.0	8.0	2.0	43.1
8.0	8.0	1.3	8.0	2.0	48.0
8.0	8.0	1.6	8.0	2.0	53.2
8.0	8.0	2.0	8.0	2.0	59.8
8.0	8.0	1.0	2.0	2.0	18.9
8.0	8.0	1.0	4.0	2.0	27.2
8.0	8.0	1.0	6.0	2.0	35.0
8.0	8.0	1.0	8.0	2.0	43.1
8.0	8.0	1.0	10.0	2.0	53.2
8.0	8.0	1.0	12.0	2.0	61.8
8.0	8.0	1.0	14.0	2.0	74.9
8.0	8.0	1.0	8.0	2.0	43.1
8.0	8.0	1.0	8.0	2.3	40.8
8.0	8.0	1.0	8.0	2.6	37.9
8.0	8.0	1.0	8.0	2.9	36.1
8.0	8.0	1.0	8.0	3.2	34.2
8.0	8.0	1.0	8.0	3.6	32.8
8.0	8.0	1.0	8.0	4.0	30.7

Experimental Error ± 4%

Effect of [His] on the Reaction Rate

The observed rate constant k_C was determined at different initial concentrations of the reductant L-histidine keeping all other reactants concentrations constant. The obtained results show that the rate constant increases with the increase in concentration of L-histidine as listed in Table 1. Plot of the observed rate constant versus [His] is linear with positive intercept confirming fractional-first order dependence with respect to the amino acid (Figure not shown).

Effect of $[H^+]$ on the Reaction Rate

The reaction rate was measured at constant [His], [HCP], [Zr(IV)], ionic strength and temperature but with various $[H^+]$ (0.2 – 2.0 mol dm⁻³). The rate of reaction was found to increase with increase in $[H^+]$ and the reaction is fractional-order dependence on $[H^+]$.

Effect of [Zr(IV)] on the Reaction Rate

The reaction rate was measured with various [Zr(IV)], (2.0 – 14.0) × 10⁻⁴ mol dm⁻³, at constant other variables. Values of k_C were found to increase with the increase of [Zr(IV)] (Table 1). The order with respect to [Zr(IV)] was found to be less than unity which was also confirmed from the linear plot of $\ln k_C$ versus $\ln [Zr(IV)]$ with a slope of 0.76 as shown in **Figure 2**.

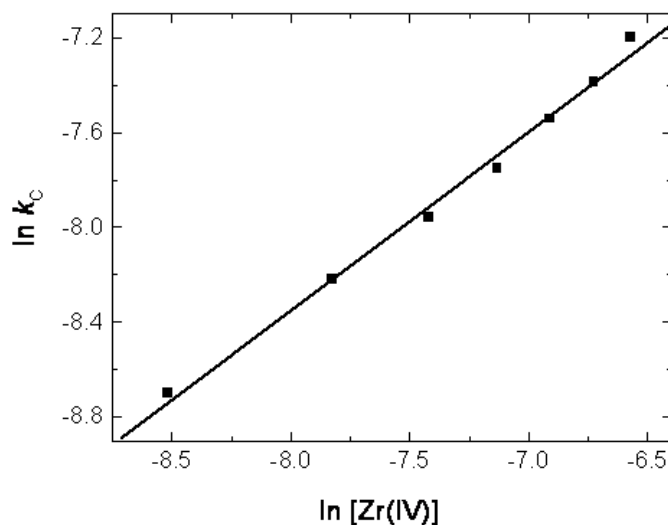


Figure 2 Plot of $\ln k_C$ versus $\ln [Zr(IV)]$ in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. [His] = 8.0 × 10⁻³, [HCP] = 8.0 × 10⁻⁵ and $[H^+] = 1.0$ mol dm⁻³ at 25°C

Effect of Ionic Strength and Dielectric Constant on the Reaction Rate

The effect of ionic strength on the reaction was studied by varying the concentration of sodium sulfate in the reaction medium at constant concentrations of His, HCP and Zr(IV), and at constant pH and temperature. The results are presented in Table 1. These results show that k_C decreases with the increase in ionic strength of the medium, and the Debye-Hückel plot was linear with negative slope, **Figure 3(a)**.

In order to determine the effect of dielectric constant (D) of the medium on the rate, the oxidation of L-histidine by HCP was studied at different solvent compositions (v/v) of acetic acid and water. The dielectric constant of the medium at different compositions was calculated using dielectric constants of water and acetic acid (78.5 and 6.15 at 25 °C, respectively). The data clearly reveals that the rate constant k_C decreases with the decrease in dielectric constant of the solvent mixture; i.e. increase in acetic acid content. The plot of $\log k_C$ versus $1/D$ was linear with a negative slope as shown in Figure 3(b).

Effect of Temperature on the Reaction Rate

The kinetics was studied at different temperatures, 15, 20, 25, 30, and 35 °C, at constant concentrations of the reactants and other conditions being constant. The obtained results indicate that the pseudo-first order rate constant increases with raising temperature. The activation parameters of the second-order rate constant k_2 ($k_2 = k_C / [\text{His}]$), were calculated using Arrhenius, **Figure 4(a)**, and Eyring, **Figure 4(b)**, plots and are listed in **Table 2**.

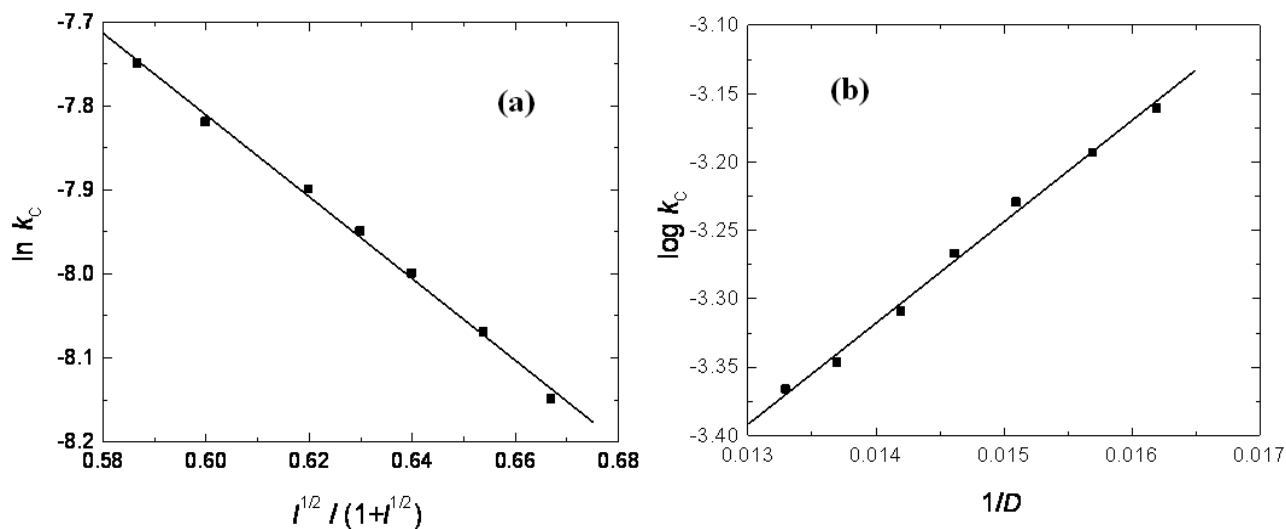


Figure 3 Effect of: (a) ionic strength, I , and (b) dielectric constant, D , in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[\text{His}] = 8.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$ and $[\text{Zr(IV)}] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 25 °C

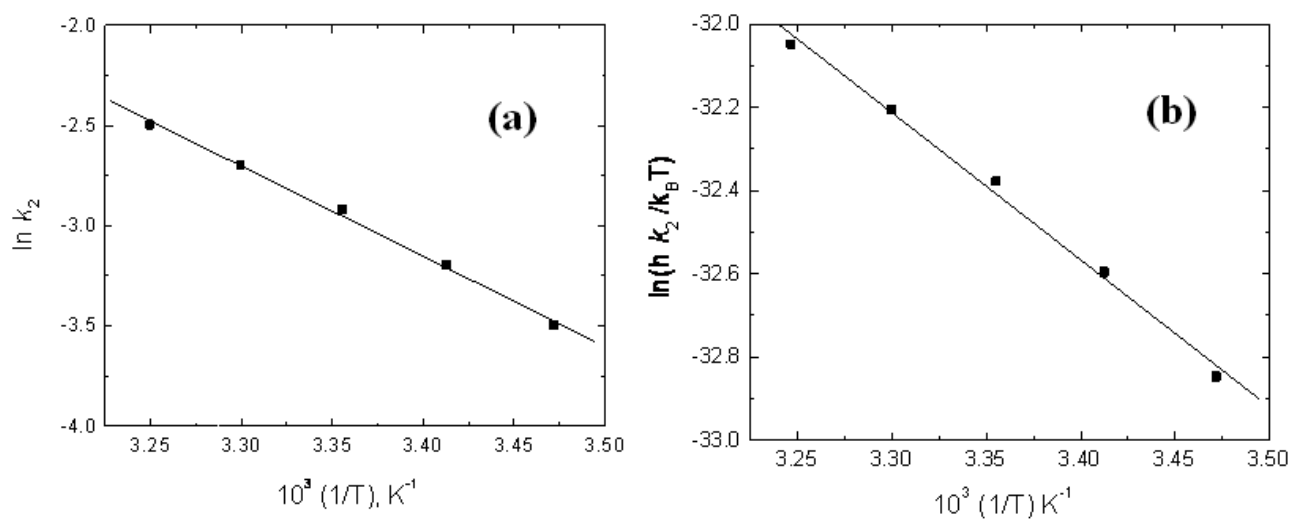


Figure 4 (a) Arrhenius plot and (b) Eyring plot in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[\text{His}] = 8.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, $[\text{Zr(IV)}] = 8.0 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$

Table 2 Activation parameters of the second-order rate constant k_2 in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. [His] = 8.0×10^{-3} , [HCP] = 8.0×10^{-5} , $[H^+] = 1.0 \text{ mol dm}^{-3}$, $[Zr(IV)] = 8.0 \times 10^{-4}$ and $I = 2.0 \text{ mol dm}^{-3}$

ΔS^\ddagger , $\text{J mol}^{-1} \text{K}^{-1}$	ΔH^\ddagger , kJ mol^{-1}	ΔG^\ddagger_{298} , kJ mol^{-1}	E_a^\ddagger , kJ mol^{-1}
-166.28	29.68	79.23	37.41

Experimental error $\pm 4\%$

Test for Free Radical Intermediate

To study the possible intervention of free radicals during the oxidation reaction, the reaction mixture to which a known amount of acrylonitrile scavenger was initially added was kept for 6 h in an inert atmosphere. On diluting the mixtures with methanol, no white precipitate was formed, thus confirming the absence of free radical intervention in the present reaction.

Discussion

Amino acids are known [29] to exist in zwitterions and predominantly tend to protonate at higher acid concentrations according to the following equilibria,



where K_1 is the protonation constant of L-histidine.

The enhancement of the reaction rates with increasing acid concentration, with a less than unit order dependence on $[H^+]$, suggests protonation of L-histidine prior to the rate-determining step.

On the other hand, in acid medium platinum(IV) species exist as $[\text{PtCl}_6]^{2-}$, which assumed to be the principal reactive oxidant [30]. The reduction of $[\text{PtCl}_6]^{2-}$ generally proceeds as follows



In this redox process, octahedral Pt(IV) is reduced to square planar Pt(II) with release of two Cl^- ions. Therefore, this reaction is better classified as reductive-elimination reaction [31].

There are two suggested alternative reaction mechanisms for the oxidation of L-histidine by hexachloroplatinate(IV). The first mechanism involves a simultaneous two-electron transfer in a single step. The second one involves two successive one-electron transfer steps. If the transition states of reductant and/or oxidant are unstable, a simultaneous two-electron transfer mechanism may be suggested such as that in the case of oxidation of uranium(IV) by $[\text{PtCl}_6]^{2-}$ [32]. In the present study, addition of acrylonitrile monomer to the reaction mixture failed to give polymerized products. It may be that the free radical like Pt(III) species is too short-lived to interact with acrylonitrile to give the polymerized product under our experimental conditions. Consequently, the two-electron transfer mechanism seems plausible.

Reaction Mechanism

The reaction between HCP and L-histidine in acid medium in the presence of zirconium(IV) catalyst exhibits a stoichiometry of 1:1 with a first order dependence on [HCP] and a fractional-first order dependences with respect to [His], [acid] and [Zr(IV)]. The observed less than unit order in [His] presumably results from a complex formation

between the catalyst zirconium(IV) and L-histidine substrate prior to the reaction with the oxidant HCP. The formation of the complex was also proved kinetically by a non-zero intercept of the plot of $[\text{Zr(IV)}]/k_c$ versus $1/[\text{His}]$ (Figure 5). The failure of a spectrophotometric detection of such intermediate complex might be explained by either lower concentrations of the reactants used and, hence, lower absorptivity of the formed complex, or fast subsequent decomposition of the intermediate relative to its rate of formation. Also, the rate of reaction decreases on increasing the ionic strength and dielectric constant of the medium, suggesting that the reaction occur between two ions with opposite charge [33].

The obtained results suggest that the amino acid substrate first protonate in a pre-equilibrium step. In the next step, the protonated L-histidine (His^+) combines with Zr(IV) species to form an intermediate complex (C) in the form of $[\text{His}^+ - \text{Zr(IV)}]$ which then reacts in a slow step with one molecule of HCP to give rise to the oxidation products with regeneration of the catalyst Zr(IV) (see Scheme I). The results are accommodated in the following sequence,

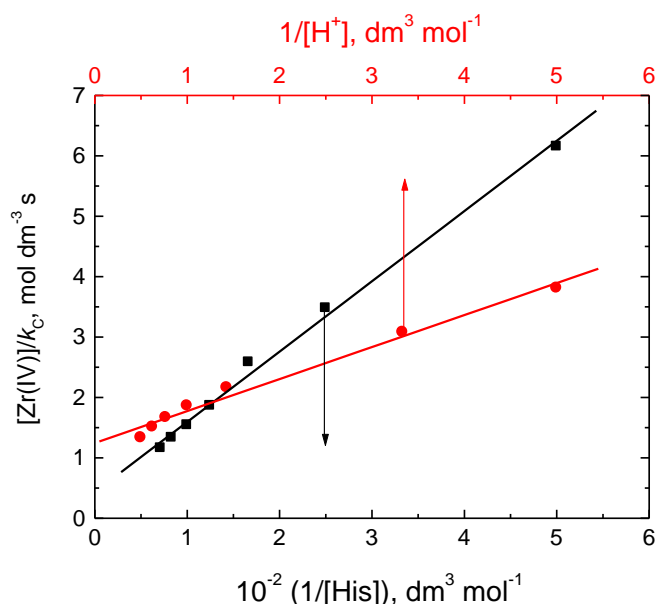
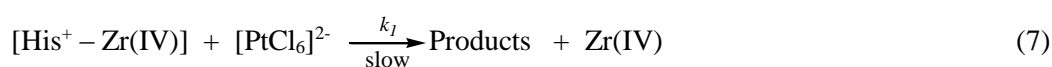
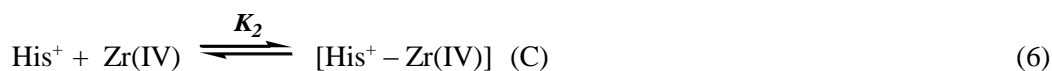


Figure 5 Verification of the rate law (11) in the form of Eqs. (14) and (15) in the zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[\text{HCP}] = 8.0 \times 10^{-5}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .



The proposed mechanism leads to the following rate law,

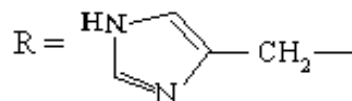
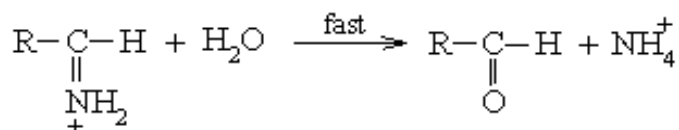
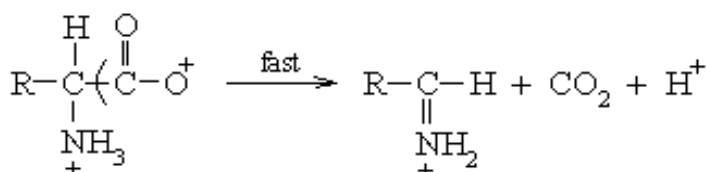
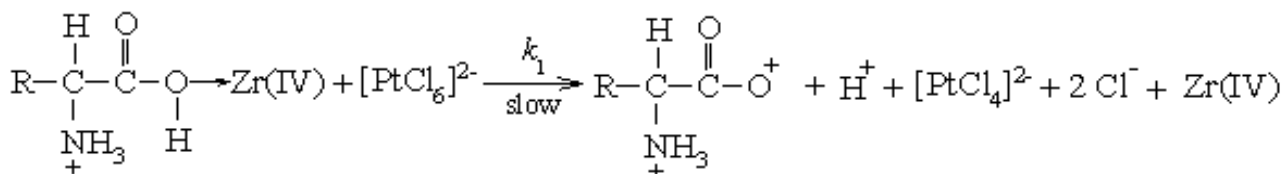
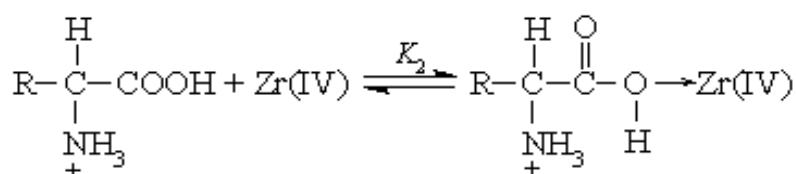
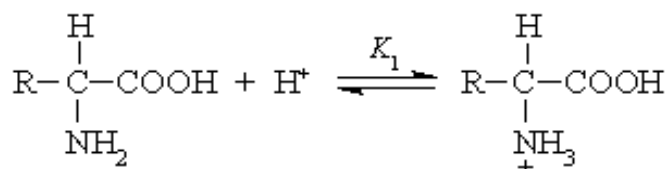
$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = k_1[\text{C}][\text{HCP}] \quad (8)$$

The relationship between the rate of complex formation and the substrate, hydrogen ion, catalyst and oxidant concentrations can be deduced to give the following rate-law equation,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{His}] [\text{H}^+] [\text{Zr(IV)}] [\text{HCP}]}{(1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{Zr(IV)}]) (1 + K_1 K_2 [\text{His}] [\text{H}^+])} \quad (9)$$

In view of low concentration of [Zr(IV)] used, the term $K_1 K_2 [\text{H}^+] [\text{Zr(IV)}]$ in the denominator can be neglected. Therefore, Eq. (9) becomes,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{His}] [\text{H}^+] [\text{Zr(IV)}] [\text{HCP}]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{His}] [\text{H}^+] + K_1^2 K_2 [\text{His}] [\text{H}^+]^2} \quad (10)$$



Scheme I Mechanism of zirconium(IV)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in sulfuric acid medium

The term $K_1^2K_2[\text{His}][\text{H}^+]^2$ in the denominator of Eq. (10) is negligibly small compared to unity in view of the low concentration of L-histidine used. Therefore Eq. (10) can be written as,

$$\text{Rate} = \frac{k_1K_1K_2[\text{His}][\text{H}^+][\text{Zr(IV)}][\text{HCP}]}{1 + K_1[\text{H}^+] + K_1K_2[\text{His}][\text{H}^+]} \quad (11)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = k_c[\text{HCP}] \quad (12)$$

Therefore,

$$k_c = \frac{\text{Rate}}{[\text{HCP}]} = \frac{k_1K_1K_2[\text{His}][\text{H}^+][\text{Zr(IV)}]}{1 + K_1[\text{H}^+] + K_1K_2[\text{His}][\text{H}^+]} \quad (13)$$

Equation (13) can be rearranged to the following form, which is suitable for verification:

$$\frac{[\text{Zr(IV)}]}{k_c} = \left(\frac{1}{k_1K_1K_2[\text{H}^+]} + \frac{1}{k_1K_2} \right) \frac{1}{[\text{His}]} + \frac{1}{k_1} \quad (14)$$

and with rearrangement,

$$\frac{[\text{Zr(IV)}]}{k_c} = \left(\frac{1}{k_1K_1K_2[\text{His}]} \right) \frac{1}{[\text{H}^+]} + \frac{1}{k_1K_2[\text{His}]} + \frac{1}{k_1} \quad (15)$$

According to Eq. (15), other conditions being constant, plots of $[\text{Zr(IV)}]/k_c$ versus $1/[\text{His}]$ at constant $[\text{H}^+]$ and $[\text{Zr(IV)}]/k_c$ versus $1/[\text{H}^+]$ at constant $[\text{His}]$ should be linear with positive intercepts which were found to be so (Figure 5) confirming the proposed mechanism.

The activation parameters listed in Table 2 may be interpreted as follows: the observed large negative values of ΔS^\ddagger confirm the compactness of the zirconium(IV)–histidine complex formed and such activated complex is more ordered than the reactants because of loss of degrees of freedom [34]. The positive values of both ΔH^\ddagger and ΔG^\ddagger 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 [35, 36]. 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 an intermediate complex of inner-sphere nature for the electron transfer mechanism with respect to the present redox reactions.

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