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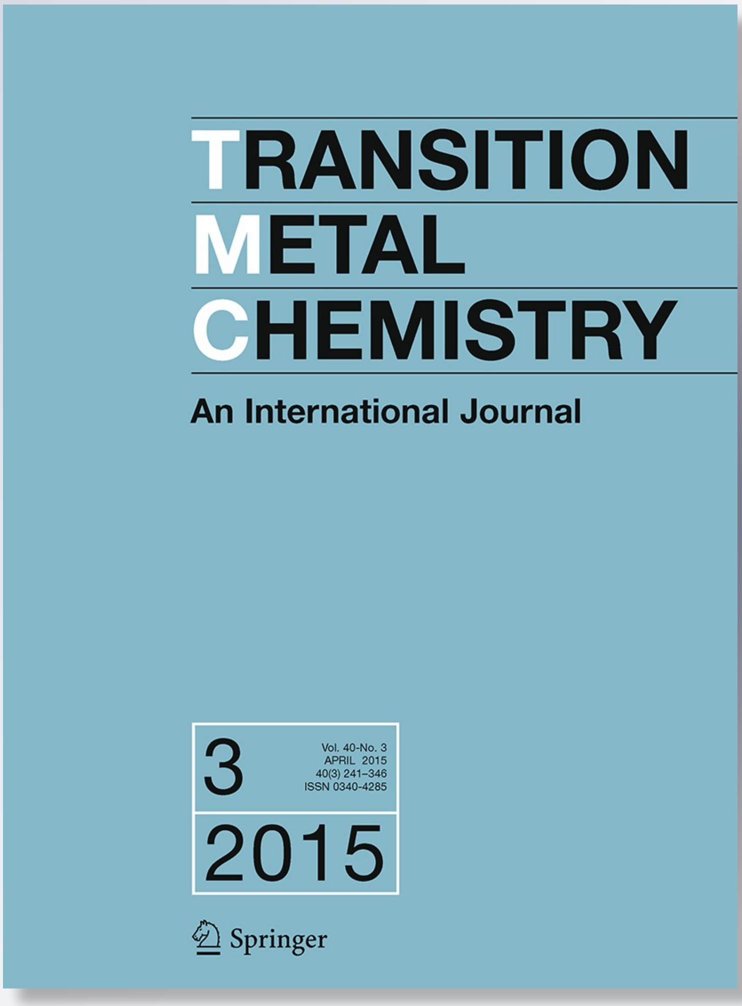

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Kinetics and mechanism of uncatalyzed and silver(I)-catalyzed oxidation of L-histidine by hexachloroplatinate(IV) in acid medium

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Abstract Kinetics of hexachloroplatinate(IV) (HCP) oxidation of L-histidine (His) in H_2SO_4 medium has been investigated in the absence and presence of silver(I) catalyst at constant ionic strength 2.0 mol dm^{-3} and temperature 25 °C. The progress of both uncatalyzed and silver(I)-catalyzed oxidation reactions has been monitored spectrophotometrically. Both uncatalyzed and catalyzed paths show first-order dependence on [HCP] and fractional-first-order dependence each on [His] and [acid]. The catalyzed path is first order in [Ag^I]. Increasing ionic strength and dielectric constant decreases the oxidation rates. The catalyzed reaction has been shown to proceed via formation of a silver(I)-histidine intermediate complex, which reacts with the oxidant by an inner-sphere mechanism leading to decomposition of the complex in the rate-determining step. The final oxidation products of histidine were identified as the corresponding aldehyde (2-imidazole acetaldehyde), ammonium ion and carbon dioxide. The mechanisms of these reactions have been proposed and the appropriate rate laws are deduced.

Introduction

The chemistry of biologically active platinum(IV) complexes has become of fundamental importance in the last decades, due to their anticancer properties [1–3]. They appear attractive because they are usually substitution inert and require reduction to Pt^{II} species to act as potential anticancer drugs. 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), $[PtCl_6]^{2-}$, as an oxidant are scarce and limited to a few cases [4–14], in which $[PtCl_6]^{2-}$ may behave as a one- or two-electron oxidant, depending upon the substrate and experimental conditions. The knowledge of the reactivity of platinum(IV) compounds toward their reduction by potential bioreductants such as histidine may be important for understanding the mechanism of their antitumor activity as well as for designing new compounds with reduced side effects.

Histidine, an α-amino acid, is one of the proteinogenic amino acids which is essential to humans and other mammals and important for growth and general tissue repair. This amino acid is necessary for the production of red and white blood cells. It finds extensive applications as a reducing agent in chemical and biochemical systems. Rate of reduction by histidine depends on the oxidant nature and pH of the medium. The oxidation of histidine has been previously studied for several reagents in different media [14–21]. In most cases, the final oxidation products of histidine were 2-imidazole acetaldehyde, ammonia and carbon dioxide. Furthermore, due to the high reactivity of its imidazole group, histidine is often found at the active sites of enzymes and involved directly in catalysis. It controls the transmission of metals in biological bases [22]. The formation and structure of histidine complexes with some transition metal ions have been studied in aqueous

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medium [23–25]. Such metal complexes are usually more active than the parent ligands.

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. The kinetic results of silver(I)-catalyzed oxidation of histidine by permanganate in acidic medium are ambiguous [21]. No work, however, has been reported on the oxidation of histidine by hexachloroplatinate(IV) in acid medium in either absence or presence of a catalyst. The present study deals with the title reaction in an attempt to understand the redox chemistry of hexachloroplatinate(IV) and to explore the kinetics and mechanistic aspects of such catalyzed reactions in strong acid medium. This study may enable us to understand the complicated biological reactions in living systems and will also help us to understand the catalytic activity of Ag^I along with the oxidative capacity of hexachloroplatinate(IV). In view of the above-mentioned arguments and the dearth of literature on the oxidation of this amino acid, we have carried out a detailed study of the title reaction.

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 solutions of the oxidant were freshly prepared before each experiment by proper dilution of an original solution which was standardized spectrophotometrically [26]. The solution was stored in a bottle away from light and re-standardized periodically. The ionic strength, I, of the reaction mixtures was adjusted to 2.0 mol dm^{-3} using Na_2SO_4. The reaction temperature (25 °C) was controlled within ±0.1 °C. 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 measurements were performed under pseudo-first-order conditions with the amino acid concentration being greater than the hexachloroplatinate(IV) concentration. The reaction solutions were thermally equilibrated in a constant-temperature water bath maintained at the desired temperature. When the solutions of HCP and His had attained the thermostat temperature, the required volumes of the reactants were syringed out and poured into the reaction cell that also contained the calculated amount of H_2SO_4 and Na_2SO_4 to maintain the required acidity and ionic strength, respectively, and silver(I) catalyst in the case of catalyzed reaction. The courses of the reactions were 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 such that the molar extinction coefficient was determined ($\varepsilon = 13117 \pm 273$ dm^3 mol^{-1} cm^{-1}) and found to be in a good agreement with that reported previously [26].

As the reduction in hexachloroplatinate(IV) by histidine in acid medium proceeds with a measurable rate in the absence of silver(I) ion, 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. The kinetic runs were followed until more than 85 % completion of the reactions. The pseudo-first-order rate constants (k_U and k_C) were determined from the gradients of ln(absorbance) versus time plots, by considering the initial straight line region. The gradients of such plots were calculated by the least-squares method. The rate constants were reproducible to within ±4 % and are the average of at least three independent kinetic runs.

The spectral changes during the courses of the reactions between histidine and hexachloroplatinate(IV) in the absence and presence of silver(I) catalyst are shown in Fig. 1a, b, respectively. Gradual decrease in $[PtCl_6]^{2-}$ absorbance at its absorption maximum with time was observed.

Results

Stoichiometry and product analysis

Reaction mixtures containing various ratios of the amino acid to $[PtCl_6]^{2-}$ were mixed at constant acidity, ionic strength and temperature, then equilibrated for 24 h in an inert atmosphere. Estimation of the unreacted $[PtCl_6{}^{2-}]$ was performed spectrophotometrically by measuring the absorbance at 262 nm. The results showed that one mole of $[PtCl_6]^{2-}$ consumed one mole of histidine in accordance with the following stoichiometric equation;

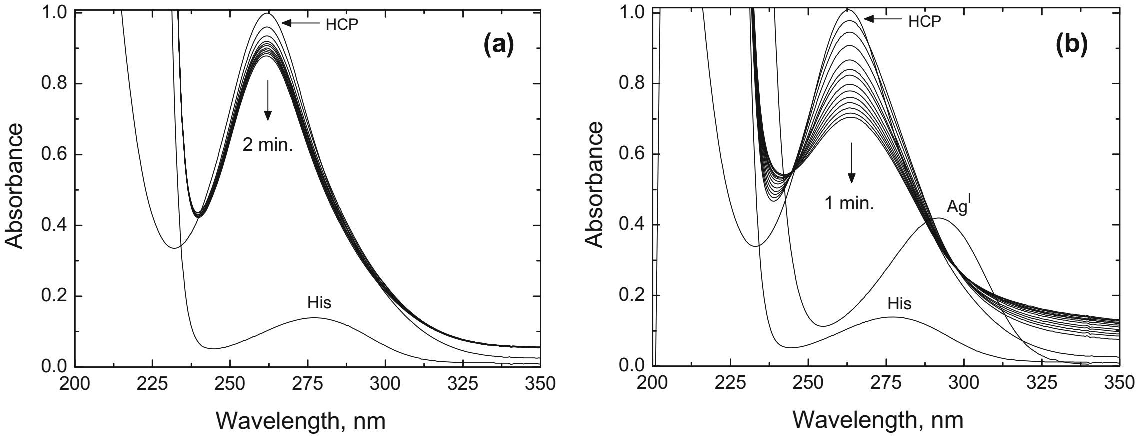


Fig. 1 Spectral changes (200–350 nm) in the oxidation of histidine by hexachloroplatinate (IV) in sulfuric acid medium. [His] = 8 × 10^{-3}, [HCP] = 7.6 × 10^{-5}, [H^+] = 1.0 and I = 2.0 mol dm^{-3} at 25 °C **a** in the absence of Ag^I, **b** in the presence of 1 × 10^{-5} mol dm^{-3} Ag^I

$$C_6H_9O_2N_3 + [PtCl_6]^{2-} + H_2O \rightarrow C_5H_6ON_2 + NH_4^+ + CO_2 + [PtCl_4]^{2-} + 2Cl^- + H^+ \quad (1)$$

where $C_6H_9O_2N_3$ and $C_5H_6ON_2$ are 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 [27]. Other products were identified as discussed earlier [28, 29]. Similar oxidation products with different experimental conditions have been also reported earlier [15–21]. On the other hand, formation of $[PtCl_4]^{2-}$ was confirmed [30] by the observed black precipitate of platinum(II) hydroxide on addition of alkali to the reaction mixture. Furthermore, a similar product was reported [30, 31] for the reaction between $[PtCl_6]^{2-}$ and different reductants.

Reaction order

The orders of the various reactants were determined from the plots of log k_U and log k_C versus log(concentration) except in [HCP] by varying the concentrations of oxidant, reductant, catalyst and acid in turn, while keeping others constant in the variation of each reactant.

The concentration of the oxidant, hexachloroplatinate(IV), was varied in the range of 4 × 10^{-5}–12 × 10^{-5} mol dm^{-3} at fixed [histidine], [Ag^I], [H^+], ionic strength and temperature. The non-variation in the pseudo-first-order rate constants at various concentrations of HCP (Tables 1, 2) indicates that the order with respect to the oxidant is confirmed to be one.

The observed rate constants (k_U and k_C) were determined at different initial concentrations of the reductant histidine keeping all other reactant concentrations constant including sliver(I) catalyst for the catalyzed reaction. The obtained results show that the values of the rate constants increased with the increase in concentration of histidine as listed in Tables 1 and 2. Plots of the observed rate constants versus [His] are linear with positive intercepts, confirming fractional-first-order dependences with respect to the amino acid for both uncatalyzed and catalyzed reactions (Figure not shown).

The reaction rates were measured at constant [His], [$PtCl_6^{2-}$], [Ag^I] (for the catalyzed reaction), ionic strength and temperature but with various [H^+] (0.2–2.0 mol dm^{-3}). The rate of reactions was found to increase with increase in [H^+]. Similarly to the case of histidine, both reactions show fractional-order dependences on [H^+].

Effect of ionic strength and dielectric constant

The effect of ionic strength on both uncatalyzed and catalyzed reactions was studied by varying the concentration of sodium sulfate in the reaction medium at constant concentrations of His, $[PtCl_6]^{2-}$ and Ag^I, and at constant pH and temperature. The results are presented in Tables 1 and 2. These results show that the pseudo-first-order rate constants (k_U and k_C) decrease with increase in the ionic strength of the medium, and the Debye–Hückel plots were linear with negative slopes (Fig. 2).

The dielectric constant or relative permittivity (ε) effect was studied by varying the *t*-butyl alcohol–water content (0–40 %) in the reaction mixture with all other conditions being constant. The data clearly reveal that the rate of the reactions retards with the increase in dielectric constant of the solvent mixture. The plots of log k_U and log k_C versus 1/ε were linear with positive slopes (figure not shown).

The reaction rate was measured with various [Ag^I] (6–14) × 10^{-6} mol dm^{-3}, at constant other variables.

Table 1 Effect of $[PtCl_6^{2-}]$, [His], $[H^+]$ and ionic strength, I, on the pseudo-first-order rate constant values in the uncatalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium at 25 °C

10^5 $[PtCl_6^{2-}]$ (mol dm^{-3})	10^3 [His] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	10^5 k_U (s^{-1})
4.0	8.0	1.0	2.0	14.3
6.0	8.0	1.0	2.0	13.9
7.6	8.0	1.0	2.0	15.0
10.0	8.0	1.0	2.0	16.2
12.0	8.0	1.0	2.0	15.4
7.6	4.0	1.0	2.0	8.5
7.6	6.0	1.0	2.0	12.1
7.6	8.0	1.0	2.0	15.0
7.6	10.0	1.0	2.0	17.3
7.6	12.0	1.0	2.0	19.5
7.6	8.0	0.2	2.0	5.3
7.6	8.0	0.5	2.0	9.4
7.6	8.0	1.0	2.0	15.0
7.6	8.0	1.5	2.0	19.2
7.6	8.0	2.0	2.0	22.9
7.6	8.0	1.0	2.0	15.0
7.6	8.0	1.0	2.5	13.8
7.6	8.0	1.0	3.0	12.1
7.6	8.0	1.0	3.5	11.3
7.6	8.0	1.0	4.0	10.6

Experimental error ±4 %

Values of k_C were found to be directly proportional to $[Ag^I]$ (Table 2). The order in $[Ag^I]$ was found to be unity which was also confirmed from the linearity of the plot of log k_C versus $\log[Ag^I]$ with a slope = 1.

Polymerization study

The intervention of free radicals during the uncatalyzed and catalyzed reactions was examined as follows: the reaction mixture to which a known amount of acrylonitrile scavenger was initially added was kept for 24 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 these reactions.

Discussion

Amino acids are known [32] to exist as zwitterions and predominantly tend to protonate at higher acid concentrations according to the following equilibria

$$\text{R-CH(NH}_2\text{)COOH} \rightleftharpoons \text{R-CH(}^+\text{NH}_3\text{)COO}^-\text{(zwitterion)} \qquad (2)$$

$$\underset{\text{(His)}}{\text{R-CH(}^+\text{NH}_3\text{)COO}^-} \underset{K_1}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(His}^+\text{)}}{\text{R-CH(}^+\text{NH}_3\text{)COOH}} \qquad (3)$$

where K_1 is the protonation constant of histidine.

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

On the other hand, in acid medium, platinum(IV) species exist as $[PtCl_6]^{2-}$, which is assumed to be the principal reactive oxidant [33]. The reduction of $[PtCl_6]^{2-}$ generally proceeds as follows

$$[PtCl_6]^{2-} + 2e^- = [PtCl_4]^{2-} + 2Cl^- \qquad (4)$$

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 [34]. The reduction potential of Pt^{IV}/Pt^{II} couple has been measured [35] as 0.68 V.

There are two suggested alternative reaction mechanisms for the oxidation of 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 $[PtCl_6]^{2-}$ [36]. 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

Table 2 Effect of $[PtCl_6^{2-}]$, [His], $[H^+]$, $[Ag^I]$ and ionic strength, I, on the pseudo-first-order rate constant values in the silver(I)-catalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium at 25 °C

10^5 $[PtCl_6^{2-}]$ (mol dm^{-3})	10^3 [His] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	10^6 $[Ag^I]$ (mol dm^{-3})	*I* (mol dm^{-3})	10^5 k_C (s^{-1})
4.0	8.0	1.0	5.0	2.0	76.7
6.0	8.0	1.0	5.0	2.0	80.1
7.6	8.0	1.0	5.0	2.0	78.0
10.0	8.0	1.0	5.0	2.0	77.3
12.0	8.0	1.0	5.0	2.0	77.9
7.6	4.0	1.0	5.0	2.0	43.1
7.6	6.0	1.0	5.0	2.0	59.4
7.6	8.0	1.0	5.0	2.0	78.0
7.6	10.0	1.0	5.0	2.0	90.9
7.6	12.0	1.0	5.0	2.0	105.1
7.6	8.0	0.2	5.0	2.0	29.3
7.6	8.0	0.5	5.0	2.0	51.7
7.6	8.0	1.0	5.0	2.0	78.0
7.6	8.0	1.5	5.0	2.0	103.0
7.6	8.0	2.0	5.0	2.0	122.2
7.6	8.0	1.0	6.0	2.0	47.2
7.6	8.0	1.0	8.0	2.0	62.0
7.6	8.0	1.0	10.0	2.0	78.0
7.6	8.0	1.0	12.0	2.0	96.3
7.6	8.0	1.0	14.0	2.0	109.6
7.6	8.0	1.0	5.0	2.0	78.0
7.6	8.0	1.0	5.0	2.5	65.5
7.6	8.0	1.0	5.0	3.0	61.1
7.6	8.0	1.0	5.0	3.5	60.3
7.6	8.0	1.0	5.0	4.0	58.7

Experimental error ±3 %

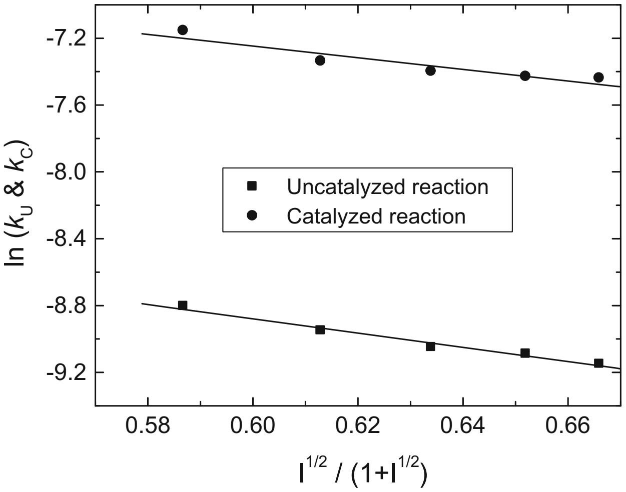


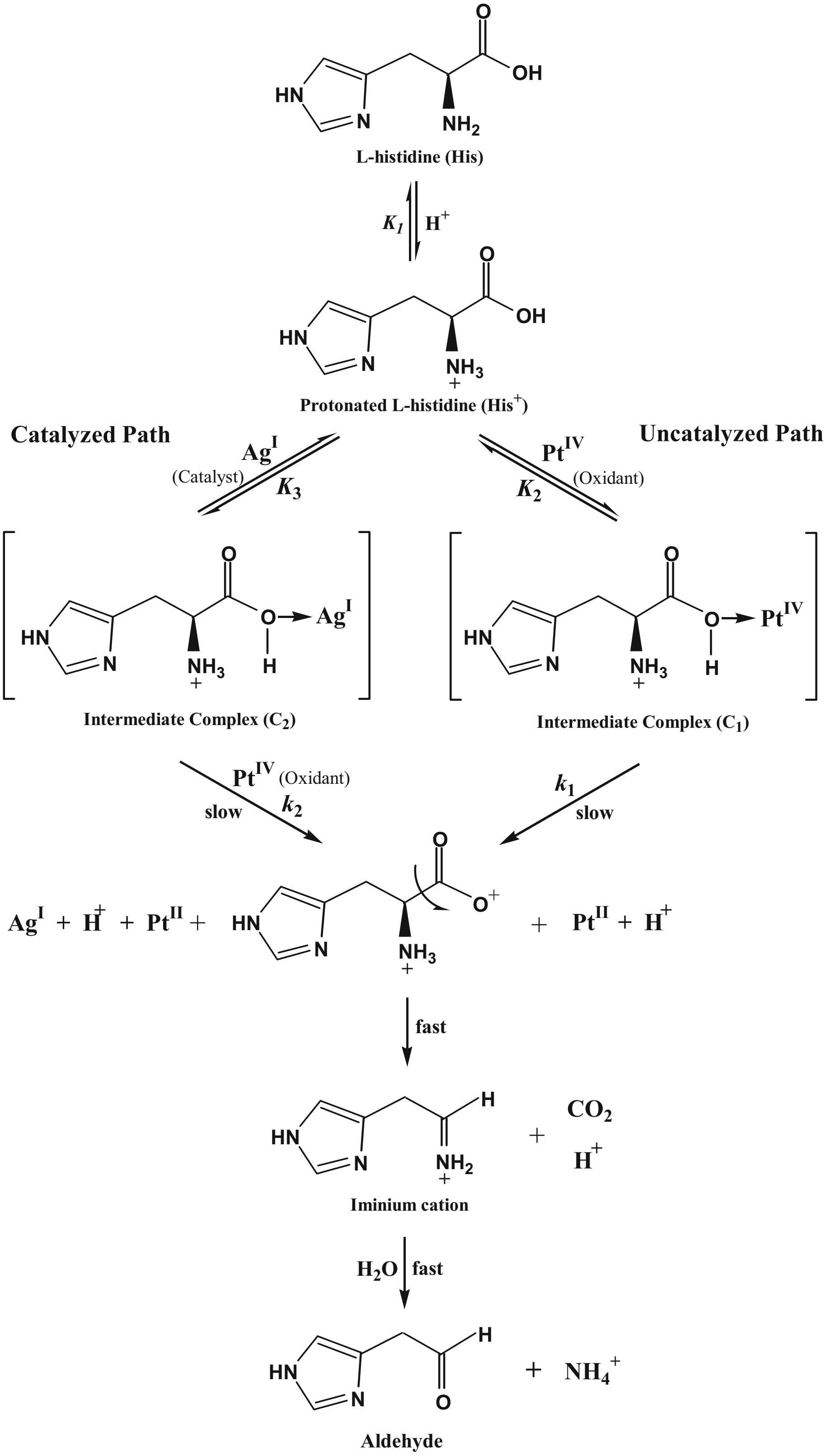
Fig. 2 Debye–Hückel plots in the uncatalyzed and silver(I)-catalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium. [His] = 8 × 10^{-3}, $[PtCl_6^{2-}]$ = 7.6 × 10^{-5} and $[H^+]$ = 1.0 mol dm^{-3} at 25 °C. $[Ag^I]$ = 1 × 10^{-5} mol dm^{-3}

to give the polymerized product under our experimental conditions. Consequently, the two-electron transfer mechanism seems plausible.

Mechanism of uncatalyzed oxidation reaction

The reaction between $[PtCl_6]^{2-}$ and histidine in acid medium in the absence of silver(I) catalyst exhibits a stoichiometry of 1:1 with a first-order dependence on $[PtCl_6^{2-}]$ and a fractional-first-order dependence on both [His] and [acid]. These results imply that the amino acid substrate first protonates in a prior rate-determining step. In the next step, $[PtCl_6]^{2-}$ combines with protonated histidine to form an intermediate complex (C_1) as shown in Scheme 1. The fractional order with respect to histidine can be attributed to this complex formation prior to the slow step. Indeed, it is noted that the plot of $1/k_U$ versus 1/[His] (Fig. 3) shows an intercept, in agreement with complex formation. Also, decreasing rate of reaction on increasing the ionic strength and dielectric constant of the medium confirms that the reaction occurs between two ions with unlike charge [37–40], i.e., between $[PtCl_6]^{2-}$ and His^+. The failure of the spectrophotometric detection of an intermediate complex (Fig. 1a) may be interpreted by either lower concentration of the reactants used and, hence, the expected lower absorptivity of the formed complex and/or the fast subsequent decomposition of the

Scheme 1 Mechanism of uncatalyzed and silver(I)-catalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium



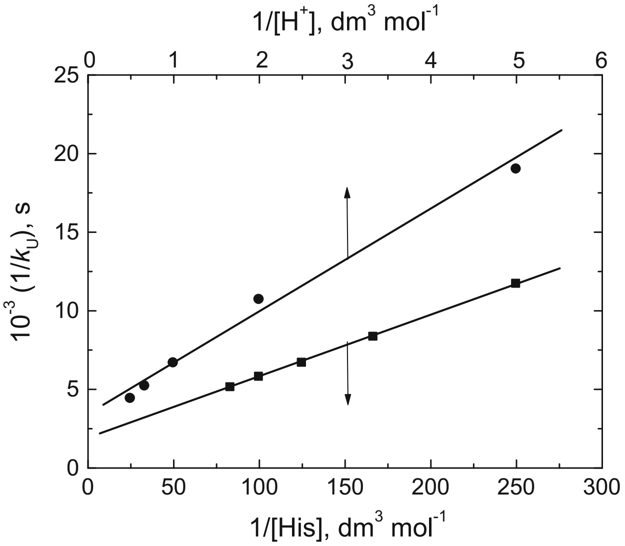


Fig. 3 Verification of the rate law (9) in the form of Eq. (11) in the uncatalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[PtCl_6^{2-}] = 7.6 \times 10^{-5}$, and $I = 2.0$ mol dm^{-3} at 25 °C

intermediate in comparison to its formation. The intermediate species decomposes in a slow step forming the oxidation products as depicted by the following equations;

$$\text{His} + \text{H}^+ \overset{K_1}{\leftrightarrows} \text{His}^+ \tag{5}$$

$$\text{His}^+ + [\text{PtCl}_6]^{2-} \overset{K_2}{\leftrightarrows} [\text{His} - \text{PtCl}_6]^- (\text{C}_1) \tag{6}$$

$$[\text{His} - \text{PtCl}_6]^- \xrightarrow[\text{slow}]{k_1} \text{Products} \tag{7}$$

The suggested mechanism leads to the following rate law;

$$\begin{aligned}\text{Rate} &= \frac{-\text{d}[\text{PtCl}_6^{2-}]}{\text{d}t}\\ &= \frac{k_1 K_1 K_2 [\text{PtCl}_6^{2-}][\text{His}][\text{H}^+]}{(1 + K_1[\text{H}^+] + K_1 K_2 [\text{PtCl}_6^{2-}][\text{H}^+])(1 + K_1 K_2 [\text{His}][\text{H}^+])}\end{aligned} \tag{8}$$

In view of the low concentration of $[\text{PtCl}_6]^{2-}$ used, the term $K_1 K_2 \left[\text{PtCl}_6^{2-}\right][\text{H}^+]$ in the denominator of Eq. (8) can be neglected. Therefore, Eq. (8) becomes

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{PtCl}_6^{2-}][\text{His}][\text{H}^+]}{(1 + K_1[\text{H}^+])(1 + K_1 K_2 [\text{His}][\text{H}^+])} \tag{9}$$

The rate law is consistent with all the observed orders with respect to different species.

Under pseudo-first-order conditions,

$$\text{Rate} = \frac{-\text{d}[\text{PtCl}_6^{2-}]}{\text{d}t} = k_\text{U}\left[\text{PtCl}_6^{2-}\right] \tag{10}$$

Comparing Eqs. (9) and (10) and on rearrangement, we obtain

$$\frac{1}{k_\text{U}} = \left(\frac{1 + K_1[\text{H}^+]}{k_1 K_1 K_2 [\text{H}^+]}\right)\frac{1}{[\text{His}]} + C \tag{11}$$

where $C = (1 + K_1[\text{H}^+])/k_1$.

According to Eq. (11), plots of $1/k_\text{U}$ against 1/[His], at constant [H$^+$], and $1/k_\text{U}$ against 1/[H$^+$], at constant [His], should be linear with positive intercepts on the $1/k_\text{U}$ axes as were observed experimentally (Fig. 3).

Due to the non-availability of the protonation constant of histidine (K_1) and/or the formation constant of the $[\text{PtCl}_6]^{2-}$–histidine complex (K_2) under the present reaction conditions and at different temperatures, evaluation of the rate constant value of the slow step (k_1) along with its activation parameters has not been possible. Some attempts were made to evaluate these constants from the experimental data, but the results were not satisfactory.

Mechanism of silver(I)-catalyzed reaction

The reaction between $[\text{PtCl}_6]^{2-}$ and histidine in acid medium in the presence of micro amounts of silver(I) catalyst is similar to the uncatalyzed reaction with respect to stoichiometry, reaction orders, the influence of ionic strength and dielectric constant; in addition, the reaction is first order with respect to silver(I) catalyst.

The observed less than unit order in [His] presumably results from a complex formation between the catalyst silver(I) and substrate prior to the reaction with the oxidant. The formation of the complex was also proved kinetically by a nonzero intercept of the plot of $\left[\text{Ag}^\text{I}\right]/k_\text{C}$ versus $1/[\text{His}]$ (Fig. 4). Further evidence for complex formation was obtained from the UV–Vis spectra shown in Fig. 1b, in which presence of two isosbestic points located at 297 and 243 nm is consistent with complex formation. Such complexes between histidine and silver(I) catalyst have been reported in earlier studies [21, 25].

In view of the above-mentioned aspects, we can suggest that the protonated histidine combines with Ag$^\text{I}$ species to form an intermediate complex in the form of $[\text{His} - \text{Ag}]^{2+}(\text{C}_2)$ which then reacts in a slow step with one mole of $[\text{PtCl}_6]^{2-}$ to give rise to the oxidation products with regeneration of the catalyst Ag$^\text{I}$ (see Scheme 1). The results are accommodated in the following sequence;

$$\text{His} + \text{H}^+ \overset{K_1}{\leftrightarrows} \text{His}^+ \tag{12}$$

$$\text{His}^+ + \text{Ag}^+ \overset{K_3}{\leftrightarrows} [\text{His} - \text{Ag}]^{2+} (\text{C}_2) \tag{13}$$

$$[\text{His} - \text{Ag}]^{2+} + [\text{PtCl}_6]^{2-} \xrightarrow[\text{slow}]{k_2} \text{Products} + \text{Ag}^+ \tag{14}$$

According to the proposed mechanism, the rate of disappearance of $[\text{PtCl}_6]^{2-}$ or formation of the intermediate

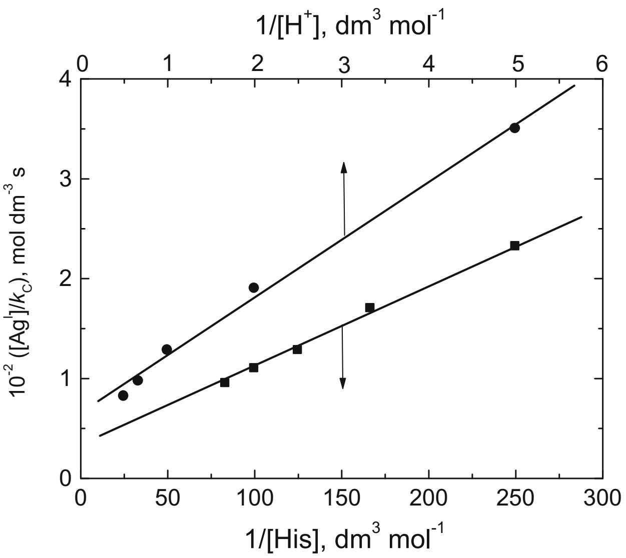


Fig. 4 Verification of the rate law (17) in the form of Eq. (19) in the silver(I)-catalyzed oxidation of histidine by hexachloroplatinate(IV) in sulfuric acid medium. $[PtCl_6^{2-}] = 7.6 \times 10^{-5}$, and $I = 2.0$ mol dm^{-3} at 25 °C

complex can be expressed by the following rate law equation;

$$\begin{aligned}\text{Rate} &= \frac{-\mathrm{d}[PtCl_6^{2-}]}{\mathrm{d}t} = \frac{+\mathrm{d}[His - Ag^{2+}]}{\mathrm{d}t}\\ &= k_2\left[His - Ag^{2+}\right]\left[PtCl_6^{2-}\right]\end{aligned} \tag{15}$$

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;

$$\text{Rate} = \frac{k_2K_1K_3[His][H^+][Ag^I][PtCl_6^{2-}]}{(1+K_1[H^+]+K_1K_3[H^+][Ag^I])(1+K_1K_3[His][H^+])} \tag{16}$$

In view of low concentration of $[Ag^I]$ used, the term $K_1K_3[H^+][Ag^I]$ in the denominator can be neglected. Therefore, Eq. (16) becomes

$$\text{Rate} = \frac{k_2K_1K_3[His][H^+][Ag^I][PtCl_6^{2-}]}{(1+K_1[H^+])(1+K_1K_3[His][H^+])} \tag{17}$$

Under pseudo-first-order conditions,

$$\text{Rate} = \frac{-\mathrm{d}[PtCl_6^{2-}]}{\mathrm{d}t} = k_C\left[PtCl_6^{2-}\right] \tag{18}$$

Comparing Eqs. (17) and (18) and rearrangement, we obtain

$$\frac{[Ag^I]}{k_C} = \left(\frac{1+K_1[H^+]}{k_2K_1K_3[H^+]}\right)\frac{1}{[His]} + C \tag{19}$$

where, $C = (1 + K_1[H^+])/k_2$.

According to Eq. (19), the plots of $\left[Ag^I\right]/k_C$ against $1/[His]$, at constant $[H^+]$, and $\left[Ag^I\right]/k_C$ against $1/[H^+]$, at constant [His], should be linear with positive intercepts on $\left[Ag^I\right]/k_C$ axes. The experimental results satisfied this requirement as shown in Fig. 4.

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