

Kinetics and Mechanism of Ruthenium(III)-Catalyzed Oxidation of L-citrulline by Hexachloroplatinate(IV) in Perchloric Acid

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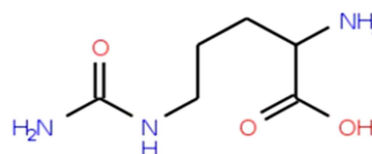
Abstract: Oxidation kinetics of L-citrulline (Cit) by hexachloroplatinate(IV) (HCP) was studied spectrophotometrically in perchloric acid solutions in the presence of ruthenium(III) catalyst at a constant ionic strength of 1.8 mol dm^{-3} and at 20°C . The reaction rate was very slow in the absence of the catalyst. The reaction showed first order kinetics in both [HCP] and [Ru(III)] and less than unit order with respect to both [Cit] and $[\text{H}^+]$. Increasing ionic strength and dielectric constant were found to increase the oxidation rate. Both spectral and kinetic evidences revealed formation of an intermediate complex between L-citrulline and ruthenium(III) prior to the rate-determining step. The complex reacts with the oxidant (HCP) by an inner-sphere mechanism leading to decomposition of the complex in the rate-determining step to give rise to the final oxidation products of L-citrulline which were identified by both spectroscopic and chemical tools as 4-(carbamoylamino) butyraldehyde, ammonia and carbon dioxide. The rate-law expression for the catalyzed reaction was deduced. The reaction constants involved in the different steps of the reaction mechanism have been evaluated. The activation parameters of the second order rate constant have been evaluated and discussed.

Keywords: L-Citrulline, Hexachloroplatinate(IV), Ruthenium(III), Oxidation, Kinetics, Mechanism

1. Introduction

Oxidation of amino acids is considered as a significant field of organic chemistry 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 [1-18], and they often undergo oxidative decarboxylation and deamination. L-citrulline (2-amino-5-(carbamoylamino) pentanoic acid, shown below) is a naturally occurring amino acid which is used for Alzheimer's disease, dementia, fatigue, muscle weakness, high blood pressure, and diabetes. It is also used for heart disease, body building, increasing energy, and for improving athletic performance. L-citrulline might help increase the supply of ingredients the body needs to making certain proteins. It is a

key intermediate in the urea cycle. In the body, L-citrulline is produced as a byproduct of the enzymatic production of nitric oxide from the amino acid arginine, catalyzed by nitric oxide synthase [19].



Biologically active platinum (IV) complexes such as hexachloroplatinate (IV) complex (HCP), $[\text{PtCl}_6]^{2-}$, have remarkable anticancer properties [20-23]. They have become attractive because they are usually substitution-inert, hence requiring reduction to Pt (II) species before they can act as

potential anticancer drugs. Their reduction with different reductants generally proceeds via a free radical one-electron transfer mechanism [24, 25]. An alternative path, whereby Pt (IV) undergoes a two-electron reduction process was also shown to occur [26]. The experimental conditions and choice of reductant determined whether a two-electron reduction process could occur. Hexachloroplatinate (IV) complex has been used to oxidize a limited number of inorganic [23-29] and organic [10-16, 30-34] compounds in different media. The knowledge of the reactivity of platinum (IV) compounds towards their reduction by potential bioreductant such as L-citrulline may be important for understanding the mechanism of where antitumor activity as well as for designing new compounds with the least side effect. Furthermore, transition metal ions have been widely employed as homogenous catalysts for oxidation of organic and inorganic substrates [8-16] by different reaction pathways such as formation of complexes with the reactants, oxidation of a substrate, or the formation of free radicals [35]. Kinetic investigations on the oxidation of amino acids catalyzed by different metal ions are an important field of chemistry due to the role played by metals in biological systems.

Literature survey reveals that there are no reports about the kinetics of oxidation of L-citrulline by any oxidant. In view of the above mentioned arguments, we have carried out a detailed study on the kinetics and mechanism of oxidation of this amino acid by hexachloroplatinate (IV) in perchloric acid medium in the presence of ruthenium (III) catalyst. This work aims to study the selectivity of the studied amino acid towards HCP in an acid medium, to check the catalytic efficiency of Ru (III) catalyst, and to elucidate a suitable oxidation mechanism.

2. Experimental

2.1. Materials

A stock solution of L-citrulline was prepared afresh by dissolving the sample (SD. Fine Chem.) 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 [36]. The solution was stored in a bottle away from light and re-standardized periodically. Sodium perchlorate and acetic acid were used to vary the ionic strength and dielectric constant of the reaction medium, respectively.

2.2. Kinetic Measurements

All kinetic investigations were performed under pseudo-first-order conditions where L-citrulline was present in a large excess over that of HCP. The ionic strength, I , of the reaction mixture was adjusted to 1.8 mol dm^{-3} using sodium perchlorate as an inert electrolyte. The reaction temperature (20°C) was controlled within $\pm 0.1^\circ\text{C}$ unless stated otherwise. The reaction was initiated by rapid addition of known

amounts of the pre-equilibrated HCP to the reaction mixture containing the required amounts of L-citrulline, perchloric acid, Ru (III) chloride, sodium perchlorate and water, thermostated at the same temperature. The solutions were then mixed and transferred to a cell with a path length of 1.0 cm. The course of the reaction was followed spectrophotometrically by monitoring the decrease in the absorbance of HCP at $\lambda = 262 \text{ nm}$, its absorption maximum, as a function of time using Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer with a cell compartment kept at constant temperature. The applicability of Beer's law was verified at 262 nm under the reaction conditions. The molar extinction coefficient, ϵ , was determined ($\epsilon = (1.319 \pm 0.07) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and was found to be in a good agreement with that reported previously [36]. In addition, there is no interference from other reagents at this wavelength. It was observed that the oxidation reaction was very slow in the absence of Ru (III) catalyst. The pseudo-first order rate constant values of the catalyzed reaction (k_c) were obtained from the linear portion of $\ln(\text{absorbance})$ versus time plots, which were the average of at least two independent kinetics runs and were reproducible to within $\pm 3\%$. Double logarithmic plots were used to determine the order with respect to each reactant. The concentration of the particular species being examined was varied while the concentrations of the other species were held fixed.

3. Results

3.1. Spectral Changes

The spectral changes during the course of the reaction between L-citrulline and HCP in the presence of Ru(III) catalyst are shown in Figure 1. The scanned spectra indicate gradual disappearance of the HCP absorption band with time as a result of its reduction. Two isosbestic points located at 242 and 305 nm are apparent in the spectra.

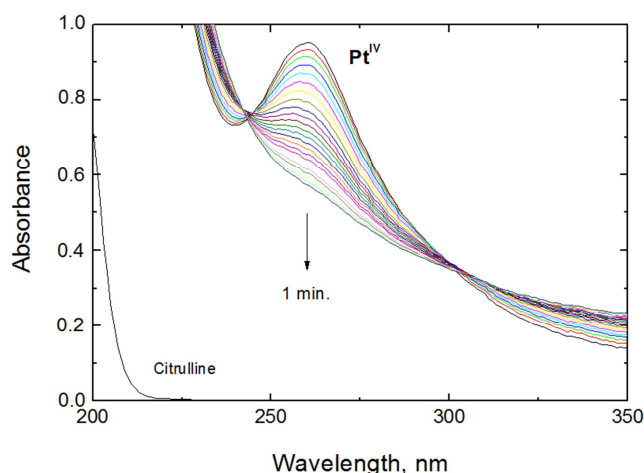
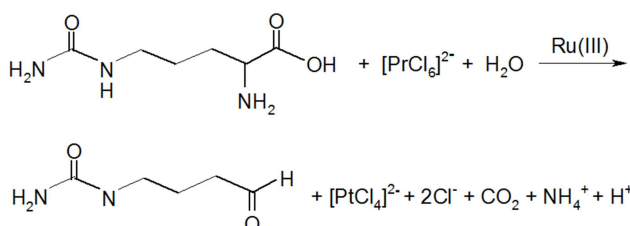


Figure 1. Time-resolved spectra during Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$, $[\text{Ru(III)}] = 5.0 \times 10^{-5}$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C . Scanning time interval = 1.0 min.

3.2. Reaction Stoichiometry and Product Analysis

Different sets of the reaction mixtures with different sets of reactants containing various amounts of HCP and L-citrulline at fixed acidity, ionic strength, and temperature were allowed to react for 24 h in an inert atmosphere. After completion of the reactions, the unreacted [HCP] was determined spectrophotometrically. Results indicated that one mole of L-citrulline consumed one mole of HCP in the predominant reaction, as represented in the following stoichiometric equation:



The above stoichiometric equation is consistent with the results of product analysis. The oxidation products of L-citrulline was identified as the corresponding aldehyde 4-(carbamoylamino) butyraldehyde, ammonia and carbon dioxide by both spectroscopic and chemical tools as reported earlier [37, 38]. On the other hand, formation of $[\text{PtCl}_4]^{2-}$ was confirmed [10-16] by the observed black precipitate of platinum(II) hydroxide on addition of alkali to the reaction mixture.

3.3. Effect of [HCP]

The concentration of the oxidant, HCP, was varied in the range of 2.0×10^{-5} to $12.0 \times 10^{-5} \text{ mol dm}^{-3}$ at constant [Cit], [Ru(III)], $[\text{H}^+]$, ionic strength and temperature. The non-variation in the observed first order rate constants at various concentrations of HCP (Table 1) indicates that the order with respect to the oxidant is confirmed to be one.

3.4. Effect of [Cit]

The observed first order rate constant (k_c) was determined at different initial concentrations of L-citrulline substrate keeping all other reactants concentration constant including Ru(III) catalyst. The results showed that the rate constant increased with increase in the L-citrulline concentration as listed in Table 1. A plot of k_c versus [Cit] was found to be linear with a positive intercept indicating less than unit order dependence with respect to L-citrulline (Figure 2).

3.5. Effect of $[\text{H}^+]$

The reaction rate was measured at constant [Cit], [HCP], [Ru(III)], ionic strength and temperature but with various $[\text{H}^+]$ ($0.3 - 1.6 \text{ mol dm}^{-3}$). The rate of reaction was found to increase as $[\text{H}^+]$ increased with less than unit order as the slope of the plot of $\log k_c$ versus $\log [\text{H}^+]$ as illustrated in Figure 3.

3.6. Effect of [Ru (III)]

The reaction rate was measured with various [Ru(III)], (1.0

$- 11.0) \times 10^{-5} \text{ mol dm}^{-3}$ at constant other variables. The reaction rate increased with the increase in [Ru(III)] (Table 1). The order with respect to [Ru(III)] was found to be unity as the slope of $\log k_c$ versus $\log [\text{Ru(III)}]$ plot (Figure 4).

Table 1. Effect of [HCP], [Cit], $[\text{H}^+]$, [Ru(III)] and ionic strength, I , on the observed first order rate constant (k_c) in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solutions at 20 °C.

$10^5 [\text{HCP}]$ (mol dm^{-3})	$10^3 [\text{Cit}]$ (mol dm^{-3})	$[\text{H}^+]$ (mol dm^{-3})	$10^5 [\text{Ru(III)}]$ (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_c$ (s^{-1})
2.0	6.0	1.0	5.0	1.8	15.9
4.0	6.0	1.0	5.0	1.8	17.1
6.0	6.0	1.0	5.0	1.8	18.3
8.0	6.0	1.0	5.0	1.8	17.6
10.0	6.0	1.0	5.0	1.8	17.5
12.0	6.0	1.0	5.0	1.8	18.1
8.0	2.0	1.0	5.0	1.8	10.2
8.0	4.0	1.0	5.0	1.8	13.3
8.0	6.0	1.0	5.0	1.8	17.6
8.0	8.0	1.0	5.0	1.8	20.6
8.0	10.0	1.0	5.0	1.8	23.9
8.0	12.0	1.0	5.0	1.8	25.9
8.0	6.0	0.3	5.0	1.8	9.1
8.0	6.0	0.5	5.0	1.8	12.4
8.0	6.0	0.7	5.0	1.8	14.6
8.0	6.0	1.0	5.0	1.8	17.6
8.0	6.0	1.3	5.0	1.8	21.2
8.0	6.0	1.6	5.0	1.8	23.0
8.0	6.0	1.0	1.0	1.8	5.1
8.0	6.0	1.0	3.0	1.8	12.5
8.0	6.0	1.0	5.0	1.8	17.6
8.0	6.0	1.0	7.0	1.8	23.6
8.0	6.0	1.0	9.0	1.8	30.4
8.0	6.0	1.0	11.0	1.8	35.9
8.0	6.0	1.0	5.0	1.8	17.6
8.0	6.0	1.0	5.0	2.1	18.8
8.0	6.0	1.0	5.0	2.4	20.5
8.0	6.0	1.0	5.0	2.7	22.1
8.0	6.0	1.0	5.0	3.0	23.4
8.0	6.0	1.0	5.0	3.3	24.7

Experimental error $\pm 3\%$

3.7. Effect of Ionic Strength and Dielectric Constant

The effect of ionic strength on the oxidation rate was studied by the addition of sodium perchlorate to the reaction medium at constant concentration of L-citrulline, HCP, Ru(III), and at constant pH and temperature. The results showed that the rate constant increased with increase in the ionic strength of the medium, and the Debye-Hückel plot was found to be linear with a positive slope as shown in Figure 5. Also, the effect of the dielectric constant (D) of the medium on the oxidation rate 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 the dielectric constants of water and acetic acid as 78.5 and 6.15, respectively, at 20 °C. The rate constant was found to decrease 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 found to be linear with a negative slope as shown in Figure 6.

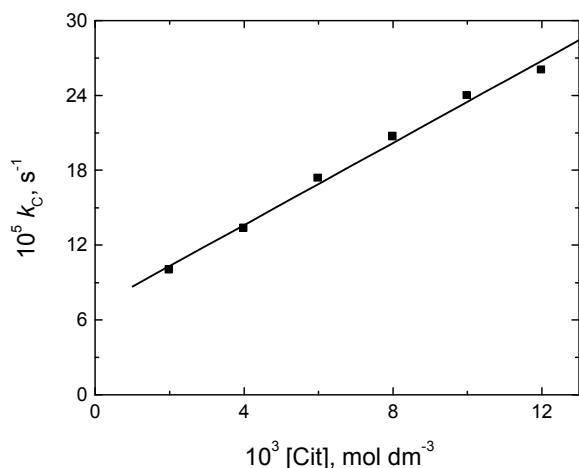


Figure 2. Plot of the observed first order rate constant (k_c) versus $[\text{Cit}]$ in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$, $[\text{Ru(III)}] = 5.0 \times 10^{-5}$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C .

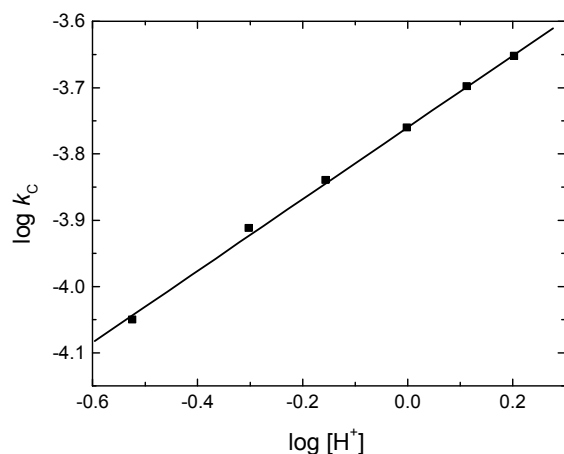


Figure 3. Plot of $\log k_c$ versus $\log [\text{H}^+]$ in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{Ru(III)}] = 5.0 \times 10^{-5}$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C .

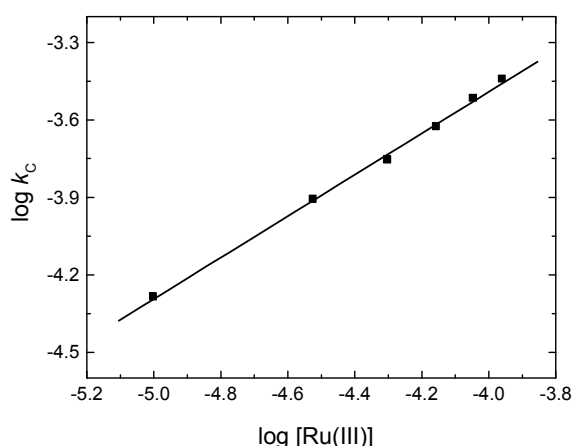


Figure 4. Plot of $\log k_c$ versus $\log [\text{Ru(III)}]$ in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C .

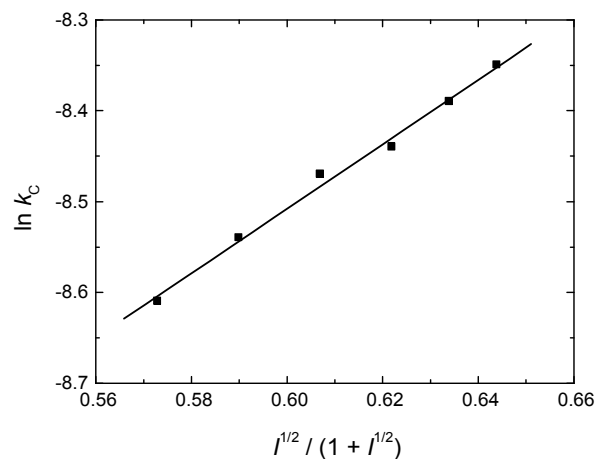


Figure 5. Debye-Hückel plots in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$ and $[\text{Ru(III)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ at 20°C .

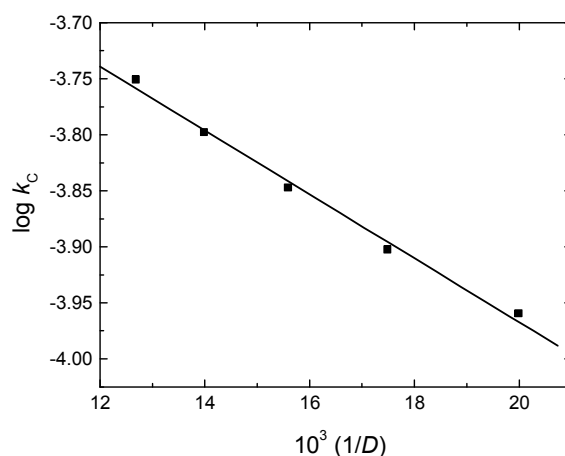


Figure 6. Effect of solvent composition on the observed first order rate constant. Plot of $\log k_c$ versus $1/D$ for the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$, $[\text{Ru(III)}] = 5.0 \times 10^{-5}$ and $I = 1.8 \text{ mol dm}^{-3}$ at 25°C .

3.8. Effect of Temperature

The rate of Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution was measured at five different temperatures (288 - 308 K). The reaction rate was found to increase with raising temperature. The activation parameters of the second order rate constants (k_2) are calculated using Arrhenius and Eyring plots and are listed in Table 2.

Table 2. Activation parameters of k_2 in the Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution.

$\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta H^\ddagger, \text{kJ mol}^{-1}$	$\Delta G^\ddagger_{293}, \text{kJ mol}^{-1}$	$E_a^\ddagger, \text{kJ mol}^{-1}$
-73.22	44.21	65.66	47.30

3.9. Test for Free Radical Intermediates

To study the possible intervention of free radicals during the oxidation reaction, the reaction mixture to which a known quantity of acrylonitrile scavenger was initially added was

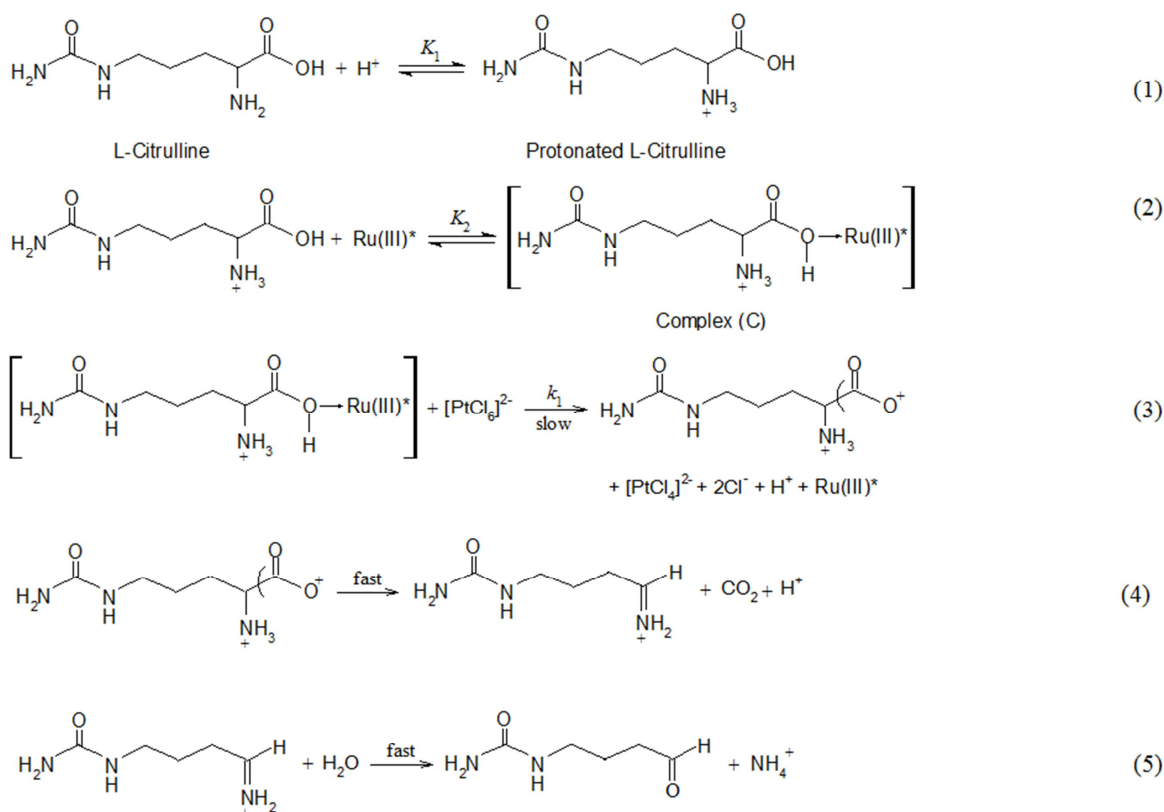
kept for 8 h in an inert atmosphere. On diluting the mixtures with methanol, no white precipitate was formed, thus confirming the absence of free radical intervention in the present reaction.

4. Discussion

It was reported [39, 40] that the reactive species of Ru(III) chloride in acid media is $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ (assigned as Ru(III)^*). Also, due to the availability of electron pairs on both oxygen atom of the carboxylate group and nitrogen atom of the amine group in L-citrulline. Within the protolytic L-citrulline system, the carboxylate and amine groups may act as nucleophiles, depending on pH of the medium. The protolytic group with the highest basicity interacts with the Ru(III) catalyst. Thus, at low pH where the amine group is protonated, the carboxylate group should be able to attack Ru(III). On the other hand, platinum(IV) species in acid medium is present as $[\text{PtCl}_6]^{2-}$, which is assumed to be the principal reactive oxidant [41]. Because platinum(IV) complexes are generally substitution-inert [42], initial complex formation between platinum(IV) and reductant prior to electron transfer can be excluded in reductive-elimination reactions. There are two alternative reaction mechanisms for the oxidation by HCP may be considered. 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 the reductant and/or oxidant are unstable, a simultaneous two-electron transfer mechanism may be suggested, such as that in the

oxidation of uranium(IV) by $[\text{PtCl}_6]^{2-}$ [28]. In the present study, addition of acrylonitrile monomer to the reaction mixture failed to give polymerized products. It may be that a free radical such as the 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.

The present reaction between HCP and L-citrulline in the presence of small amounts of Ru(III) catalyst had a stoichiometry of 1:1 with a first order dependence on both $[\text{HCP}]$ and $[\text{Ru(III)}]$, and less than unit orders with respect to both $[\text{Cit}]$ and $[\text{H}^+]$. The observed increase in the reaction rate upon increasing acid concentration suggests protonation of L-citrulline substrate prior to the rate-determining step to form protonated L-citrulline as a more reactive species, which plays the main role in the reaction kinetics [43] as illustrated by step (1) in the mechanistic Scheme 1. The less than unit order with respect to $[\text{Cit}]$ suggests formation of an intermediate complex between L-citrulline substrate and Ru(III) catalyst prior to the reaction with the oxidant, step (2). Complex formation was proved kinetically by the non-zero intercepts of the plots of $[\text{Ru(III)}]/k_c$ versus $1/[\text{Cit}]$ (Figure 7) [44]. Spectroscopic evidence to support complex formation between L-citrulline and Ru(III) which obtained from the UV-Vis spectra was the observed appearance of two isosbestic points as shown in Figure 1. Also, the oxidation rate increased upon increasing both ionic strength and dielectric constant of the medium, suggesting that the rate-determining step of the reaction occurred between two similarly charged ions [45, 46].



Scheme 1. Mechanism of Ru(III)-catalyzed oxidation of L-citrulline by HCP in perchloric acid solution.

The suggested mechanism shown in Scheme 1 involves combination of the protonated L-citrulline with the reactive species of the catalyst, Ru(III)^* , to form an intermediate complex (C). The complex reacts in a slow step with HCP leading to formation of L-citrulline cation with regeneration of the catalyst Ru(III)^* , step (3), which rapidly hydrolyze to give rise to the oxidation products of L-citrulline 4-(carbamoylamino) butyraldehyde, ammonia and carbon dioxide as illustrated by step (5).

The suggested mechanism leads to the following rate-law expression:

$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = \frac{+d[\text{C}]}{dt} = k_1[\text{C}][\text{HCP}] \quad (6)$$

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 expression:

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{Cit}][\text{H}^+][\text{Ru(III)}][\text{HCP}]}{(1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+][\text{Ru(III)}])(1 + K_1 K_2 [\text{Cit}][\text{H}^+])} \quad (7)$$

In view of low concentration of $[\text{Ru(III)}]$ used, the term $K_1 K_2 [\text{H}^+][\text{Ru(III)}]$ in the denominator can be neglected. Therefore, Eq. (7) becomes,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{Cit}][\text{H}^+][\text{Ru(III)}][\text{HCP}]}{1 + K_1[\text{H}^+] + K_1 K_2 [\text{Cit}][\text{H}^+]} \quad (8)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[\text{HCP}]}{dt} = k_c[\text{HCP}] \quad (9)$$

Comparing Eqs. (8) and (9) and rearrangement, we obtain,

$$\frac{[\text{Ru(III)}]}{k_c} = \left(\frac{1}{k_1 K_1 K_2 [\text{H}^+]} + \frac{1}{k_1 K_2} \right) \frac{1}{[\text{Cit}]} + \frac{1}{k_1} \quad (10)$$

$$\frac{[\text{Ru(III)}]}{k_c} = \left(\frac{1}{k_1 K_1 K_2 [\text{Cit}]} \right) \frac{1}{[\text{H}^+]} + \frac{1}{k_1 K_2 [\text{Cit}]} + \frac{1}{k_1} \quad (11)$$

According to Eqs. (10) and (11), the plots of $[\text{Ru(III)}]/k_c$ versus $1/[\text{Cit}]$, at constant $[\text{H}^+]$, and $[\text{Ru(III)}]/k_c$ against $1/[\text{H}^+]$, at constant $[\text{Cit}]$, should be linear with positive intercepts on $[\text{Ru(III)}]/k_c$ axes. The experimental results satisfied this requirement as shown in Figures 7 and 8. From the slopes and intercepts of these Figures, the values of the rate constant of the slow step (k_1) and the equilibrium constants involved in the first two steps of the mechanistic Scheme 1 (K_1 & K_2) can be evaluated.

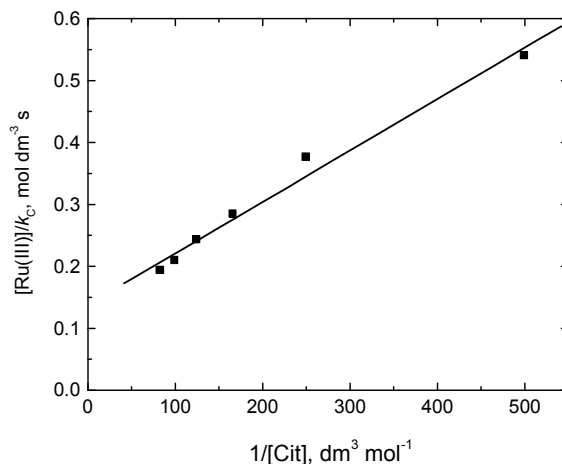


Figure 7. Plot of $[\text{Ru(III)}]/k_c$ versus $1/[\text{Cit}]$ in the Ru(III) -catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 1.0$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C .

The obtained negative value of ΔS^\ddagger indicates that there is a decrease in the randomness during the oxidation process. This leads to the formation of compacted intermediate complex and such activated complex is more ordered than the reactants due to loss of degree of freedom [47, 48]. Again, the negative values of both ΔH^\ddagger and ΔG^\ddagger indicate the exothermic formation of the intermediate and its spontaneity, respectively.

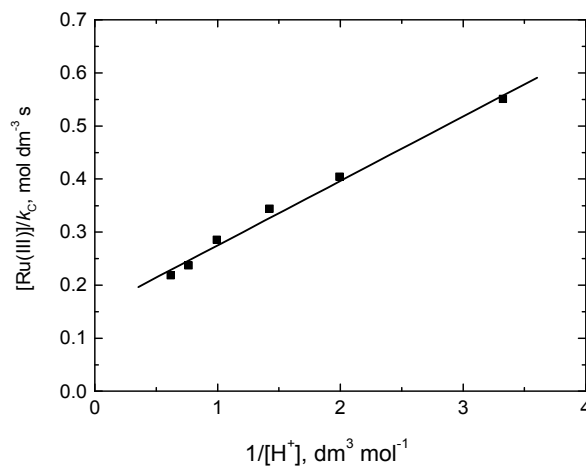


Figure 8. Plot of $[\text{Ru(III)}]/k_c$ versus $1/[\text{H}^+]$ in the Ru(III) -catalyzed oxidation of L-citrulline by HCP in perchloric acid solution. $[\text{Cit}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$ and $I = 1.8 \text{ mol dm}^{-3}$ at 20°C .

5. Conclusions

The reaction between L-citrulline and hexachloroplatinate (IV) in perchloric acid solution was very slow in the absence of Ru(III) catalyst. Plausible mechanistic scheme of the catalyzed reaction has been proposed. The final oxidation products of L-citrulline was identified as 4-(carbamoylamino) butyraldehyde, ammonia and carbon dioxide.

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