

Kinetics and Mechanism of Palladium(II)-Catalyzed Oxidation of Inositol by Hexachloroplatinate(IV) in Perchlorate Solutions

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To cite this article:

Ahmed Fawzy, Ishaq A. Zaafarany, Khalid S. Khairou, Sheigha S. Ashour, Naeema Yarkandi. Kinetics and Mechanism of Palladium(II)-Catalyzed Oxidation of Inositol by Hexachloroplatinate(IV) in Perchlorate Solutions. *American Journal of Applied Chemistry*.

Vol. 4, No. 5, 2016, pp. 185-191. doi: 10.11648/j.ajac.20160405.15

Received: August 29, 2016; Accepted: September 8, 2016; Published: September 24, 2016

Abstract: Oxidation of inositol (INOS) by hexachloroplatinate(IV) complex (HCP) in perchlorate solutions in the presence of palladium(II) catalyst was studied spectrophotometrically. The reaction rate was very slow in the absence of the catalyst. The reaction exhibited a first order dependence on [HCP], and fractional-first order dependences with respect to [INOS], [H⁺] and [Pd(II)]. Increasing ionic strength and dielectric constant was found to increase the oxidation rate. A probable oxidation mechanism has been suggested and the rate-law expression has been derived. Both spectral and kinetic evidences revealed formation of a 1:1 intermediate complex between INOS and Pd(II) prior to the rate-controlling step. The final oxidation product of inositol was identified by both spectral and chemical analyses as the corresponding monoketone derivative, namely inosose. The activation parameters of the second order rate constant were evaluated and discussed.

Keywords: Inositol, Hexachloroplatinate(IV), Oxidation, Palladium(II), Kinetics, Mechanism

1. Introduction

Anticancer platinum(IV) complexes have attracted many researchers in the last decades [1-4]. Hexachloroplatinate(IV) complex is considered as one of the most important platinum(IV) complexes applicable to oxidize various organic and inorganic compounds in different media [2-15]. The kinetics and mechanism of antitumor activity of platinum(IV) compounds can be understood by investigating the reactivity of these compounds toward their reduction by bio-reductants such as amino acids [5-15].

Inositol is a water soluble six membered cyclic polyol, which is synthesized by both eukaryotes and prokaryote [16]. In humans most inositol is synthesized in the kidneys. Inositol and some of its mono and polyphosphates function as the basis for a number of signaling and secondary

messenger molecules [17, 18]. These are involved in insulin signal transduction, gene expression, breakdown of fats and reducing blood cholesterol [19]. Oxidation of inositol was studied by different oxidants like alkaline potassium periodate [20], alkaline diperiodatocuprate(III) [21], alkalinepermanganate [22], V(V) in acid medium [23] and chromic acid [24].

Kinetic studies on the oxidation of organic compounds catalyzed by various metal ions are considered as a significant field of chemistry because of the role of metals in biological systems [25-32]. One of the important metal catalysts is palladium which is a rare and lustrous silvery-white metal referred to platinum group metals. Catalysis by Palladium is very significant in organic chemistry [33] e.g. medicinal chemistry [34] and the preparation of fine chemicals [35]. It is a versatile metal applied inhomogeneous catalysis. Most studies using palladium as catalyst have

employed it in the form of palladium(II) chloride [31, 36-38] which exists as $[\text{PdCl}_4]^{2-}$ in acidic media.

The present title deals with the kinetics of oxidation of inositol by hexachloroplatinate(IV) complex in perchlorate solutions in the presence of palladium(II) catalyst. This work aims to study the selectivity of inositol towards HCP in acidic medium, to check the catalytic efficiency of Pd(II) catalyst and to elucidate a probable oxidation mechanism.

2. Experimental

2.1. Materials

Reagent grade chemicals and bidistilled water have been employed in the present work. A stock solution of inositol was prepared by dissolving the sample (E. Merck) in bidistilled water. Chloroplatinic acid solution (Johnson Matthey) was freshly prepared by dilution of the original solution with bidistilled water and standardized spectrophotometrically [39]. Sodium perchlorate and acetic acid solutions have been used to study the effects of ionic strength and dielectric constant of the medium, respectively.

2.2. Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions, where $[\text{INOS}] \gg [\text{HCP}]$. The ionic strength, I , of the reaction mixture was adjusted to 1.0 mol dm^{-3} . The course of the reaction was followed spectrophotometrically by monitoring the decrease in the absorbance of HCP at $\lambda = 263 \text{ nm}$, using a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer.

It was observed that the oxidation reaction was proceeded very slowly in the absence of Pd(II) catalyst. The observed rate constants of the catalyzed reaction (k_c) were obtained from the linear portion of $\ln(\text{Abs.}) - \text{time}$ plots. These values were the average of at least two independent kinetics runs and were reproducible to within $\pm 3\%$. Reaction orders were calculated from the slope of $\log k_c$ versus $\log(\text{Conc.})$ plots by varying the concentrations of INOS, HClO_4 and Pd(II) in turn and keeping all other concentrations and conditions constant.

The spectral changes throughout palladium(II)-catalyzed oxidation of inositol by HCP in perchlorate solutions are illustrated in Figure 1. The scanned spectra indicate gradual disappearance of the HCP absorption band with time. Two isosbestic points were also observed in the spectra.

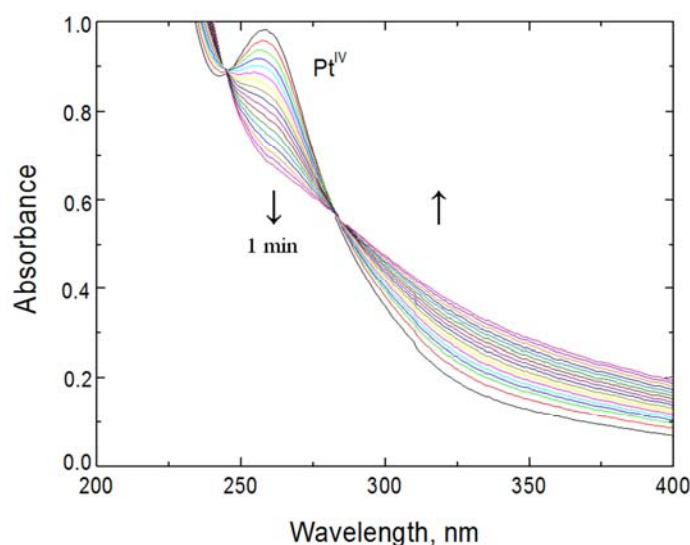
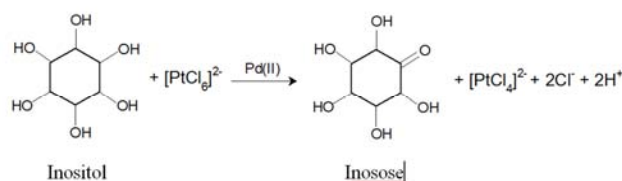


Figure 1. Spectral changes during palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[\text{INOS}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 0.5$, $[\text{Pd(II)}] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

3. Results

3.1. Stoichiometry and Product Analysis

Different sets of the reaction mixture containing various amounts of HCP and INOS at fixed acidity, $[\text{Pd(II)}]$, ionic strength, and temperature were allowed to react for about 24 h. After completion of the reaction, the unreacted $[\text{HCP}]$ was determined spectrophotometrically. The obtained results showed that the reaction stoichiometry is 1:1, as represented by the following stoichiometric equation:



The oxidation product of inositol was identified by both spectral and chemical analyses [40, 41] as the corresponding monoketone derivative, namely inosose. Also, the formed $[\text{PtCl}_4]^{2-}$ was confirmed as reported elsewhere [9-15].

3.2. Effect of [HCP]

The effect of the hexachloroplatinate(IV) oxidant was investigated by varying its concentration in the range of $(2.0 - 10.0) \times 10^{-5} \text{ mol dm}^{-3}$, at constant [INOS], $[\text{H}^+]$, [Pd(II)], ionic strength and temperature, and measuring the values of k_C . The non-variation in k_C at different [HCP] (Table 1) indicates that the order with respect to the oxidant is confirmed to be one.

3.3. Effect of [INOS]

The rate constant (k_C) was determined at various inositol concentrations keeping others constant. The results showed that k_C increases with increasing [INOS] as listed in Table 1. The plot of k_C versus [INOS] were found to be linear with non-zero intercepts indicating fractional-first order kinetics in [INOS] (Figure 2).

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

The oxidation rate was measured at constant concentration of INOS, HCP, Pd(II) but with various $[\text{H}^+]$ ($0.1 - 0.9 \text{ mol dm}^{-3}$). The reaction rate was found to increase as $[\text{H}^+]$ increased with less than unit order as found from the plot of $\log k_C$ versus $\log [\text{H}^+]$ (Figure 3).

3.5. Effect of [Pd(II)]

The rate of reaction was measured with various concentration of palladium(II) catalyst in the concentration range of $(2.0 - 10.0) \times 10^{-5} \text{ mol dm}^{-3}$ at constant other variables. The oxidation rate was found to increase with increasing [Pd(II)] as listed in Table 1. The order with respect to [Pd(II)] was less than unity as found from the plot of $\log k_C$ versus $\log [\text{Pd(II)}]$ as illustrated in Figure 4.

3.6. Effect of Ionic Strength and Dielectric Constant

The effect of ionic strength on the oxidation rate was investigated by addition of NaClO_4 to the reaction medium at constant other variables. The results showed that the observed rate constant increases with increasing ionic strength, and the Debye-Hückel plot was found to be linear with a positive slope as shown in Figure 5. Also, the effect of dielectric constant (D) of the reaction medium on the oxidation rate was examined by measuring the oxidation rate at different solvent compositions (v/v) of acetic acid and water. The rate constant decreased 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.

Table 1. Effect of variation of [HCP], [INOS], $[\text{H}^+]$, [Pd(II)] and ionic strength, I , on the observed first order rate constant (k_C) in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solutions at 25°C.

| 10^5 [HCP] (mol dm ⁻³) | 10^3 [INOS] (mol dm ⁻³) | $[\text{H}^+]$ (mol dm ⁻³) | 10^5 [Pd(II)] (mol dm ⁻³) | I (mol dm ⁻³) | $10^5 k_C$ (s ⁻¹) |
|--------------------------------------|---------------------------------------|--|---|-----------------------------|-------------------------------|
| 2.0 | 6.0 | 0.5 | 6.0 | 1.0 | 29.2 |
| 4.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 6.0 | 6.0 | 0.5 | 6.0 | 1.0 | 30.4 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 10.0 | 6.0 | 0.5 | 6.0 | 1.0 | 27.7 |
| 8.0 | 2.0 | 0.5 | 6.0 | 1.0 | 11.1 |
| 8.0 | 4.0 | 0.5 | 6.0 | 1.0 | 21.0 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 8.0 | 8.0 | 0.5 | 6.0 | 1.0 | 36.3 |
| 8.0 | 10.0 | 0.5 | 6.0 | 1.0 | 42.0 |
| 8.0 | 6.0 | 0.1 | 6.0 | 1.0 | 8.4 |
| 8.0 | 6.0 | 0.3 | 6.0 | 1.0 | 19.5 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 8.0 | 6.0 | 0.7 | 6.0 | 1.0 | 35.1 |
| 8.0 | 6.0 | 0.9 | 6.0 | 1.0 | 43.2 |
| 8.0 | 6.0 | 0.5 | 2.0 | 1.0 | 12.3 |
| 8.0 | 6.0 | 0.5 | 4.0 | 1.0 | 21.5 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 8.0 | 6.0 | 0.5 | 8.0 | 1.0 | 37.1 |
| 8.0 | 6.0 | 0.5 | 10.0 | 1.0 | 45.3 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.0 | 28.9 |
| 8.0 | 6.0 | 0.5 | 6.0 | 1.5 | 33.0 |
| 8.0 | 6.0 | 0.5 | 6.0 | 2.0 | 35.3 |
| 8.0 | 6.0 | 0.5 | 6.0 | 2.5 | 38.0 |
| 8.0 | 6.0 | 0.5 | 6.0 | 3.0 | 40.1 |

Experimental Error $\pm 3\%$

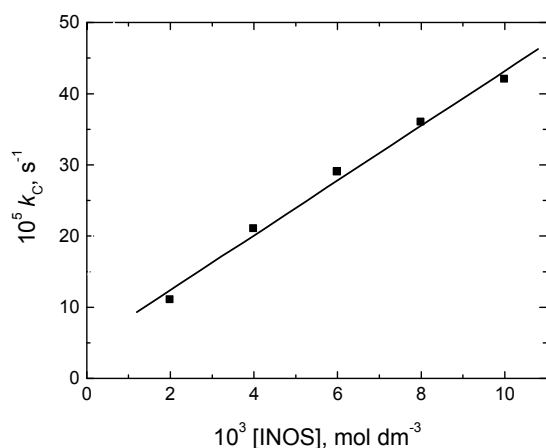


Figure 2. Plot of k_C versus $[INOS]$ in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[HCP] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Pd(II)] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

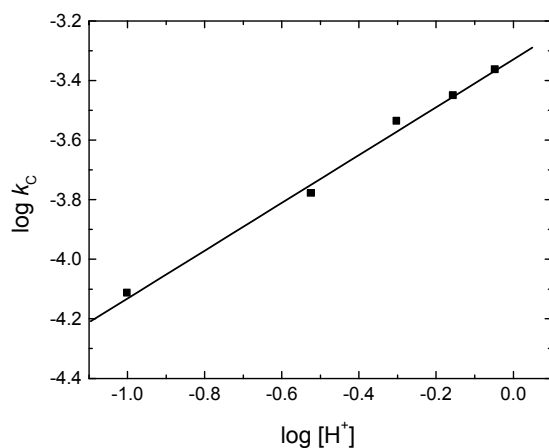


Figure 3. Plot of $\log k_C$ versus $\log [H^+]$ in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[INOS] = 6.0 \times 10^{-3}$, $[HCP] = 8.0 \times 10^{-5}$, $[Pd(II)] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

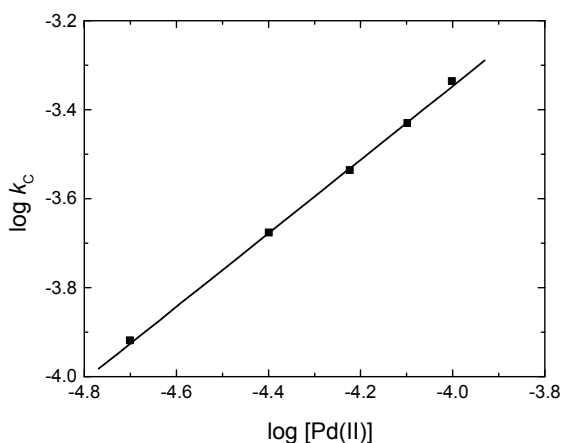


Figure 4. Plot of $\log k_C$ versus $\log [Pd(II)]$ in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[INOS] = 6.0 \times 10^{-3}$, $[HCP] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

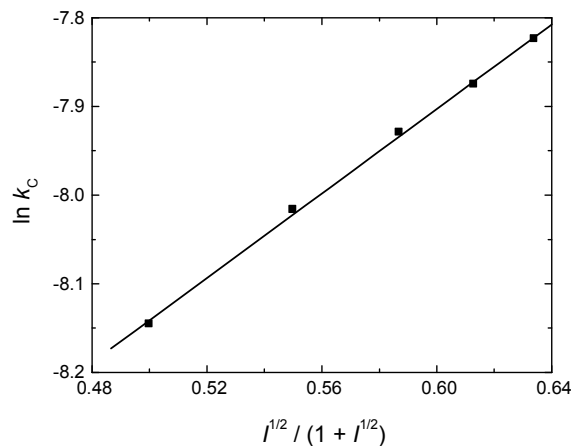


Figure 5. Debye-Hückel plot in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[INOS] = 6.0 \times 10^{-3}$, $[HCP] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Pd(II)] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

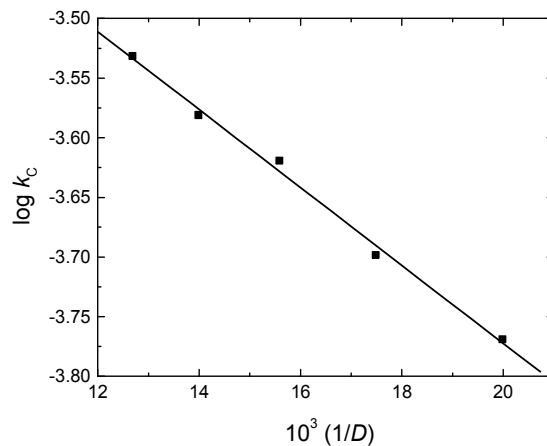


Figure 6. Plot of $\log k_C$ versus $1/D$ for the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[INOS] = 6.0 \times 10^{-3}$, $[HCP] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Pd(II)] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

3.7. Effect of Temperature

The oxidation rate was performed at five different temperatures in the range of 288 - 308 K, at constant concentrations of the reactants. 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 the second order rate constants k_2 in the palladium(II)-catalyzed oxidation of inositol by hexachloroplatinate(IV) in perchlorate solution. $[INOS] = 6.0 \times 10^{-3}$, $[HCP] = 8.0 \times 10^{-5}$, $[H^+] = 0.5$, $[Pd(II)] = 6.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$.

| $\Delta S^\ddagger, \text{J mol}^{-1}\text{K}^{-1}$ | $\Delta H^\ddagger, \text{kJ mol}^{-1}$ | $\Delta G^\ddagger_{298}, \text{kJ mol}^{-1}$ | $E_a^\ddagger, \text{kJ mol}^{-1}$ |
|---|---|---|------------------------------------|
| -89.12 | 47.46 | 74.41 | 50.11 |

3.8. Polymerization Test

The involvement of free radicals in the oxidation reaction was examined by the polymerization test. The reaction mixture to which a known quantity of acrylonitrile monomer was added initially and was kept for about 6 h. Upon diluting

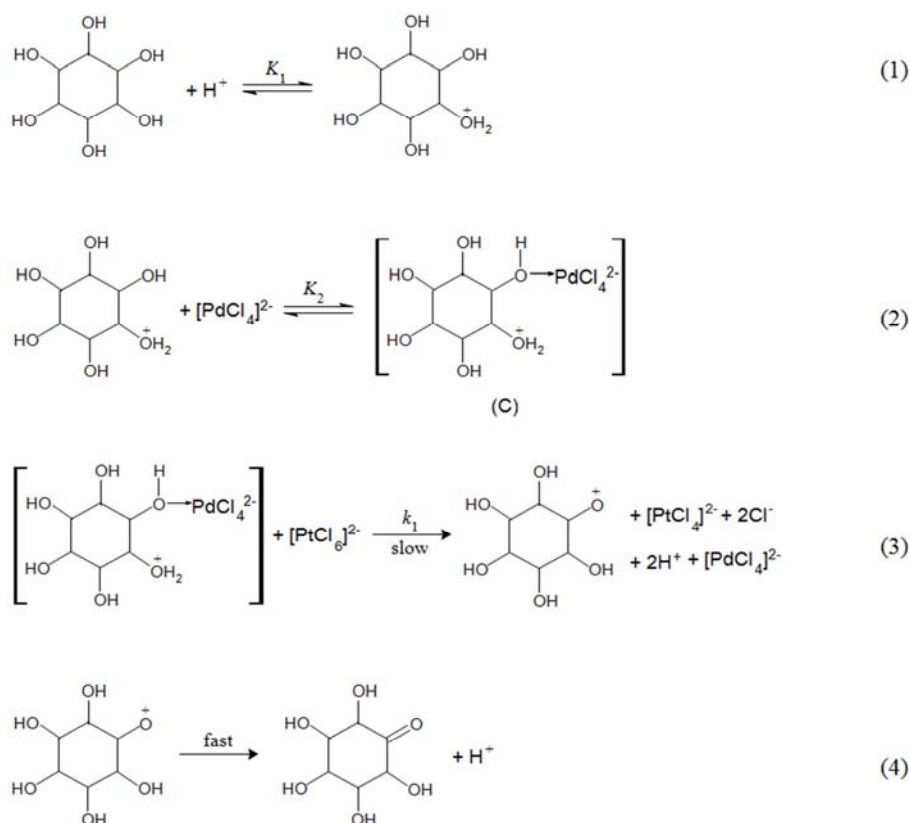
the reaction mixture with methanol, there was no white precipitate formed, suggesting absence of free radical intervention during the oxidation reaction. This indicates that the reaction was not routed through free radical path.

4. Discussion

The present reaction between inositol and hexachloroplatinate(IV) in perchlorate solution have a stoichiometry of 1:1. The reaction exhibited a first order dependence with respect to [HCP], less than unit order dependences with respect to [INOS], $[H^+]$ and [Pd(II)]. The observed enhancement of the oxidation rate upon increasing acid concentration with less than unit order dependence suggests that the protonated form of inositol substrate may be considered as the kinetically reactive species in the rate-determining step, which play the main role in the reaction kinetics. The less than unit order dependences with respect to both inositol and palladium(II) concentrations suggests

formation of an intermediate complex between inositol and the active species of Pd(II) catalyst, $[PdCl_4]^{2-}$, as reported earlier [31, 36-38]. Complex formation was proved kinetically by the non-zero intercept of the plot of $[Pd^{II}]/k_C$ versus $1/[INOS]$ (Figure 7). Spectroscopic evidence to support complex formation was obtained from the UV-Vis spectra as the appearance of two isosbestic points as shown in Figure 1.

Owing to the experimental results and the above-mentioned arguments, the oxidation mechanism illustrated in Scheme 1 suggests that the protonated inositol combines with $[PdCl_4]^{2-}$ to form an intermediate complex (C). Such complex slowly reacts with one molecule of HCP to give the oxidation product of inositol with regeneration of the catalyst Pd(II). Increasing the oxidation rate with increasing both ionic strength and dielectric constant of the reaction medium suggests that the reaction in the rate-determining step occur between two similarly charged ions [42, 43], i.e. between the negatively charged complex (C) and $[PtCl_6]^{2-}$.



Scheme 1. Mechanism of palladium(II)-catalyzed oxidations of inositol by hexachloroplatinate(IV) in perchlorate solutions.

According to the suggested mechanistic Scheme 1, the relationship between the rate of oxidation and the concentrations of inositol, hydrogen ion, palladium(II) catalyst and hexachloroplatinate(IV) oxidant may be represented by the following rate-law expression,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{INOS}][H^+][\text{Pd(II)}][\text{HCP}]}{(1 + K_1[H^+])(1 + K_1 K_2 [\text{INOS}][H^+])} \quad (5)$$

Under pseudo-first-order conditions, the rate law can be

expressed as,

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

Comparing Eqs. (5) and (6) leads to Eq. (7),

$$k_C = \frac{k_1 K_1 K_2 [\text{INOS}][H^+][\text{Pd(II)}]}{(1 + K_1[H^+])(1 + K_1 K_2 [\text{INOS}][H^+])} \quad (7)$$

and with rearrangement it becomes,

$$\frac{[\text{Pd(II)}]}{k_c} = \left(\frac{1 + K_1[\text{H}^+]}{k_1 K_1 K_2 [\text{H}^+]} \right) \frac{1}{[\text{INOS}]} + K' \quad (8)$$

$$\frac{[\text{Pd(II)}]}{k_c} = \left(\frac{1}{k_1 K_1 K_2 [\text{INOS}]} \right) \frac{1}{[\text{H}^+]} + \frac{1}{k_1 K_2 [\text{INOS}]} + K' \quad (9)$$

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

According to equations (8) and (9), the plots of $[\text{Pd(II)}]/k_c$ against $1/[\text{INOS}]$, at constant $[\text{H}^+]$, and $[\text{Pd(II)}]/k_c$ against $1/[\text{H}^+]$, at constant $[\text{INOS}]$, should be linear with positive intercepts on $[\text{Pd(II)}]/k_c$ axes. The experimental results satisfied this requirement as shown in Figures 7 and 8, respectively.

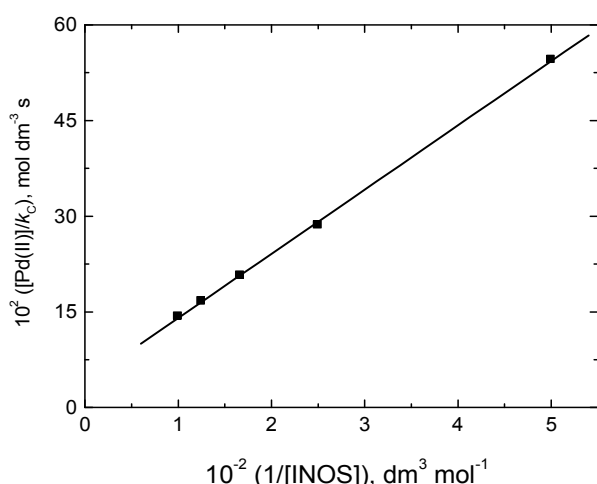


Figure 7. Verification of equation (8) in the palladium(II)-catalyzed oxidations of inositol by hexachloroplatinate(IV) in perchlorate solutions. $[\text{HCP}] = 8.0 \times 10^{-5}$, $[\text{H}^+] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

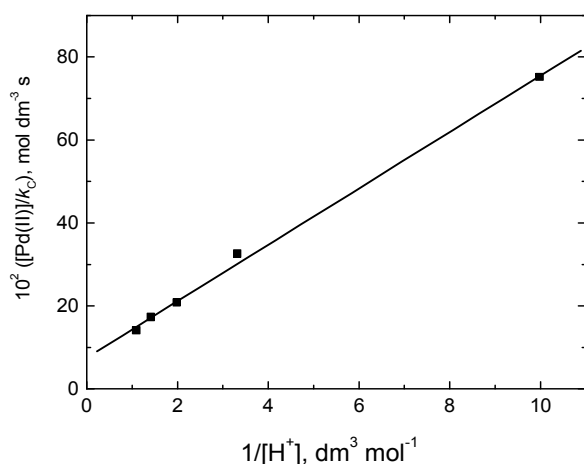


Figure 8. Verification of equation (9) in the palladium(II)-catalyzed oxidations of inositol by hexachloroplatinate(IV) in perchlorate solutions. $[\text{INOS}] = 6.0 \times 10^{-3}$, $[\text{HCP}] = 8.0 \times 10^{-5}$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

The activation parameters listed in Table 2 may be interpreted as follows. The obtained negative values of ΔS^\ddagger suggest that the reactions point towards the inner-sphere pathway [44]. The positive values of both ΔH^\ddagger and ΔG^\ddagger confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

5. Conclusions

The kinetics of oxidation of inositol by hexachloroplatinate(IV) has been investigated in perchlorate solutions in the presence of palladium(II) catalyst. The reaction was proceeded very slowly in the absence of the catalyst. A probable oxidation mechanism has been suggested. The oxidation product of inositol substrate identified as the corresponding mono ketone, namely inosose.

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