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Kinetics and Mechanistic Approach to Palladium (II)-Catalyzed Oxidative Deamination and Decarboxylation of Leucine and Isoleucine by Anticancer Platinum (IV) Complex in Perchlorate Solutions

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Abstract

Oxidations of two aliphatic α-amino acids (AA), namely, leucine and isoleucine by hexachloroplatinate (IV) as an anticancer platinum (IV) complex has been studied using a spectrophotometric technique in perchlorate solutions in the presence of palladium (II) catalyst at a constant ionic strength of 1.0 mol dm^{-3} and at 25°C. The reactions did not proceed in the absence of the catalyst. The reactions of both amino acids showed a first order dependence on both [Pt^{IV}] and [Pd^{II}], and less than unit order dependences with respect to both [AA] and [H^+]. Increasing ionic strength and dielectric constant of the reactions medium increased the rates of the reactions. A probable oxidations mechanism has been suggested and the rate law expression has been derived. Both spectral and kinetic evidences revealed formation of 1:1 intermediate complexes between AA and Pd^{II} before the rate-controlling step. The oxidation products of the investigated amino acids were identified as the corresponding aldehyde, ammonium ion and carbon dioxide. The activation parameters of the second order rate constants were evaluated and discussed.

Keywords: α-Amino acids; Palladium (II); Platinum (IV); Oxidation; Kinetics; Mechanism

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].

Amino acids act as the building blocks in the synthesis of proteins and play a vital role in the metabolism. In the metabolism, amino acids are subjected to various reactions and supply precursors for many endogenous substances, e.g., haemoglobin in blood. They undergo different reactions, depending on whether a particular amino acid contains non-polar groups or polar substituents. Leucine (Leu) and isoleucine (Ile) (their structure shown below) are essential amino acids. They are considered as active site residues of enzymes, and can help in maintaining correct conformation of enzymes by keeping them in their proper ionic states. Therefore, their oxidation can help in understanding the enzyme kinetics [16-19]. The kinetics of oxidation of amino acids is also of interest as the products differ depending on the oxidants [20-35].

Palladium is a rare and lustrous silvery-white metal referred to as the platinum group metals. Palladium-catalyzed reactions have found widespread use in many areas of organic chemistry [36], medicinal chemistry [37] and in the preparation of fine chemicals [38]. It is a versatile metal applied in homogeneous catalysis. Most studies using palladium as catalyst have employed it in the form of palladium(II) chloride [32,39-41] which exists as $[PdCl_4]^{2-}$ in aqueous solutions. Kinetic investigations on the oxidation of amino acids catalyzed by different metal ions [9-16] are considered as a significant field of chemistry because of the role of metals in biological systems.

The present investigation deals with the kinetics of oxidations of leucine and isoleucine by an anticancer platinum (IV) complex in perchlorate solutions, in the presence of palladium (II) catalyst. This work aims to study the selectivity of the studied amino acids towards platinum (IV) in acid medium, to check the catalytic efficiency of Pd^{II} catalyst, and to elucidate a probable reactions mechanism.

Experimental

Materials

Reagent grade chemicals and doubly distilled water were used throughout the work. A stock solution of the investigated α-amino acids were prepared by dissolving the amino acids samples (E. Merck) in bidistilled water. Chloroplatinic acid solution (Johnson Matthey) was freshly prepared by dilution of the original solution with doubly distilled water and standardized spectrophotometrically [42]. Sodium pechlorate and acetic acid solutions have been used to study the effects of the ionic strength and dielectric constant of the medium, respectively.

Kinetic measurements

The kinetic runs have been carried out under pseudo-first order conditions, i.e., the amino acid concentration>>platinum (IV) concentration. The ionic strength, I, of the reactions mixtures was adjusted to 1.0 mol dm^{-3}. The reactions temperature (25°C) was

controlled within ± 0.1°C unless stated otherwise. The reactions were initiated by rapid addition of known amounts of the pre-equilibrated Pt^{IV} to the reactions mixtures containing the required amounts of the investigated amino acid, perchloric acid, palladium (II) 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 cm. The courses of the reactions were followed spectrophotometrically by monitoring the decrease in the absorbance of Pt^{IV} at λ=261 nm, its absorption maximum, as a function of time using a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. The molar extinction coefficient, ε, was determined, ε=(1.32 ± 0.04) × 10^4 dm^3 mol^{-1} cm^{-1}, and was found to be in a good agreement with that reported previously [42]. It was observed that the oxidation reactions were not proceed in the absence of palladium (II) catalyst. The observed rate constants of the catalyzed reactions (k_C) were obtained from the linear portion of ln (Abs.) - time plots. These values were the average of at least two independent kinetics runs and were reproducible to within ± 2-3%.

Results

Spectral changes

The spectral changes throughout palladium (II)-catalyzed-oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions are shown in Figure 1 respectively. The scanned spectra indicate gradual disappearance of the Pt^{IV} absorption band with time as a result of its reduction. A hyposchromic shift in the Pt^{IV} band as well as two isosbestic points were observed in the both spectra.

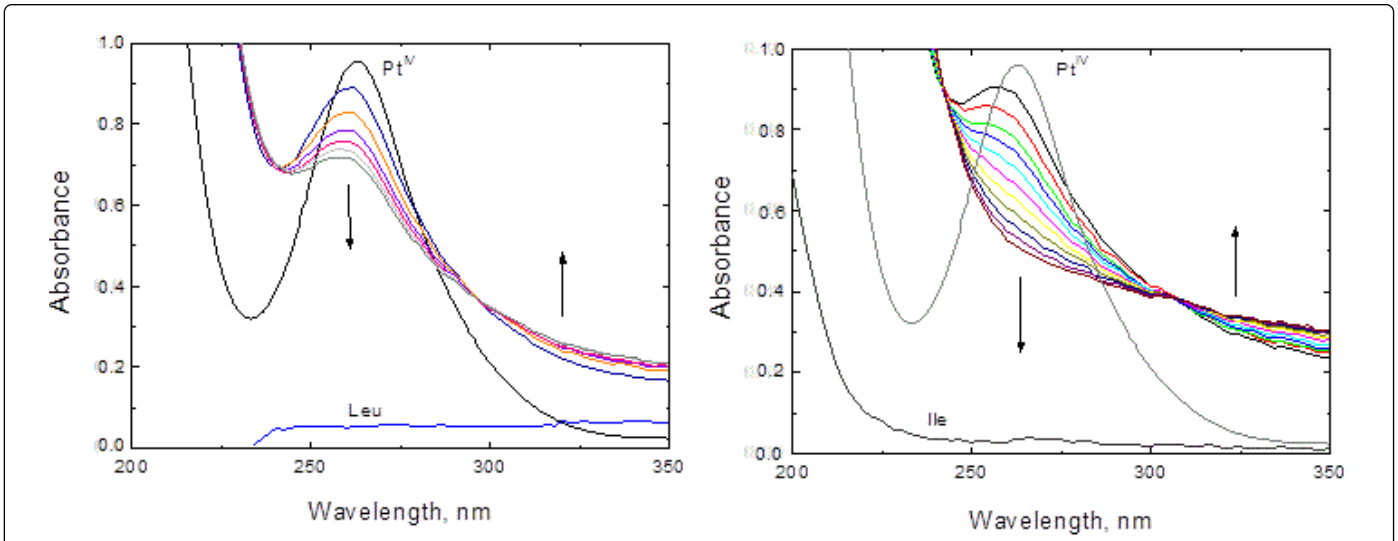
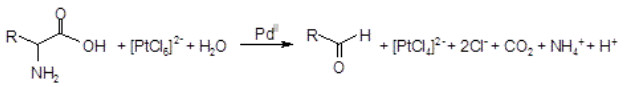


Figure 1: Time-resolved spectra during the palladium (II)-catalyzed oxidations of: (a) leucine, and (b) isoleucine by platinum (IV) in perchlorate solutions. [AA]=3.0 × 10^{-3}, [Pt^{IV}]=8.0 × 10^{-5}, [H^+]=0.5, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

Reaction stoichiometry and product identification

Different sets of the reactions mixtures containing various amounts of Pt^{IV} and AA at fixed acidity, ionic strength, and temperature were allowed to react for about 24 h. After completion of the reactions, the unreacted [Pt^{IV}] was assayed spectrophotometrically. The obtained results showed that the reaction stoichiometry is 1:1, as represented by the following stoichiometric equation:



Where R=CH $(CH_3)CH_2CH_3$ for leucine, and R=$CH_2CH(CH_3)_2$ for isoleucine.

The corresponding aldehydes were identified as reported earlier [43,44]. The other products were identified as ammonia by Nessler's reagent and CO_2 by lime water. On the other hand, the formation of $[Pt^{II}Cl_4]^{2-}$ was also confirmed as reported elsewhere [9-15].

Orders of the reactions

Double logarithmic plots were used to determine the orders with respect to the reactants. The concentration of the particular reactant being examined was varied and the concentrations of the other reactants were held fixed.

The effect of the platinum (IV) oxidant was varied in the range of 2.0 × 10^{-5} to 10.0 × 10^{-5} mol dm^{-3} at constant [AA], [Pd^{II}], [H^+], ionic strength and temperature. The non-variation in the observed first order rate constants at various concentrations of Pt^{IV} (Table 1) indicates that the order with respect to the oxidant is confirmed to be one.

The observed first order rate constant (k_C) was determined at different initial concentrations of the reductants leucine and isoleucine keeping all other reactants concentration constant. The results showed that the rate constants increased with increasing the amino acids concentrations as listed in Table 1. The plots of k_C versus [AA] were found to be linear with non-zero intercepts indicating fractional-first order dependences with respect to the amino acids (Figure 2).

The rates of the reactions were measured at constant concentrations of amino acids, PtIV, PdII, ionic strength and temperature but with

various $[H^+]$ (0.1–0.9 mol dm^{-3}). The rates were found to increase as $[H^+]$ increased with less than unit orders as found from the plots of log k_C versus log $[H^+]$ (Figure 3).

The oxidation rates were measured with various concentrations of palladium (II) catalyst in the concentration range of (2.0–10.0) × 10^{-5} mol dm^{-3} at constant other variables. The oxidation rates were found to increase with increasing $[Pd^{II}]$ as listed in Table 1. The order with respect to $[Pd^{II}]$ was approximately unity as found from the plots of log k_C versus log $[Pd^{II}]$ as illustrated in Figure 4.

Effect of ionic strength and dielectric constant

The effect of ionic strength on the oxidation rates was investigated by the addition of sodium perchlorate as an inert electrolyte to the reactions medium at constant concentrations of AA, Pt^{IV} and Pd^{II}, and at constant pH and temperature. The results showed that the observed rate constants increase with increasing ionic strength and the Debye–Hückel plots were found to be linear with positive slopes as shown in Figure 5.

10^5 $[Pt^{IV}]$ (mol dm^{-3})	10^3 [AA] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	10^5 $[Pd^{II}]$ (mol dm^{-3})	I (mol dm^{-3})	10^5 k_C (s^{-1})	
					leucine	Isoleucine
2.0	3.0	0.5	6.0	1.0	107.0	102.6
4.0	3.0	0.5	6.0	1.0	109.2	104.0
6.0	3.0	0.5	6.0	1.0	108.7	101.4
8.0	3.0	0.5	6.0	1.0	107.3	102.6
10.0	3.0	0.5	6.0	1.0	110.7	103.1
8.0	2.0	0.5	6.0	1.0	47.0	36.2
8.0	4.0	0.5	6.0	1.0	78.2	69.0
8.0	6.0	0.5	6.0	1.0	107.3	102.6
8.0	8.0	0.5	6.0	1.0	135.1	131.2
8.0	10.0	0.5	6.0	1.0	159.8	155.6
8.0	3.0	0.1	6.0	1.0	38.3	35.4
8.0	3.0	0.3	6.0	1.0	78.0	74.2
8.0	3.0	0.5	6.0	1.0	107.3	102.6
8.0	3.0	0.7	6.0	1.0	125.1	119.3
8.0	3.0	0.9	6.0	1.0	139.7	126.0
8.0	3.0	0.5	2.0	1.0	31.2	29.9
8.0	3.0	0.5	4.0	1.0	63.9	61.2
8.0	3.0	0.5	6.0	1.0	107.3	102.6
8.0	3.0	0.5	8.0	1.0	141.2	137.2
8.0	3.0	0.5	10.0	1.0	174.1	159.9
8.0	3.0	0.5	6.0	1.0	107.3	102.6
8.0	3.0	0.5	6.0	1.5	113.3	106.0
8.0	3.0	0.5	6.0	2.0	117.7	111.2
8.0	3.0	0.5	6.0	2.5	123.1	115.6
8.0	3.0	0.5	6.0	3.0	128.0	118.0

Table 1: Effect of variation of $[Pt^{IV}]$, [AA], $[H^+]$, $[Pd^{II}]$ and ionic strength, I, on the observed first order rate constant (k_C) in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. Experimental Error ± 3%.

Also, the effect of the dielectric constant (D) of the reactions medium on the oxidation rates was examined by measuring the oxidation rates at different solvent compositions (v/v) of acetic acid and water. The rate constants decreased with the decrease in dielectric constant of the solvent mixture, i.e., increase in acetic acid content. The

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plots of log kC versus 1/D was found to be linear with negative slopes as shown in Figure 6.

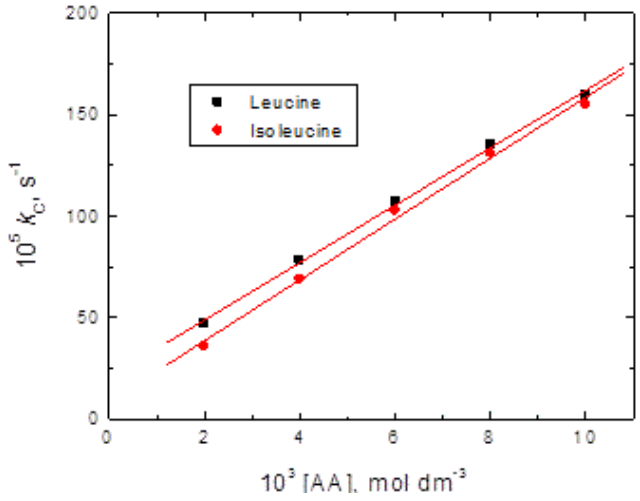


Figure 2: Plots of the observed first order rate constant *(k_C)* versus [AA] in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [PtIV]=8.0 × 10^{-5}, [H^+]=0.5, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

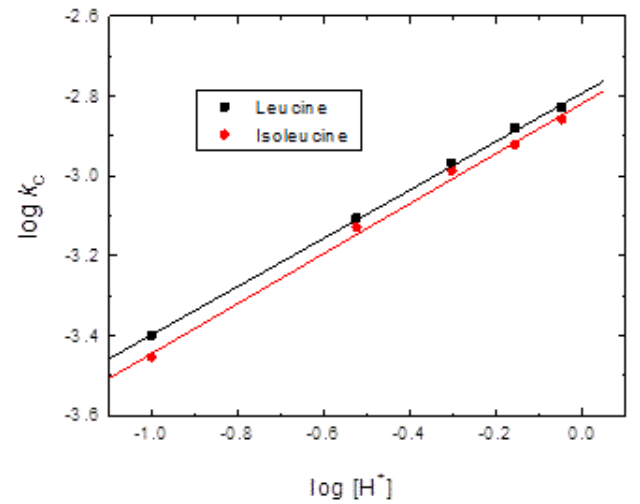


Figure 3: Plots of log k_C versus log [H^+] in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=6.0 × 10^{-3}, [PtIV]=8.0 × 10^{-5}, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

Effect of temperature

The oxidation rates were 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.

Amino acid	$\Delta S^{\neq}$, J $mol^{-1}K^{-1}$	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}	$E_a^{\neq}$, kJ mol^{-1}
Leucine	-87.12	47.47	73.43	49.01
Isoleucine	-95.07	44.11	72.44	45.97

Table 2: Activation parameters of the second order rate constants k_2 in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=3.0 × 10^{-3}, [Pt^{IV}]=8.0 × 10^{-5}, [H^+]=0.5, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3}. Experimental error ± 3%.

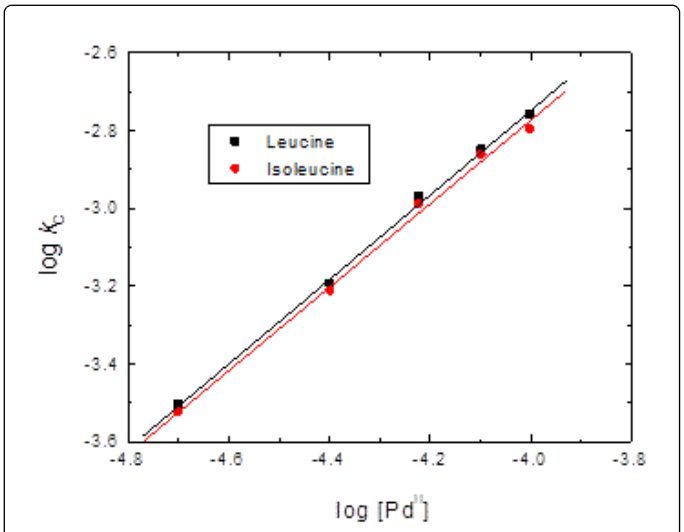


Figure 4: Plots of log k_C versus log [Pd^{II}] in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=6.0 × 10^{-3}, [Pt^{IV}]=8.0 × 10^{-5}, [H^+]=0.5 and I=1.0 mol dm^{-3} at 25°C.

Polymerization test

The involvement of free radicals in the oxidation reactions in both acids was examined by the polymerization test. The reactions mixtures to which a known quantity of acrylonitrile scavenger has been added initially and was kept in inert atmosphere for 4 h. Upon diluting the reactions mixtures with methanol, there were no white precipitates formed, suggesting absence of free radicals intervention during the oxidation reactions. This indicates that the reactions were not routed through free radical path.

Discussion

It is also reported [45] that the platinum(IV) species in acid medium is present as $[PtCl_6]^{2-}$, which is assumed to be the principal reactive oxidant. The reduction of $[PtCl_6]^{2-}$ generally proceeds as follows:

$$[PtCl_6]^{2-} + 2e^- = [PtCl_4]^{2-} + 2Cl^-$$

In this reduction process, Pt^{IV} is reduced to Pt^{II} with release two Cl^- ions. Therefore, this reaction is better classified as a reductive–elimination reaction [2,3]. Due to Pt^{IV} complexes are substitution-

inert [46], initial complex formation between Pt^{IV} and reductant before electron transfer can be excluded in reductive–elimination reactions.

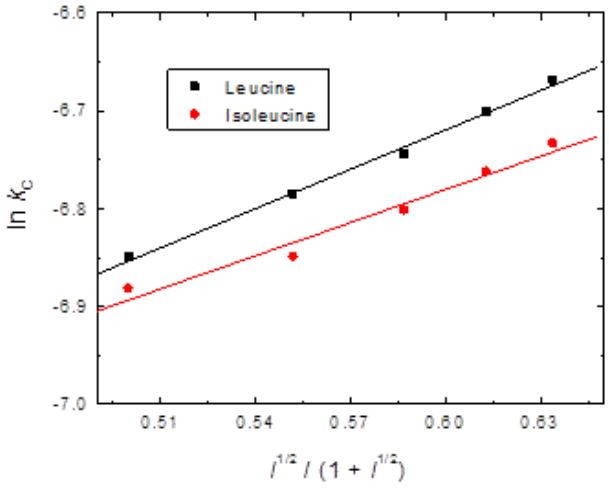


Figure 5: Debye–Hückel plots in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=3.0 × 10^{-3}, [Pt^{IV}]=8.0 × 10^{-5}, [H+]=0.5, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

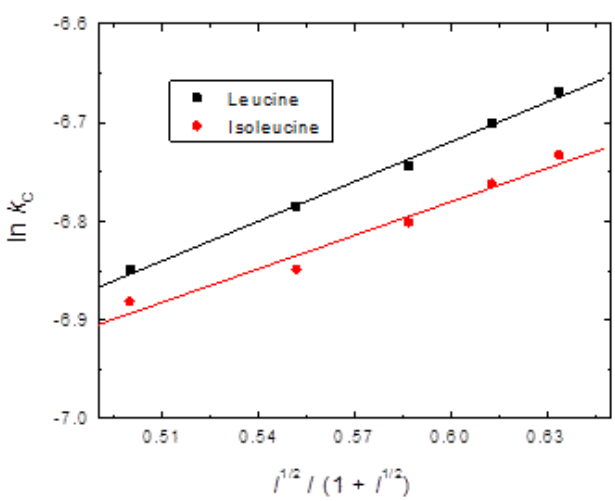
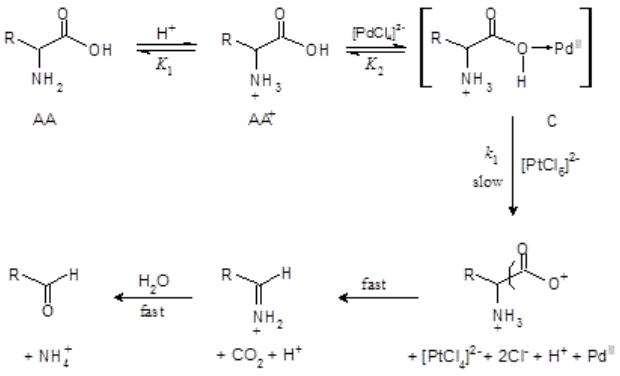


Figure 6: Plots of log k_C versus 1/D for the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=3.0 × 10^{-3}, [PtIV]=8.0 × 10^{-5}, [H^+]=0.5, [Pd^{II}]=6.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

The present reactions of leucine and isoleucine with Pt^{IV} in perchloriate solutions have a 1:1 stoichiometry. The reactions exhibited a first order dependence with respect to both [Pt^{IV}] and [Pd^{II}], less than unit order dependences with respect to both [AA] and [H^+]. The observed enhancement of the oxidation rates upon increasing acids concentration with the less than unit order dependences suggests [47] that the protonated forms of the amino acids may be considered as the kinetically reactive species in the rate-determining step, which play the main role in the reactions kinetics. The less than unit order dependences with respect to the concentrations of the amino acids suggests formation of intermediate complexes between the amino acids and the active species of Pd^{II} catalyst, $[PdCl_4]^{2-}$, as reported earlier [32,39-41]. Complexes formation was proved kinetically by the non-zero intercepts of the plots of $[Pd^{II}]/k_C$ versus 1/[AA] (Figure 7). Spectroscopic evidence to support complexes formation was obtained from the UV-Vis spectra where hyposchromic shifts in the wavelength with the appearance of two isosbestic points as shown in Figure 1.

Based on the experimental results and the above-mentioned arguments, the oxidation mechanism illustrated in Scheme 1 suggests that the protonated amino acid combines with $[PdCl_4]^{2-}$ to form an intermediate complex (C). Such complex slowly reacts with one mole of Pt^{IV} to give the products with regeneration of the catalyst Pd^{II}. Increasing the oxidation rates with increasing ionic strength and dielectric constant of the reactions medium suggests that the reactions in the rate-determining step occur between two similarly charged ions [48,49], i.e., between the positively charged complex and $[PtCl_6]^{2-}$.



Where R=$CH(CH_3)CH_2CH_3$ for leucine, and R=$CH_2CH(CH_3)_2$ for isoleucine.

Scheme 1: Mechanism of palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum(IV) in perchlorate solutions.

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

$$Rate = \frac{k_1 K_1 K_2 [AA][H^+][Pd^{II}][Pt^{IV}]}{(1 + K_1[H^+])(1 + K_1 K_2 [AA][H^+])} \quad (1)$$

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

$$Rate = \frac{-d[Pt^{IV}]}{dt} = k_c[Pt^{IV}] \quad (2)$$

Comparing Eqs. (1) and (2), the following relationship is obtained,

$$kc = \frac{k_1 K_1 K_2 [AA][H^+][Pd^{II}]}{(1 + K_1[H^+](1 + K_1 K_2 [AA])[H^+])} \quad (3)$$

and with rearrangement it becomes,

$$\frac{[Pd^{II}]}{k_c} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 [H^+]}\right)\frac{1}{[AA]} + K' \quad (4)$$

$$\frac{[Pd^{II}]}{k_c} = \left(\frac{1 + K_1[H+]}{k_1 K_1 K_2 [AA]}\right)\frac{1}{[H^+]} + \frac{1}{k_1 K_2 [AA]} + K' \quad (5)$$

where K'=(1+K1[H+]) / k1.

According to equations (4) and (5), the plots of $[Pd^{II}]/k_C$ against 1/[AA], at constant $[H^+]$, and $[Pd^{II}]/k_C$ against $1/[H^+]$, at constant [AA], should be linear with positive intercepts on $[PdII]/k_C$ axes. The experimental results satisfied this requirement as shown in Figures 7 and 8, respectively.

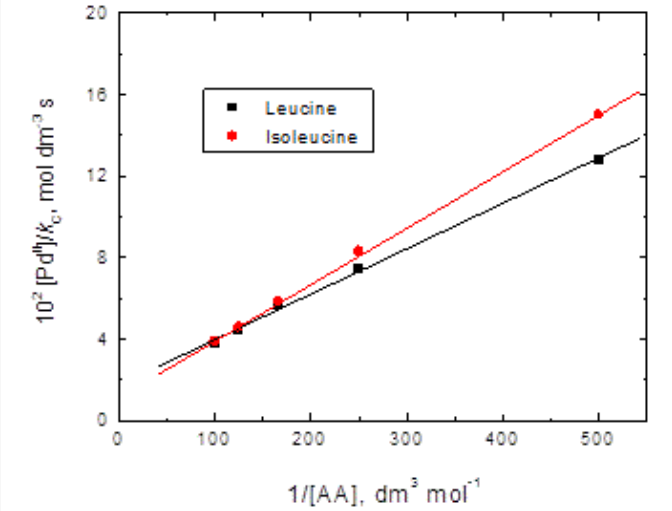


Figure 7: Verification of equation (4) in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C [PtIV]=8.0 × 10^{-5}, $[H^+]$=0.5 and I=1.0 mol dm^{-3} at 25°C.

The activation parameters listed in Table 2 may be interpreted as follows. The obtained negative values of $\Delta S\neq$ suggest that the reactions point towards the inner-sphere pathway [50]. The positive values of both $\Delta H\neq$ and $\Delta G\neq$ confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

Conclusions

The kinetics of oxidations of leucine and isoleucine by platinum (IV) has been investigated in perchlorate solutions in the presence of palladium (II) catalyst. The reactions were not proceeding in the absence of the catalyst. A probable oxidations mechanism has been suggested. The oxidation products of the studied amino acids were identified as the corresponding aldehyde, ammonium ion and carbon dioxide.

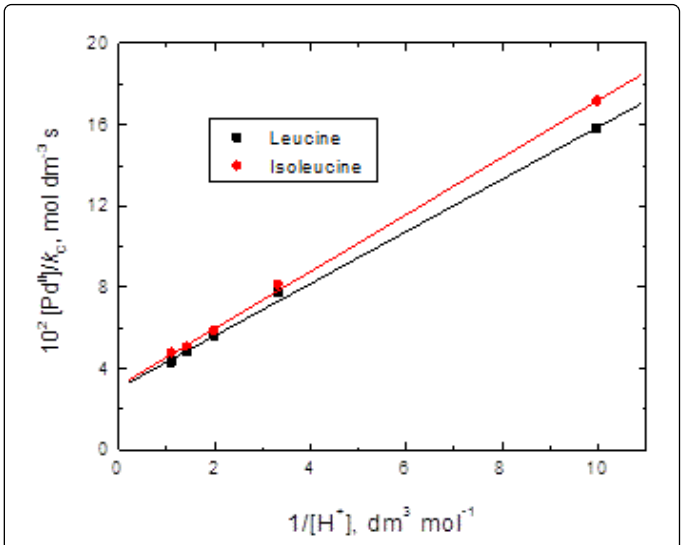


Figure 8: Verification of equation (5) in the palladium (II)-catalyzed oxidations of leucine and isoleucine by platinum (IV) in perchlorate solutions at 25°C. [AA]=3.0 × 10^{-3}, [Pt^{IV}]=8.0 × 10^{-5} and I=1.0 mol dm^{-3} at 25°C.

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