

# A COMPARATIVE STUDY OF PALLADIUM(II) CATALYSED OXIDATION OF L-LEUCINE AND L- ISOLEUCINE BY ALKALINE PERMANGANATE. A KINETIC AND MECHANISTIC APPROACH

Adarsha JR<sup>1</sup>, Sailashree S<sup>2</sup>, Surekha M<sup>3</sup>

<sup>1,2,3</sup>Global Academy of Technology, Bangalore, Sairam College of Engineering, Bangalore,  
The Oxford College of Engineering, Bangalore (India)

## ABSTRACT

*The kinetics of the Palladium(II) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate were studied and compared, spectrophotometrically using a rapid kinetic accessory. The reaction is first order with respect to [oxidant] and [catalyst] with an apparently less than unit order in [substrate] and [alkali] respectively. The results suggest the formation of a complex between the amino acid and the hydroxylated species of Palladium (II). The complex reacts further with the alkaline permanganate species in a rate-determining step, resulting in the formation of a free radical, which again reacts with the alkaline permanganate species in a subsequent fast step to yield the products. The reaction constants involved in the mechanism were calculated. There is a good agreement between observed and calculated rate constants under different experimental conditions. The activation parameters with respect to the slow step of the mechanism for both the amino acids were calculated and discussed. Of the two amino acids, leucine is oxidized at a faster rate than isoleucine.*

## I INTRODUCTION

Potassium permanganate is widely used as an oxidizing agent in synthetic as well as in analytical chemistry, and also as a disinfectant. The permanganate reactions are governed by the pH of the medium. Among the six oxidation state of manganese (2+ to 7+). Permanganate, manganese intermediates are relatively easy to identify when they have sufficiently long life times, oxidation states of the intermediates permit useful conclusions to be drawn as to the possible reaction mechanism, including the nature of intermediates.

Oxidation by permanganate ion is applied extensively in organic synthesis [1-7] especially since the advent of phase transfer catalysis [3, 4, 6]. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by the results referring to unsaturated acids both in aqueous [1,3,7] and non aqueous media [8].

During oxidation, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which the multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium [9] used for the study. In strongly alkaline medium, the stable reduction product [10,11] of the permanganate ion is manganate ion  $\text{MnO}_4^{2-}$ . No mechanistic information is available to distinguish between a direct one-electron reduction to manganese (VI) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of the hypomanganate ion [12].

Amino acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism. In metabolism, amino acids are subjected to many reactions and can supply precursors for many endogenous substances, e.g. Hemoglobin in blood. Amino acids can undergo many types of reaction, depending on whether a particular amino acid contains non-polar groups or polar substituent. Leucine and isoleucine are essential amino acids. They are active site residues of enzymes, and help in maintaining the correct conformation of enzymes by keeping them in their proper ionic states. Thus, their oxidation may help in understanding enzyme kinetics. The oxidation of amino acids is also of interest as the products differ depending on the oxidants [13, 14].

Palladium(II) is known to catalyze various reactions [7]. Most studies using Palladium(II) as a catalyst have employed it in the form of Palladium(II) chloride [8] and the nature of its active form in such reactions remains obscure. Hence, the effect of chloride on the reaction was studied in order to establish the active species of palladium in chloride medium. Micro amount of Palladium(II) is sufficient to catalyze the reaction in alkaline medium and varieties of mechanisms are possible. The reaction in alkaline medium and varieties of mechanisms is possible. The redox potentials of the couples,  $\text{H}_3\text{IO}_6^{2-}$ (VII)/  $\text{H}_2\text{IO}_6^{5-}$ (V) and Pd(IV)/Pd(II), in alkaline medium make the Palladium(II) catalyst for oxidation of dimethyl sulfoxide by periodate more feasible.

## II EXPERIMENTAL

Since the reaction was too fast to be monitored by the usual methods, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

Stock solutions of L-leucine and L-isoleucine (S.D. Co., fine chemicals) were prepared by dissolving the appropriate amount of sample in doubly distilled water. The solution of  $\text{KMnO}_4$  (BDH) was prepared and standardized with  $(\text{CO}_2\text{H})_2$  [18]. A potassium manganate solution was prepared as described by Carrington and Symons [19]. The solution was standardized by measuring the absorbance on a Hitachi 150-20 spectrophotometer with a 1 cm quartz cell at 608 nm ( $\epsilon = 1530 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

A palladium(II) stock solution was prepared by dissolving a known weight of Palladium(II) chloride (S.D. Fine Chem) in  $0.20 \text{ mol dm}^{-3}$  HCl and standardized against EDTA [9]. For some kinetic runs in the absence of chloride, the chloride ion in the palladium(II) stock solution was precipitated with  $\text{AgNO}_3$  and removed by repeated centrifugation. The resulting clear palladium(II) solution contained less than  $5.0 \times 10^{-5}$  and  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Cl}^-$  and  $\text{Ag}^+$ . Such extremely

low concentrations of  $\text{Cl}^-$  and  $\text{Ag}^+$  were found to have no significant effect on the reaction. The chloride concentration was maintained between  $2.0 \times 10^{-5}$  and  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$  with KCl. Iodate standard solution was prepared by dissolving a known amount of potassium iodate (Rechem) in doubly distilled water.

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of the samples in double distilled water. NaOH and  $\text{NaClO}_4$  were used to provide the required alkalinity and to maintain the ionic strength respectively.

### III KINETIC STUDIES

All kinetic measurements were performed under pseudo first order conditions with  $[\text{amino acid}]:[\text{MnO}_4^-] \geq 10:1$  at constant ionic strength ( $0.50 \text{ mol}^{-1} \text{ dm}^3$ ). The reaction was initiated by mixing previously thermostatted solutions of  $\text{MnO}_4^-$ , Palladium(II) and amino acids, which also contained the necessary quantities of NaOH and  $\text{NaClO}_4$ . The temperature was maintained at  $30 \pm 0.1^\circ\text{C}$ . The course of reaction was followed by monitoring the decrease in absorbance of  $\text{MnO}_4^-$  in the 1 cm quartz cell of a Hitachi model 150-20 spectrophotometer at its absorption maximum, 526 nm, as a function of time. Earlier it was verified that negligible interference occurs from other reagents at this wavelength. The application of Beer's law to permanganate at 526 nm had been verified, giving  $\epsilon = 2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (literature  $\epsilon = 2200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). [10]. The first order rate constants,  $K_{\text{obs}}$  were evaluated by plots of  $\log[\text{MnO}_4^-]$  versus time. The first order plots in almost all cases were linear to 80% completion of the reaction and  $K_{\text{obs}}$  values were reproducible within  $\pm 5\%$ . During the course of measurements, the solution changed from violet to blue and then to green. The spectrum of the green solution was identical to that of  $\text{MnO}_4^-$ . It is probable that the blue originated from the violet of permanganate and the green of the manganate, excluding the accumulation of hypomanganate.

The effect of dissolved oxygen on the reaction rate was checked by preparing the mixture and following the reaction in an atmosphere of dinitrogen. No significant difference between the results obtained under the nitrogen and in the presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. Nevertheless as a precaution, fresh solutions were used when conducting kinetic experiments. In the view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

### IV RESULTS

#### Stoichiometry

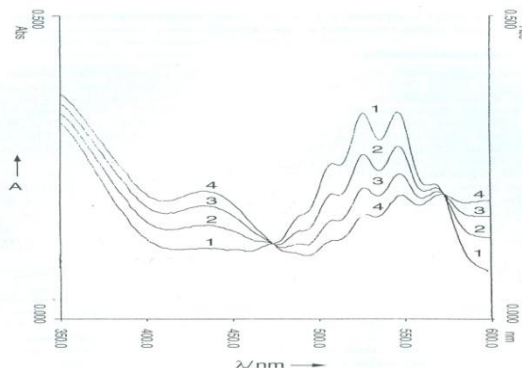
The reaction mixture containing an excess of permanganate over amino acids, and  $0.05 \text{ mol}^{-1} \text{ dm}^3$  were allowed to react for ca. 2 h at  $30 \pm 0.1^\circ\text{C}$  under an inert atmosphere. After completion of the reaction, the remaining  $\text{MnO}_4^-$  was then

analyzed spectrophotometrically. Some results indicated that 2 mol of  $MnO_4^-$  were consumed per mole of each amino acid. Other results indicated that 4 mol of  $MnO_4^-$  were consumed per mole of amino acid. The reaction products for the first series were identified as aldehyde [21], by b.p., spot test and ammonia [22] by Nessler's reagent, and manganate by its visible spectrum.  $CO_2$  was qualitatively detected by bubbling  $N_2$  gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water [23]. The product aldehyde was quantitatively estimated to ca. 78%, evidence for which is provided by its 2,4-DNP derivative [24]. The nature of the aldehyde was confirmed by its IR spectrum [25] carbonyl stretch at  $1729\text{ cm}^{-1}$  and by a band at  $2928\text{ cm}^{-1}$  due to the aldehyde stretch. The reaction product from the second series were identified as the carboxylic acid by its b.p., spot test [26], ammonia by Nessler's reagent and manganate by its visible spectrum,  $CO_2$  was qualitatively detected by bubbling  $N_2$  gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water. The nature of the carboxylic acid was confirmed by its IR spectrum which showed a carbonyl (C=O) stretch at  $1657\text{ cm}^{-1}$  and  $OH^-$  stretch at  $2854\text{ cm}^{-1}$ . The same type of aldehyde as above was obtained when the product analysis was carried under pseudo-first order conditions for leucine and isoleucine separately. It was also observed that the aldehyde does not undergo further oxidation under the present kinetic conditions. A test for corresponding acid was negative, so it is concluded that the stoichiometry of the reaction under kinetic study is:



where  $R = CH_2CHMe_2$  for L-leucine and  $R = CHMeEt$  for L-isoleucine

The permanganate in alkaline medium exhibits various oxidation states, such as  $Mn^{VII}$ ,  $Mn^V$  and  $Mn^{VI}$ . The solution changed from violet to blue and then to green, excluding the accumulation of hypomanganate. The violet colour originates from the pink of permanganate and blue from hypomanganate. The change of  $KMnO_4$  solution from violet  $Mn^{VII}$  ion to dark green  $Mn^{VI}$  ion through the blue  $Mn^V$  ion has been observed. The spectral changes during the reaction are shown in Figure 1. It is evident that  $[Mn^{VII}]$  decreases at 526 nm whereas  $[Mn^{VI}]$  increases at 608 nm during the reaction. Regression analysis of experimental data to obtain the regression coefficient  $r$ , and standard deviation  $r$ , of points from the regression line was performed using a Pentium-III personal computer.



**Fig.1 Spectral Changes during the reaction**

## Reaction order

The reaction orders were determined from the slopes of  $\log k_{\text{obs}}$  versus  $\log$  concentration plots, by varying the concentration of reductant, catalyst and alkali, while keeping others constant. The oxidant (potassium permanganate) concentration was varied in the  $1.0 \times 10^{-4}$ – $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> range as shown in Table 1. The plots of  $\log [\text{MnO}_4^-]$  versus time, for different initial concentrations of  $\text{MnO}_4^-$  are found to be linear. ( $r > 0.9964$ ,  $r < 0.021$ ), and the fairly constant  $k_{\text{obs}}$  values indicate that the order with respect to  $[\text{MnO}_4^-]$  was unity. This fact was also confirmed by varying  $[\text{MnO}_4^-]$  which did not show any change in pseudo-first order constants ( $k_{\text{obs}}$ ) values as shown in Table 1.

The substrates, L-leucine and L-isoleucine were varied in the  $1.0 \times 10^{-3}$ – $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> range at 30°C, keeping all other concentrations and the catalyst concentration constant. The rate constant,  $k_{\text{obs}}$  increased with increase in concentration of amino acids, indicating a less than unit order dependence on both the substrates concentration.

## Effect of alkali

The effect of alkali on the reaction was studied at constant amino acids (L-leucine and L-isoleucine) and potassium permanganate concentrations and at a constant ionic strength of 0.50 mol dm<sup>-3</sup> at 30°C. The rate constants increased with the increase in [alkali], as given in Table 1.

## Effect of catalyst

The Palladium(II) concentration was varied over the  $2.0 \times 10^{-7}$ – $2.0 \times 10^{-6}$  mol dm<sup>-3</sup> range. The linearity of plots ( $r > 0.9983$ ,  $\sigma < 0.0341$ ) of  $\log k_{\text{obs}}$  versus  $\log [\text{Pd(II)}]$  with unit slope showed unit order (table 1) dependence on  $[\text{Pd(II)}]$ . Under the conditions used, the uncatalysed reaction rate is negligible compared to the catalysed reaction rate.

## Effect of initially added products

Externally added products such as manganate, ammonium hydroxide and aldehyde did not show any significant effect on the rate of the reaction.

## Effect of ionic strength and dielectric constant

The effect of ionic strength was studied by varying the sodium perchlorate concentration from 0.05 to 0.50 mol dm<sup>-3</sup> at constant permanganate, amino acids, alkali and catalyst concentrations. It was found that the rate constants decreased with increase in concentration of  $\text{NaClO}_4$  and the plot of  $\log k_{\text{obs}}$  versus  $I^{1/2}$  was linear with negative slope. See Figure 2 ( $r > 0.9989$ ,  $r < 0.031$ ). It was found that the rate constants did not change with increase in the dielectric constant of the medium.

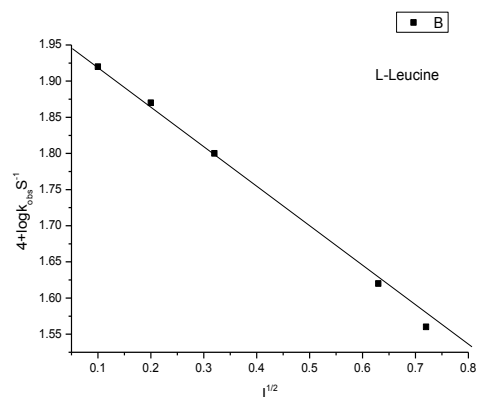
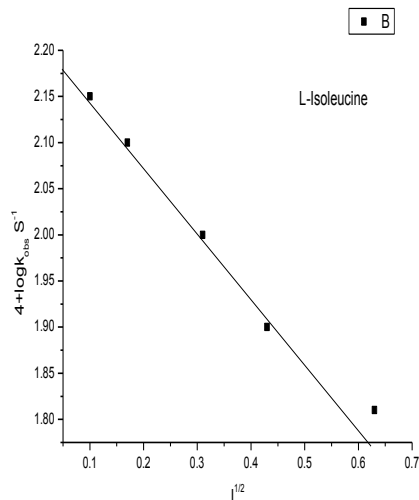


Fig.2 L-Isoleucine

L-Leucine

### Test for free radicals

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 h in an inert atmosphere. On diluting with methanol, a white precipitate formed indicating the intervention of free radicals in the reaction.

### Effect of temperature

The reaction rate was measured at three different temperatures with varying [substrate], keeping other conditions constant. The rate was found to increase with increasing temperature. The rate constants,  $k$  of the slow step of Scheme 1 were obtained from the intercept of the plots of  $[Pd(II)] / k_{obs}$  versus  $1/[L-leu]$  for different temperatures. The energy of activation corresponding to these constants was evaluated from the plot of  $\log k$  versus  $1/T$ , from which the activation parameters were calculated and are given in Table 2.

The thermodynamic quantities of the first step of Scheme 1 can be evaluated as follows. The hydroxyl ion concentration (as in Table 1) was varied at several temperatures, and  $K_1$  values were determined at each temperature. The values for leucine at 293, 298 and 303 K are, 1.1, 1.4 and 1.7 mol dm<sup>-3</sup> respectively, and the values for isoleucine at 293, 298 and 303 K are 3.02, 4.44 and 6.50 mol dm<sup>-3</sup> respectively. The van't Hoff plot was drawn for the variation of  $K_1$  with temperature ( $\log K_1$  versus  $1/T$ ;  $r > 0.9972$ ,  $r < 0.0231$ ). The values of thermodynamic quantities are given in Table 3. A comparison of these values with those values obtained for the slow step shows that the reaction before the rate-determining step is fairly slow in the case of leucine and fast in the case of isoleucine. This is again confirmed by the comparison of  $K_1$  values of leucine and isoleucine.

**Table 1. Effect of variation of [MnO<sub>4</sub><sup>-</sup>], [amino acid], [Pd(II)] and [OH<sup>-</sup>] on [Pd(II)] catalysed oxidation of leucine and L isoleucine by KMnO<sub>4</sub> in aqueous alkaline medium at 30<sup>o</sup>C and I = 0.50 mol dm<sup>-3</sup>**

10 <sup>4</sup> [MnO <sub>4</sub> <sup>-</sup> ] mol dm <sup>-3</sup>	10 <sup>-3</sup> [AA] mol dm <sup>-3</sup>	[OH <sup>-</sup> ] mol dm <sup>-3</sup>	10 <sup>6</sup> [Pd <sup>II</sup> ] mol dm <sup>-3</sup>	10 <sup>2</sup> xk <sub>obs</sub> (s <sup>-1</sup> )			
				Found		calculated	
				Leu	(I-leu)	Leu	(I-leu)
1.0	4.0	0.05	1.0	1.43	0.88	1.33	0.92
2.0	4.0	0.05	1.0	1.38	0.91	1.30	0.93
4.0	4.0	0.05	1.0	1.32	0.89	1.31	0.92
8.0	4.0	0.05	1.0	1.35	0.87	1.32	0.94
10.0	4.0	0.05	1.0	1.38	0.88	1.33	0.93
4.0	1.0	0.05	1.0	0.65	0.47	0.64	0.47
4.0	2.0	0.05	1.0	0.91	0.67	0.95	0.73
4.0	4.0	0.05	1.0	1.32	0.88	1.35	0.93
4.0	8.0	0.05	1.0	1.55	1.15	1.65	1.15
4.0	10.0	0.05	1.0	1.68	1.26	1.73	1.23
4.0	4.0	0.02	1.0	0.88	0.59	0.88	0.68
4.0	4.0	0.04	1.0	1.23	0.82	1.23	0.88
4.0	4.0	0.05	1.0	1.35	0.87	1.31	0.93
4.0	4.0	0.10	1.0	1.59	1.12	1.56	1.12
4.0	4.0	0.20	1.0	1.75	1.25	1.73	1.18
4.0	4.0	0.05	0.2	0.33	0.23	0.28	0.21
4.0	4.0	0.05	0.6	0.87	0.59	0.79	0.62
4.0	4.0	0.05	1.0	1.34	0.92	1.35	0.95
4.0	4.0	0.05	1.5	1.95	1.26	1.93	1.35
4.0	4.0	0.05	2.0	2.43	1.58	2.64	1.65

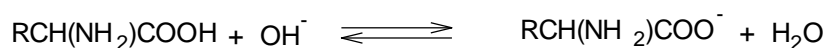
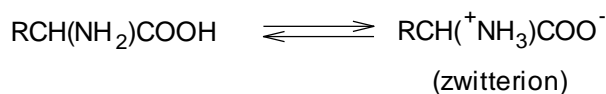
**Table 2. Activation parameters with respect to slow step of Scheme 1**

Activation parameters	Leucine	Isoleucine
$E_a(\text{kJ}^{-1}\text{mol}^{-1})$	$45.5 \pm 4.0$	$42.3 \pm 4.0$
Log A	$15 \pm 2.0$	$12.0 \pm 2.0$
$\Delta H^\ddagger(\text{kJ}^{-1}\text{mol}^{-1})$	$35.5 \pm 3.5$	$32.6 \pm 3.5$
$\Delta S^\ddagger(\text{kJ}^{-1}\text{mol}^{-1})$	$-73 \pm 15$	$-82 \pm 15$
$\Delta G^\ddagger(\text{kJ}^{-1}\text{mol}^{-1})$	$56.4 \pm 3.5$	$56.6 \pm 3.5$

### III DISCUSSION

Permanganate ion,  $\text{MnO}_4^-$ , is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at  $\text{pH} > 12$ , the reduction product of manganese(VII) is stable and further reduction of manganese(VI) might be stopped [12, 13]. Diode array rapid scan spectrophotometric (DARSS) studies have shown that at  $\text{pH} > 12$ , the product of manganese(VII) is manganese(VI) and no further reduction was observed as reported [12, 13] by Simandi et al. However, on prolonged standing, green manganese(VI) is reduced to manganese(IV) under our experimental conditions.

It is known that in aqueous solution, amino acid exists as zwitterionic [27] form whereas in aqueous alkaline medium it exists as the anionic form according to the following equilibria.



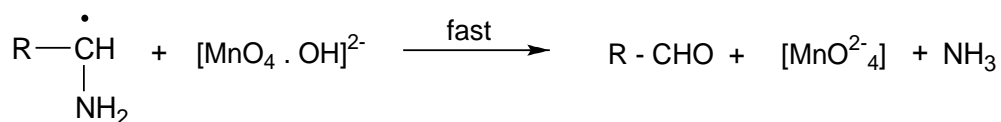
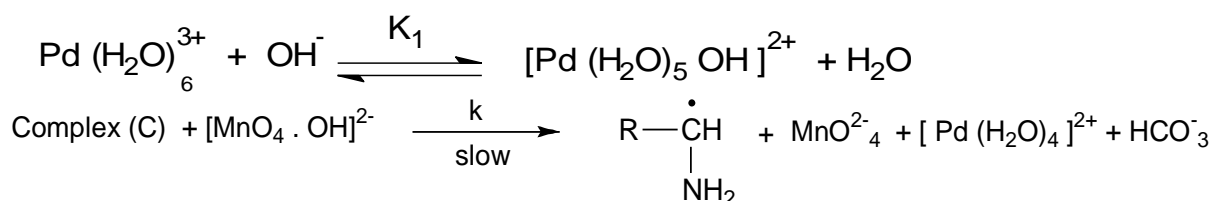
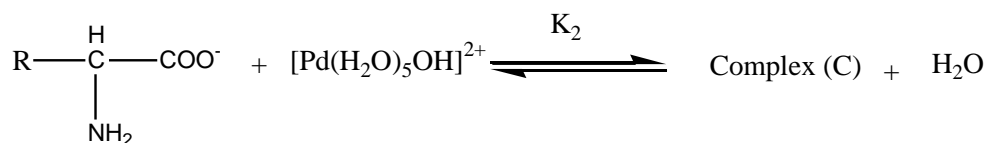
The reaction between permanganate and amino acids under study in alkaline medium has a 2:1 stoichiometry with a first order dependence on both  $[\text{MnO}_4^-]$  and Palladium(II) and less than unit order dependence on both the [alkali] and [amino acid]. No effect of added products such as aldehyde and ammonia was observed. It is interesting to identify the probable Palladium(II) chloride species in alkaline medium. In the present study it is quite probable that the species

$[\text{Pd}(\text{H}_2\text{O})_5\text{OH}]^{2b}$  might assume the general form  $[\text{Pd}(\text{II})(\text{OH})_x]^{3x}$ . The value of  $x$  would always be less than six because there are no definite reports of any hexahydroxy species of Palladium. The remainder of the coordination sphere will be filled by water molecules. Hence under the conditions  $\frac{1}{2}\text{OH}^-$  &  $\frac{1}{2}\text{Pd}(\text{II})$ , Palladium(II) is mostly present [28] as the hydroxylated species,  $[\text{Pd}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ .

Increase in rate with increase in  $[\text{OH}^-]$  indicates the presence of the hydroxylated species of Palladium(II) as a reactive species, which is shown by the following equilibrium in accordance with the earlier work [29].



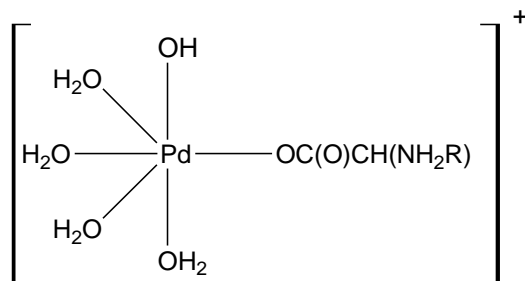
The results suggest the formation of a complex between the amino acid and the hydroxylated Palladium(II) species. Such complex formation between substrate and catalyst has also been observed in earlier work [30]. Evidence is provided by the fractional order found in [amino acid]. The spectral evidence for complex formation between catalyst and substrate was obtained from the u.v.–vis. spectra of the catalyst. And a mixture of catalyst and amino acid in the alkaline medium. A bathochromic shift of 5 nm from 398 to 403 nm is observed for leucine and a bathochromic shift of 5 nm from 386 to 391 nm is observed for isoleucine. The formation of the complex was also proved kinetically by the non-zero intercept of the plot of  $[\text{Pd}(\text{II})]/K_{\text{obs}}$  versus  $1/[\text{amino acid}]$ . The observed modest enthalpy of activation and a relatively low value of the entropy of as well as a higher rate constant for the slow step, indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by the earlier observation [31]. Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of one electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work on the alkaline permanganate oxidation of amino acids [32]. It is also known that permanganate ion in alkaline medium [33] exists as  $(\text{MnO}_4 \text{OH})^{2-}$ . The complex formed further reacts with the alkaline species of permanganate in a rate-determining step, resulting in the formation of a free radical, which again reacts with the alkaline species of permanganate in a subsequent fast step to yield the products. In agreement with the experimental results obtained a mechanism, as set out below, may be envisaged



Scheme 1.

Where R = -CH<sub>2</sub>-CHMe<sub>2</sub> for L-leucine and R = -CH<sub>2</sub>-CHMeEt for L-isoleucine.

The probable structure of the complex C is,



Scheme 1 leads to rate law (2)

$$\text{Rate} = - \frac{d[\text{MnO}_4^-]}{dt}$$

$$= \frac{kK_1K_2[MnO_4.OH]^{2-} [Pd^{II}]_T [OH^-]_T [AA]_T}{\{1 + K_1K_2[Pd^{II}]_T [OH^-]_T\} \{1 + K_1[Pd^{II}]_T\} \{1 + K_1[OH^-]_T + K_1K_2[AA]_T [OH^-]_T\}} \quad (1)$$

The terms  $(1 + K_1K_2[Pd(II)]_T[OH^-]_T)$  and  $(1 + K_1[Pd(II)]_T)$  in the denominator of equation (1) approximate to unity in view of the low concentration of Palladium(II) used. Therefore Equation (1) becomes Equation (2).

$$k_{obs} = \frac{\text{Rate}}{[MnO_4.OH]^{2-}} = \frac{kK_1K_2[Pd^{II}]_T [OH^-]_T [AA]_T}{1 + K_1[OH^-]_T + K_1K_2[AA]_T [OH^-]_T} \quad (2)$$

Further, the Equation (2) can be rearranged to Equation (3) (by omitting the subscript 'T') which is suitable for verification.

$$\frac{Pd^{III}}{K_{obs}} = \frac{1}{kK_1K_2[OH^-][AA]} + \frac{1}{kK_2[AA]} + \frac{1}{k} \quad (3)$$

According to Equation (3), the plots of  $[Pd(II)]/k_{obs}$  versus  $1/[amino\ acid]$  and  $[Pd(II)]/k_{obs}$  versus  $1/[OH^-]$  are linear with non-zero intercepts which are verified in Figures 3 and 4. From slopes and intercepts of such plots  $k$ ,  $K_1$  and  $K_2$  values are obtained at 30 LC as  $1.96 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1}$ , 1.7 and  $5.6 \cdot 10^3 \text{ mol dm}^{-3}$  respectively for leucine and  $1.39 \times 10^4 \text{ mol dm}^{-3} \text{ s}^{-1}$ , 6.5 and  $1.7 \times 10^3 \text{ mol dm}^{-3}$  for isoleucine. Using these values the calculated rate constants are in reasonable agreement with the experimental values as given in Table 1. The  $K_1$  value is in the neighborhoods with the earlier work [34].

The decrease in the reaction rate with increase in the ionic strength qualitatively explains the reaction between two oppositely charged ions as seen in Scheme 1. The moderate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are both favorable for electron transfer reactions. Negative  $\Delta S^\ddagger$  values for radical reactions have been ascribed to the nature of electron pairing and unpairing reactions and to the loss of degrees of freedom by formation of a rigid transition state [35]

The activation parameters for the oxidation of some amino acids by  $MnO_4^-$  are summarised in Table 4. The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by changes in the enthalpy and/or entropy of activation. Changes in rate are caused by changes in both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , but these quantities

Vary extensively in a parallel fashion. A plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  is linear according to equation,  $\Delta H^\ddagger = \beta \Delta S^\ddagger + \text{constant}$

$\beta$  is called the isokinetic temperature; it has been asserted that apparently linear correlation of  $\Delta H^\ddagger$  with  $\Delta S^\ddagger$  are sometimes misleading and the evaluation of  $b$  by means of the above equation lacks statistical validity [36]. Exner [37] advocates an alternative method for the treatment of experimental data. If the rates of the several reactions in a series have been measured at two temperatures and  $\log k_2$  (at  $T_2$ ) is linearly related to  $\log k_1$  (at  $T_1$ ) i.e.  $\log k_2 = \frac{1}{4} a + b \log k_1$ , he proposes that  $\beta$  can be evaluated from the equation,  $\beta = T_1 T_2 (b-1) / T_2 \cdot b - 1$ .

We have calculated the isokinetic temperature as 217 K by plotting  $\log k_1$  at 298 K versus  $\log k_2$  at 303 K (Figure 5,  $r > 0.9987$ ,  $r < 0.023$ ). The value of  $b$  (217 K) is much lower than the experimental temperature (303 K). This indicates that the rate is being governed by the entropy of activation [38]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested. Among the two amino acids leucine and isoleucine, the former is found to be oxidized faster than the latter. This is due to the presence of the branched chain, making molecules less reactive because of the increase in the steric crowding.

The activation parameters are compared with the uncatalysed reaction [17]. The difference in the activation parameters for the catalysed and uncatalysed reactions, explains the catalytic effect on the reaction. The catalyst alters the reaction path by lowering the energy of activation, i.e. it provides an alternative pathway with lower activation parameters for the reaction.

## IV CONCLUSION

It is interesting that the oxidant species  $[\text{MnO}_4^-]$  requires  $\text{pH} > 12$ , below which the system becomes disturbed  $\text{pH} > 12$ , below which the system becomes disturbed and the reaction proceeds further to give a reduced oxidation product as manganese (IV), which slowly develops a yellow turbidity. Hence, it becomes apparent that, in carrying out this reaction, the role of  $\text{pH}$  in the reaction medium is crucial. Palladium (II) is found to be an efficient catalyst, (especially in alkaline medium) which catalyses the reaction with a measurable velocity at a concentration of  $10^{-6} \text{ mol dm}^{-3}$ . It is also note-worthy that, under the conditions studied, the reaction occurs in two successive one-electron reduction (Scheme 1) steps rather than a two-electron reduction in a single step.

## Appendix

According to scheme 1

$$\text{Rate} = K [\text{MnO}_4 \cdot \text{OH}]^{2-} \times C$$

$$= k K_1 K_2 [\text{AA}]_f [\text{Pd}^{\text{II}}]_f [\text{MnO}_4 \cdot \text{OH}]^{2-} [\text{OH}^-]_f \quad (\text{A1}) \quad \text{total concentration for amino acid is given by}$$

$$\begin{aligned}
 [AA]_T &= [AA]_f + [C] \\
 &= [AA]_f + K_2[AA]_f [Pd(OH)]^{2+} \\
 &= [AA]_f + K_1 K_2 [AA]_f [Pd^{II}] [OH^-]_f \\
 &= [AA]_f \{ 1 + K_1 K_2 [Pd^{II}] [OH^-]_f \}
 \end{aligned}$$

Therefore,  $[AA]_f = \frac{[AA]_T}{1 + K_1 K_2 [Pd^{II}]_f [OH^-]_f}$  A1a

Similarly,  $[OH^-]_f = \frac{[OH^-]_T}{1 + K_1 [Pd^{II}]_f}$  A1b

and  $[Pd^{II}]_f = \frac{[Pd^{II}]_T}{1 + K_1 [OH^-]_f + K_1 K_2 [AA]_f [OH^-]_f}$  A1c

Substituting equations (A1a)-(A1c) in equation (A1), we get

$$\begin{aligned}
 \text{Rate} &= - \frac{d[MnO_4^-]}{dt} \\
 &= \frac{k K_1 K_2 [MnO_4 \cdot OH]^{2-} [Pd^{II}]_T [OH^-]_T [AA]_T}{\{ 1 + K_1 K_2 [Pd^{II}]_T [OH^-]_T \} \{ 1 + K_1 [Pd^{II}]_T \} \{ 1 + K_1 [OH^-]_T + K_1 K_2 [AA]_T [OH^-]_T \}} \quad (A1d)
 \end{aligned}$$

The terms  $( 1 + K_1 K_2 [Pd^{II}]_T [OH^-]_T )$  and  $( 1 + K_1 [Pd^{II}]_T )$  in the denominator of Equation (A 1 d) approximate to unity in view of low concentration of Pd(II) used. Therefore Equation (A 1 d) becomes equation (A<sub>2</sub>).

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{MnO}_4 \cdot \text{OH}]^{2-}} = \frac{kK_1K_2[\text{Pd}^{\text{II}}]_{\text{T}} [\text{OH}^-]_{\text{T}} [\text{AA}]_{\text{T}}}{1 + K_1[\text{OH}^-]_{\text{T}} + K_1K_2[\text{AA}]_{\text{T}} [\text{OH}^-]_{\text{T}}} \quad (\text{A2})$$

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