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Kinetics and Mechanism of Palladium (II) Catalysed Oxidation of Valine by N- Bromosuccinimide in Perchloric Acid Medium



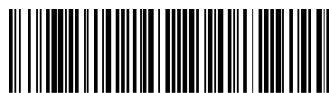
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ABSTRACT

The kinetics of Pd(II) catalysed oxidation of L-valine by N-bromosuccinimide(NBS) was studied in the presence of perchloric acid and Hg(II) at 35°C. The rate of reaction decreased with increase in perchloric acid concentration. The reaction shows first order kinetics with respect to NBS and Pd(II). The first order kinetics with respect to amino acid obtained at its lower concentration changes to zero order at its higher concentration. Variation in [Hg(II)], [NHS], [Cl⁻], ionic strength has no effect on the rate of reaction. NBS itself and [PdCl₄]²⁻ have been postulated as the reactive species of NBS and Pd(II) chloride in acidic medium respectively. The main oxidation products of the reaction have been identified as isobutaldehyde and ammonia. A mechanism supported by kinetic and spectrophotometric data has been proposed. Various activation parameters have been calculated and on the basis of these parameters, a suitable explanation of the reaction mechanism has been given.

INTRODUCTION

Oxidation reactions of α –amino acid are one of the most relevant biochemical reactions because such reactions serve as models for protein oxidations¹⁻³. A number of uncatalyzed⁴⁻¹⁰ and catalyzed¹¹⁻¹⁶ kinetic studies have been reported on the oxidation of amino acids by different oxidants. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants¹⁷⁻¹⁹ such as N Bromosuccinimide, diperiodatoargentate(III), hexacyanoferrate (III) etc. These oxidation reactions display diverse reaction mechanisms, oxidative deamination and decarboxylation. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant.

N-Bromosuccinimide(NBS) has been used as a brominating and oxidizing agent in synthetic organic chemistry as well as analytical reagent especially in acid medium²⁰⁻²⁶. Though there are several reports²⁷⁻²⁹ on the oxidation of amino acids by N-halo compounds, no information is available where the use of chloro complex of Pd(II) as catalyst has been made in the oxidation of amino acids by N-bromosuccinimide in acidic medium. Pd(II) is known as a catalyst for many reactions³⁰⁻³⁴ but the nature of its active form in such reactions remains obscure and a little is known about the mechanism of reactions involving Pd(II) as a homogenous catalyst.

The above literature survey shows that oxidation of amino acid have been studied using various oxidants but catalyzed oxidation using transition metals as catalyst have not been studied in detail by using oxidants like N-bromosuccinimide. This prompted us to undertake systematic study of kinetics of Pd(II) catalyzed oxidation of valine by acidic solution of NBS with a view to formulate the mechanistic steps and to know the active form of Pd(II) and NBS in acidic medium.

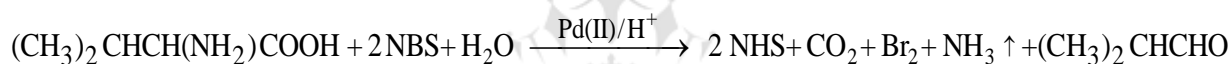
MATERIALS AND METHODS

An aqueous solution of NBS (E.Merck) was prepared afresh by dissolving a weighed amount in doubly distilled water. The solution was standardized iodometrically against standard solution of sodium thiosulphate using starch as an indicator. The reaction mixture was prepared in a black- coated vessel to avoid photochemical deterioration. A Pd(II) stock solution was prepared by dissolving a known weight of palladium chloride (Johnson Matthey) in 0.20 mol dm^{-3} hydrochloric acid and stored in black bottle to prevent photochemical decomposition. HClO_4 (E.Merck) was used as a source of hydrogen ions.

NaClO₄ (E.Merck) was used to maintain required ionic strength. Aqueous solution of amino acids was prepared by dissolving a weighed amount in doubly distilled water. A standard solution of mercuric acetate (E.Merck) was acidified with 20% acetic acid. All other reagents used were of analytical grade and highest available purity.

An electrically operated thermostated water bath was used to maintain the desired temperature to within $\pm 10^{\circ}\text{C}$. Requisite volumes of all reagents except NBS were introduced into reaction vessel and equilibrated at 35°C . A measured volume of NBS solution already equilibrated separately at the same temperature was rapidly poured into the reaction vessel. The progress of the reaction was followed by measuring the unconsumed NBS iodometrically using starch as indicator.

Reaction mixture containing an excess [NBS] over [amino acid] used here in different ratios were allowed to equilibrate at 35°C for 48 hours and then analysed. Estimation of unconsumed NBS indicated that two mole of NBS were consumed to oxidise one mole of valine. Accordingly, the following stoichiometric equations may be written as-



The main reaction products were succinimide, iso-butylaldehyde, ammonia and CO₂. Liberated ammonia was identified by Nessler's reagent where a brownish colour was observed indicating a deamination reaction³⁵. CO₂ was identified by freshly prepared lime water and the solution turned milky, indicating a decarboxylation reaction³⁶.

Iso-butylaldehyde was confirmed by the IR spectrum of the corresponding hydrazone. (Fig.1). The reaction mixture was treated with acidified 2,4 - DNP solution which yielded a hydrazone. The IR spectrum of the hydrazone was superimposed on the spectrum of a corresponding hydrazone of a standard sample of iso-butylaldehyde. The IR value for -CO group stretching is 1617 cm^{-1} and for the two -C-H stretchings one at 2970 cm^{-1} and the other at 2871 cm^{-1} . Further, aldehyde group was confirmed with qualitative test such as Tollen's reagent³⁷. The product has also been confirmed by UV-Vis spectra (Fig.2). The reaction was carried out and spectra taken at different time interval. The product appears near 320 nm.

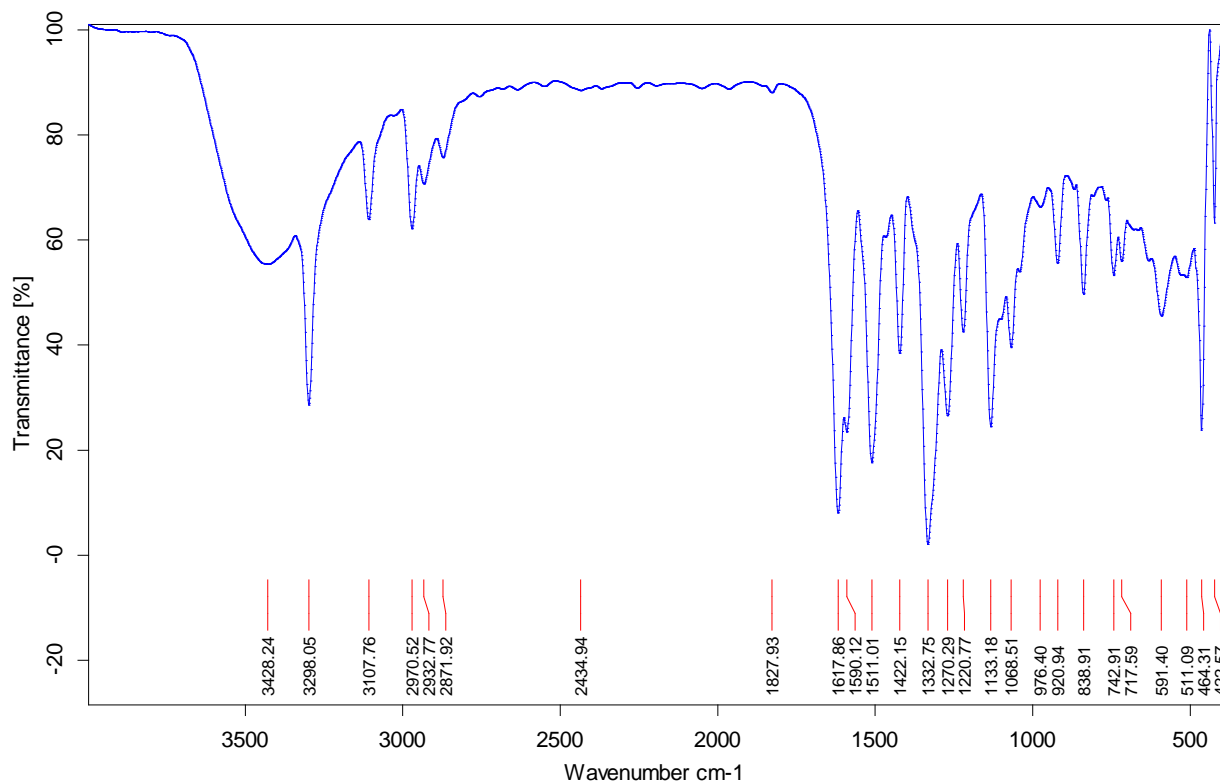


Fig. 1- IR Spectra of hydrazone of Iso-butylaldehyde

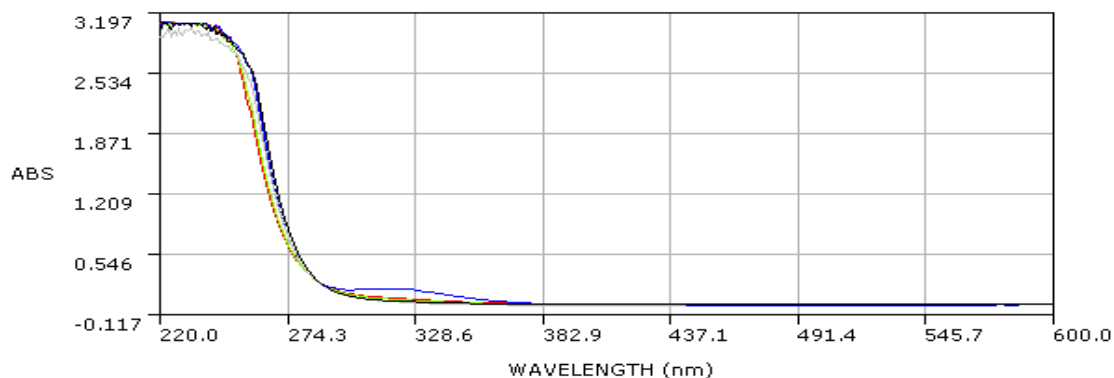


Fig. 2-UV-spectra of NBS in acid medium and [Pd(II).NBS] complex

Kinetics of oxidation of valine using chloro complex of Pd(II) as homogeneous catalyst in acidic medium have been investigated at 35°C. The rate of reaction of each kinetic run was determined by the slope of the linear plot of log [NBS] vs time. The value of pseudo first order rate constant

$$k_{\text{obs}} = \frac{-d[\text{NBS}] / dt}{[\text{NBS}]}$$

RESULTS AND DISCUSSION

The kinetics of oxidation of valine was studied under pseudo first order conditions, keeping the concentration of valine in a large excess over that of [NBS]. The reaction was studied at different initial [NBS] and at fixed concentration of all other reagents. Increase of concentration of NBS yields constant pseudo first order rate constants confirming the first order dependence on NBS (Table 1). When $\log [\text{NBS}]_t$ was plotted against time, very good linear plots were obtained which also proves first order with respect to [NBS] (Fig. 3). At constant [NBS], $[\text{H}^+]$, [Pd (II)] and mercuric acetate, kinetic runs were carried out with different initial concentration of valine at three temperatures 30°C, 35°C and 40°C respectively. The plot of $\log k_{\text{obs}}$ vs $\log [\text{val}]$ was a straight line with fractional slope. The results show first order dependence of the reaction on amino acid at low concentration, which shifts towards zero order at its higher concentration. The formation of the complex was kinetically proven by Michaelis-Menten plot that is non-zero intercept of the plot of $1/\text{rate}$ vs $1/[\text{val}]$. The complex formation between oxidant and reductant was also reported in literature³⁸. Keeping concentration of all reactants fixed, perchloric acid concentration was varied and kinetic runs were taken at fixed ionic strength ($I = 0.5 \text{ mol dm}^{-3}$). The result showed a negative effect with respect to $[\text{H}^+]$ (Fig. 4). The plot of $\log k_{\text{obs}}$ vs $\log [\text{H}^+]$

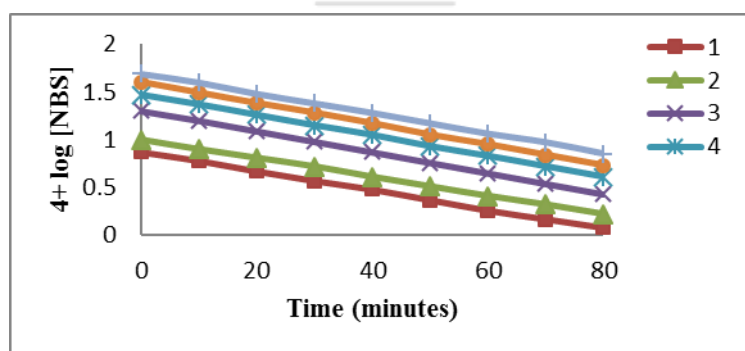


Fig. 3-Pseudo first order plots for the variation of NBS

$$[\text{Val}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3},$$

$$[\text{H}^+] = .10 \text{ mol dm}^{-3},$$

$$[\text{Pd(II)}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3},$$

$$I = .25 \text{ mol dm}^{-3}, \text{ Temp.} =$$

$$[\text{NBS}] = (1) 0.75 \times 10^{-3} \text{ mol dm}^{-3},$$

$$(2) 1.0 \times 10^{-3} \text{ mol dm}^{-3},$$

$$(3) 2.0 \times 10^{-3} \text{ mol dm}^{-3},$$

$$(4) 3.0 \times 10^{-3} \text{ mol dm}^{-3},$$

$$(5) 4.0 \times 10^{-3} \text{ mol dm}^{-3},$$

$$(6) 5.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Table-1: Effect of variation of [NBS], [Val], [Pd(II)] and [H⁺] on the palladium(II) catalysed oxidation of valine by NBS at 35°C

10 ³ [NBS] mol dm ⁻³	10 ² [Val] mol dm ⁻³	10 ⁵ [Pd(II)] mol dm ⁻³	[H ⁺] mol dm ⁻³	10 ⁴ (K _{obs}) sec ⁻¹
0.75	2.0	2.0	0.10	3.76
1.0	2.0	2.0	0.10	3.72
2.0	2.0	2.0	0.10	3.74
3.0	2.0	2.0	0.10	3.74
4.0	2.0	2.0	0.10	3.76
5.0	2.0	2.0	0.10	3.72
2.0	0.50	2.0	0.10	1.54
2.0	0.70	2.0	0.10	1.90
2.0	1.0	2.0	0.10	2.50
2.0	2.0	2.0	0.10	3.74
2.0	3.0	2.0	0.10	4.10
2.0	4.0	2.0	0.10	4.25
2.0	5.0	2.0	0.10	4.31
2.0	2.0	0.50	0.10	0.99
2.0	2.0	1.0	0.10	1.92
2.0	2.0	2.0	0.10	3.74
2.0	2.0	3.0	0.10	5.66
2.0	2.0	4.0	0.10	7.61
2.0	2.0	5.0	0.10	9.40
2.0	2.0	2.0	0.05	4.75
2.0	2.0	2.0	0.075	4.25
2.0	2.0	2.0	0.10	3.74
2.0	2.0	2.0	0.20	2.25
2.0	2.0	2.0	0.30	1.25
2.0	2.0	2.0	0.40	0.58
2.0	2.0	2.0	0.50	0.50

is linear and yields a fractional slope. First order kinetics with respect to [Pd(II)] is evident from the observed values of k_{obs} which show increase in the same proportion in which the concentration of [Pd(II)] is increased (Fig.5). Negligible effects of [Hg(II)], [Cl⁻], [succinimide] and ionic strength on the rate have been observed. The effect of temperature on the rate of reaction was studied in the range 303-313 K and various activation parameters computed. $E_a = 26.80 \text{ KJ mol}^{-1}$, $\Delta H^\ddagger = 24.24 \text{ KJ mol}^{-1}$, $\Delta S^\ddagger = -147.20 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger = 69.57 \text{ KJ mol}^{-1}$

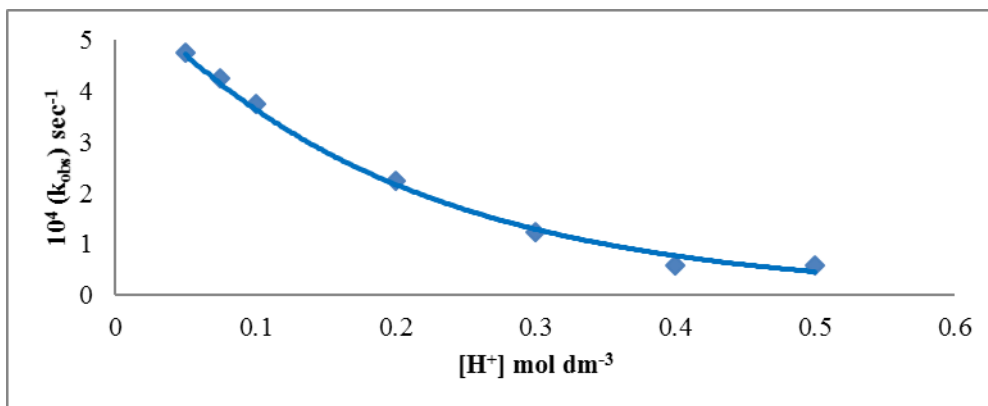


Fig. 4- Variation of hydrogen ion

[NBS] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$; [Val] = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$

[Pd(II)] = $2.0 \times 10^{-5} \text{ mol dm}^{-3}$; I = 0.25 mol dm^{-3} ; Temp. = 35°C

is linear and yields a fractional slope. First order kinetics with respect to [Pd(II)] is evident from the observed values of k_{obs} which show increase in the same proportion in which the concentration of [Pd(II)] is increased (Fig.5). Negligible effects of [Hg(II)], [Cl⁻], [succinimide] and ionic strength on the rate have been observed. The effect of temperature on the rate of reaction was studied in the range 303-313 K and various activation parameters computed. $E_a = 26.80 \text{ KJ mol}^{-1}$, $\Delta H^\ddagger = 24.24 \text{ KJ mol}^{-1}$, $\Delta S^\ddagger = -147.20 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger = 69.57 \text{ KJ mol}^{-1}$.

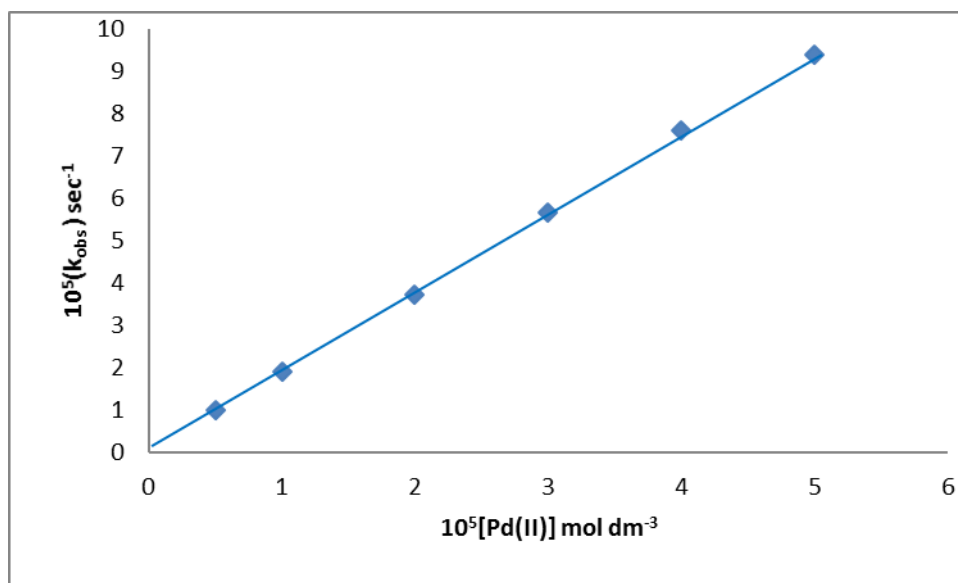


Fig. 5- Variation of palladium(II)

$[\text{NBS}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Val}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$;

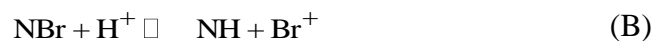
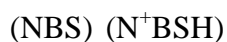
$I = 0.25 \text{ mol dm}^{-3}$; Temp. = 35°C

Mechanism

Before formulating the reaction mechanism for the reaction under investigation, it is necessary to ascertain the reactive species of NBS, Pd(II) chloride and amino acid in acidic medium

Reactive species of NBS

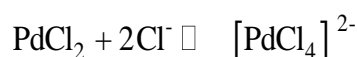
It is reported that the nature of halogen atom, the groups attached to the nitrogen, pH of the medium and also the reaction conditions play a very important role to know the actual reactive species of NBS. In the present study, the pH of the reaction was maintained between 2 to 3. In acidic media, NBS is known to exist in three different forms³⁹⁻⁴¹. NBS itself, Br^+ or N^+BSH in the following way



The observed kinetic results show negligible effect of succinimide which rules out the possibility of Br^+ being the reaction species. The negative effect of acid on the reaction rate rules out N^+BSH as the reactive species. Thus NBS species remains as the reactive species of NBS. This conclusion finds support from UV-VIS spectra obtained for various solutions of NBS with different $[\text{H}^+]$ where a single peak was obtained at 220 nm.

Reactive species Pd(II) chloride in acidic medium

In most of studies using Pd(II) chloride as a homogeneous catalyst, it has been employed in the form of Pd(II). Pd(II) chloride is rather insoluble in aqueous solution but soluble in HCl and exists as⁴²⁻⁴³ $[\text{PdCl}_4]^{2-}$ according to the equilibrium⁴⁴.



Such species using Pd(II) chloride has also been reported in the oxidation of amino acids by Cerium(IV)⁴⁵, Chloramine-T⁴⁶, N-bromophthalimide⁴⁷, acid bromate⁴⁸ and some sugars by N-bromosuccinimide⁴⁹ and N-bromoacetamide⁵⁰ and oxidation of EDTA by NBS⁵¹.

Reactive species amino acid in acidic medium

The chemistry of amino acids consist transformation a functional group present in the molecule. There is high reactivity of the functional groups relative to inertness of the hydrocarbon chain. The amino acid is known to exist in the following equilibrium in aqueous solution.

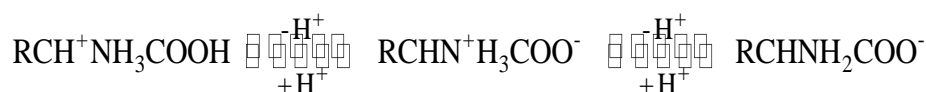


Amino acid (S)

Anion (S⁻)

Zwitterion (S⁰)

The dissociation of amino acid depends upon the pH of the solution. In strongly acidic or strongly alkaline solution, amino acid dissociates as shown in below:



Cation (S⁺ H)

Zwitterion (S⁰)

Under the experimental conditions, the concentration of anion-form will be very low and the possible reactive reducing species may either be the cationic-form, zwitterionic form of

amino acid or simple amino acid. If S^+H is the main reactive species then H^+ ion should show first order dependence but our results are contrary to it so the only possible active species controlling the rate of oxidation seems to be valine itself.

Various complexes formed during the studied reactions

To ascertain the formation of possible complex or complexes during the course of reaction, spectra were obtained by using systronics UV-VIS Spectrophotometer 2203 spectra for NBS solution with 2 different concentration of $[H^+]$ such as 0.1 and 0.5. It is evident from the spectra that with the increase in concentration of hydrogen ion there is decrease in the absorbance from 2.724 to 2.616. This supports the inverse dependence of hydrogen ion. UV-Vis spectra of NBS and H^+ solutions with three different concentration of Pd (II) chloride shows an increase in absorption from 2.54, 2.71, 2.90. This confirms the formation of complex(a) formed through equilibrium between $[PdCl_4]$ and a NBS molecule which shifts towards the right with more and more formation of $[PdCl_4.NBS]^{2-}$ complex which is the sole factor for the increase in absorbance $NBS + [PdCl_4]^{2-} \rightleftharpoons [PdCl_4.NBS]^{2-}$

Further, when the spectrum of NBS, H^+ and Pd(II) chloride solution was compared with the spectra of NBS, H^+ and Pd(II) chloride with three different concentration of valine, an increase in absorbance from 2.48 to 2.60 and 2.65 was noted. This indicate the formation of unstable activated complex $[NBS.PdCl_4.NH_3CHCH(CH_3)_2COOH]$.

Further, the spectra of the reaction mixture at different time interval was studied at $35^\circ C$, NBS concentration decreased gradually with time (Fig.6) and there is a sharp decrease in concentration with the product formation when the catalyst concentration was increased to 5×10^{-4} indicating the fast completion of the solution with the increase in catalyst concentration.

The possibility of formation of 1:1 complex between NBS and $[PdCl_4]^{2-}$ was ascertained by Job's plot^(52,53) where $1/\Delta A$ values were plotted against $1/(PdCl_4)^{2-}$ in the oxidation of valine. A straight was obtained with positive intercept on y-axis which proves formation of 1:1 complex.

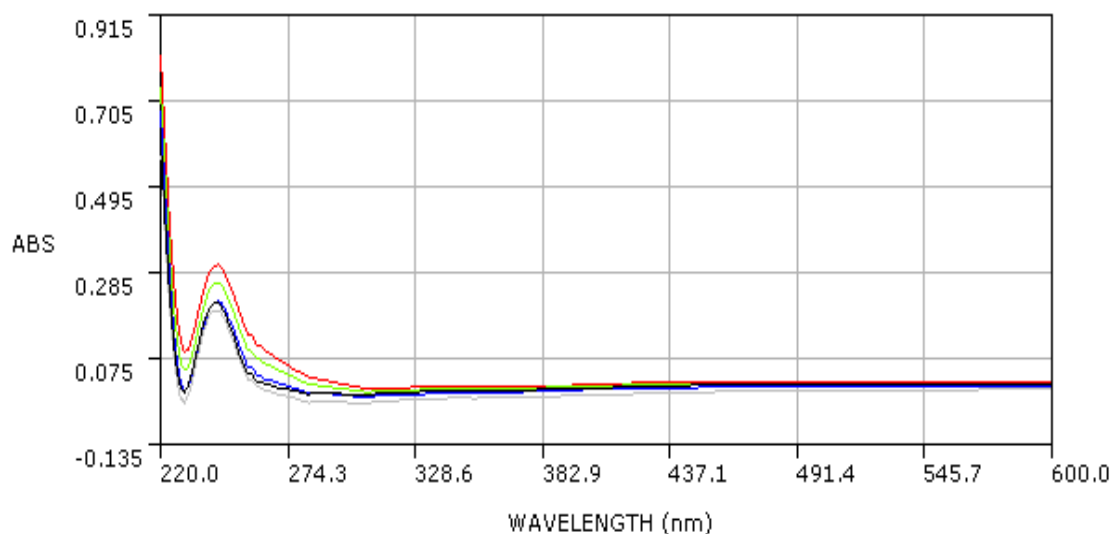
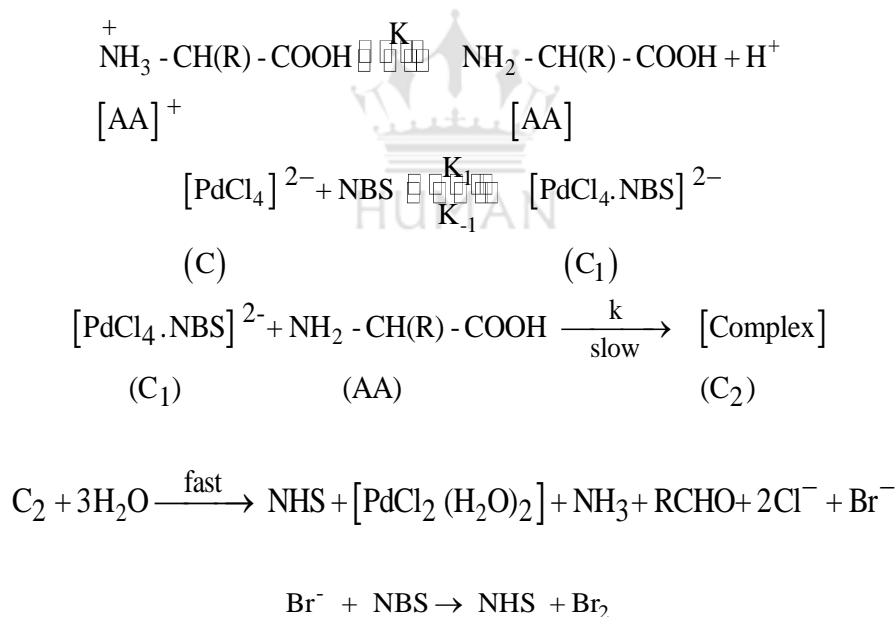


Fig. 6- Spectra of the reaction mixture at time interval

On the basis of above spectral evidences and kinetic results, a probable reaction mechanism has been proposed for Pd(II) catalysed oxidation valine by NBS in acidic medium.



Scheme-1

Since all the kinetic studies are conducted in the presence of mercuric acetate, the liberated Br₂ during the course of reaction can be removed in the form of HgBr₄²⁻ or HgBr₂ complexes because Hg(OAc)₂ acts as a scavenger for Br⁻ formed in the reaction.

$$\text{rate} = \frac{-d[\text{NBS}]}{dt} = 2k[\text{C}_1][\text{AA}] \quad \text{----- (1)}$$

On applying the law of chemical equilibrium, we get

$$K = \frac{[AA][H^+]}{[AA]^+}$$

$$\text{or } [AA]^+ = \frac{[AA][H^+]}{K} \quad \dots\dots(2)$$

On applying steady-state approximation to $[C_1]$, we have

$$\frac{d[C_1]}{dt} = K_1[NBS][C] - K_{-1}[C_1] - k[C_1][AA] = 0$$

$$\text{or } K_1[NBS][C] = K_{-1}[C_1] + k[C_1][AA]$$

$$= [C_1] [(K_{-1} + k[AA])]$$

$$\text{or } C_1 = \frac{K_1[NBS][C]}{K_{-1} + k[AA]} \quad \dots\dots(3)$$

Substituting the value of $[C_1]$ from Eq. (3) to Eq. (1) we get Eq. (4).

$$\text{rate} = \frac{-d[NBS]}{dt} = \frac{2kK_1[NBS][C][AA]}{K_{-1} + k[AA]} \quad \dots\dots (4)$$

The total concentration of Pd (II) i.e. $[Pd(II)]_T$ at any time in the reaction can be given by

$$[Pd(II)]_T = [C] + [C_1] \quad \dots\dots (5)$$

In reaction $C \gg C_1$, So concentration of $[C]$ can be taken as equal to total concentration of

$[Pd(II)]$. i.e. $[Pd(II)]_T$. Thus Eq. (4) can be written as:

$$\frac{-d[NBS]}{dt} = \frac{2kK_1[NBS][Pd(II)]_T[AA]}{K_{-1} + k[AA]} \quad \dots\dots (6)$$

According to scheme, the total concentration of amino acid $[AA]_T$ can be given as

$$[AA]_T = [AA] + [AA]^+ \quad \dots\dots(7)$$

Substituting the value of $[AA]^+$ from Eq. (2) to Eq. (7).

$$[AA]_T = [AA] + \frac{[AA][H^+]}{K}$$

$$[AA]_T = [AA] \frac{K + [H^+]}{K}$$

$$\text{or } [AA] = \frac{K + [AA]_T}{K + [H^+]} \dots\dots\dots(8)$$

Substituting [AA] from Eq. (8) to Eq. (6).

$$\text{rate} = \frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T [AA]_T}{K_{-1}[K + (H^+)] + kK[AA]_T}$$

$$\text{rate} = \frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T [AA]_T}{KK_{-1} + K_{-1}[H^+] + kK[AA]_T} \dots\dots (9)$$

$$\text{or rate} = \frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T [AA]_T}{K_{-1}[H^+] + K [K_{-1} + k [AA]_T]} \dots\dots(10)$$

Under reaction conditions, the $k [AA]_T \gg K_{-1}$, so Eq. (10) changes into Eq. (11).

$$\frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T [AA]_T}{K_{-1}[H^+] + kK[AA]_T} \dots\dots\dots (11)$$

Equation (11) clearly confirms our experiment results i.e. first order with respect to [NBS] [Pd(II)]_T and [AA]_T at lower concentration of amino acid as well as inverse order with respect to [H⁺].

$$k_{obs} = \frac{-d[NBS] / dt}{[NBS]}$$

$$k_{obs} = \frac{2kKK_1 [Pd(II)]_T [AA]_T}{K_{-1} [H^+] + kK [AA]_T} \dots\dots\dots (12)$$

$$k' = \frac{2kKK_1 [(AA)_T]}{K_{-1} [H^+] + kK [(AA)_T]} \dots\dots\dots (13)$$

Where k_{obs} is the first order rate constant and k' is the second order rate constant.

A plot of $[k']^{-1}$ v/s $[AA]_T^{-1}$ was made from equation (13) and a straight line with non zero intercept (Fig. 7) was obtained yielding the value of K_1 to be 12.5×10^{-4} , 14.7×10^{-4} 17.2×10^{-4} mol dm⁻³ sec at 30°C, 35°C and 40°C respectively. The thermodynamic quantities were evaluated from the plot of log K_1 v/s $1/T$ which were $E_a = 24.12$ KJ mol⁻¹, $\Delta H^\ddagger = 21.56$ KJ mol⁻¹, $\Delta S^\ddagger = -144.50$ J K⁻¹ mol⁻¹ and $\Delta G^\ddagger = 66.06$ KJ mol⁻¹. The kinetic data shows the increasing rate

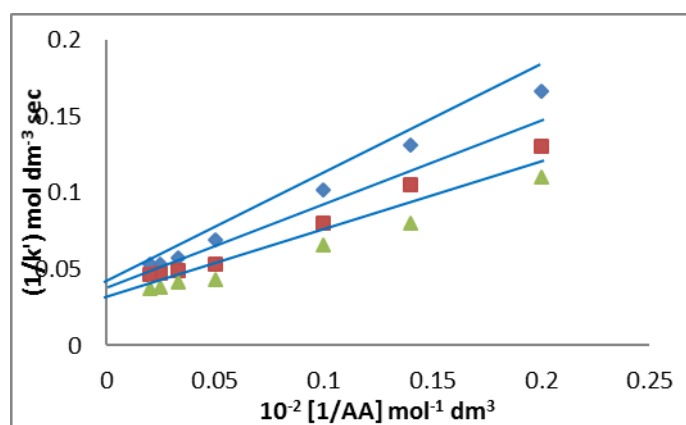


Fig.7- Variation of valine at three different temperatures

$[NBS] = 2.0 \times 10^{-3}$ mol dm⁻³; $[H^+] = .10$ mol dm⁻³

$[Pd(II)] = 2.0 \times 10^{-5}$ mol dm⁻³; $I = 0.25$ mol dm⁻³; Temp. (♦) 30°C, (■) 35°C and (▲) 40°C

of reaction on increasing temperature. The fairly high value of negative ΔS^\ddagger suggest the formation of more ordered activation complex whereas the high positive value of the free energy of activation (ΔG^\ddagger) and enthalpy of activation (ΔH^\ddagger) indicate that the transition state is highly solvated

The catalyst Pd(II) alters the path of the reaction by lowering the energy barrier i.e. it provides an alternative pathway which lowers activation parameters for the reaction. K increase with increase in temperature indicating the reaction is endothermic which is consistent with $\Delta H > 0$. The moderate value of ΔH and ΔS favours electron transfer process.

It is known fact⁵⁵ that the reaction between ions of opposite charge, there is generally an increase in entropy in going from reactant to activated complexes and for ions of like charges, there is entropy decrease.

CONCLUSION

From the above study, we concluded that the NBS oxidation of valine in perchloric acid medium has the stoichiometry 2:1 in oxidant to reductant. The reaction is very slow at room temperature but the reaction occurs in measurable quantities at 35°C in the presence of Pd(II) catalyst. The order w.r.t. to oxidant and catalyst is one and fractional order is seen with the substrate. Inverse order is found in the case of hydrogen ions. The reactive species are valine, NBS, PdCl₄²⁻. The decomposition of complex in the slow step followed by fast step to give the products. The derived mechanism is consistent with all experimental results.

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