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Kinetics and Mechanism of Pd(II)-Catalyzed Oxidation of L-Proline by N-bromoacetamide in Perchloric Acid Medium

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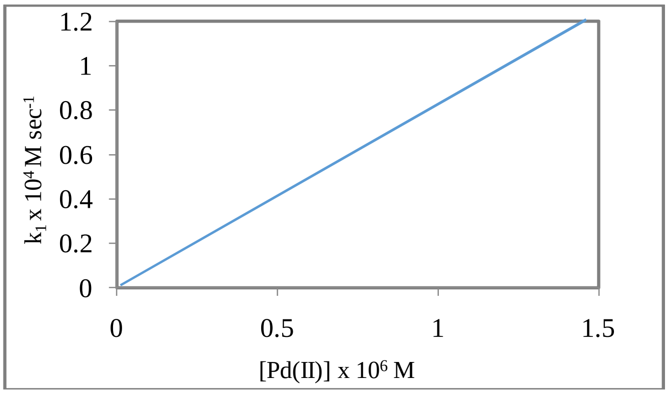
ABSTRACT

Kinetic study of oxidation of proline, a biologically active organic compound, by N- bromoacetamide (NBA) using Pd(II) as homogeneous catalyst in acidic medium have been made at 35°C± 0.1°C . The kinetic results shows first-order kinetics with respect to [NBA], [Proline] and [Pd(II)] throughout their variations. Inverse fractional order with respect to $[H^+]$ *was observed. Variations of mercuric acetate, acetamide (NHA),* $[Cl^-]$*, ionic strength (μ) and dielectric constant (D) show nil effects on rate of the reaction. Further increase in temperature markedly increased the reaction velocity. On the basis of observed kinetic data proline and NBA as such and* $[PdCl_4]^{2-}$ *have been reported as the reactive species of proline, NBA and Pd(II) chloride respectively in acidic medium. Kinetic results and proposed mechanism are well supported by spectrophotometric evidences.*

Graphical Abstract



Plot between $k1$ and [Pd(II)] at 35°C.

Keywords: Bromoacetamide, Mechanism, Pd(II)chloride, Perchloric acid medium, Proline.

INTRODUCTION

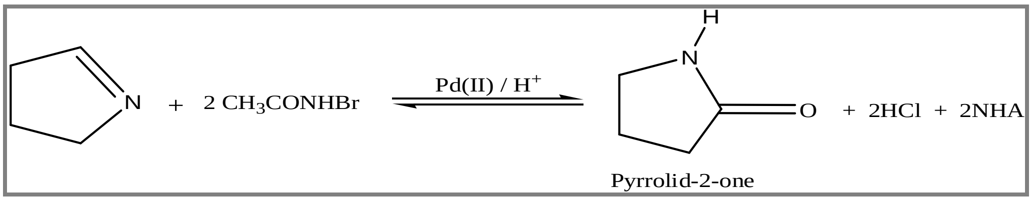
Amino acids are the final class of biomolecules whose oxidation makes a significant contribution towards generation of metabolic energy. Oxidation of amino acid has been carried out in acidic as well as alkaline medium by different oxidants using transition metal ions [**1, 2**] as homogeneous catalyst. The generation and reactivity of N-halo compounds and their importance in biological systems have been reviewed [**3, 4**]. The reactivity of amino acid with brominating agents has been known for some time and reaction with N-bromoacetamide has been used as a method for decarboxylation [**5, 6**].The species responsible for such oxidizing character may be different depending on the pH of the medium. Transition metals are convenient for the coordination of amino acids[**7, 8**]. In recent years transition metal ions such as osmium, ruthenium and irridium have been applied in the oxidation of several redox processes [**9-11**]. Palladium (II) chloride as a non toxic and homogeneous catalyst in the oxidation of organic compounds by acidic solution of NBS [**12, 13**] and NBA [**14-17**] are available in literature. The main objective of the present investigation is to elucidate suitable mechanism and to put forward a rate law consistent with experimental data.

MATERIALS AND METHODS

Chemicals and solutions: The stock solutions of NBA, $HClO_4$, Proline, $NaClO_4$, KI, $Hg(OAc)_2$ and KCl were prepared by dissolving the known amount of reagent in double distilled water. The stock solution of L(-) proline was freshly prepared daily. The solution of palladium(II) chloride (Sigma Aldrich) was prepared by dissolving 1 g of sample in hydrochloric acid (HCl) of 3M strength and the strength of palladium(II) chloride was found to be 5.64×10^{-3} M.

Kinetic measurements: All the kinetic measurements were carried out at constant temperature 35°C in the thermostatic bath. The reaction mixture containing the desired volume of all reactants except proline was taken in conical flask, kept in the thermostatic bath. Proline solution was also placed within the same thermostatic bath. After 30 min., the required volume of proline solution was poured into reaction mixture to initiate the reaction. 5 mL aliquot of the reaction mixture was quenched with 4% potassium iodide and perchloric acid solution and titrated against a standard solution of hypo using starch solution as an indicator. Reaction rates were measured by following the decrease of NBA concentration with time (iodometrically).

Stoichiometry and product analysis: Several sets of experiments with different [NBA]:[amino acid] ratio under the condition [NBA]>>[amino acid], were performed at room temperature for 72 h. Estimation of unconsumed [NBA] was made iodometrically. On the basis of stoichiometric experiments it was found that 2 mole of NBA were required to oxidize 1 mole of L- proline. Accordingly, the following stoichiometric equation can be formulated as-

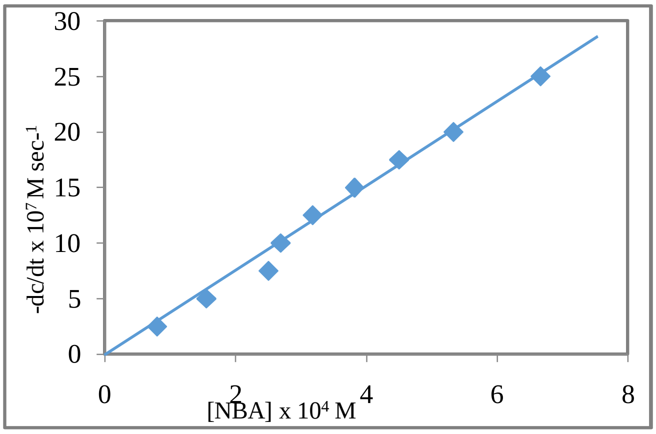


RESULTS AND DISCUSSION

In order to propose a reaction mechanism for Pd (II)-catalyzed oxidation of L-proline by NBA in acidic medium, a series of experiments were performed at constant temperature of 35°C. The order of reaction with respect to each reactant was determined by varying the concentrations of NBA L-proline, Pd (II), H^+ ions, Cl^- ions, mercuric acetate and NHA one by one in different sets keeping

concentration of all other reactants constant at a constant temperature 35°C. To investigate the dependence of rate on NBA in Pd (II)-catalyzed oxidation of L-proline, the concentration of NBA was varied from $2.5x10^{-4}$ to $25.00x10^{-4}$ M at constant concentration of all other reactants at 35°C. Initial rates have been calculated from the slopes of the plots of unconsumed NBA versus time and first-order rate constant, k_1 was calculated as:
k_1= (-dc/dt) / [NBA].

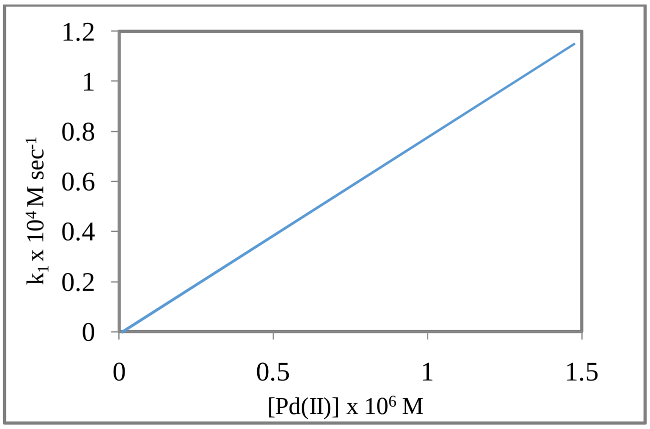
The observed values of –dc/dt clearly show that there is first-order kinetics with respect to NBA. This result is further verified by the plot made between (-dc/dt) values and [NBA], where a straight line passing through the origin was observed (Figure 1).



[Proline] = 1.00×10^{-3} M, $[H^+] = 5.00\times10^{-2}$ M; [NHA] = 5.50×10^{-4} M,
$[Hg(OAc)_2] = 5.50\times10^{-4}$ M, [Pd(II)] = $5.64x10^{-6}$ M, [NaClO4] = 0.50 M

Figure 1. Plot between –dc/*dt* and [NBA] at 35°C.

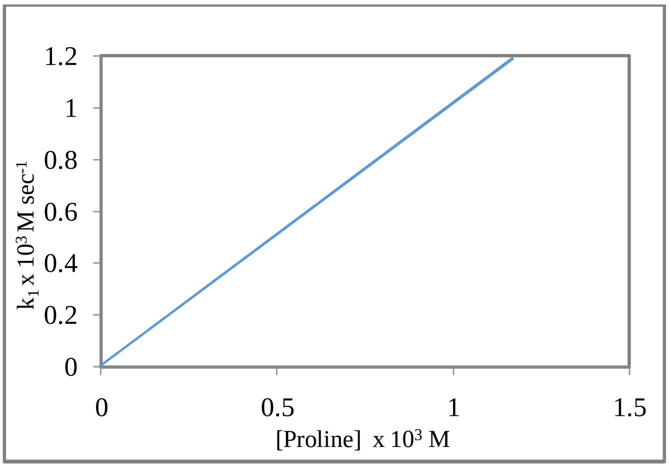
The direct proportionality between $k_1$and [Pd(II)] indicates that the order with respect to Pd(II) is unity as is evident from the plot of k_1 vs [Pd(II)] , where a straight line passing through the origin is obtained in figure 2.



[NBA] = 5.00×10^{-4} M, [Proline] = 1.00×10^{-3} M, $[H^+] = 5.00\times10^{-2}$M,
[NHA] = 5.50×10^{-4} M, $[Hg(OAc)_2] = 5.50 \times10^{-4}$ M, [NaClO4] = 0.50 M

Figure 2. Plot between *k*1 and [Pd(II)] at 35°C.

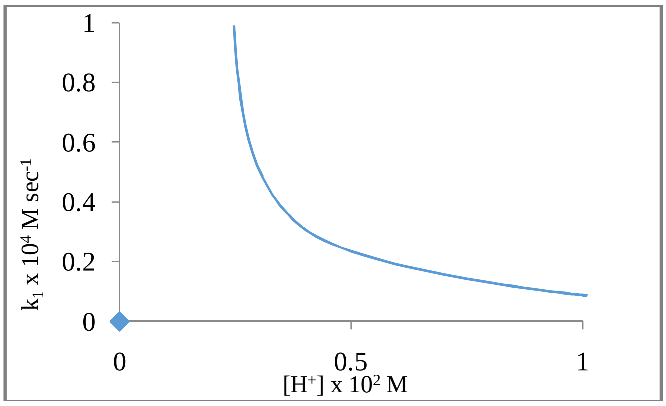
The results obtained for oxidation of substrate shows first order dependence of the reaction in [Proline], (Figure 3).



[NBA] = 5.00×10^{-4} M, [H^+] = 5.00×10^{-2}M, [NHA] = 5.50×10^{-4} M,
[Hg(OAc)2] = 5.50×10^{-4} M, [Pd(II)] = 5.64x10^{-6}M, [NaClO4] = 0.5 M

Figure 3. Plot between *k*1 and [Proline] at 35°C.

Negative effect of [H^+] on the rate of oxidation was observed throughout its variation (Fig.4).



[NBA] = 5.00×10^{-4}M, [Proline] = 1.00×10^{-3}M, [NHA] = 5.50×10^{-4} M,
[Hg(OAc)2] = 5.50×10^{-4} M,[Pd(II)] = 5.64x10^{-6}M, [NaClO4] = 0.5M.

Figure 4. Plot between *k*1 and [H+] at 35°C.

Successive addition of NHA, mercuric acetate [Hg^{++}] and Cl^- shows a negligible effect on the rate of oxidation. On changing the ionic strength (μ) of the medium, the values of k_1 remain constant throughout the variation showing nil effect of ionic strength (μ) on the rate of oxidation of L-proline. In order to find out the influence of temperature on the reaction rate, the reaction was studied at four different temperatures i.e. 35, 40, 45 and 50°C. The values of first-order rate constant, k_1, obtained at four different temperatures were utilized to calculate activation parameters such as specific rate constant (k_r), Arrhenius frequency factor (A), energy of activation (E_a), enthalpy of activation ($\Delta H^\#$), entropy of activation ($\Delta S^\#$) and Gibb's free energy of activation ($\Delta G^\#$) at 35°C (Table 1).

Table 1. Activation parameters of Pd(II)- catalysed oxidation of L- proline by NBA in acidic medium

Amino acid	**Kr (s^{-1})**	**A ($mol^{-1}ls^{-1}$)**	**Ea ($kcalmol^{-1}$)**	**$\Delta H^\#$ ($kJmol^{-1}$)**	**$\Delta S^\#$ ($Jmol^{-1}$)**	**$\Delta G^\#$ ($kJmol^{-1}$)**
L(-) Proline	1.23×10^4	2.87×10^{19}	21.81	21.19	120.08	143.11

Reactive species of NBA: Two sets of equilibria showing the existence of NBA in acidic medium are reported [18] as under

$$CH_3CONHBr + H_2O \rightleftharpoons CH_3CONH_2 + NOBr \quad \text{(i)}$$

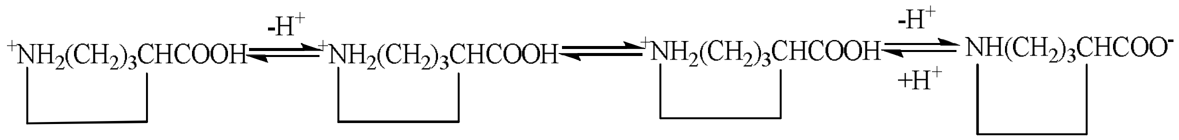
$$HOBr + H^+ \rightleftharpoons H_2OBr^+ \quad \text{(ii)}$$

$$CH_3CONHBr + H^+ \rightleftharpoons (CH_3CONH_2Br)^+ \quad \text{(iii)}$$

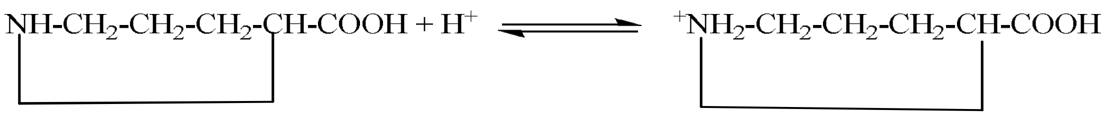
$$(CH_3CONH_2Br)^+ + H_2O \rightleftharpoons CH_3CONH_2 + H_2OBr^+ \quad \text{(iv)}$$

From the above two sets of equilibria, it is clear that there are four possible reactive species, i.e NBA itself, HOBr, $(CH_3CONH_2Br)^+$ and $(H_2OBr)^+$ of NBA in acidic medium. Here zero effect of [NHA] on the rate of reaction does not allow us to assume HOBr and $(CH_3CONH_2Br)^+$as reactive species. The species $(H_2OBr)^+$ can also not be considered as the reactive species because if with this reactive species, a reaction scheme is formulated and a rate law is derived then this rate law will show first-order kinetics with respect to $[H^+]$, which is contrary to the observed negative effect of $[H^+]$ on the rate of reaction, At this stage we are left with no option but to assume NBA itself as reactive species in the oxidation of Proline, the derived rate law explains the fractional negative order in $[H^+]$.

Reactive species of Proline in acidic medium: The amino acids are known to exist in Zwitter ionic form in equilibrium with anionic and cationic forms depending upon the pH of the solution It is known that L-proline exists in the form of Zwitter ion [19] in aqueous medium. In highly acidic medium, it exists in the protonated form, whereas in highly basic medium, it is in the fully deprotonated form medium.



On the basis of the facts reported above, equilibrium of the type shown below can be assumed for the existence of L- Proline in acidic medium.



Observed negative effect with respect to $[H^+]$ forced us to conclude that L- Proline itself is the reactive species in Pd(II)-catalyzed oxidation of L-proline by NBA in acidic medium.

Reactive species of palladium chloride in perchloric acid medium: Pd(II) is the most common oxidation state of palladium and certainly the most important in the chemistry of its homogeneous catalysis. It is reported [20] that much of its catalytic chemistry is related to the fact that Pd(II) is an oxidant. Pd(II) is a d^8 ion and it prefers to form four co-ordinate square planar complexes. The equilibrium constants corresponding to the following equilibria have been determined and found in agreement with a value of log β between 11 and 12 at 25°C.

$$Pd^{2+} + Cl^- \rightleftharpoons PdCl^+ \quad K_1 \qquad \text{(a)}$$

$$PdCl^+ + Cl^- \rightleftharpoons PdCl_2 \quad K_2 \qquad \text{(b)}$$

$$PdCl_2 + Cl^- \rightleftharpoons PdCl_3^- \quad K_3 \qquad (c)$$

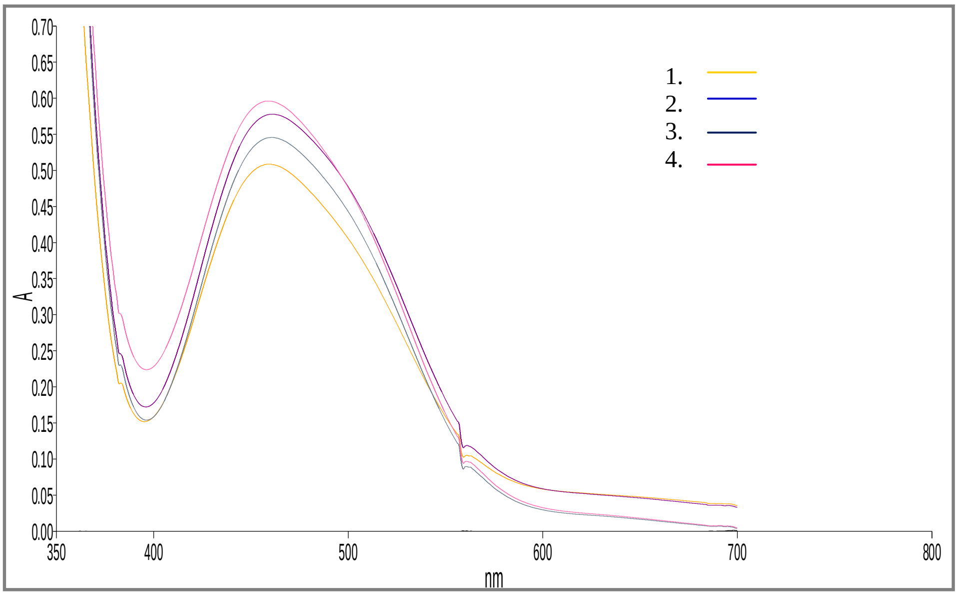
$$PdCl_3^- + Cl^- \rightleftharpoons PdCl_4^{2-} \quad K_4 \qquad (d)$$

Elding [21]studied both the stability constants and rates of reaction and determined values of log K_1 to log K_4 as 4.47, 3.29, 2.41 and 1.37, respectively, with log β_4 equal to 11.54. Grinberg *et al.* [22] were also determined values of aforesaid stability constants and found as 4.3, 3.54, 2.68 and 1.68, respectively. On the basis of above equilibria, we can write

$$Pd^{2+} + 4Cl^- \overset{\beta_4}{\rightleftharpoons} PdCl_4^{2-} \qquad (e)$$

Where β_4 is equal to $K_1K_2K_3K_4$

Ayres reported [23] that when a concentration ratio 2:1 for sodium chloride to palladium (II) chloride is maintained, it will result in the formation of tetrachloropalladate(II), $[PdCl_4]^{2-}$. Since throughout the study of oxidation of L(-)proline, the aforesaid concentration ratio was maintained, hence it is reasonable to assume that the catalyst palladium(II) chloride in the reaction under investigation remains in the form of $[PdCl_4]^{2-}$. Taking into consideration the observed catalytic role of Pd(II) chloride, it can be concluded that $[PdCl_4]^{2-}$ is the reactive species of Pd(II) chloride in the oxidation of L(-)proline by NBA in presence of perchloric acid. This result is further verified by the spectrophotometric evidences (Figure 5and 6).

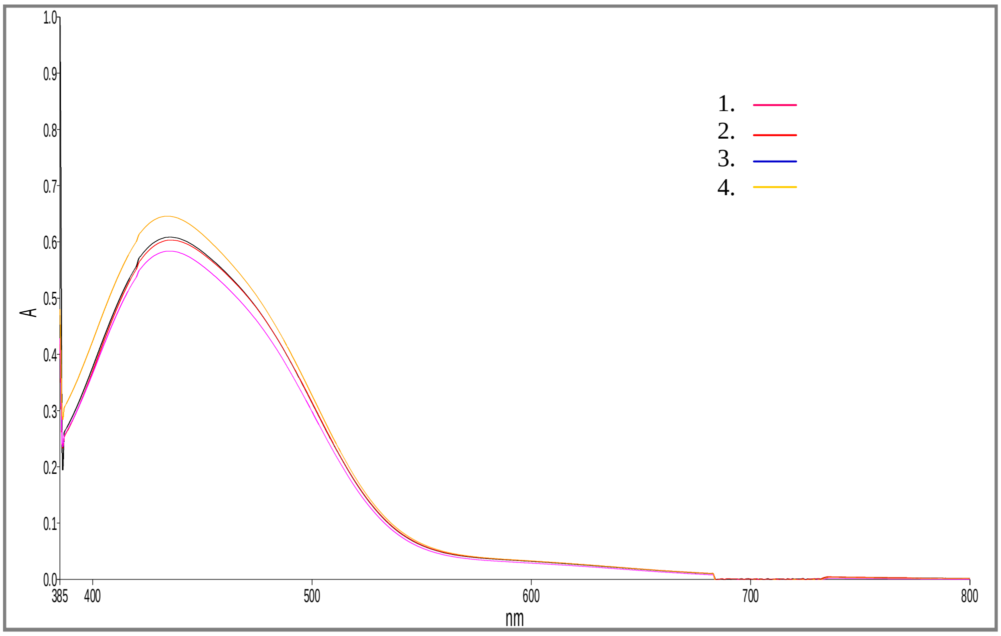


(1). [Pd(II)] =5.64 x 10^{-6} M, $[H^+]$ = 5.00x10^{-3} M (2). [Pd(II)] =5.64 x 10^{-6} M, $[H^+]$ = 10.00x10^{-2} M
(3). [Pd(II)] = 5.64 x 10^{-6}M, $[H^+]$ = 5.00x10^{-3} M (4). [Pd(II)] = 5.64 x 10^{-6}M , $[H^+]$ = 5.00x10^{-3} M
[NBA] = 0.5x10^{-4} M [NBA] = 1.0x10^{-4} M

Figure 5. Spectroscopic evidence for the formation of complexes during the course of reaction.

On the basis of the above discussion made for the reactive species of NBA and Pd(II) chloride, spectral information collected for the possible formation of complex or complexes in the reaction and kinetic informations about the effect of [NBA], [Proline], [Pd(II)] and $[H^+]$ on the rate of reaction, the reaction shown in scheme(1) has been proposed.

Scheme -1



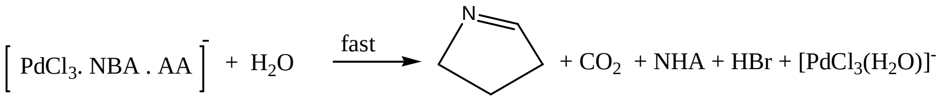
(1). [Pd(II)] = 5.64 x 10^{-6}M, (2). [Pd(II)] = 5.64 x 10^{-6}M, [H^+] = 5.00x10^{-3} M, [H^+] = 5.00x10^{-3} M
[NBA] =1.0x10^{-4} M, [NBA] = 1.0x10^{-4} M, [Proline]= 1.0x10^{-4} M, [Proline] = 2.0x10^{-4} M

(3). [Pd(II)] = 5.64 x 10^{-6}M, (4). [Pd(II)] = 5.64 x 10^{-6}M, [H^+] = 5.00x10^{-3} M, [H^+] = 5.00x10^{-3} M
[NBA] = 1.0x10^{-4} M, [NBA] = 1.0x10^{-4} M, Proline] = 6.0x10^{-4} M, [Proline] = 8.0x10^{-4} M

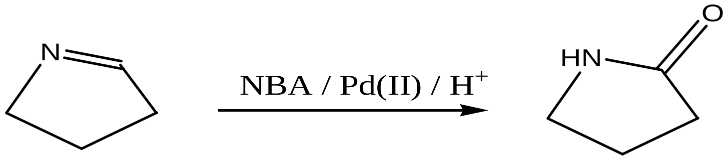
Figure 6. Spectroscopic evidence for the formation of complexes during the course of reaction.

$$\underset{(C_2)}{[PdCl_4.NBA]^{2-}} + AA \xrightarrow[r.d.s]{k_3} \underset{(C_3)}{\left[PdCl_3.\ NBA\ .\ AA\right]^{-}} + Cl^{-} \qquad (III)$$

where AA stands for amino acid.



(IV)



(V)

On the basis of the above mechanism, the rate in terms of disappearance of NBA can be expressed as -

$$\text{Rate} = \frac{-\,d[NBA]}{dt} = n\,k_3\,[C_2]\,[AA] \qquad (1)$$

On applying the law of chemical equilibrium to step (I) and steady- state approximation to steps (II) and (III) the rate law in terms of concentration of reaction component can be derived as –

$$K_1 = \frac{[C_2]}{[NBA]\,[C_1]} \qquad (2)$$

$$[C_2] = K_1 [NBA] [C_1] \qquad (3)$$

Substituting the value of $[C_2]$from equation (3) to equation (1), we get equation (4)

$$r = n k_3 [AA] K_1 [NBA] [C_1] \qquad (4)$$

On applying the law of chemical equilibrium to step (II) we have equation (5)

$$K_2 = \frac{[AA]\ [H^+]}{[AA^+]}$$

$$[AA] = \frac{K_2 [AA^+]}{[H^+]} \qquad (5)$$

Now substituting the value of (5) in equation (4) we get equation (6)

$$r = \frac{n k_3 K_1 [NBA] [C_1] K_2 [AA^+]}{[H^+]} \qquad (6)$$

According to the proposed mechanism, the total concentration of Pd(II), i.e., $[Pd(II)]_T$ can be expressed as-

$$[Pd(II)]_T = [C_1] + [C_2] \qquad (7)$$

On substituting the value of $[C_2]$ from equation (3) to equation (7) we obtain equation (8)

$$[Pd(II)]_T = [C_1] \{1 + K_1 [NBA]\}$$

$$[C_1] = \frac{[Pd(II)]_T}{1 + K_1 [NBA]} \qquad (8)$$

$$[AA^+] = \frac{[AA]_T [H^+]}{[H^+] + K_2} \qquad (9)$$

On Putting the value of $[C_1]$ and $[AA^+]$ in equation (6) we get-

$$r = \frac{n k_3 K_1 K_2 [NBA] [Pd(II)]_T [AA]_T}{(1 + K_1 [NBA]) ([H^+] + K_2)} \qquad (10)$$

Under an experimental condition the inequality $K_1[NBA] << 1$ can be assumed is valid one and under this condition above equation will be reduced to-

$$\text{Rate} = \frac{2 k_3 K_1 K_2 [NBA] [Pd(II)]_T [AA]_T}{(K_2 + [H^+])} \qquad (11)$$

Equation (9) is the final rate law which is in agreement with the kinetic observations made for the effect of [NBA], $[Pd (II)]_T$, $[H^+]$ and $[AA]_T$ on the rate of oxidation of proline.

On reversing equation (9), we have equation (10)

$$\frac{[NBA]\,[Pd(II)]_T\,[AA]_T}{Rate} = \frac{1}{2k_3K_1} + \frac{[H^+]}{2k_3K_1K_2} \qquad (12)$$

When a plot between $[NBA][Pd(II)]_T[AA]_T$/rate and $[H^+]$, was made, according to equation (12), a straight line having positive intercept on *y*-axis was obtained (Figure 7).This not only proves the validity of rate law (11) but also gives support to the proposed reaction scheme 1. From the slope and intercept of the straight line, the values of $2k_3K_2$ and K_2were calculated and found as 2.17×10^5 mol L^{-1} sec^{-1} and 3.28×10^{-2} mol Lt^{-1}, respectively. Utilizing these values of rate constants, the reaction rates for the variation of $[H^+]$, has been calculated on the basis of the rate law (11) and found to be in close agreement with the observed rates (Table 2).This further proves the validity of rate law (11) and hence the proposed mechanism.

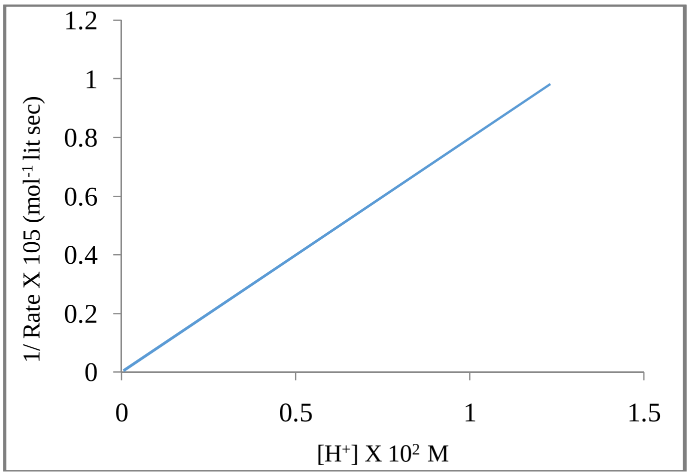


Figure 7. a plot between $[NBA][Pd(II)]_T[AA]_T$/rate and $[H^+]$.

Table 2. Comparison of observed rates with the rates calculated for the variation of $[H^+]$ in the Pd(II)-catalysed oxidation of Proline at 35°C.

$[H^+]$ x 10^2(mol lit^{-1})	− d*c*/d*t* (×10^7 mol lit^{-1} s^{-1})	
	Experimental	Calculated on the basis of rate law (9)
1.00	4.77	4.69
3.00	3.65	3.20
5.00	2.00	2.43
7.00	1.96	1.95
9.00	1.66	1.63
11.00	1.47	1.40
15.00	1.41	1.10

Comparative studies: The findings of the present study of oxidation of proline by NBA in presence of Pd(II) as homogeneous catalyst have been compared with the results reported for Pd(II) catalyzed [24] oxidation of glucose and fructose by NBA in acidic medium and Ru(III) catalyzed [25] oxidation of proline by hexacyanoferrate(III) in aqueous alkaline medium. When the present study has been made for the effect of [NBA] on the rate of oxidation, it is found that the rate is directly proportional to [NBA] contrary to the first to zero order kinetics in [NBA] for Pd(II)-catalyzed [24] oxidation and unity order of hexacyanoferrate(III) on the rate of reaction for Ru(III) catalyzed [25] oxidation. Observed first order kinetics in [substrate] in the present study is same as the Pd(II)-catalyzed [24] oxidation of sugar whereas contrary to the reported zero order kinetics in Ru(III)- catalyzed [25]. In the present study first-order kinetics with respect to [Pd(II)] has been observed throughout its variation. This result is similar to the reported first order kinetics with respect to[Pd(II)] and [Ru(III)] catalyzed oxidation of sugar by NBA in acidic medium and hexacyanoferrate(III) in aqueous alkaline medium respectively. On the basis of observed kinetic data and spectroscopic evidence, it has been assumed that the species $[PdCl_4]^{2-}$ is the reactive species of Pd(II)-chloride in the oxidation of Proline, which is similar to the reported Pd(II)-catalysed oxidation of sugar. Whereas $[Ru(H_2O)_5(OH)]^{2+}$ is the reactive species of Ru(III)-chloride [25] in the oxidation of L- Proline by hexacyanoferrate(III) in aqueous alkaline medium. Inverse fractional order kinetics of $[H^+]$ in the present study is similar to the Pd(II)-catalyzed oxidation of sugar and contrary to fractional positive order in the Ru(III) catalyzed oxidation of L-Proline. Nil effect in dielectric constant of the medium was observed in the present study. But this is in contrary with the effect reported in first order rate constant decreases with an increase in the dielectric constant of the medium in Pd(II)-catalyzed [24] oxidation of sugar and where an increase in the rate with increase in dielectric constant of the Ru(III) catalyzed [25] oxidation of L- proline. In view of the facts mentioned above, it can be said that the present study is different in many respect from the other two studies reported earlier.

APPLICATION

Industrial applications of amino acids are due to the large number of natural antibiotics containing amino acids isolated mainly from bacteria, the majority of applications of these compounds are related to antimicrobial activities.

CONCLUSION

Based on kinetic results and spectroscopic evidence and observe entropy of activation, a most probable reaction path for Pd (II)- catalyzed oxidation of L-Proline by N-Bromoacetamide (NBA) in acidic medium has been proposed.

1. NBA itself and $[PdCl4]^{2-}$ have been assumed as the reactive species of NBA and Pd (II) chloride in acidic medium, respectively.
2. The complex $[PdCl_3.NBA.AA]^-$ instep(III) in scheme(1) has been proposed as the most reactive activated complex in the oxidation of L(-) Proline by NBA in acidic medium.
3. The rate of oxidation of L-Proline is unaffected by the ionic strength of the medium.
4. Pyrrolid-2-onewas identified as the oxidation product of the reaction under investigation.

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