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Kinetics and Mechanism of Pd (II) Chloride Catalyzed Oxidation of L-Proline by N-Chlorosuccinimide in Acidic Medium

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ABSTRACT

The kinetics of oxidation of Proline by N-Chlorosuccinimide (NCS) in presence of Pd (II)-chloride as homogeneous catalyst in acidic medium has been investigated at 35^0C. The reaction is found to be first-order with respect to (NCS) and [Pd (II)]. The first order kinetics with respect to amino acid obtained at its lower concentrations changes to zero order at its higher concentrations. Inverse fractional order with respect to $[H^+]$ and $[Cl^-]$ were obtained, while $[Hg(OAc)_2]$ and (NHS) variations show negligible effect on the reaction rate. Rate of reaction is not influenced by the change in ionic strength (µ) and dielectric constant (D) of the medium. The reaction has been studied at four different temperatures and observed values of the first-order rate constants were utilized to calculate various activation parameters. $[PdCl_4]^{2-}$, (NCS) itself and Proline as such were considered as the reactive species of Pd (II) chloride, NCS and Proline in acidic medium respectively. A reaction scheme consistent with the kinetic data, spectroscopic information and activation parameters was proposed.

Keywords: Kinetics, Pd (II) chloride, Catalyzed oxidation, N- Chlorosuccinimide, Mechanism.

INTRODUCTION

N-halo compounds have been used successfully not only as halogenating agents, but several of them have been found to be effective agents for oxidations and dehydrogenations. Attention has been focused on the diverse nature of the chemistry of N-halo compounds [1] owing to their ability to act as source of halogenonium cations, hypohalite species and nitrogen anions which act both as bases and nucleophiles.

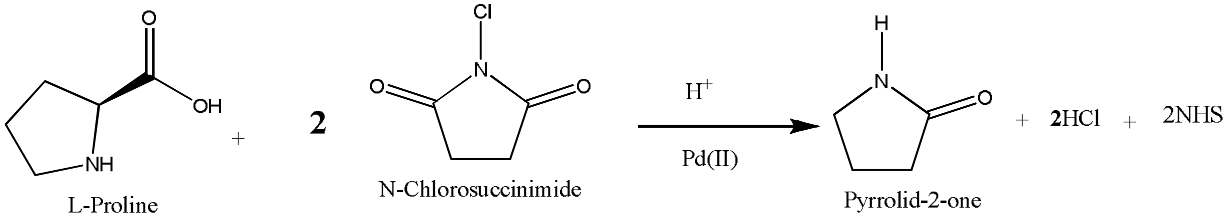
N-halo compounds oxidations of organic substrates are complicated by parallel chlorine oxidation which is obviated by Hg (II). Reports are available on oxidative capacity of N-halo compounds in catalyzed [2-7] and uncatalyzed [8-10] processes. The study of amino acids becomes important because of their biological significance. Amino acids have been oxidized by a variety of oxidizing agents [11-13]. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [14, 15]. L- Proline is a non- essential amino acid and is an important constituent of collagen. As per recent report [16], L-proline is considered to be the world's smallest natural enzyme and it is used in catalyzing the aldol condensation of the acetone to various aldehydes with high stereo-specificity Palladium (II) is known as catalyst for many reactions [17-19]. Recently, kinetic investigations on oxidation of L-proline has been reported [20-22] but so far , no attempt has been made to probe the catalytic role of Pd(II) in the oxidation of L-proline using NCS as an oxidant. The present work reports the kinetic data obtained in Pd (II) catalyzed oxidation of L-Proline in hydrochloric acid medium in presence of mercuric acetate and mechanistic routes in light of Pd(II) catalysis have been discussed.

MATERIALS AND METHODS

Materials: Stock solution of Palladous chloride i.e. Palladium (II) chloride (Qualigens 'Glaxo' Chem.) was prepared by dissolving its sample in known volume of hydrochloric acid. The overall strength of hydrochloric acid was maintained at 11.71×10^{-2}M and the strength of Pd(II) chloride was 5.64×10^{-3}M. N-Chlorosuccinimide (NCS) solution was prepared by weighing and dissolving it in doubly distilled water every day. Standardization of NCS solution was done iodometrically by titrating it against standard sodium thiosulphate (hypo) solution. Amino acid i.e. L-Proline solution was prepared daily by weighing and dissolving it in doubly distilled water. The aqueous solution of mercuric acetate (loba chemicals) was acidified with 20% acetic acid solution. All other reagents namely HCl, $NaClO_4$, $HClO_4$, acetamide and KCl were prepared from their samples (E. Merck) in doubly distilled water.

Kinetic measurements: A black coated reaction vessel, containing requisite volumes of solution of NCS, HCl, Pd (II)chloride, KCl, $NaClO_4$ and $Hg(OAc)_2$, was placed in an electrically operated thermostatic water both maintained at $35^0C\pm0.1^0C$ for thermal equilibrium. Another conical flask containing substrate solution was also placed in the same thermostat at the same temperature for thermal equilibrium. Requisite amount of substrate solution (L-Proline) was added to the reaction vessel containing all other thermally equilibrated reactants to initiate the reaction. The progress of the reaction was determined by estimating the unconsumed N-Chlorosuccinimide iodometrically in the aliquots withdrawn from reaction mixture at regular time intervals.

Stoichiometry: Different sets of experiments were performed with varying [NCS]: [Proline] ratios under the condition [NCS] >>>[Proline] . Estimation of unconsumed NCS indicated that two moles of NCS were consumed to oxidize one mole of Proline .Accordingly the following stoichiometric equation is suggested:



RESULTS AND DISCUSSION

Kinetic results and Discussion: In order to propose a reaction mechanism for Pd (II)-catalyzed oxidation of L-Proline by NCS in acid medium, a series of experiments were performed at constant temperature35°C. The order of reaction with respect to each reactant was determined by varying the concentrations of NCS, L-Proline, Pd (II), H^+ ions, Cl^- ions, mercuric acetate and N-Hydrosuccinimide one by one in different sets keeping concentrations of all other reactants constant at a constant temperature 35^0 C. To investigate the dependence of rate on NCS in Pd (II)-catalyzed oxidation of L-Proline, the concentration of NCS was varied from 1.00×10^{-3} to 10.00×10^{-3}M at constant concentration of all other reactants at 35^0C. Initial rates have been calculated from the slopes of the plots of unconsumed NCS, time and first-order rate constant, k_1 was calculated as:

$$k_1 = (-dc/dt) / [NCS]$$

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

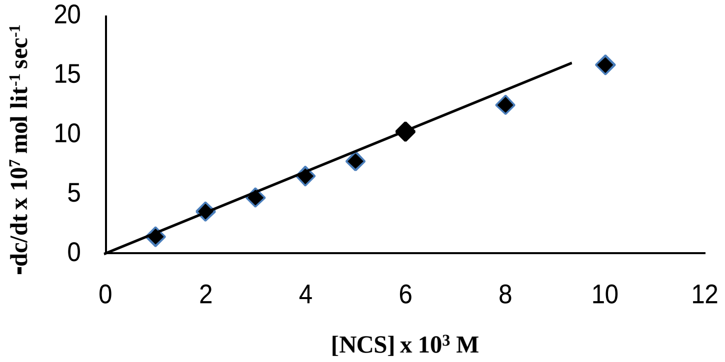


Fig1. Plot between –dc/dt and [NCS] at 35 ^{0}C,
[Pd(II)]= $5.64X10^{-6}$M ,[Proline] = 5×10^{-2}M, $[H^+] = 20\times 10^{-2}$ M, μ = 0.3 M, [NHS]= 10.50×10^{-3} M
[KCl]= $1.5X10^{-3}$M , $[Hg(OAc)_2] = 10.50\times10^{-3}$ M

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 (Fig.-2).The results obtained for oxidation of Proline show first order dependence of the reaction on Proline at low concentrations , which shift towards zero order at its higher concentrations (Fig.3). Negative effect of H^+ on the rate of oxidation was observed throughout its variation (Fig.4). Negative effect of $[Cl^-]$ was observed by varying the concentration of Cl^- ions in the Pd(II)-catalysed oxidation of L -Proline by NCS (Fig.5). Successive addition of NHS and mercuric acetate $[Hg^{++}]$ 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. 30, 35, 40 and 45^0C. 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 35^0C (Table 1).

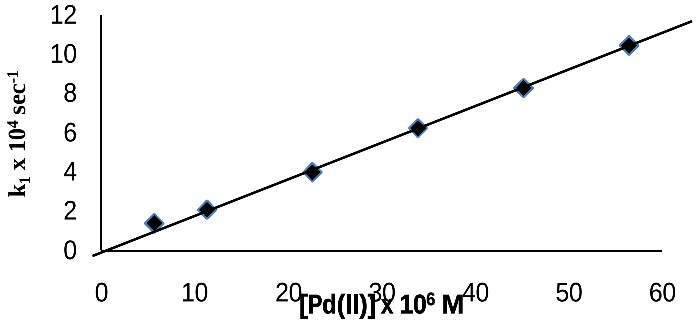


Fig. 2: Plot between k_1 and [Pd (II)] at 35°C
$[NCS] = 1\times10^{-3}$ M, $[H^+] = 20\times10^{-2}$ M, $[Proline] = 5\times10^{-2}$ M, $[NHS] = 1.25\times10^{-3}$ M,
$[Hg(OAc)_2] = 1.25\times10^{-3}$ M, μ =0.3 M , [KCl]= $1.5X10^{-3}$ M

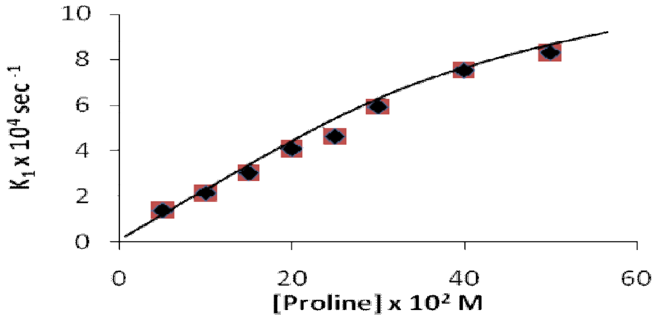
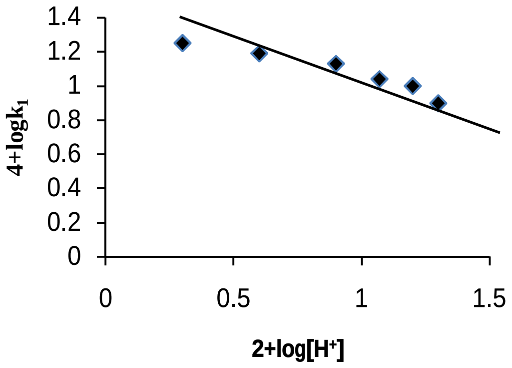


Fig. 3: Plot between k_1 and [Substrate] at 35°C
[NCS] = 1×10^{-3} M, [Pd(II)] = 5.64×10^{-6} M, $[H^+]$ = 20×10^{-2} M, [NHS] =1.25×10^{-3} M,
$[Hg(OAc)_2]$ = 1.25×10^{-3} M,μ =0.3 M, [KCl]= $1.5X10^{-3}$M



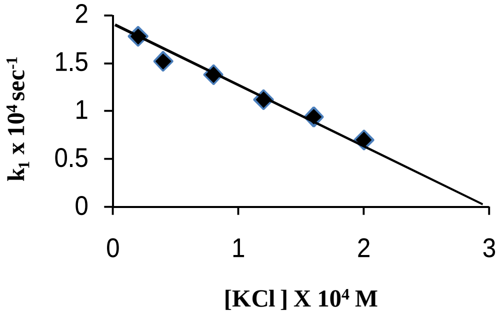


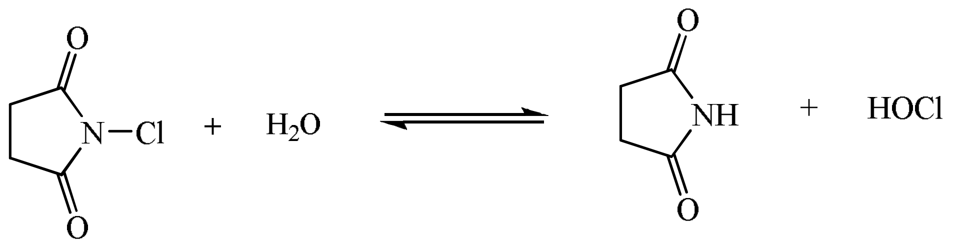
Fig 4 : Plot between logk_1 and log[H^+] at 35°C
[NCS] = 1×10^{-3}M, [Proline] = 5×10^{-2}M
[Pd(II)] = 5.64×10^{-6} M, μ =0.3 M,
[NHS] =1.25×10^{-3} M, [KCl]= $1.5X10^{-3}$M
$[Hg(OAc)_2]$ = 1.25×10^{-3} M

Fig 5 : Plot between k_1 and [KCl] at 35°C
[NCS] = 1×10^{-3} M, $[H^+]$ = 20×10^{-2}M,
[Pd(II)] = 5.64×10^{-6} M, μ =0.3 M ,
$[Hg(OAc)_2]$ = 1.25×10^{-3} M [NHS] =1.25×10^{-3} M,
[Proline] = 5×10^{-2}M

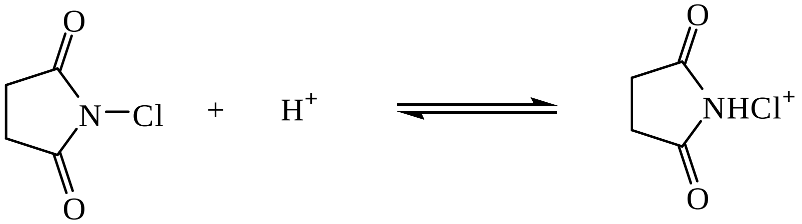
Table 1. Thermodynamic parameters for Pd (II)–Catalyzed oxidation of L-Proline by NCS in acidic medium at 35^0C

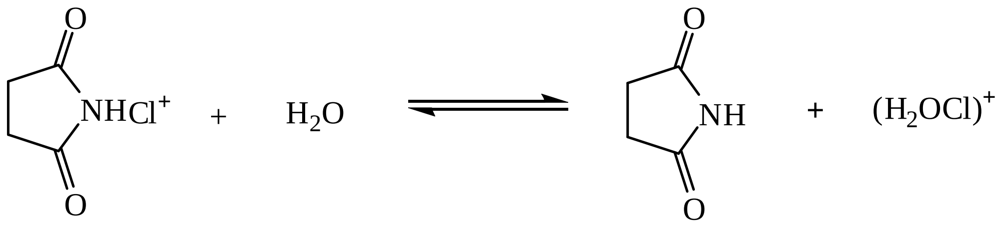
Parameters	Proline
Ea (kJMol^{-1})	*82.11*
$\Delta S^\#$ (JK^{-1}Mol^{-1})	*19.57*
$\Delta H^\#$(kJMol^{-1})	*79.43*
$\Delta G^\#$(kJMol^{-1})	*73.75*
A (Mol^{-4} l^4 sec^{-1})	*1.45* x 10^{14}

Reactive species of N- chlorosuccinimide in acidic medium: When NCS is dissolved in water, it exits in the following equilibrium [23].


(a)

In the presence of acid, the following equilibrium can be assumed to exit


(b)


(c)

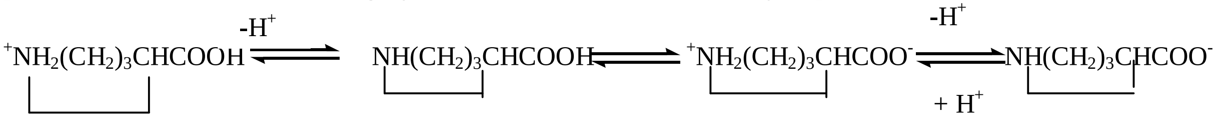
From the above sets of equilibria (a, b& c) it is clear that NCS in acidic medium exists in four different forms i.e. NCS itself, HOCl, NH Cl$^+$ and $(H_2OCl)^+$. Here zero effect of [NHS] on the rate of reaction does not allow us to assume HOCl and H_2O^+Cl as reactive species. On the other hand if N$^+$HCl is taken as the reactive species of NCS , it will lead to a positive effect of $[H^+]$ on the rate of oxidation which is contrary to the observed negative effect of $[H^+]$ on the rate of oxidation. Thus, out of NCS itself, HOCl , NHCl$^+$ and $(H_2OCl)^+$, the only choice left before us is to choose NCS itself as the reactive species for the oxidation of aforesaid amino acid in acidic medium using Pd(II) as homogeneous catalyst. This assumption also finds further support from the spectral evidence where single peak was found for NCS solution in acidic medium (Fig.6).

Reactive species of Pd (II) chloride in acidic medium: Before formulating the reaction mechanism for the reaction under investigation, it is necessary to ascertain the reactive species of Pd(II) chloride in acidic medium. It is reported [24] that Pd (II) is the most common oxidation state for palladium and certainly the most important in the chemistry of its homogeneous catalysis. It is also reported 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. From crystal field splitting diagrams it is predicted that these complexes are diamagnetic. Various mononuclear complexes namely $[PdLCl_3]$, $[PdL_2Cl_2]$, $[PdL_3Cl^+]$ and $[PdCl_4]^{2+}$ (Where L represents a ligand like amine, phosphine, thioether etc. are reported [25] in literature. In most of the studies using Pd (II) as homogeneous catalyst, it has been employed in the form of Pd (II) Chloride. Pd (II) chloride is rather insoluble in aqueous solution but is soluble in hydrochloric acid and exits [26] as $[PdCl_4]^{2-}$, according to the equilibrium [27]

$$[PdCl_2] + 2\,Cl^- \rightleftharpoons [PdCl_4]^{2-}$$

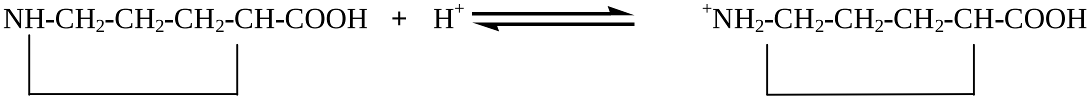
The existence of $PdCl_2$ exclusively in the form of $PdCL_4$ is also supported by Ayers [28] in 1953, who observed that when a concentration ratio of 2:1 for sodium chloride(Cl^-) to palladium(II)chloride is maintained, it will result in the formation of tetrachloropalladate (II), $[PdCl_4]^{2-}$. Since 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 $[PdCl_4]^{2-}$. Thus it is concluded that $[PdCl_4]^{2-}$ is the reactive species of Pd (II) chloride in the oxidation of L-Proline by NCS in presence of hydrochloric acid.

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 [29] 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.



$$^{+}NH_2(CH_2)_3CHCOOH \overset{-H^+}{\rightleftharpoons} NH(CH_2)_3CHCOOH \rightleftharpoons {}^{+}NH_2(CH_2)_3CHCOO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} NH(CH_2)_3CHCOO^-$$

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.



$$NH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}COOH + H^+ \rightleftharpoons {}^{+}NH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}COOH$$

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 NCS in acidic medium. In order to show the negative effect of $[H^+]$ on the rate of oxidation.

Spectroscopic information for the verification of various complexes formed during the course of reactions: After ascertaining the reactive species of NCS and also of L-Proline in acid medium, efforts have been made to find out the possible formation of complex or complexes between various reactive species of reactants in the reactions under investigation. In this regard, when spectra of NCS and H^+ ions solutions with three different concentrations of Pd(II) chloride solution were recorded peak numbers, it was observed that there is an increase in absorbance from 0.523 to 0.585, 0.662 and 0.773 (Fig. 6 (1) and Fig.7(3,4 and 5**))**. This confirms the existence of the complex, $[NCS.PdCl_3]^-$ formed through equilibrium presented below in the reaction under investigation.

$$NCS + PdCl_4^{2-} \rightleftharpoons PdCl_3^-.NCS + Cl^-$$

Further, when spectrum of NCS, H^+ and Pd (II)-chloride solution was compared with the spectra of NCS, H^+ and Pd(II)-chloride with two different concentrations of Proline an increase in absorbance from 0.773 to 0.785 and 0.959 was noted (Fig 7 (5) and Fig.8(6 and 7)**)** .On the basis of this information, the existence of the following equilibrium in the reaction can be assumed.

$$[PdCl_3^-.NCS] + \underset{\text{(L-Proline)}}{AA} \rightleftharpoons [PdCl_3.NCS.AA]^-$$

Kinetic data demonstrate that the possibility of the reverse reaction shown above is remote and hence it will be most appropriate to consider the above equilibrium reaction as irreversible reaction in the reaction scheme proposed for the catalyzed oxidation of L- Proline.

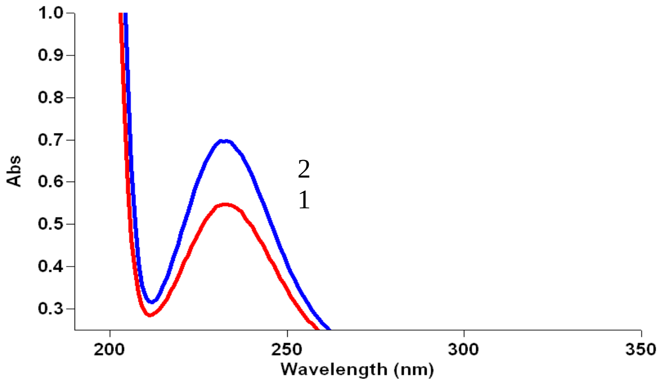


Fig 6: Spectra of solutions of NCS in acidic medium recorded at room temperature
(1) [NCS] = 1 ×10^{-4} M (2) [NCS] = 1 ×10^{-4} M
$[H^+]$ = 0.2 M $[H^+]$ = 0.4 M

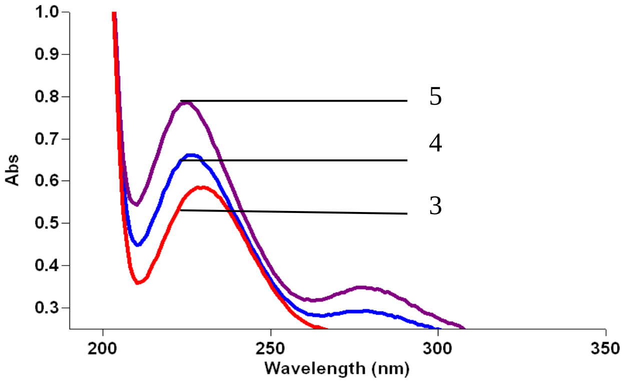


Fig.7: Spectra of solutions [3, 4 and 5] recorded at room temperature
(3) [NCS] = 1×10^{-4} M (4) [NCS] = 1×10^{-4} M (5) [NCS] = 1x 10^{-4} M
$[H^+]$ = 0.2 M $[H^+]$ = 0.2 M $[H^+]$ = 0.2 M
[Pd(II)] = 5.64×10^{-6} M [Pd(II)] = 11.28 × 10^{-6} M [Pd(II)]=16.92 x 10^{-6} M

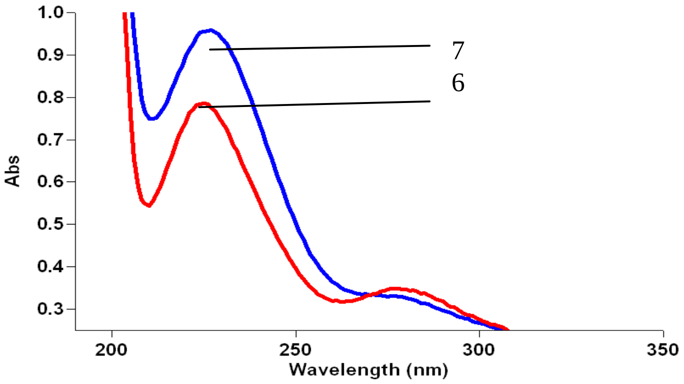
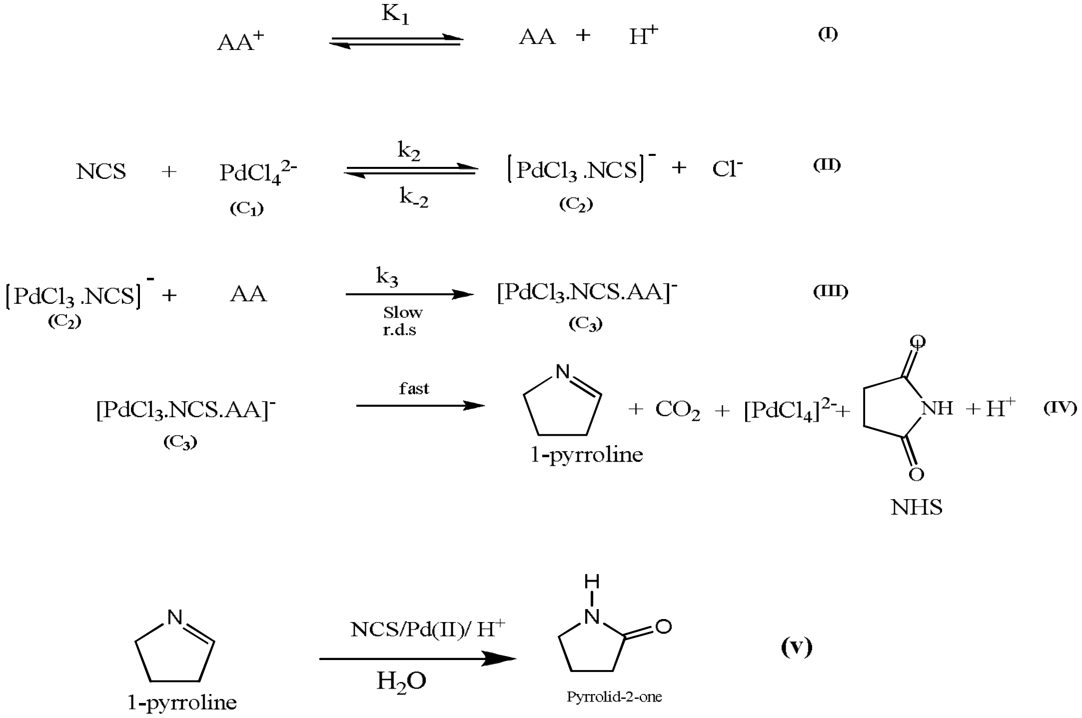


Fig. 8: Spectra of solutions [6 and 7] recorded at room temperature
(6) [NCS] = 1×10^{-4} M (7) [NCS] = 1×10^{-4} M
$[H^+]$ = 0.2 M $[H^+]$ = 0.2 M
[Pd(II)] = 5.64×10^{-6} M [Pd(II)] = 5.64 × 10^{-6} M
[L- Proline] = 2.5 ×10^{-3} M [L-Proline] = 5 ×10^{-3}

On the basis of kinetic order with respect to each reactant taking part in the reaction, spectral information collected for the probable formation of complex or complexes in the reaction and taking into consideration the observed values of activation parameters, a reaction Scheme 1 for the reactions under investigation can be proposed in the following way:



Scheme 1

Equivalence studies and the reaction scheme proposed above clearly show that the rate in terms of decrease in concentration of NCS can be expressed as

$$-\frac{d[NCS]}{dt} = 2\ k_3[AA]\ [C_2] \qquad (1)$$

On applying the law of chemical equilibrium to step (I), we get equation (2)

$$K_1 = \frac{[AA][H^+]}{[AA^+]}$$

or
$$[AA^+] = \frac{[AA][H^+]}{K_1} \qquad (2)$$

On applying steady-state approximation to [C_2], we have

$$0 = \frac{d[C_2]}{dt} = k_2[NCS][C_1] - k_{-2}[C_2][Cl^-] - k_3[C_2][AA]$$

or
$$k_2[NCS][C_1] = [C_2](k_{-2}[Cl^-] + k_3[AA])$$

$$[C_2] = \frac{k_2\,[NCS]\,[C_1]}{[Cl^-]\,k_{-2} + k_3\,[AA]}$$

or (3)

On substituting the value of [C_2] from equation (3) to equation (1), we get equation (4) as given below

$$-\frac{d[NCS]}{dt} = \frac{2k_3\,k_2\,[NCS]\,[C_1]\,[AA]}{[Cl^-]\,k_{-2} + k_3\,[AA]} \qquad (4)$$

According to the reaction mechanism, total concentration of Pd(II) i.e. $[Pd(II)]_T$ at any moment in the reaction can be expressed as

$$[Pd\,(II)]_T = [C_1] + [C_2] \qquad (5)$$

$[C_2]$ being very reactive will not accumulate in the reaction, hence $[C_2]$ will always be less than $[C_1]$ and under this condition the concentration of C_1 can be taken as approximately equal to total concentration of Pd(II) i.e. $Pd(II)_T$.

Thus, when $[C_1] = [Pd\,(II)]_T$, equation (4) can be written as

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2k_2k_3[NCS][Pd(II)]_T[AA]}{k_{-2}[Cl]+k_3[AA]} \qquad (6)$$

Reaction scheme-1 clearly shows that the total concentration of amino acid i.e. $[AA]_T$ can be expressed as

$$[AA]_T \;=\; [AA] + [AA^+] \qquad (7)$$

On substituting the value of $[AA^+]$ from equation (2) to equation (7), we have equation (8) in the following form

$$[AA]_T = [AA] + \frac{[AA][H^+]}{K_1}$$

$$\text{or}\;\; [AA]_T = [AA]\,\frac{K_1+[H^+]}{K_1}$$

$$\text{or}\;\; [AA] = \frac{K_1[AA]_T}{K_1+[H^+]} \qquad (8)$$

Now equation (6) together with equation (8) will give equation (9) as given below

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2K_1k_2k_3[NCS][Pd(II)]_T[AA]_T}{[Cl]k_{-2}(K_1+[H^+])+k_1k_3[AA]_T}$$

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2K_1k_2k_3[NCS][Pd(II)]_T[AA]_T}{[Cl]K_1k_{-2}+k_{-2}[H^+][Cl]+k_1k_3[AA]_T} \qquad (9)$$

Equation (9) can also be written as

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2k_2k_3K_1[NCS][Pd(II)]_T[AA]_T}{[Cl]k_{-2}[H^+]+K_1\{k_{-2}[Cl]+k_3[AA]_T\}} \qquad (10)$$

Under our experimental conditions the inequality $k_3[AA] >> k_{-2}$ can be assumed as valid one and under this condition equation (10) will take the shape of equation (11)

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2k_2k_3K_1[NCS][Pd(II)]_T[AA]_T}{k_{-2}[Cl][H^+]+k_3K_1[AA]_T} \qquad (11)$$

Equation (11) is the final rate law which clearly explains our experimental findings

On reversing equation (11) , we have equation (12)

$$\frac{[Pd(II)]\,[NCS]}{\text{rate}} = \frac{k_{-2}\,[Cl^-]\,[H^+]}{2k_2\,k_3\,K_1\,[AA]_T} + \frac{1}{2k_2} \qquad (12)$$

According to equation (12) if plot is made between $[Pd(II)]_T\,[NCS]/\text{rate}$ and $[H^+]$ /or 1 $[AA]_T$, a straight line having positive intercept on $[Pd(II)]_T\,[NCS]/\text{rate}$ axis will be obtained. When plots were made between $[Pd(II)]_T\,[NCS]/\text{rate}$ and 1 $[AA]_T$ and also between $[Pd(II)]_T\,[NCS]/\text{rate}$ and $[H^+]$

straight lines having intercepts on Y- axis were obtained. From the intercepts and slopes of straight lines ,the values of k_{-2}/k_3 K_1 and k_2 were calculated and found as 2.5x 10^3 mol^{-1} l^1 and 0.625 x 10^{-2} mol^{-1} l^1 sec^{-1}, respectively .On substituting the values of k_{-2}/k_3 K_1 and k_2 the rates for the variation of $[H^+]$ and $[AA]_T$ were calculated with the help of rate law (11) and found as very close to experimental rates (Table 2). This clearly proves the validity of rate law (11) and hence the proposed reaction scheme 1.

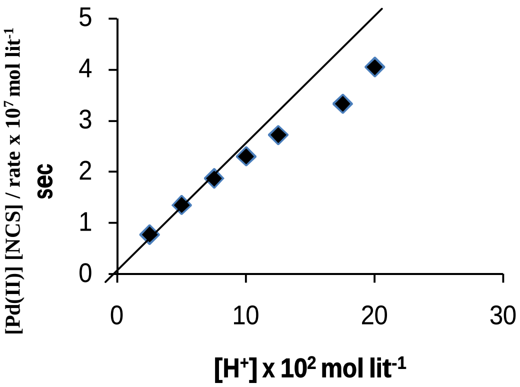


Fig 9: Plot between [Pd(II)][NCS]/ rate and $[H^+]$ at 35 ^{0}C

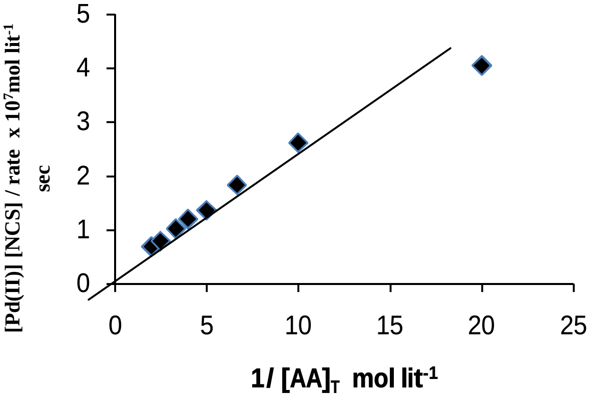


Fig 10: Plot between [Pd(II)][NCS]/rate and $1/[AA]_T$ at 35 ^{0}C

Solution Conditions

$[NCS] = 1\times10^{-3}M$, $[Pd(II)] = 5.64\times10^{-6}M$,
$[NHS] = 1.25\times10^{-3}$ M,
$[KCl] = 1.5X10^{-3}M$, $\mu = 0.3M$,
$[Hg(OAc)_2] = 1.25\times10^{-3}$ M,
[L-Proline] = 5 $\times10^{-2}$ M

$[NCS] = 1\times10^{-3}M$, $[Pd(II)] = 5.64\times10^{-6}M$,
$[NHS] = 1.25\times10^{-3}$ M,
$[KCl] = 1.5X10^{-3}$, $\mu = 0.3$ M ,
$[Hg(OAc)_2]$ = 1..25$\times10^{-3}$ M
$[H^+]$ = 20 $\times10^{-2}$ M

Observed positive entropy of activation is due to interaction of a charged species C_3 and a neutral molecule AA in the rate determining step, which further supports kinetic data and hence the proposed mechanism

Table 2: Comparison of experimental rates and the rates calculated on the basis of rate law (11) for $[H^+]$ and $[AA]_T$variations in the oxidation of Proline at 35^{o}C.

$[H^+]$x10^2 (mole lit^{-1})	$[AA]_T\times10^2$ (mole lit^{-1})	-dc/dt x 10^7 (mole lit^{-1} sec^{-1})	-dc/dt x 10^7 (mole lit^{-1} sec^{-1})
		Rate calculated on the basis of rate law(11)	Experimental rates
20.00	5.00	1.15	1.39
20.00	10.00	2.16	2.15
20.00	15.00	3.08	3.05
20.00	20.00	3.88	4.10
20.00	25.00	4.62	4.64
20.00	30.00	5.32	5.45
20.00	40.00	6.48	7.02
20.00	50.00	7.42	8.00
2.50	5.00	6.63	7.29
5.00	5.00	4.02	4.16
7.50	5.00	2.89	3.01
10.00	5.00	2.25	2.45
12.50	5.00	1.84	2.07
17.50	5.00	1.35	1.69
20.00	5.00	1.20	1.39

Solution Condition

[NCS] = 1×10^{-3} M, [Pd(II)] = 5.64×10^{-6}M, [NHS] =1.25×10^{-3} M, [KCl]= $1.5X10^{-3}$ M, μ =0.3 M, $[Hg(OAc)_2]$ = 1.25×10^{-3} M,

APPLICATIONS

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

CONCLUSIONS

The following conclusions were drawn from the observed kinetic data and from the spectroscopic information collected for Pd(II)-catalyzed oxidation of L- Proline by NCS in acidic medium.

1. NCS itself and $[PdCl_4]^{2-}$ have been assumed as the reactive species of NCS and Pd (II) chloride in acidic medium, respectively
2. The complex $[PdCl_3.NCS.AA]^-$ has been proposed as the most reactive activated complex in the oxidation of L(-) Proline by NCS in acidic medium.
3. Positive entropy of activation clearly supports step (III) of the purposed reaction scheme 1
4. The rate of oxidation of L-Proline is unaffected by the ionic strength of the medium.
5. Pyrrolid-2-one was identified as the oxidation product of the reaction under investigation.

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REFERENCES

[1] B. Singh, M. Mishra, S.P. Singh, J. Singh, Ashish, *Oxid.Commun,* **2006,** 29(2), 410-418.
[2] Rashmi Tripathi, Neelu Kambo, S.K. Upadhyay, *Trans. Met. Chem*, **2004**, 29, 861-866.
[3] Ashok Kumar Singh, Reena Singh, Jaya Srivasatava, Shahla Rahmani, Ranju Pradhan, *J Applicable Chem.,* **2015**, 4 (2), 587-600.
[4] Ashok Kumar Singh, Priyanka Singh, Jaya Srivastava, Shahla Rahmani, Ravi Prakash, *J Applicable Chem.,***2015,** 4 (5), 1507-1521.
[5] Ashok Kumar Singh, Rajesh Kumar Singh, Jaya Srivastava, Rakesh Patel and Shahla Rahmani, *J Applicable Chem.,***2016**, 5 (1)**,** 204-218 .
[6] A.K. Singh, T. Gupta, V. K. Singh, S. Rahmani, D. Kesarwani, B. Singh, *Oxid. Comm,* **2000**, 23(3), 416-422.
[7] A.K. Singh, S. Rahmani, V.K. Singh, V. Gupta, D. Kesarwani, B. Singh, *Ind. J. Chem*, **2001,** 40A, 519-523.
[8] K. S. Rangappa, M. P. Raghvendra, D. S. Mahadevappa, D. C. Gowda, *Carbohydrate Research,***1998,** 306, 57-67.
[9] T.A. Iyengar, Puttaswamy, D.S. Mahadewappa, *Carbohydr. Res*, **1990**, 204, 197-206.
[10] T.A. Iyengar, Puttaswamy, D.S. Mahadevappa, *Cabohydr. Res*, **1990**, 197, 119- 130.
[11] D. S. Mahadevappa, K. S. Rangappa, N. N. M. Gowda, B. Thimmegouda, *Int. J. Chem. Kinet*, **1986,** 60, 589.
[12] Puttaswamy, Nirmala Vaz, Proc. *Indian Acad. Sci. (Chem. Sci*.), **2001**, 113(4), 325–332.
[13] Ahmed A. Abdel-Khalek, Adel A. Mohamed, Hassan A. Ewais, *Transition Met. Chem*, **1999**, 24, 233-238.
[14] Rosap Ascualm,' Iguela . Herraeza, N D Emilioc Alle, *Can. J. Chem*, **1989,** 67.

[15] Veeresh C.Seregar, Chanabasayya, G.A.Hiremath, S.T.Nandibewoor, *Transition metal Chemistry*, **2006**, 31, *541-548.*

[16] B. List, R. A. Lerner, C. F. Barbas, J. *Am. Chem.Soc*, **2000**, 122, 2395.

[17] I.S. Ahmed, C. Mohammad, *J Chem Kinet*, **1985**, 11, 813.

[18] N.N haligudi, S.M. Desai, S.T.Nandibewoor, *Indian J Chem*, **1999**, 38A, 943-946.

[19] A.K. Singh, D. Chopra, S.Rahmani, B.Singh, *Carbohydr Res*, **1998**, 314,157.

[20] Ammar J. Mohammed,Hassan Hadi, *Journal of Al-Nahrain University*, **2007,** 10(2), 66-72.

[21] SUN, Han-Wen SHI, Hong-Mei, SHEN, Shi-Gang, KANG, Wei-Junb GUO, Zhi-Feng, *Chinese Journal of Chemistry*, **2008**, 26, 615—620.

[22] M.I.Heremath, R.S.Shettar, Nandibewoor, *E-Journal of Chemistry***, 2004**, 1(5), 216- 227.

[23] Ashish, Chhaya Singh, Ashok Kumar Singh, Bharat Singh, *Indian Journal of Chemistry*, **2005**, 44, 476-482.

[24] Patrick M. Henry, "Palladium Catalysed Oxidation of Hydrocarbons", **2**, D.Reidel Publishing Company, Holland**, 1928,** pp. 6.

[25] F.A**.** Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Edn (Wiley Interscience, New York, **1988,** pp.1026.

[26] G.P. Tikhonova, S.N. Bovkovets, *Russ J Inorg Chem*, **1973,** 23, 813.

[27] V.I. Schlenskaya, A.A. Biryukov, *Russ J Inorg Chem*, **1966,** 11, 28.

[28] G.H. Ayres, Anal Chem, **1953,** 24, 1622.

[29] R. Chang , Physical Chemistry with applications to Biological systems; McMillan; New York, **1981**, 326.

CITATIONS

[1] Ashok Kumar Singh, Priyanka Singh, Jaya Srivastava, Shahla Rahmani, Ravi Prakash, Rh(III)-Catalysis in The Kinetic Studies of Oxidation of D-Xylose by N-Bromosuccinimide in Acidic Medium, *J Applicable Chem.*, **2015**, 4 (5), 1507-1521.

[2] Ashok Kumar Singh, Rajesh Kumar Singh, Jaya Srivastava, Rakesh Patel , Shahla Rahmani, Kinetics Of Oxidation Of Trehalose By Protonated N-Bromosuccinimide Using Rh (III) Chloride As Homogeneous Catalyst, *J Applicable Chem.*, **2016**, 5 (1), 204-218.

[3] Ashok Kumar Singh, Manjula Singh, Jaya Srivastava, Shahla Rahmani, Rupam Yadav, The Kinetics of Rh(III)-Catalyzed Oxidation of D(+) Melibiose By Cu(II) Bipyridyl Complex In Alkaline Medium, *J Applicable Chem.*, **2015**, 4 (2), 510-524.

[4] Ashok Kumar Singh, Reena Singh, Jaya Srivasatava, Shahla Rahmani, Ranju Pradhan, A Kinetic Approach for $(H_2OBr)^+$ Oxidation of Glucose in Presence of $[RhCl_4(H_2O)_2]^{1-}$ as Catalyst, *J Applicable Chem.*, **2015**, 4 (2), 587-600.

[5] Jagdish V. Bharad, Balaji R. Madje, Milind B. Ubale, Kinetics and Mechanistic Study of Oxidation of 1-Phenylethanols by N-Bromophthalimide in Aqueous Acetic acid, *J Applicable Chem.*, **2014**, 3 (4), 1776-1781.

[6] Birla Anjaiah, P. Srinivas, Kinetics and mechanism of oxidation of aminoalcohols with N-Bromopthalimide in aqueous acetic acid, *J Applicable Chem.*, **2014**, 3 (5), 2123-2130.

[7] Prashant A. Magdum, Basavraj S. Gundapalli, Maruthi M. Kurubar and Sharanappa T. Nandibewoor, Kinetics And Mechanistic Investigation of Oxidation of D-Mannitol By Periodate In Aqueous Alkaline Medium, *J Applicable Chem.*, **2014**, 3 (4), 1744-1755.

[8] L. N. Malviya, V. K. Siriah, M. K. Badole, Kinetics and mechanism of oxidation of lactic acid by N-bromoanisamide, *J Applicable Chem.*, **2013**, 2 (3), 636-639.

[9] Manoj Kumar Ghosh, Surendra K. Rajput, Study of Palladium (II) Catalysed Oxidation of D-(+) Ribose by Cerium (IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Approach, *J Applicable Chem.*, **2013**, 2 (2),280-290.

[10] Ajay Sharma, A. Meena, J. Khatri, P. Swami, Vinita Sharma, Kinetics and Mechanism of the Oxidation of DL-Methionine by Quinolinium Chlorochromate, *J Applicable Chem.*, **2012**, 1 (1), 70-78.

[11] Surendra K. Rajput, Sonal Choubey,Kinetic Study of Oxidation of Milk Sugar by Ceric Ammonium Sulphate in Acidic Medium, *J Applicable Chem.*, **2012**, 1 (1), 79-96.

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