A KINETIC STUDY OF OXIDATION OF AMINO ACIDS BY N-BROMOSUCCINIMIDE (NBS) USING TRANSITION METAL CATALYSTS IN AQUEOUS MEDIUM

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Thesis

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UNIVERSITY OF KOTA

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Submitted by
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I, **Rashmi Gupta**, hereby certify that the research work presented in my Ph.D. thesis entitled **"A KINETIC STUDY OF OXIDATION OF AMINO ACIDS BY N-BROMOSUCCINIMIDE (NBS) USING TRANSITION METAL CATALYSTS IN AQUEOUS MEDIUM"** which is carried out by me under the supervision of **Dr. Manju Bala Yadav,** Professor, Department of Chemistry, Govt. College, Kota and submitted in the partial fulfillment of the requirement for the award of the degree of Doctor of Philosophy of the University of Kota, represents my ideas in my own words and where others' ideas or words have been included in this thesis, I have adequately cited and referenced the original sources.

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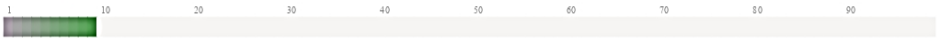

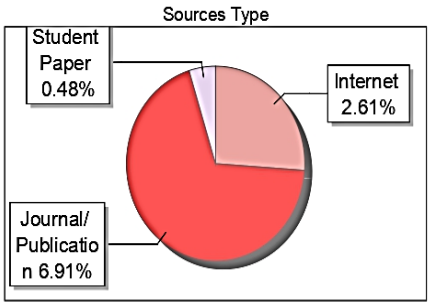

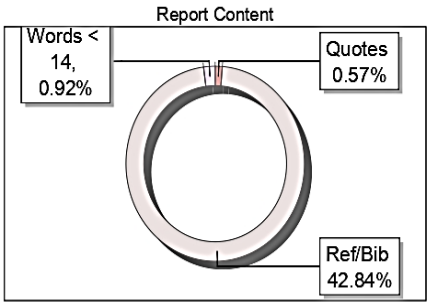

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A WORD OF GRATITUDE

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Rashmi Gupta

(Research Scholar)

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HARD WORK + DREAMS + DEDICATION = SUCCESS

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ABSTRACT

This thesis presents a comprehensive study on the oxidation of amino acids by N-Bromosuccinimide (NBS) in the presence of palladium (II) and palladium nanoparticles as catalysts in presence of perchloric acid, with the aim of understanding the mechanistic, kinetic and catalytic roles of palladium in facilitating this significant transformation. NBS, a mild oxidising agent, was employed to oxidise a range of amino acids to their corresponding aldehydes.

It also presents the experimental procedures involved in the synthesis of palladium nanoparticles using the chemical reduction method. The synthesized nanoparticles are subjected to morphological and structural characterization using various techniques, including UV-Visible Spectroscopy, FT-IR Spectroscopy and Transmission Electron Microscopy (TEM).

Kinetic studies were conducted under pseudo first order conditions, maintaining large excess of the amino acids. The reactions were monitored titrimetrically by following the decrease in concentration of NBS. The results indicate that the oxidation reaction follows first order kinetics with respect to NBS and catalyst, fractional and negative order w.r.t amino acid and acid respectively and the observed rate constants significantly increase in the presence of catalyst as compared to aqueous medium.

Using Pd (II), this enhancement is attributed to complex formation between NBS and Pd (II) which then reacts with amino acid in the rate determining step to form another complex which in subsequent steps give products. On the basis of observed kinetic orders and spectral analysis information collected for the possible formation of complex or complexes in the reaction, a probable reaction path has been proposed.

In case of palladium nanoparticles there is large surface-to-volume ratio with many active sites that can adsorb both the oxidant (NBS) and the substrate (amino acid) at the same time. Further, adsorption weakens certain bonds (e.g., C–H, N–H) in the substrate, that makes easier for the oxidizing agent to attack. Pd nanoparticles may undergo dynamic redox conversion between Pd^0 and Pd^{2+} states during the reaction. These redox transitions enable efficient regeneration of Br^+ species from NBS and facilitating repeated oxidative events. The homogeneous medium increases this effect due to high dispersion and surface availability of Pd, ensuring close contact with both NBS and amino acid molecules. All these factors drastically reduce the activation energy of the reaction thereby explaining the observed catalytic acceleration.

Activation parameters such as Activation energy (E_a), Enthalpy ($\Delta H^{\neq}$), Entropy ($\Delta S^{\neq}$) and Gibbs free energy ($\Delta G^{\neq}$) of activation were calculated from temperature dependent studies, proving insights into the transition state.

Overall, this research demonstrated that oxidation of amino acid by NBS is a slow oxidation process that can be accelerated using Pd (II) and palladium nanoparticles. The rate is very fast with palladium nanoparticles as compared to Pd (II).

CONTENT

ABBREVIATION

NBS	N-Bromosuccinimide
Val	Valine
Ser	Serine
Asp	Aspartic acid
Arg	Arginine
Pdnps	Palladium nanoparticles
PVP	Polyvinylpyrrolidone
KD	Kilodalton
KHz	Kilohertz
rpm	Rotation per minute
KI	Potassium iodide
$HClO_4$	Perchloric acid
$NaClO_4$	Sodium perchlorate
Hypo	Sodium thiosulphate ($Na_2S_2O_3$)
2,4 – DNPH	2,4 Dinitrophenylhydrazine
$PdCl_2$	Palladium chloride
HCl	Hydrochloric acid
KCl	Potassium chloride
MA	Mandelic acid
DMF	N, N-Dimethyl formamide
BINAP	2,2'-Bis (diphenlyphasphino)-1,1'-binaphtyl
PdO	Palladium (II) oxide
SSS	Silica Starch Subtrate
NCS	N-Chlorosuccinimide
PANI-H	Polyaniline-hydrochloride

k_{obs}	Pseudo first order rate constant
I	Ionic strength
EDTA	Ethylenediamine tetra acetic acid
HRTEM	High Resolution Transmission Electron Microscope
UV-Vis	Ultra-Violet Visible
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission Electron Microscope

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CHAPTER 1

INTRODUCTION

ABSTRACT

The present chapter gives a review on the kinetic studies of the oxidation of amino acids by N-Bromosuccinimide (NBS) in the presence of palladium (II) and palladium nanoparticles as catalysts. This review describes a brief discussion of various transition metal nanoparticles and their applications in different reactions. The literature examined encompasses foundational insights into the structural classification and functional diversity of amino acids and also presents a curated compilation of scholarly references that provide a comprehensive overview of amino acids and oxidants.

1.1 CHEMICAL KINETICS

Chemical Kinetics is the study of the rate at which a chemical process occurs and quantitative study of chemical systems that are changing with time. It concerns itself with the measurement of rate of reactions proceeding under given condition of temperature, pressure and concentration [1]. If a reaction is able to take place, we want to understand how far the reaction will proceed, and how rapid it will manifest. The aim of chemical kinetics is twofold, to determine the macroscopic rate law of the overall reaction along with the numerical values of the rate constants and to analyze the reaction mechanism. Kinetics takes into consideration the time required for transformation of reactants from one state to another. Some reactions take place rapidly within fraction of seconds while some are extremely slow like rusting of iron. Reactions which take reasonable time for completion can be studied conveniently by suitable methods. There are different types of chemical reactions and wide varieties of physical and chemical methods to investigate them. In all these methods, decreasing concentration of reactant and increasing concentration of product is measured at different time intervals as the reaction proceeds.

Numerous researchers [2-4] have made significant contributions in the science of chemical kinetics. This area of study is important for understanding reactions in gaseous, liquid and solid phases. Engineers from various industries as well as organic and particularly inorganic chemists have shown great interest in this field. Liquid phase reactions have received considerable attention due to their relevance to both organic and inorganic chemists and industry professionals [5-7]. The study of various thermodynamic parameters- such as activation energy (ΔE), entropy of activation (ΔS) and free energy of activation (ΔG) can help in elucidating reaction mechanisms. The mechanism is often determined by analyzing various kinetic parameters such as order of the reaction with respect to various reactants, influence of catalyst concentration, ionic strength [8], solvent effects [9-10], dielectric permittivity [11-14] and the presence of free radicals [15-16]. The key factors to understand the mechanisms involving in the reactions are stoichiometry determination, influence of substituents on the reaction rate and identification and estimation of the products. In reactions involving multiple elementary steps, the slowest step i.e., rate determining step controls the overall reaction.

The reaction rate is significantly influenced by the presence of a catalyst. Heterogenous catalyst is a well- established area, with numerous notable examples demonstrating its vital role in industrial development. In catalyzed reactions, several short-lived intermediates can be formed alongside the catalyst. Consequently, the reaction pathway in a catalyzed process may differ from that of an uncatalyzed one, even though the final products are crucial for understanding the reaction mechanism.

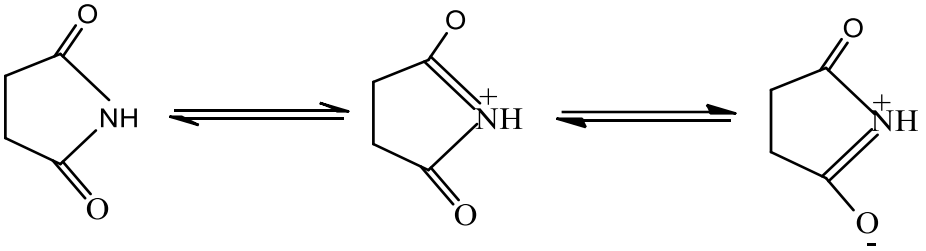
The current study clarifies how chemical kinetics can be used to investigate the intricate chemistry of amino acids. The oxidation of amino acids, specifically valine, serine, arginine, and aspartic acid, by NBS in the presence of Pd (II) catalyst and Pd nanocatalyst is the broad scope of our investigation. A lot of experimental data is gathered, standard kinetic quantities are calculated, and the mechanism explaining the different steps in the solution phase is derived.

1.2 NBS (N-BROMOSUCCINIMIDE)

Pure NBS (Mol.Weight 178) is a colourless solid melting at 176-177˚C free from sodium bromide and occluded bromine. It contains 44.5%-44.9% active bromine depending on its purity. NBS is soluble in various solvents such as water (1.48g/100ml), carbon tetrachloride (0.025g/100ml), benzene (1.12g/100ml) and n-hexane (0.003g/100ml). N-Bromo succinimide shows its solubility in different organic solvents like chloroform, ethanol, pyridine, glacial acetic acid and nitromethane. In most solvents, NBS undergoes decomposition when exposed to air, light or acids. This process is accelerated at higher temperatures and can often be noticed by a change in the solution's color to pale yellow due to the release of bromine which is accompanied by a strong bromine odor. N-Bromosuccinimide is a potential oxidizing agent [17-21] and analytical agent. It has also been used in the estimation of several organic as well as inorganic compounds. This reagent has been exploited as an oxidant for a variety of substrates in both acidic and alkaline medium [22, 23]. In acidic medium N-Bromosuccinimide is involved in multiple equilibria [24, 25] and one needs to know the active form of NBS in the reaction.

The N-Br bond in NBS is basically covalent. The acidic behaviour of succinimide **(Eqn. 1)** is accounted by the stability of the anion **(Eqn. 2)**, which permits charge distribution rather than charge separation. It is also impossible to completely rule out the contribution of N-Bromosuccinimide's anionic form, especially when it comes to

polar solvent solutions.



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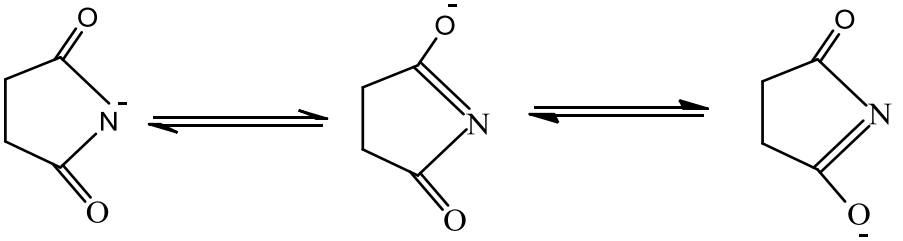


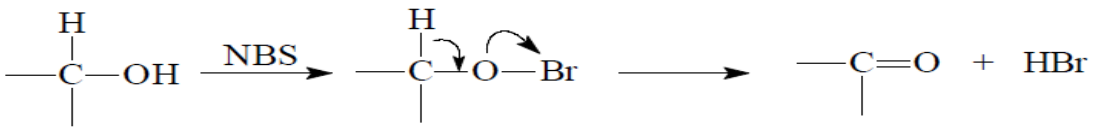
(2)

In N–halogen compounds, an increase in the electronegativity of the nitrogen atom increases its ability to withdraw electron density from the covalently bonded halogen. thereby increasing the partial positive charge on the halogen, making it more electrophilic and a stronger oxidizing agent. While the N-Br bond in other halomides is often polar, it is nearly non-polar in N-bromo succinimide. The molecules of succinimide and N-Bromosuccinimide are entirely planer than those of several other N-bromoimides [26]. The modest quantity of bromine released by N-bromo succinimide makes it a very selective bromination agent that can be used in both electrophilic addition of unsaturated systems and free radical replacement. Attaching nitrogen to specific electron-withdrawing groups, like acyl groups, increases its electronegativity even more. The mechanisms and active oxidizing species are dependent on the reaction environment, the groups bonded to the nitrogen, and the behavior of the halogen atom. The species causing this oxidizing nature could depend on the medium's pH changes. In alkaline solutions, the likely reactive species [27] of NBS are >NH, HOX and OX^-, while in acidic solutions, they are >NX, H_2OX^+, $>N^+HX$ or HOX.

Most of the investigations of NBS oxidations of organic substances have assumed that the molecular NBS acts only through its positive polar end [28] producing Br^+, which is subsequently solvated. Thus H_2O^+Br has been considered as the effective oxidizing species of NBS in acidic medium. Protonated form of NBS, i.e., N^+BSH has also been considered [29] as reactive species of NBS in acidic medium in presence of mercuric acetate.

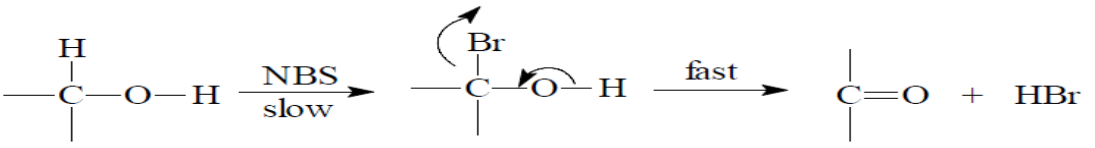
1.2.1 Kinetics Studies of NBS with Different Compounds

Although events involving the addition of oxygen have been reported, the majority of N-Bromosuccinimide oxidation reactions involve the abstraction of hydrogen from C-H, O-H, N-H, or S-H bonds. The identification of several chemical compounds has made considerable use of these reactions. NBS has been employed for oxidation at comparatively lower pH values because it is comparatively more stable in neutral, aqueous or slightly acidic media (pH 4.5). NBS undergoes a straightforward two-electron reduction during the oxidation reactions, producing succinimide and bromide ions as byproducts that do not affect the identification of organic molecules. It is widely acknowledged that the attacking species in polar media is a "positive" halogen, through which oxidation processes occur. But NBS can also hydrolyze gradually to produce hypobromite. The reactive species may even be molecular NBS or molecular bromine. The oxidation of steroidal alcohols by N-Bromosuccinimide (NBS) was systematically studied by Fieser and Rajagopalan [30–31] and Srinivasan et al. [32] and Barakat and Mousa [33] reported that primary and secondary alcohols undergo NBS oxidation to the corresponding aldehyde and ketones. As seen in **[Scheme 1]**, Kruse et al. [34] suggested a provisional mechanism for the oxidation of alcohols by NBS that involves the formation of intermediate hypobromite and the quick loss of hydrogen bromide to create carbonyl compounds.



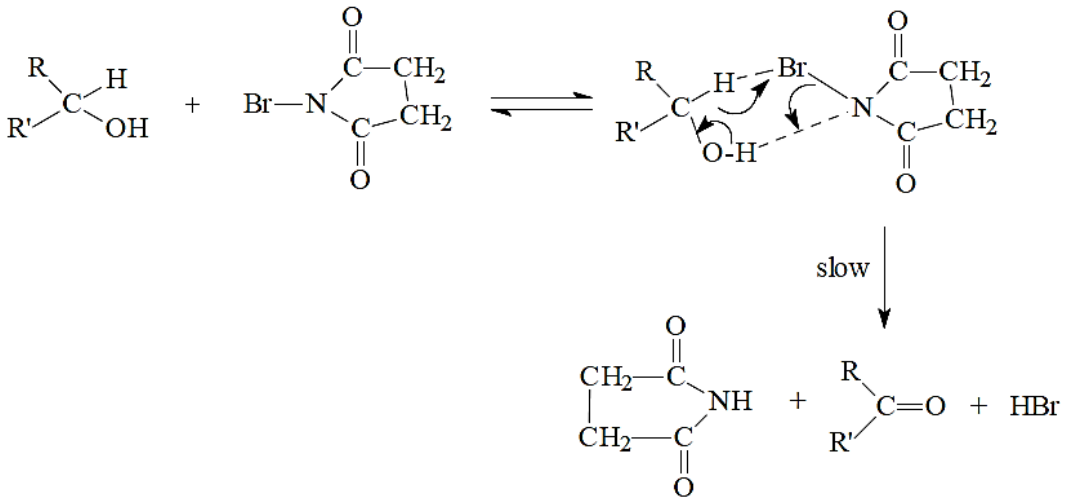
Scheme 1: Hypobromite intermediate

According to a different route outlined by Lecomte and Gault [35], the oxidation process continues by replacing a hydrogen atom on the carbon atom bearing –OH group with bromine of NBS, with a quick loss of hydrogen bromide. C-H bond cleavage to create a bromo intermediate in this process was regarded as the step that determines the rate **[Scheme 2]**.



Scheme 2: Bromo intermediate

The study on the oxidation of several aromatic and aliphatic alcohols by NBS was reported under kinetic conditions [36]. The reaction was first order in terms of [alcohol] and [NBS], and overall, it was second order kinetics. Two stages of the reaction were observed, with the first stage primarily fast which is caused by Br_2 oxidation. In the second step, initial addition of mercuric acetate acts as a scavenger for any bromine generated in the reaction, $HgBr_4$ or $HgBr_2$, fully suppressed the second step and ensured pure NBS oxidation. It was suggested that the rate-determining step involves a mechanism **[Scheme 3]** in which the loss of secondary hydrogen takes place as a hydride ion.



Scheme 3: Oxidation of Alcohols by NBS

Ganapathy et al. have investigated the kinetics of allyl alcohol oxidation to acrolein by NBS [37]. First order dependence on both [NBS] and allyl alcohol was seen in the reaction. It was seen that the proposed mechanism in the reaction involved the abstraction of hydrogen as a hydride ion by [$NBSH^+$] **(Eqns.3-5)**.

$$CH_2=CH-CH_2-OH_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2C=CH-CH_2-OH + H^+ \quad (3)$$

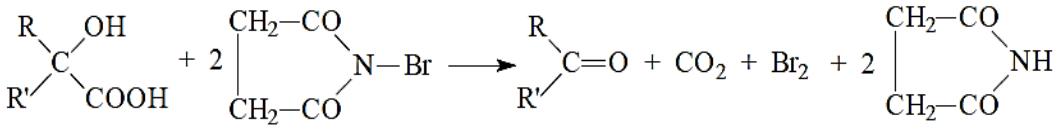
$$NBS + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (NBSH)^+ \quad (4)$$

$$CH_2=CH-CH_2-OH + (NBSH)^+ \xrightarrow[\text{slow}]{k_3} CH_2=CH-CHO + (CH_2CO)_2NH + 2H^+ + Br^- \quad (5)$$

The following rate law was derived from the above mechanism

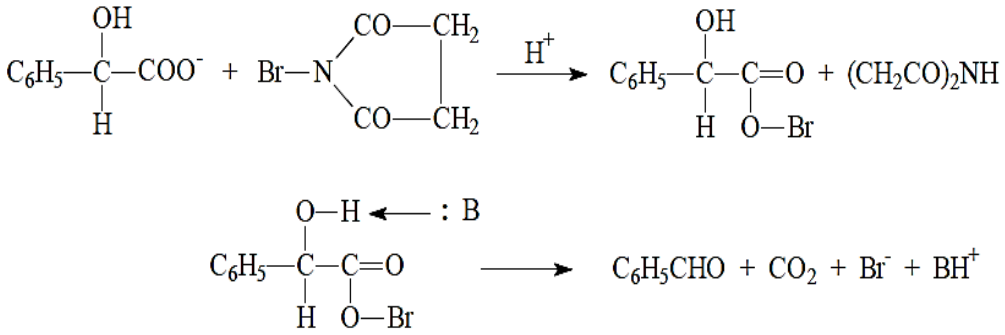
$$-\frac{d[NBS]}{dt} = \frac{k_1k_2k_3[NBS][Alcohol]}{k_{-1}k_{-2}} \quad (6)$$

NBS converts α-hydroxy acids to aldehydes or ketones with one less carbon atom than the parent acid in an aqueous solution [38]. The following [**Scheme 4**] can be used to illustrate the oxidation reaction.



Scheme 4: Oxidation of α– hydroxy acids by NBS

In H_2SO_4 medium, Venkatasubramanian and Natarajan [39] examined the kinetics of NBS-induced oxidation of mandelic acid (MA). The reaction showed a whole second order dependence under experimental conditions, with the first order being related to [MA] and [NBS]. Carbon dioxide and benzaldehyde were determined to be oxidation products. As the pH increased, so did the rate of oxidation. These findings have led to the proposal of the following mechanism [**Scheme 5**].



Scheme 5: Oxidation of Mandelic acid (MA) by NBS

A.K. Singh [40] noted first order kinetics in the Ir (III) catalyzed oxidation of aspartic acid by NBS in [NBS], [Ir (III)], [aspartic acid], and on [Cl^-]. It was found that the reaction rate dropped when $HClO_4$ and acetic acid were added one after the other. Waqarchand et al. conducted comparable kinetic research [41]. Zero order kinetics in [Ru (III)] were observed by Reshmi et al. [42] in the Ru (III)catalyzed oxidation of certain hydroxyl acids in the presence of Cl^- ions. N-Bromosuccinimide in carbon tetra chloride, oxidizes thiols to the equivalent disulphides [43].

Oxidation in an aqueous acetic acid solution yields the same oxidation products, and the process has been used to identify thiols, including thiophenols [44]. According to Barkat and Mousa [33], primary amines and NBS react violently in an aqueous medium

at room temperature to produce the appropriate aldehyde. They suggested the following process (**Eqns. 7-9**).

$$(CH_2CO)_2N-Br + RCH_2-NH_2 \longrightarrow RCH_2-NHBr + (CH_2CO)_2NH \quad (7)$$

$$RCH_2-NHBr \longrightarrow RCH=NH + HBr \text{ (Aldmine)} \quad (8)$$

$$R-CH=NH \xrightarrow{H_2O} R-CHO + NH_3 \quad (9)$$

According to Kruse et al. [34], secondary amines easily undergo N-bromination with NBS, which is typically followed by HBr removal. According to reports, aldehyde and secondary amines are produced when tertiary amines undergo C-N fission [34, 45]. In acid medium solutions, the kinetics of NBS oxidation of primary aliphatic amines [46] demonstrated a first-order dependence on [Amine] and [NBS]. The rate rose somewhat with an increase in $[H^+]$. As the medium's dielectric constant decreased, the rate of reaction increased. According to stoichiometric analyses, one mole of amine converted one mole of NBS into one mole of ammonia and carbonyl molecule.

Ru (III) catalyzed aliphatic amine oxidation by NBS in a perchloric acid media is one recent report [47]. In a perchloric acid solution with the presence of mercuric acetate, the kinetics of the Ru (III) catalyzed oxidation of diethylene glycol (DG) and ethyl diethylene (EDG) by NBS have been examined [48]. A plausible mechanism that aligns with the kinetic findings has been suggested. A first order dependence on [aldose] and [NBS] was found in the kinetics of aldose oxidation [49,50] by NBS in H_2SO_4. According to reports, NBS uses hydride ion transfer to oxidize hydroxyl groups more quickly than equatorial ones [51]. Sunita Manjari Padma has examined the kinetics and mechanistic analysis of 5-oxoacid oxidation by NBS in aqueous acetic media [52]. First order dependence is observed in [NBS], [5-Oxo acid], and $[H_2SO_4]$. According to the suggested mechanism, protonated species of N-Bromosuccinimide $[H_2O^+Br]$ attack the enol form of 5-oxo acids, forming a carbocationic reaction centre by carbon – carbon bond cleavage yield corresponding benzoic acids in the fast step **(Eqn. 10)**.

$$\frac{1}{k} = \left[\frac{[\text{succinimide}]}{k_{obs}[\text{Oxoacid}][\text{NBS}][H_3O^+]} \right] \quad (10)$$

1.3 AMINO ACID

Proteins are among the most prevalent organic molecules in biological systems and are considerably more diversified in structure and function than other types of macromolecules. The human body uses proteins, which are polymers of amino acids, for a variety of structural and functional purposes. Amino acids are vital building blocks of proteins in the body, useful for the growth and repair of damaged cells / tissues, synthesis of enzymes, plasma proteins, antibodies and some hormones. One of the most fascinating areas in organic chemistry is the study of amino acids. Numerous metabolic processes, including the formation of proteins, polypeptides, and nucleotides, depend on amino acids [53]. Therefore, a promising field for in-depth research is the mechanism of analogs of non-enzymatic chemical reactions in the oxidation of amino acids [54].

Amino acids form a group of neutral products that are distinct from other natural compounds both chemically and biochemically because of their ampholytic properties and their role as protein. A carboxylic acid that has an aliphatic primary amino group in the α position to the carboxyl group [55] and a side chain (R group) linked to the α-carbon is called an amino acid. All 20 amino acids, with the exception of glycine, possess L-configuration, as the α-carbon is chiral for all but one amino acid. Glycine is not optically active due to the absence of an asymmetric carbon atom; thus, it is neither designated as D nor L. Nine amino acids cannot be produced by the body and must thus be included in the food for protein synthesis to take place. The essential amino acids include valine, histidine, leucine, isoleucine, lysine, methionine, phenylalanine, threonine, and tryptophan. Arginine, glutamine, tyrosine, cysteine, glycine, proline, serine, ornithine, alanine, asparagine, and aspartate are non-essential amino acids that the body can generate on its own and hence do not always need to be obtained through diet. Depending on whether an amino acid has polar substituents or non-polar groups, it can undergo a variety of reactions.

Strict genetic regulation is used to biosynthesize proteins from a system of twenty amino acids. As a result, the fundamental building block of proteins is amino acids. Only 20 of the more than 300 amino acids that are found in nature are typical and found in proteins due to gene coding. Additional amino acids are non-protein amino acids called modified amino acids. Some are amino acids found in living things but not as

protein constituents; others are residues that have undergone post-translational changes after a protein has been produced.

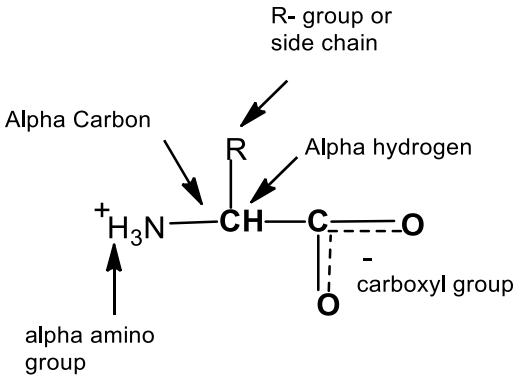


Figure 1.1: Structure of Amino Acid

Chains of amino acids are proteins which are joined by amide bonds called peptide linkages. The unique property of each amino acid is due to difference in the side-chain group or R-group. The distinctiveness of different proteins is then determined by the amino acids it contains, how these amino acids are organized in a chain, and further complex interactions the chain makes with itself and the environment.

Because of their amphoteric nature, amino acids have both basic and acidic characteristics. Neutral amino acids have been demonstrated to exist as inner salts with the dipolar structure of H_3NCOO^-. These occur even in solid form and are referred to as "Zwitter ions." This ion is also present in a straightforward solution created by dissolving the amino acid in water. In aqueous solutions, amino acids are known to exist in the following equilibrium:**(Eqns. 11- 12)**.

$$RCHNH_2COOH \rightleftharpoons RCHNH_2COO^- + H^+ \rightleftharpoons RCH(NH_3^+)COO^- \quad (11)$$

These amino acids dissociate according to pH.

$$RCH(NH_3^+)COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCH(NH_3^+)COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_2COO^- \quad (12)$$

Cation **Zwitter ion** **Anion**

Amino acid exists in the form of Zwitter ion in aqueous medium while in highly acidic medium, it exists in the protonated form, whereas in highly basic medium it remains in the anionic form. The pH of the dilute solution of Zwitterions is determined by its basic strength and acidic strengths **(Eqn. 13)**.

$$\mathrm{pH} = \frac{\mathrm{pK}_{a1} + \mathrm{pK}_{a2}}{2} \tag{13}$$

where its basic and acidic groups' acid dissociation constants are denoted by pK_{a1} and pK_{a2}, respectively. The pH of the diluted alanine solution is 6.11, while pK_{a1} and pK_{a2} for alanine are 2.35 and 9.87, respectively. The isoionic point of alanine is pH 6.11, where the number of negative charges on the protolysis-produced molecule is equal to the number of positive charges needed for proton acquisition. This value is also referred to as the isoelectric point since the alanine molecule at this pH is electrophoretically mobile and does not carry any net charge [57]. The role of various amino acids used in our study are described below.

1.3.1 Arginine amino acid

L-Arginine (L-Arg), one of the essential amino acids, is most importantly useful in child growth. L-arginine plays a vital role in synthesizing urea in mammals, the principal form in which these species excrete nitrogen. It also finds applications in the field of medicine.

1.3.2 Serine amino acid

The oxidation of serine has drawn a lot of interest because it produces a fatty acid coating around nerve fibers and strengthens the immune system by producing antibodies. It was demonstrated that serine was mostly transformed into CO_2 and then transferred to muscle glycogen. Pyruvate and ammonia were produced as a result of the anaerobic deamination of serine using various biological preparations.

1.3.3 Valine amino acid

Valine, α-amino acid, is used in the biological synthesis of the proteins. It contains an α-amino group, an α-carboxylic acid group and an isopropyl group side chain, making it a non-polar aliphatic amino acid. It is essential in humans, but the body cannot synthesize it, so it must be obtained from the diet. It promotes muscle growth and tissue repair. It acts as a precursor in the penicillin biosynthetic pathway.

1.3.4 Aspartic amino acid

Aspartic acid (or aspartate) is a non-essential amino acid, which means that it is readily and naturally synthesized by mammals. It plays a critical role in generating cellular activity and in improving metabolism. It plays important role in hormone production and nervous system functioning.

1.4 PALLADIUM (II)

Palladium is a rare and lustrous silvery-white metal with the symbol Pd. Palladium, rhodium, platinum, osmium, ruthenium and iridium belong to the group of elements known as platinum group metals (PGM). Referred to as the platinum, they share similar chemical characteristics; however, palladium is the least dense of them and has the lowest group melting point. Palladium constitutes only 0.85% of the total naturally available PGMs.

Palladium dissolves slowly in concentrated nitric acid, in hot concentrated sulphuric acid, and when finely ground, in hydrochloric acid [58]. It readily dissolves in aqua regia at room temperature. Palladium does not react with oxygen at normal temperature (thus does not tarnish in air). Palladium heated to 800>°C will produce a layer of palladium (II) oxide (PdO). It may slowly develop a slight brownish coloration over time due to formation of a surface layer of its monoxide.

The main sources of palladium compounds are in the oxidation states of 0 and 2. Other less well-known states are acknowledged as well. In general, palladium compounds resemble those of platinum more than any other elements. Palladium (II) most probably acts as either a catalyst or as a reductant having the reduction potential of the palladium (IV)/palladium (II) couple in diluted acid as 0.532V.

Palladium has reported exhibit extraordinary catalytic and corrosion resistance properties, both as a metal and as an alloy, which have led to its widespread applications [59]. Over half of the supply of palladium and its congener platinum goes into catalytic converters, which convert 90% of harmful gases from auto exhaust (hydrocarbons, carbon monoxide and nitrogen dioxide) into less harmful substances (carbon dioxide, nitrogen and water vapour). As a catalyst, palladium is employed in various industrial processes such as Petroleum cracking [60], alkaline oxidation, selective low oxide formation [61,62] reduction of C≡C to C=C without further reduction to carbon-carbon single bond [63], Suzuki coupling [64], Heck reaction [65] and carbon– fluoride bond formation [66]. Palladium is regarded as a superior electro-catalyst for alcohol oxidation in alkaline media [67, 68]. Palladium is an important hydrogenation and dehydrogenation catalyst in organometallic chemistry. Palladium is also used in electronics, dentistry, hydrogen purification, chemical applications and groundwater treatment [**Fig. 1.2**].

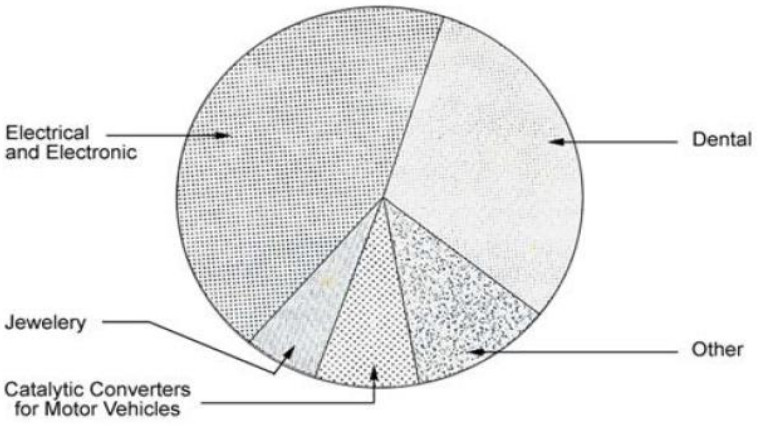


Figure 1.2: Application of palladium

Palladium plays a key role in the technology used for fuel cells, which combine hydrogen and oxygen to produce electricity, heat and water. Further, palladium can adsorb 800 times its volume of gaseous hydrogen to give material useful as a reducing agent which makes this metal, a suitable material for hydrogen [69]. Palladium is combined with a wide variety of ligands and used for selective chemical transformation. The use of platinum group metal ions, such as iridium, ruthenium, and osmium, either alone or in binary combinations, as catalysts in a variety of redox processes has garnered a lot of attention lately [70]. Transition metal ion compounds [71–73] have been widely employed as homogeneous catalysts. Although it is known that palladium (II) may catalyze a variety of processes [74–76], it is still unknown what its active form is in these reactions. Most studies using Pd (II) as a catalyst have been used in the form of palladium (II) chloride [77]. Therefore, to identify the catalyst's active species, the impact of chloride on the reaction was investigated. It is known that Pd (II) can catalyze in both acidic and alkaline media.

Palladium chloride is quite soluble in HCl and exists [78] primarily as $[PdCl_4]^{2-}$. Various mononuclear complexes, namely $[PdLCl_3]$, $[PdL_2Cl_2]$, $[PdLCl]^+$ and $[PdL_4]^{2+}$ (where L represent amine, phosphine, thioether, etc.) are well known. Oxidation of olefins by palladium (II) employed as a heterogenous catalyst, has been widely investigated [79, 80].

This study will enable us to understand the complicated biological reactions in living systems and will also help us to understand the catalytic activity of Pd (II) along with oxidative capacity of NBS in aqueous medium.

1.4.1 Review of Pd (II) studies

Suresh M. Tuwar and Co-workers [81] have reported Os (VIII) / Pd (II) catalysis of the Ce^{IV}–allyl alcohol (AA) reaction in acidic media which depends both on the rate enhancement and product distribution and the catalyst used. Os (VIII) results mainly in acrolein, whereas Pd (II) gives acrylic acid. Complex formation between the catalyst, palladium (II) and allyl alcohol is suggested by the experimental rate law (**Eqns.14-16**). The reaction is fractionally ordered in the oxidant and palladium (II) and zero order in the allyl alcohol.

$$Pd^{II} + AA \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Complex } C_I \tag{14}$$

$$Ce^{IV} + C_I \overset{K_{II}}{\rightleftharpoons} \text{Complex } C_{II} \tag{15}$$

$$C_{II} \xrightarrow{K_r} AA^0 + Ce^{III} + Pd^{II} \tag{16}$$

S. A. Chimatadar et al [82] have studied kinetics of palladium (II) catalysed oxidation of mercury (I) by iron (III) – 2,2- bipyridyl complex spectrophotometrically in aqueous nitric acid and methanol media. The reaction is first order each in [iron (III) – 2,2-bipyridyl] and [palladium (II)] and zero order in mercury (I).

Ashish et al [83] have reported the kinetic study of Pd (II) catalysed oxidation of maleic and crotonic acids by N-Chlorosuccinimide (NCS) in perchloric acid. Analysis of the results shows zero order dependence on [substrate] and $[H^+]$ and first order dependence of the reaction on NCS at its lower concentration that tends to zero order in its higher concentration range. The rate of the reaction increases with increase in [Pd (II)] but the order in [Pd (II)] is less than unity. On the basis of above kinetic results, the following mechanism **(Eqns. 17-21)** has been proposed.

$$PdCl_4^{2-} + NCS \underset{}{\overset{K_1}{\rightleftharpoons}} \left[PdCl_4 . NCS \right]^{2-} \tag{17}$$

C_1 $\qquad\qquad$ C_2

$$\left[PdCl_4 . NCS\right]^{2-} \xrightarrow[\text{slow}]{k} \left[PdCl_3 . NCS\right]^{-} + Cl^{-} \tag{18}$$

C_2 $\qquad\qquad$ C_3

$$\left[PdCl_3 . NCS\right]^{-} + S \xrightarrow[\text{fast}]{3H_2O} \left[PdCl_2\left(H_2O\right)_2\right] + 2Cl^{-} + NHS + \text{Intermediate}(X) \tag{19}$$

Where X stand for RCHCH(OH)COOH in which R= $–CH_3$ for crotonic acid and R= –COOH for maleic acid.

$$X + NCS \xrightarrow{[PdCl_3]^{2-}/H^+} Products \quad (20)$$

$$\left[PdCl_2(H_2O)_2\right] + 2Cl^- \longrightarrow \left[PdCl_4\right]^{2-} + 2H_2O \quad (21)$$

R. A. Singh et al [84] have studied the kinetics and mechanism of Pd (II) catalysed oxidation of Valine and Leucine by acidic solution of chloramines–T. The dependence of reaction is first order each in [CAT], [Pd (II)], [AA] but the acidic medium [H^+] shows inverse first order. The results suggest the formation of complex between the catalyst and the substrate **(Eqns. 22-23)**.

$$\left[PdCl_4\right]^{2-} + AA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[PdCl_4\text{-}AA\right]^{3-} + H^+ \quad (22)$$

C_1 C_2

$$C_2 + CAT \xrightarrow{k} \left[PdCl_4\right]^{2-} + Product \quad (23)$$

Where AA represents amino acids.

Ajaya K. Singh and co-workers [85] reported kinetics of Pd (II) catalysed oxidation of valine by N-Bromophthalimide (NBP) in acidic medium at 303K. The rate of the reaction shows first order kinetics with respect to [Pd (II)] whereas negative effects for the variation of [H^+] were observed on the reaction rates.

Pushpanjali Singh [86] has investigated kinetics of Pd (II) catalysed oxidation of dl-serine and dl- threonine by acidic solution of potassium bromate in the presence of mercuric acetate as a scavenger in the temperature range of 30–45˚C. The rate shows zero order kinetics in bromate [BrO_3^-] and first order with respect to substrate and Pd (II) respectively. A transition complex is formed between [$PdCl_2$] and amino acid **(Eqns. 24-28)**.

$$PdCl^+ + Cl^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \left[PdCl_2\right] \quad (24)$$

C_1 C_2

$$R\text{-}CH(NH_2)COOH + \left[PdCl_2\right] \xrightarrow[\text{slow}]{k_2} \left[S\text{-}PdCl_2\right] \quad (25)$$

rate – determining step

[S] Complex

$$Complex + HBrO_3 \xrightarrow{fast} R\text{-}C(BrO_2) = NH\text{-}COOH + \left[PdCl_2\right] + H_2O \quad (26)$$

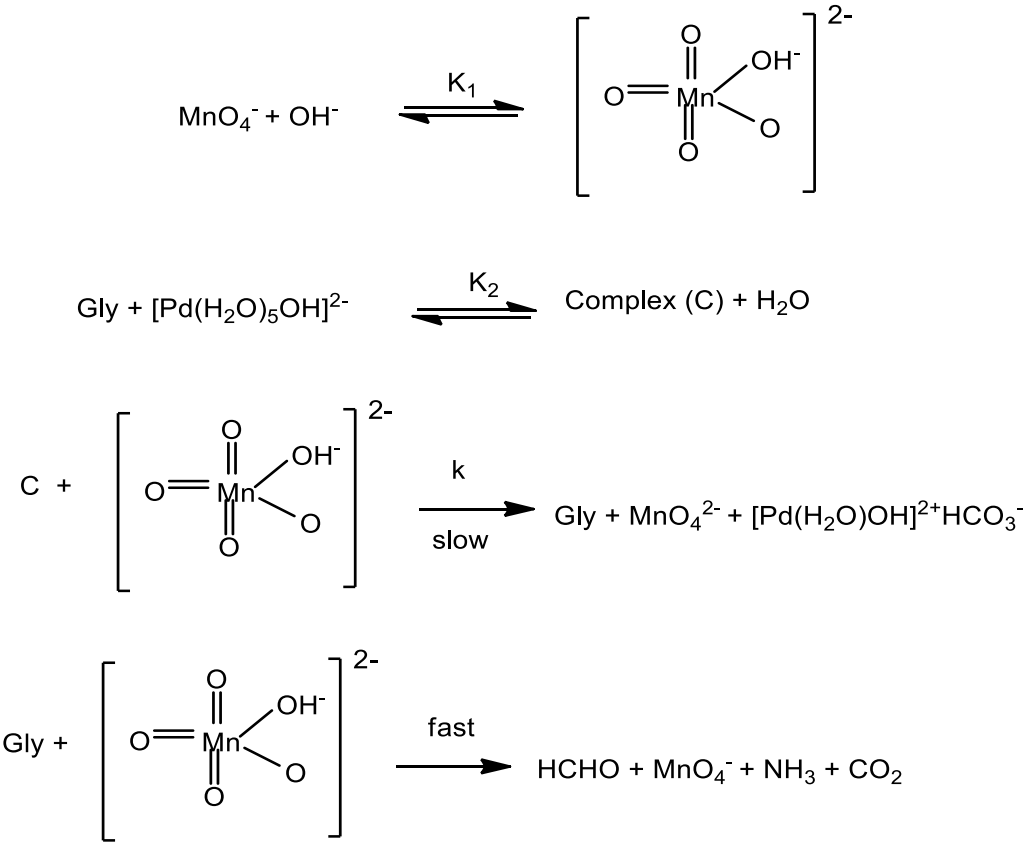
$$PdCl^+ + Cl^- + HBrO_3 \xrightarrow[H^+]{fast} \left[PdCl_2\right]^- + H_2O + HBrO_2^- \quad (27)$$

$$R\text{-}C(BrO_2) = NH\text{-}COOH + H_2O \xrightarrow[H^+]{fast} R\text{-}CHO + NH_3 + CO_2 + HBrO_2^- \quad (28)$$

Where R= CH_2OH- for dl-serine and

R= CH_3-CH(OH)- for dl- threonine

The kinetics of Pd (II) catalyzed glycine oxidation by permanganate have been investigated spectrophotometrically by Adarsha J.R. et al. [87]. It was discovered that the reaction shows less than unit order in [glycine] and [alkali] and first order dependence on [catalyst] and [oxidant]. According to the data, the catalyst and substrate form a complex, which subsequently reacts with one mole of permanganate in a slow step to produce a glycine free radical and then a fast step to produce the products [**Scheme 6**].



Scheme 6: Oxidation of glycine by permanganate

1.5 METAL NANOPARTICLES

Nanotechnology is a promising science with wide applications from cosmetics, food products, clothing and household appliances to fuel catalysts, disease treatment and renewable energies. Nanomaterials are found to be important and keep growing in the research area of nanoscience & nanotechnology. Over the past few decades, this field of nanocatalysts—both in homogeneous and heterogenous catalysis—has experienced rapid expansion [88,89]. The synthesis of nanoparticles is generally carried out by chemical reduction, which is effective. Due to their higher conductivity than metal oxides, metal nanoparticles have attracted a lot of scientific attention. Because of its special characteristics and wide range of uses, nanoparticle research has drawn a lot of attention [90, 91]. Metal nanoparticles do not represent a metal – metal chemical bond and defined as isolated particles between 1-100 nm sizes. Metal nano particles (NPs) with narrow size distribution have valuable technological importance because of their unique physi- chemical properties and applications in the field of catalysis [92-94], information storage, quantum devices [95], sensors [96-98], fine synthesis, oil refining processes and fuel cell technology [99] etc. Metal nanoparticles with high specific catalytic activity are abundant in modern synthetic organic chemistry during the recent decades [100]. Nanoparticles constitute the key factors, so efforts have been focused on the synthesis of noble metal nanoparticles (NPs) with well controlled morphology. Now a days researchers are focusing on metal nanoparticles, nanostructures and nanomaterial synthesis because of their noticeable properties.

In nanoparticles synthesis, there are two approaches one is top–down and another is bottom–up approach [101].Top–down approach describes nanoparticles synthesis from bulk material into smaller ones [102].Various physical and chemical treatment reduces the size while bottom up strategy suggest that nano particles are synthesised to the required material from smaller molecules, In this approach first entities formed are joined to produce the final particles and particles size are in nanometre range [103]. The techniques are categorized into physical, chemical and biological techniques for synthesizing nanoparticles from top–down and bottom–up approaches [**Fig. 1.3**].

1.5.1 Remarkable Properties of Nanoparticles

The main objective of research on nano catalysis is to produce catalysts with 100% selectivity, extremely high activity, low energy consumption and long lifetime. This

can be attained by precisely controlling the size, shape, surface composition, electronic structure, thermal and chemical stability of the different nanocomponents [**Fig. 1.4**].

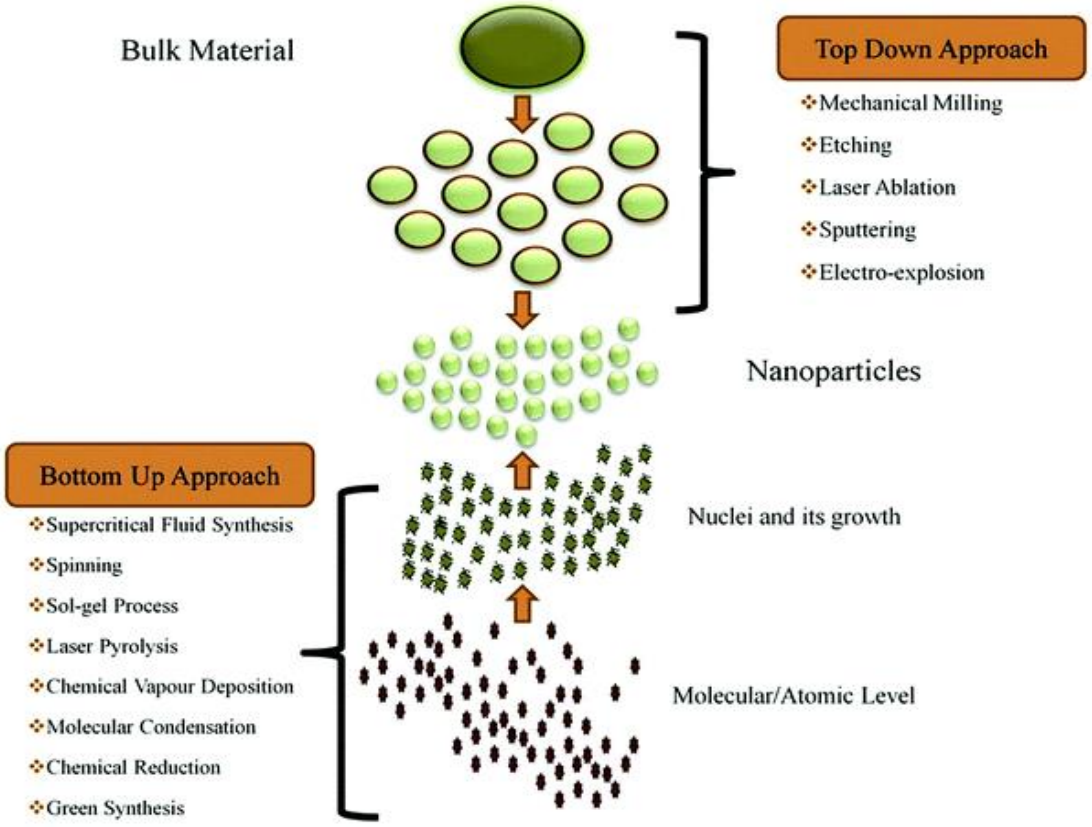


Figure 1.3: Various approaches for fabrication of Metal Nanoparticles

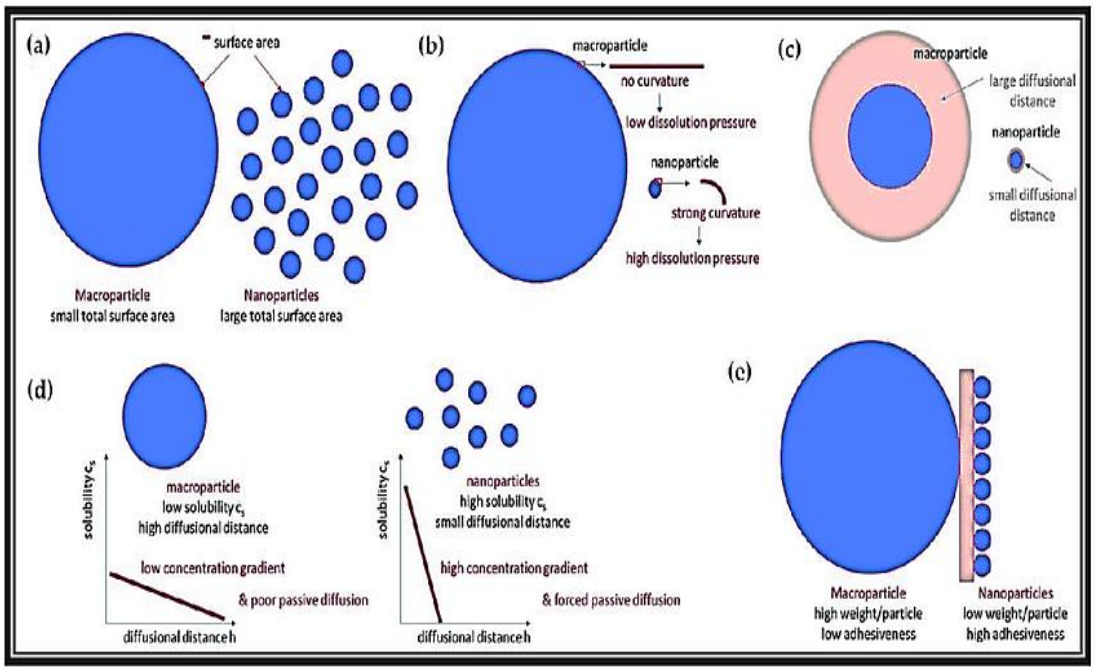


Figure 1.4: Properties of Nanoparticles

Magnetic properties

- Magnetic nanoparticles are widely used in number of applications such as in biomedicine, induction heating, sensors, magnetic fluids, data storage magnetic resonance imaging (MRI), and environmental remediation The magnetic property of nanoparticles depends on the uneven electronic distribution of nanoparticles, ferrite nanoparticles being the most explored examples.

Optical

- Optical properties of nanomaterial such as absorption, transmission, reflection, and light emission .The optical properties of metal nanoparticles are administered by collective excitation of the conduction electrons. The electrons oscillate coherently through irradiation by light in the visible and near-IR regions of the electromagnetic spectrum. Their optical properties are reported to be dependent on the size, which gives different colours due to absorption in the visible region.

Hardness Strength for Nanostructured Films

- The quantum confinement effect is observed when the size of the particle is too small as compared to the wavelength of the electron. Quantum confinement produces unique optical and electronic properties that enhance solar cell or photovoltaic. This property of nanoparticles is used in several technologies such as sensors behaving like quantum dots, nano stimulators, memory applications and electronics etc.

Quantum confinement effect

- The greater surface area of the nanoparticles allows greater space for storage or reactions. Nanoparticles are harder in comparison to the bulk as it prevents the particles from the bending due to good affinity between the nanoparticles and the matrix. Dislocation movement in the metal matrix is blocked which in turn increases the wear resistance. Addition of nanoparticles which are smaller in size can fill the matrix pores thereby reducing its porosity and increase its density.

Surface area to volume ratio

- Nanoparticles have high surface area to volume ratio due to which they are more chemically reactive. Surface area of nanoparticles are important in different application such as catalysis. Materials are found to be inert in their bulk form and are reactive when change into nanoscale form.

1.6 NANOCATALYSIS

Catalyst is a substance that increases the speed of reactions by lowering the activation energy (E_a) which is the minimum energy required to convert reactants into products. The desired product can be obtained faster by using a catalyst. Nanocatalyst is defined as a material which has catalytic properties on at least one nanoscale dimension. They possess vast surface-to-volume ratio because of their small size, due to which they act as attractive catalysts. They also have applications in the field of photochemistry, nanoelectronics, optics etc [**Fig.1. 5**].

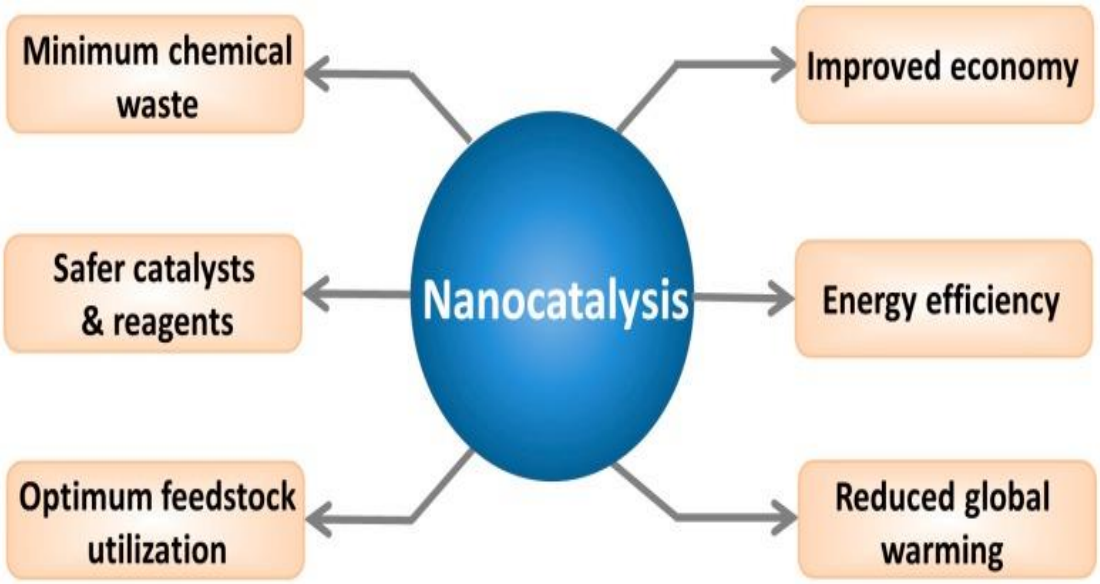


Figure 1.5: Application of Nanocatalysis

1.6.1 Classification of Nanocatalysis

The last decades have seen an enormous expansion in the field of nanocatalysis, encompassing both homogeneous and heterogeneous catalysis [104-108] due to large surface to volume ratio. They are now easy to prepare with desired size, structure, morphology and composition. Both forms of catalysis have benefits and drawbacks of their own. The primary benefit of homogeneous catalysis is its great efficiency; nevertheless, it has the drawback of potentially recovering the catalyst from the reaction mixture, which eliminates the possibility of recycling and increases the risk of product poisoning [109]. Although the catalyst efficiency will be somewhat lower in a heterogeneous environment, it can still be effectively collected from the reaction mass and regenerated.

1.6.1.1 Homogeneous catalysis

When the catalyst and reactants are in the same phase, this is known as homogeneous catalysis. Transition metal nanoparticles in colloidal solutions are employed as catalysts in homogeneous catalysis. These nanoparticles are finely distributed in an organic or aqueous solution or a mixture of solvents. In this system it is essential to prevent its aggregation when designing a nano-catalyst for use in a solution. Nanoparticles have a characteristic to agglomerate and will cluster together to form larger particles, if not prevented properly, nanoparticles drop their large surface area, catalytic activity and other significance. Homogenously catalysed aerobic oxidation has been reviewed for oxovanadium [110], Pd [111], Cu [112].

1.6.1.2 Heterogeneous catalysis

The reactants and catalysts will be in distinct phases when heterogeneous catalysis occurs. They are prepared by adsorption of nanoparticles on to support and fabrication of nanostructures on the supports by lithographic techniques. The nano-catalyst in heterogeneous system may be a solid immobilized on a solid inert matrix. A heterogeneous catalyst can behave as a catalytic reservoir in a solution phase process, releasing molecular catalytic species for catalysis and re-depositing them when a catalytic cycle is finished [113].

Because of their small size, nanocatalysts have a large surface area that keeps them evenly distributed throughout the reaction medium, increasing catalytic efficiency. At the same time, they are easily recovered from the reaction mixture by centrifugation, filtration, or magnetic separation, and they can be recycled [114].

Heterogeneous catalysis is highly desirable for commercial applications and has over the last decade, a variety of new types of nanocatalysts have been investigated, including well-defined magnetic nanocatalysts, single-atom catalysts, core–shell and yolk–shell nanocatalysts, silica-based hybrid catalysts, and graphene-based materials [115-119].

1.6.1.3 Quasi Homogenous catalysis

Quasi-heterogeneous/homogeneous catalysts are basically mixtures of a homogeneous catalyst and a heterogeneous catalyst which would act as a bifunctional catalyst.

Quasi-homogeneous catalysts are made of three-dimensional free metal nanoparticles in solvents and protected by a stabilizer. catalytic performance may be affected by the

preparation method, stabilizer, temperature which controls the size and morphology of nanoparticles. Nowadays, quasi-homogeneous catalysis has been applied to various reactions, e.g., hydrogenation, oxidation., C-C coupling reaction, etc., exhibiting excellent catalytic performance (e.g., high activity and high selectivity) [120].

Palladium nanoparticles stabilised by BINAP-thioether- derivatives have also been used in the (quasi)homogenous C-C coupling reactions [121] [**Fig. 1.6**].

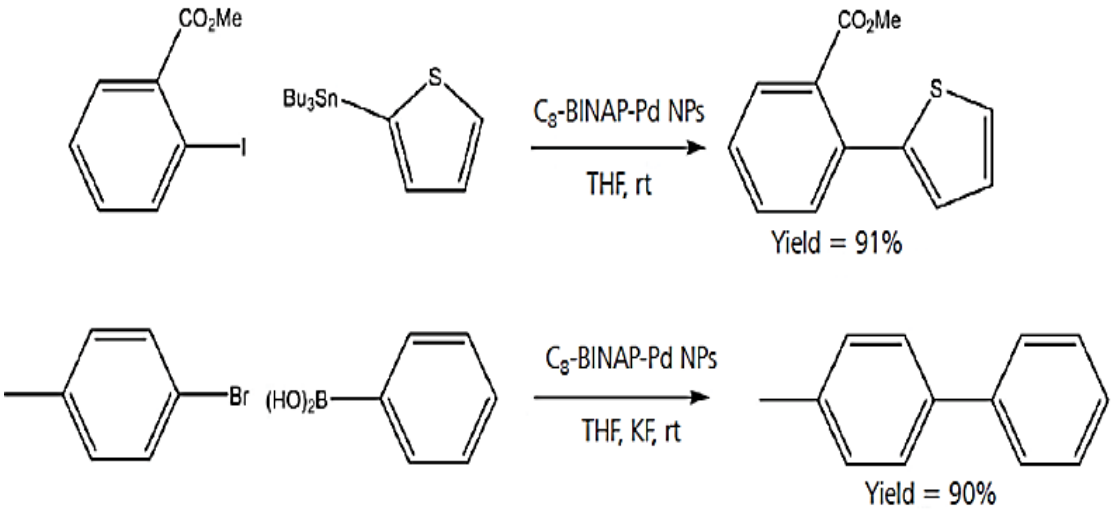


Figure 1.6: (Quasi) – homogenous carbon- carbon coupling reactions undertaken by BINAP thioether-derivatised palladium nanoparticles

1.7 FUNCTIONS OF TRANSITION METAL NANOPARTICLES IN CATALYSIS

Transition metal Au, Ag, and Cu, are commonly used as homogeneous and heterogeneous catalysts in majority of chemical reactions [122,123]. The main reason for this is the variable oxidation states offered by them and good adsorption properties essential for heterogeneous catalysis. These two properties enable the transition metal nanoparticles to act as electron channel for the reactants adsorbed on the surface of the transition metals, specifically precious noble metals such as Pt, Pd, Ti, V, V, Fe, Rh, and Ru.

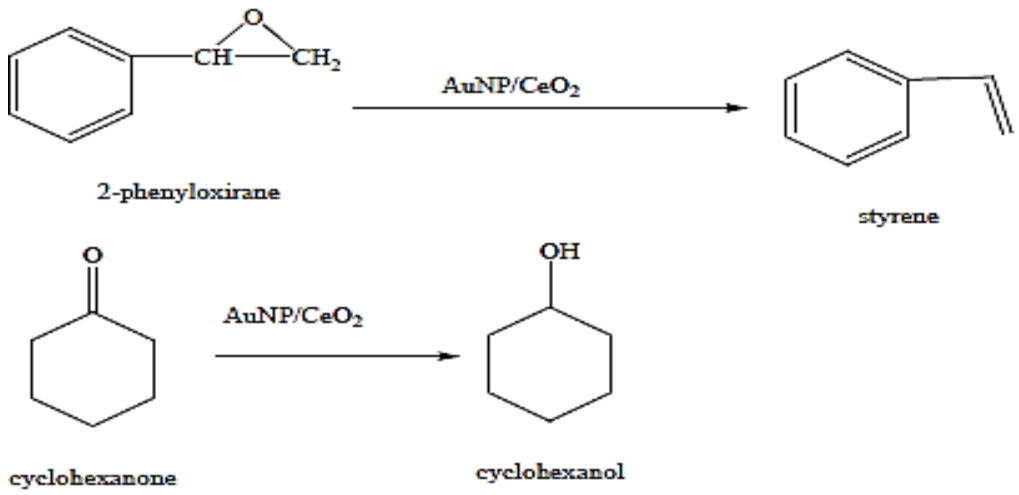
The broad range of applications in the synthesis of different compounds, which is crucial in the pharmaceutical, agrochemical, polymer, and natural product sectors, makes transition metal-based nanocatalysis relevant in many catalysis domains [124,125]. Transition metals are ideal for catalysis because of their high melting and

boiling temperatures, ability to exhibit a variety of oxidation states, and capacity to form stable complexes [126].

1.7.1 Different Transition metals used for making nanocatalysts

Iron, vanadium, nickel, platinum and palladium are examples of transition metal catalysts. Transition metals and their compounds act as catalysts because their electronic configurations permit them to temporarily exchange electrons with reacting species.

Oxidation-reduction reactions require one molecule to lose electrons and another to gain electrons. Many oxidation-reduction reactions proceed at a very slow rate in the absence of catalysts as oxidative species encountering a reductive species to exchange electrons is very low. The d-shell outer electrons of transition metal catalysts are easily lost and gained. They lend electrons to the species undergoing reduction and take electrons from those undergoing oxidation. This facilitation of electron exchange speeds up the reaction. Transition metals are not used up when they act as catalysts. Rather, they undergo a temporary change in their oxidation numbers. Based on their catalytic properties, we classified the metal nanoparticles into four groups: (1) Ti, V, Cr, Mn, Zr, Nb and W (2) Fe, Co and Ni (3) Ru, Rh and Ir (4) Ag, Au and Cu.



Scheme 7: (i) Synthesis of styrene from 2-phenyl oxirane
(ii) Synthesis of cyclohexanol from cyclohexanone

Ti, V, Cr, Mn, Zr, Nb and W as nanocatalyst-

- A major advantage of these early transition metal nanoparticles in catalysis is their cheap price. Ti, Zr, Nb and Mn nanoparticles are prepared in THF by $K[BEt_3H]$ reduction from metal halide precursors [127]. Zr nanoparticles show applications in space and is an alternative for titanium in components of liquid rocket engines .
- In the past few years, attention has been paid to one-dimensional Nb_2O_5, including nanotubes, nanowires, nanofibers and nanorods, due to their exceptional shape-dependent physical, chemical and optical properties.

Fe, Co and Ni

- The nanoparticle films of transition metals such as iron, nickel or cobalt may be used to catalyse the progress of carbon nanotube. Hot iron nanoparticles could be used to carve electronic circuits out of graphene sheets [128]. The excellent electronic properties of graphene have prompted scientists to try cutting it into 'nanoribbons', which might be used in future electronic devices. Working with nickel is because it responds to electrochemistry, has good mechanical and corrosion properties and is cheap. It is strong and easily processed in this particular style.
- Nickel nanoparticles could be used in biomedical applications, such as implants that dispense drugs, though the metal would likely be coated to prevent possible allergic reactions. The metal's magnetic properties make it a usual choice for magnetic applications [129].

Ru, Rh and Ir

- Ruthenium nanoparticles (RuNP) have attracted substantial scientific attention as they have outstanding size dependant properties [130]. have been extensively used for practical applications in many fields such as catalysis, biosensors, capacitors and electrochemical reactions [131]. Rhodium nanoparticles adsorbed on to titanium dioxide supports are synthesized using water as the solvent [132].

Ag, Au and Cu

- The nobility of gold and its resistance to surface oxidation makes it ideal material for wide range applications in nanotechnology. Gold nanoparticles are a prevalent choice for medical research, diagnostic testing and cancer treatment. Gold nanoparticles [133] improves the drug delivery efficiency of anticancer drug. Reactions using Au nanoparticle [134] are mentioned **[Scheme 7].**

High electrical and thermal conductivity, chemical stability, catalytic activity, antimicrobial activity, and improved visual qualities are only a few of the special physicochemical characteristics of silver nanoparticles [135]. Applications for silver nanoparticles in electrical, photonic, antibacterial, and disinfection fields have made use of these characteristics.

Cu-based nanocatalysts have found many applications in nanotechnology, including catalytic organic transformations and electrocatalysis [136]. Hydrotalcite-supported gold, silver, and copper nanoparticles have been employed as catalysts for the ecologically safe aerobic oxidation of alcohols [137].

1.8 PALLADIUM NANOPARTICLES

Palladium nanoparticles (PdNPs), one of the transition metal nanoparticles are well-known for their strong catalytic activity in a range of organic transformations that are significant for both academia and industry.

The synthesis of palladium catalyst as an organometallic complex [138] and the synthesis of palladium catalyst as nanoparticles [139] are two major designs among the various ways that have been used to incorporate palladium in a catalytic system. In the first scenario, palladium salt will be utilized to build a complex with a ligand system; in the second scenario, a reducing agent will be used to create palladium nanoparticles from palladium salts.

Pd nanoparticles (Pd NPs) are being used as catalysts for alkylation, dehydrogenation, hydrogenation and selective oxidation reactions of compounds for the conversion of hydrocarbons [140-145]. Pd nanocatalysts retain their catalytic properties when left unsupported in an aqueous suspension [146], making them suitable to study the size dependency of catalytic behaviour without the influence of supports based on new oxides and ceramics. Pd NPs catalyse other reactions when they are supported on a suitable material which can interact with the metal [147,148].

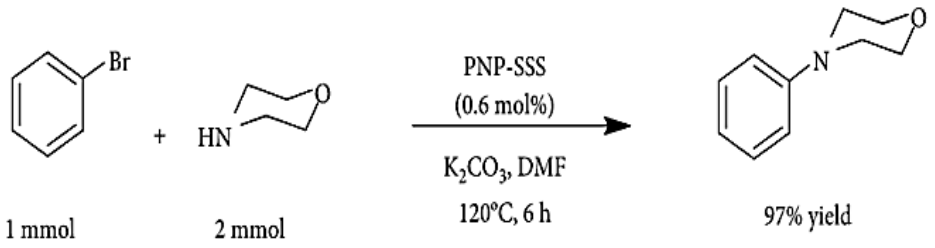
Pd NPs occupy very important position in the area of biomedical applications because of their high catalytic and sensor activities. The relatively large abundance of Pd over other noble metals such as Au and Pt makes it a cheaper substitute for application in various electrochemical sensing and biosensing platforms [149].

Owing to unique electronic properties, enhanced catalytic and selective sensing performance, several Pd nanomaterials such as nanocomposites, bimetallic NPs, metal

oxide nanomaterials and carbon nanomaterials with variable composition have been examined for the detection of numerous biomarkers over the past decade [150].

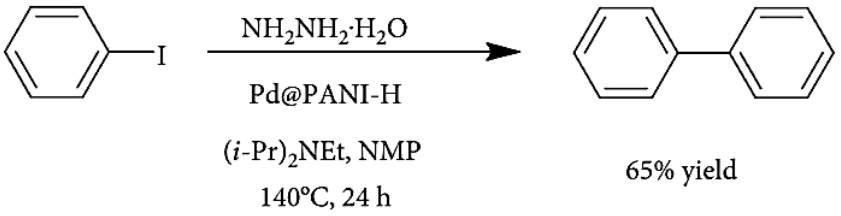
The hydrodechlorination process of chloroarenes in trichloroethene [151] and water [152] can be catalyzed by Pd nanoparticles. Additionally, Suzuki, Heck, and Sonogashira reactions were catalyzed by these palladium nanoparticles [153]. The Ullmann reaction of an aryl chloride to produce biaryls has been catalyzed by palladium nanoparticles [154].

The palladium nanoparticles were used as catalysts for the Stille coupling reaction in aqueous solvent [155], Heck reaction of haloarenes and olefins [156] in Heck cross-coupling reactions, aerobic oxidation of different alcohols in water to form ketones, aldehydes, and carboxylic acids [157]. The applications of palladium go beyond catalysis. For example, the propensity of palladium to adsorb hydrogen has also led to palladium nanoparticles being utilised in hydrogen storage [158,159] and sensing application [160,161]. The use of palladium nanocatalysts in carbon-heteroatom cross-coupling processes, including Buchwald-Hartwig amination, has proven successful. Panahi et al. recently reported that an immobilized palladium nanocatalyst on a silica-starch substrate (PNP-SSS) has good catalytic activity and reusability and is an effective catalyst for carbon-nitrogen cross-coupling processes through Buchwald-Hartwig amination [162] **[Scheme 8].**



Scheme 8: Buchwald- Hartwig animation using PNP-SSS

To create biaryls by the Ullmann homocoupling reaction of aryl iodides, Liu et al. synthesized a number of palladium nanocatalysts supported by polyaniline. It was found that adding electron-donating groups could adjust the catalyst's activity [163] [**Scheme 9**].

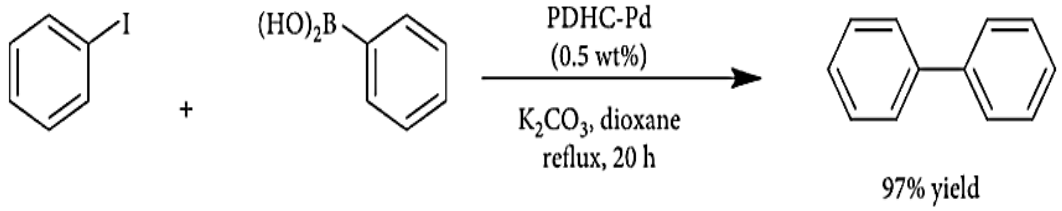


Scheme 9: Ullmann homocoupling

A palladium nanocatalyst mounted on a magnetic few-layer graphene support was recently synthesized and used in cross- and homocoupling processes, according to Rafiee et al. [164]. It was discovered that the catalyst system remained active for up to six runs without losing its catalytic activity [**Scheme 10**].

Scheme 10: Homocoupling reactions

In the fields of catalysis, total synthesis, fine chemicals, and supramolecular chemistry, the biaryl formation process is crucial [165]. A common feature of natural products, colors, medications, and agrochemicals is the link between two aryl groups. A popular technique for creating biaryls is the copper-catalyzed homocoupling reaction, although it necessitates severe reaction conditions. Palladium nanoparticles on nitrogen-doped graphene (Pd-NP-HNG) for an Ullmann-type homocoupling process in water were reported by Movahed et al. [166] [**Scheme 11**].



Scheme 11: Ullmann – type homocoupling reaction in water

1.9 OXIDATION OF AMINO ACID

Oxidation Reactions are of fundamental importance in nature and are key transformations in organic synthesis. Oxidation of amino acids is one of the most prevalent forms of chemical reactions and is susceptible to modification by a wide array of oxidants. Since the oxidation products vary depending on the oxidant, it is interesting. These oxidation processes exhibit a variety of reaction pathways, including decarboxylation and oxidative deamination [167]. Depending on whether an amino acid has polar or nonpolar substituents, it can undergo a variety of reactions. Since the hydrocarbon moiety (RCH-) is less reactive than the amino and carbonyl functional groups of amino acids, these functional groups undergo chemical change.

One of the most fascinating areas in organic chemistry is the study of amino acids. They are important for several metabolic processes, including the creation of proteins, polypeptides, and nucleotides. Therefore, one possible topic of research is the mechanism of nonenzymatic chemical reactions in the oxidation of amino acids [168]. In the presence of mercuric acetate, Bhargava and colleagues [169] investigated the kinetics of N-Bromosuccinimide's (NBS) oxidation of glycine, α-alanine, β-alanine, phenylalanine, and other compounds in an acid-water mixture. Mushran et al. [170] studied the oxidation of alanine and valine in which zwitter ion of the amino acid reacted with NBS in the rate determining step to give a short-lived unstable intermediate which in a fast step reacted another molecule of NBS giving corresponding nitriles.

Gopalkrishan and co-workers [171] reported the kinetics of NBS oxidation of glycine, valine and alanine as a function of pH. Amino acids exist in the protonated form and the oxidising species HOBr and H_2O^+Br formed by nucleophilic attack of water on the protonated NBS. A mechanism involving the formation of acyl hypobromite, its slow decomposition to an imine and fast conversion of imine to product was proposed **[Scheme 12]**.

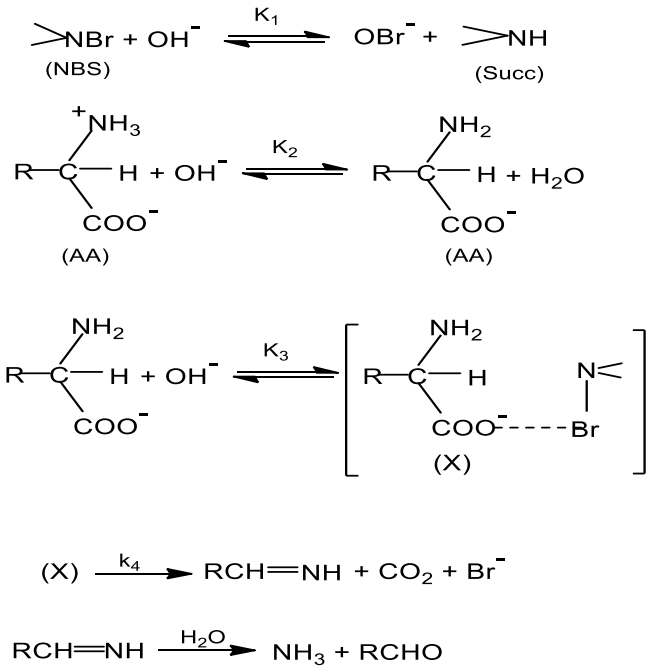
$$NH_3^+\text{-}CHR\text{-}COOBr \underset{}{\overset{k_1}{\rightleftharpoons}} Br^+ + NH_3^+\text{-}CHR\text{-}COO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$Br\text{-}NH_2^+\text{-}CHR\text{-}COO^- \xrightarrow{k_2} NH_2^+ = CHR \xrightarrow{k_3} Products$$

Scheme 12: Oxidation of Amino acids by NBS

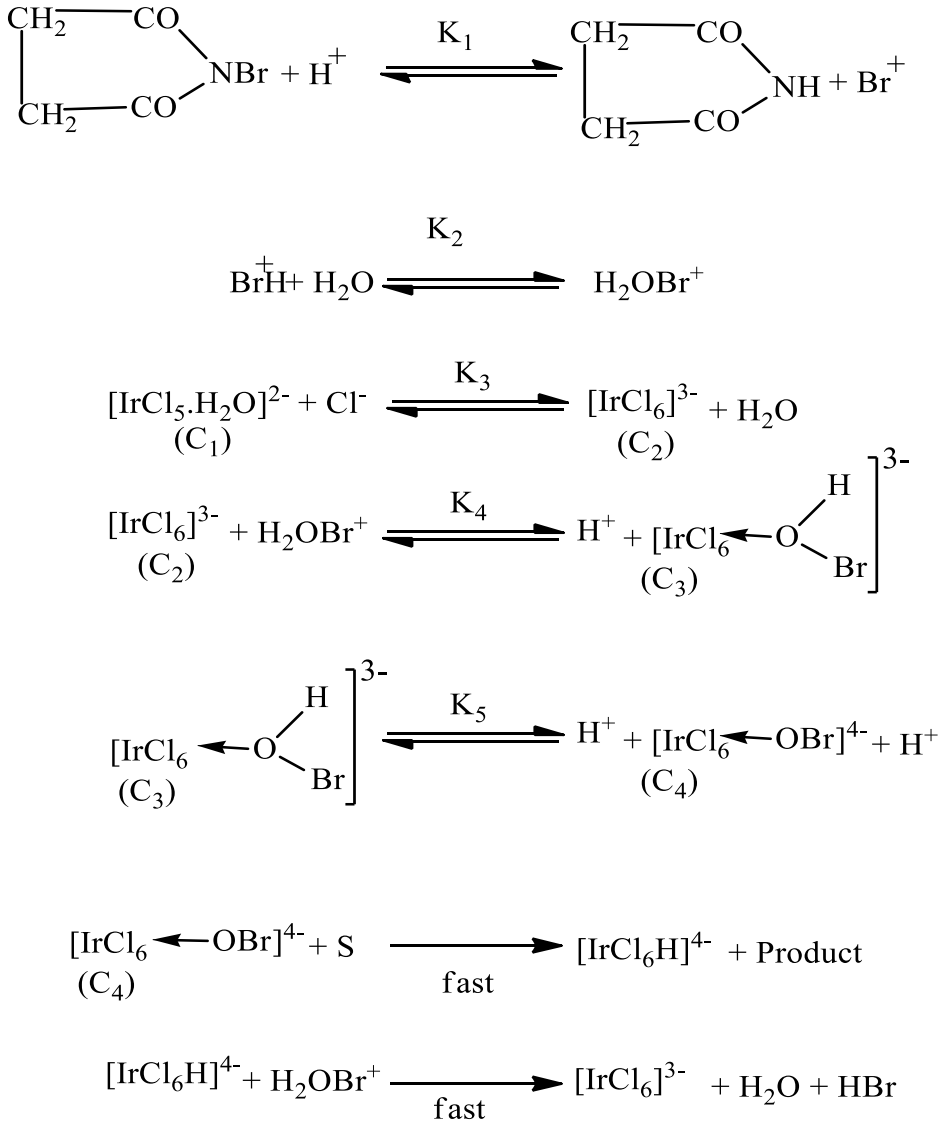
In the study of Kinetics of oxidation of glycine, alanine, Leucine and arginine by NBS in perchloric acid medium, formation of alkyl cyanides was reported by Radhakrishnamurti and his co- workers [172].

Harihar et al [173] have studied the Kinetics and mechanism of NBS oxidation of L-arginine in aqueous acidic medium. A mechanism including the unprotonated NBS as the reactive species of oxidant has been proposed [**Scheme 13**]. Neelu Kambo and co-workers [174] have reported the Kinetics of oxidation of amino acid (AA), viz. alanine, phenylalanine and valine by NBS have been studied in alkaline medium. The reaction in first order in NBS. The order of reaction with respect to amino acid and alkali decreases from unity to zero at higher [AA] and [OH^-] respectively. The rate is accelerated in presence of succinimide (product of NBS) at lower $[succinimide]_0$, while that becomes independent to succinimide at higher $[succinimide]_0$. A mechanism consistent with kinetic data has been derived.



Scheme 13: Oxidation of L- arginine by N-Bromosuccinimide (NBS) in aqueous acidic medium

A.K. Singh [175] investigated kinetics and mechanism of oxidation of aspartic acid by N-Bromosuccinimide (NBS) catalysed iridium (III) under isolation condition at 30°C. The observed kinetic findings show first order reaction kinetics with respect to oxidant catalyst and chloride ion in each case, whereas it shows zero order reaction kinetics with respect to substrate. Successive addition of succinimide in the reaction shows negative effect. On the basis of above kinetic results following reaction path have been suggested [**Scheme 14**].



Scheme 14: Oxidation of Aspartic acid by N-Bromosuccinimide (NBS) catalysed by Iridium (III)

According to A.K. Singh and colleagues [176], NBS oxidizes glycine and valine with Rh (III) acting as a catalyst. According to the paper, the reactions with NBS and Rh (III) follow first order kinetics. At larger concentrations, the amino acid's first order kinetics, which were found at lower concentrations, become zero order. The oxidation of glycine and valine catalyzed by Rh (III) showed inverse fractional order with respect to $[H^+]$. [Hg (II)], [NHS], $[Cl^-]$, ionic strength, and the medium's dielectric constant have no bearing on the rate of oxidation. It has been proposed that the reactive species of NBS and Rh (III) chloride in an acidic media are NBS itself and $[RhCl_5(H_2O)]^{2-}$.

R.V. Nadh and M. Sireesha [177] have investigated the kinetics of the catalyzed and uncatalyzed oxidation of DL-alanine by NBS utilizing Ru (III) in aqueous acetic acid in the presence of perchloric acid and Hg (II). The kinetic orders found in both Ru (III)

catalyzed and uncatalyzed oxidations were fractional order in the substrate and first order in NBS. As the concentration of perchloric acid increased and halide ions were added, the rate of the reaction reduced. Regarding Ru (III), the reactions showed fractional order.

The exceptional chemical, physical, and catalytic capabilities of metallic nanoparticles make them highly desirable. Various oxidants have been used to oxidize amino acids in the presence of various metallic nanoparticles. Hexacyanoferrate (III) oxidation of amino acids in an alkaline media was used to assess the catalytic activity of colloidal iridium nanoparticles [178] [**Fig.1. 7**].

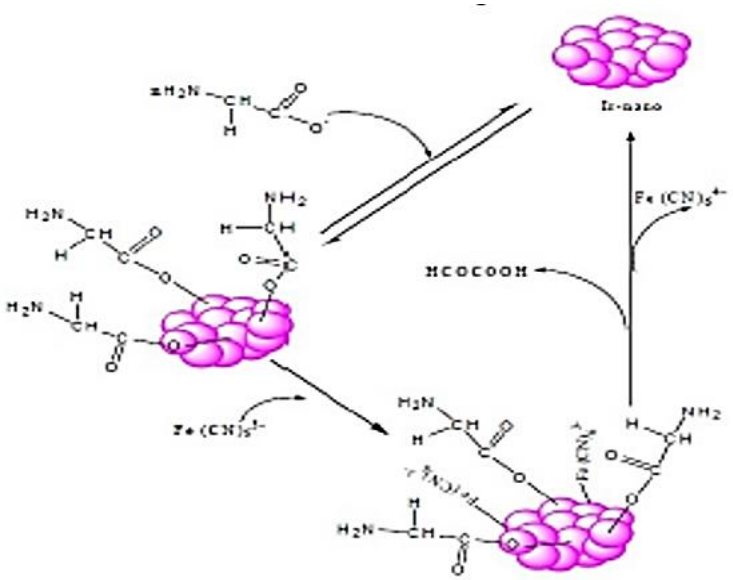


Figure 1.7: Proposed catalytic cycle of the oxidation of Glycine in the presence of Iridium nanoparticles

Catalytic cycle for glycine oxidation is suggested when iridium nanoparticles are present. In this case, iridium nanoparticles function as a more effective catalyst than an equivalent quantity of iridium precursors. In the presence of surfactant-stabilized Au and Ag nanoparticles, the oxidation of L-leucine by hydrogen peroxide as an oxidant was investigated [179]. The kinetics of the reactions gave pseudo first order with respect to the amino acid. Au nanoparticles exhibited very good catalytic activity, but bimetallic Au-Ag catalysts gave higher selectivity than pure Au-Ag. Shikha et.al studied the kinetics of copper nanoparticles catalysed oxidation of serine [180], alanine [181] and threonine [182] by peroxomonosulphate in aqueous medium. Very good catalytic activity was exhibited by copper nano catalyst, and the oxidation rate followed first order kinetic with respect to amino respect to amino acid and peroxomonosulphate.

Very few investigations have been conducted on the oxidative deamination of amino acids in the presence of metal nanoparticles, based on previous observations of amino acid oxidation. For the crucial alkylation, dehydrogenation, and oxidation processes of the molecule for the conversion of hydrocarbons, palladium nanoparticles (Pd-NPS) have been employed as catalysts [183–185]. When left unsupported in an aqueous suspension, Pd nanocatalysts maintain their catalytic capabilities. However, there isn't much research in the literature on how NBS oxidizes amino acids when palladium nanoparticles are present.

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CHAPTER 2

MATERIALS AND INSTRUMENTATION

ABSTRACT

This chapter describes the fundamental experimental details of the studies carried out in this thesis. The first part deals with the details of the reagents, chemicals and their solutions with other specifications employed in kinetic study of various reactions. The second part deals with the details of various characterization techniques which include UV- Visible Spectroscopy, Transmission Electron Microscopy (TEM) and FT-IR Spectroscopy that are important to characterize the synthesized nanocatalyst. This part also describes the basic theories and principles of the main analytical methods, electron microscopy and description of instrument which are used for analysis.

2.1 PREPARATION OF SOLUTIONS

2.1.1 N- Bromosuccinimide (NBS)

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 solution prepared was stored in a black-coated vessel to avoid photo chemical deterioration.

2.1.2 Palladium (II) Chloride ($PdCl_2$)

A Pd (II) stock solution was prepared by dissolving the known weight of Palladium (II) chloride (Johnson Matthey) in 0.20 mol dm^{-3} hydrochloric acid and assayed by complexometric titration with EDTA. Dilute solutions of palladium (II) were made from the stock solution as required and stored in black bottle to prevent photo chemical decomposition.

2.1.3 Perchloric acid ($HClO_4$)

Stock solution of $HClO_4$ was prepared by diluting 70% perchloric acid (E. Merck) in doubly distilled water. Solution was standardized against sodium hydroxide using phenolphthalein as an indicator. Solution of required concentration is obtained by dissolving requisite amount of salt.

2.1.4 Sodium Perchlorate ($NaClO_4$)

Sodium perchlorate solutions of required concentration were prepared by neutralizing perchloric acid with necessary amount of sodium carbonate (BDH, AR grade) up to the pH of the resulting solution to reach ~ 6.8. The dissolved CO_2 in the solution was expelled on heating before making up the required volume. This solution was used to maintain required ionic strength.

2.1.5 Mercuric acetate [$(CH_3COO)_2Hg$]

A standard solution of mercuric acetate (E. Merck) was acidified with 20% glacial acetic acid.

2.1.6 Starch indicator

Place 100 mL of distilled or deionized water in a 250 mL beaker and bring to boiling on a hot plate. Make a smooth paste with 1 g of soluble starch and pour this paste slowly into the boiling water with constant stirring with the help of glass rod. Allow the starch solution to cool to room temperature before use.

2.1.7 Potassium iodide (KI) solution

Dissolve 2 grams of potassium iodide in 10 mL of deionized water and dilute to 100 mL. Prepare fresh solution each day. Its solution was used in titrimetric analysis.

2.1.8 2, 4-Dinitrophenylhydrazine

Add 3 grams of 2,4-dintrophenylhydrazine, 20 mL of water and 70 mL of 95 % ethanol to a clean, dry 125 mL Erlenmeyer flask and place it on magnetic stirrer for rapid mixing. Place the flask in an ice bath in a beaker, stir and allow the mixture to cool. When the temperature reaches 10°C, slowly add 15 mL concentrated sulfuric acid with constant rapid stirring, trying to avoid boiling. If the temperature goes above 20°C, stop adding till the temperature goes back to 10°C. When all the sulfuric acid has been added, turn off the stirrer, remove the ice-bath and keep the flask on a stirrer-hotplate. Stir and warm the flask until the 2,4-dintrophenylhydrazine stops dissolving or the temperature reaches 60°C, whichever comes first, then continue stirring without heating. When the solution has cooled, filter through a funnel, if necessary.

2.1.9 Sodium Hydroxide (NaOH)

The solution of sodium hydroxide was prepared by dissolving approximately weighed pellets of NaOH (BDH, AR grade) in doubly distilled water. The solution was standardized by titrating its known aliquot sample against the oxalic acid solution using phenolphthalein [1] as an indicator. However, sodium hydroxide solutions were always used after standardizing because their concentration changes on standing at ambient temperature.

2.1.10 Phenolphthalein Indicator ($C_{20}H_{14}O_4$)

Phenolphthalein (BDH, AR grade) was used as an end point indicator for acid base titration.

2.1.11 Sulphuric acid [H_2SO_4]

Solution of sulphuric acid was prepared by dissolving the requisite volume of concentrated sulphuric acid (Ranbaxy, AR grade) in doubly distilled water and standardized against pre-standardized solution of sodium hydroxide employing phenolphthalein as an indicator.

2.1.12 Oxalic Acid [$(COOH)_2$]

Oxalic acid (BDH, AR grade) is a primary standard and yields a stable solution in doubly distilled water. It is used to standardize sodium hydroxide solutions.

2.1.13 Preparation of Sodium Thiosulphate Solution-

Dissolve required amount of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) in small quantity of distilled water and shaking for approximately 15 minutes. Make up the desired volume.

2.1.14 Valine [$NH_2CH\ (COOH)\ (CH_3)_2\ CH$]

The solution was prepared by dissolving the required amount of valine (s d fine-chem., AR grade) in doubly distilled water to obtain the solution of desired concentration. The lesser solubility of valine in water was avoided by preparing its solution in presence of 0.1 mol dm^{-3} perchloric acid.

2.1.15 Aspartic acid [$COOH\ CH_2\ CH(NH_2)\ (COOH)$]

The solution was prepared by dissolving the required amount of aspartic acid (s d fine-chem., AR grade) in doubly distilled water to obtain the solution of desired concentration.

2.1.16 Serine [$NH_2CHCH_2OH(COOH)$]

Solution of required concentration of serine was prepared by dissolving the requisite amount of serine (s d fine-chem., AR grade) in a known volume of doubly distilled water.

2.1.17 Arginine [$H_2N(HN)\ CN(H)(CH_2)_3CH(NH_2)\ CO_2H$]

Aqueous solution of arginine was prepared by dissolving requisite weighed amount (s d fine-chem., AR grade) in doubly distilled water. It is a water-soluble amino acid.

2.2 EQUIPMENT & TECHNIQUE

2.2.1 Electronic balance

Citizen electronic balance (model – CX 220) was used for weighing. The least count of balance is 0.001 mg, and the maximum count of balance is 220 gm.

2.2.2 Thermostat

Serological water bath (Macro scientific) temperature range 30°-110°C was used. The thermostat is a rectangular stainless-steel tank with double walled convection heating phenomenon. The tank was filled with water, stirred continuously and heated electrically. The unit is provided with a top opening cover made of steel with steel concentric rings. All kinetic studies were done using thermostats at temperatures varying from 30°C to 50°C. Temperature inside our water bath is controlled with a sensitivity of ± 0.50°C (With PID Controller).

2.2.3 pH meter

Systronics digital pH meter, model 335 was used for the determination of pH of the reaction mixture and synthesized nanoparticles with the maximum uncertainty in pH of ±0.01 unit. Before using the pH meter, first calibrate it using buffer solutions of different pH such as 7.0, 4.0, 9.2. Wash the pH electrode thoroughly between measurements with distilled water to avoid carryover impurity of the tested solutions. Softly wipe the electrode with tissue paper to remove the excess rinse water and do not rub the bulb to avoid build-up static charge.

2.2.4 Magnetic stirrer with Hot Plate

Magnetic stirrer with hot plate was used for the synthesis of nanoparticles (MSW-313, MAC) at 600 rpm (Range 0-1200 rpm). The stirrer used 220/230 volts AC supply and temperature range was 0-100°C. The synthesis process of

nanoparticles and size of nanoparticles are affected by speed of stirring and the reaction temperature.

2.2.5 Iodometric Titration

Iodometry, also known as iodometric titration, is a method of volumetric chemical analysis. This type of titration is a derivative of redox titration where the appearance or disappearance of elementary iodine indicates the end point. The indicator that is usually chosen for titrations involving iodine is starch.

Potassium iodide (KI) oxidizes the iodide ion in acidic medium to equivalent amount of iodine. The iodine formed in the reaction oxidizes sodium thiosulphate ($Na_2S_2O_3$) to sodium tetrathionate ion and the end point is detected by starch solution.

As the sodium thiosulphate (hypo) solution is added from burette drop by drop, the iodine solution in the conical flask gradually becomes pale yellow as the end point is approached. We add two drop starch solution; the reaction mixture turns dark blue to indicate that iodine is still present. Now we can continue to add sodium thiosulphate drop by drop until the blue colour disappears completely indicating that all the iodine has just reacted.

2.2.6 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is one of the most efficient techniques available for studying the morphological characteristics of nanoparticles. TEM provides images obtained by a beam of electrons transmitted through a thin specimen, thus allowing the detailed visualization of the interior of the sample. TEM is a suitable method to directly assess nanoparticle size, grain size, size distribution and morphology.

TEM consists of an emission source or cathode, which may be a tungsten filament or needle, or a lanthanum hexaboride (LaB_6) single crystal source [2]. The gun is connected to a high voltage source (60-300 KV) and given sufficient current [3], the gun will begin to emit electrons either by thermionic or field electron emission into the vacuum. After it leaves the gun, the beam is classically accelerated by a series of electrostatic plates till it reaches its final voltage and enters the next part of the microscope-The Condenser lens system [4] **[Fig. 2.1]**.

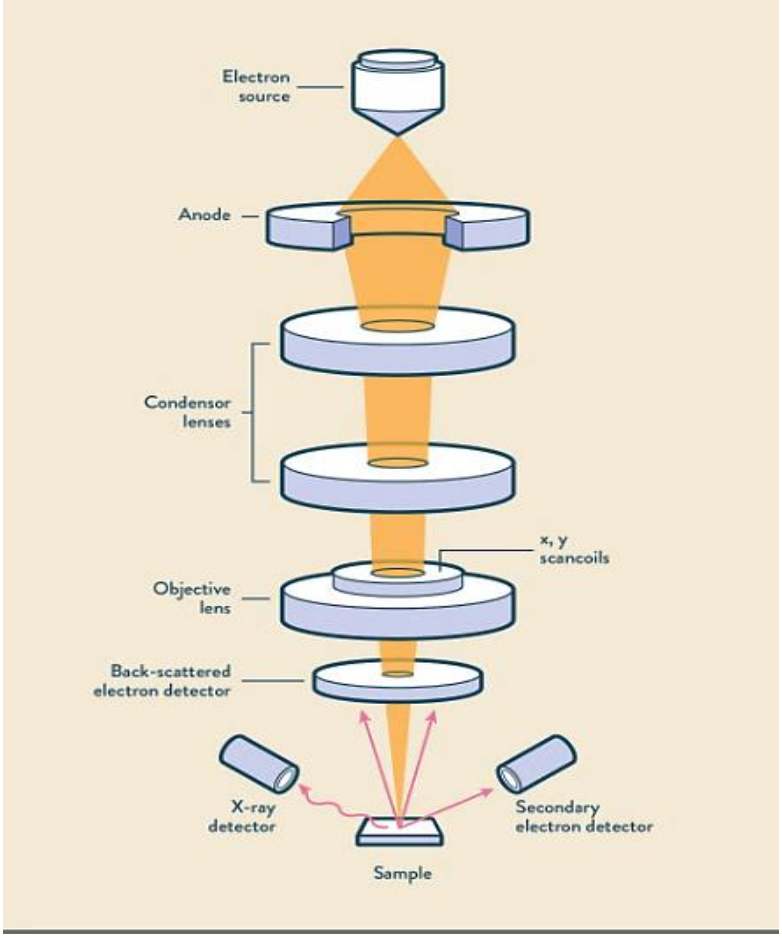

Figure 2.1: Schematic diagram of a Transmission Electron Microscope

The lenses of a TEM are what gives it its flexibility of operating modes and ability to focus beams down to the atomic scale and magnify them back up to get an image on a camera. A lens is usually made of a solenoid coil nearly surrounded by ferromagnetic materials. When an electron enters and leaves the magnetic field, it spirals around the curved magnetic field lines in a way that acts very much as an ordinary glass lens does for light – it is a converging lens. A TEM consists of three stages of lensing- condenser lenses, the objective lenses, and the projector lenses. The condenser lenses are responsible for primary beam formation, while the objective lenses focus on the beam that comes through the sample itself. The projector lenses are used to expand the beam onto the phosphor screen or other imaging device, such as film.

The magnification of the TEM is due to the ratio of the distances between the specimen and the objective lenses image plane [5]. The magnified image is

recorded on inflorescent screen or CCD. The high contrast image is called Bright field image **[Fig. 2.2]**.

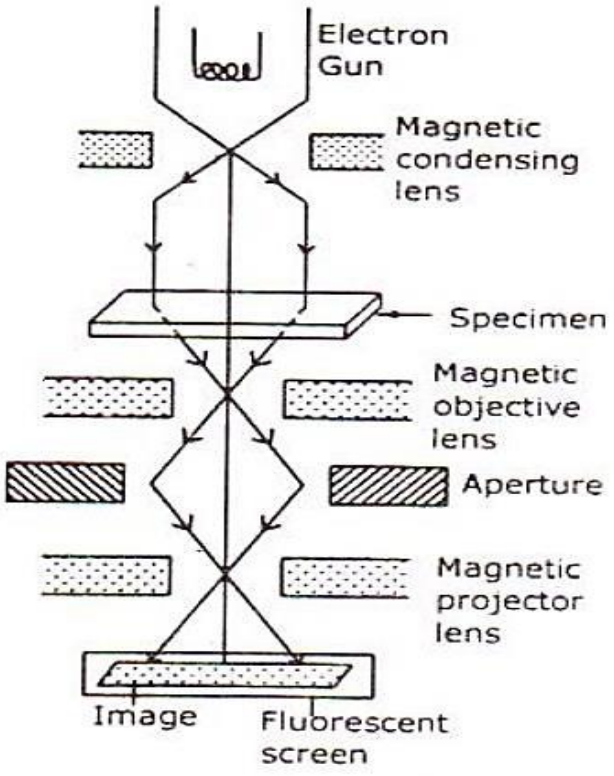

Figure 2.2: Ray diagram of a Transmission Electron Microscope for imaging and diffraction modes

Also, it must be noted that the bright field image obtained is purely due to the elastic scattering (no energy change) i.e., due to transmitted beam alone.

Nowadays there is increasing demand to produce images with atomic resolution so that the lattice arrangements within crystalline materials can be visualized. One well known technique for this is high resolution TEM (HRTEM). A very high magnification is necessary to obtain a high-resolution atomic image. HRTEM gives information on the crystalline structure, defects, grain boundaries, particle shape/structure/ distribution. First, TEM column alignment needs to be carried out as accurately as possible, which includes electron gun and condenser lens alignment, plus astigmatism correction of condenser lenses and objective lenses. Secondly, in HRTEM, an atomic image of a crystal is only possible if certain conditions are satisfied, one of which, choosing the optimum focus, is crucial.

For the work presented in this thesis, transmission electron microscope Model – FEI Techni G2S2 Twin with CCD camera and plate film camera instrument and 200 KV has been used which is located at University of Kochi, Kerala (India) to get information regarding particle size, shape and determining the size distribution of palladium particles.

Samples for TEM were prepared by dissolving a palladium nanoparticle suspension in ethanol and placing a drop of the obtained mixture onto a carbon-coated copper grid, followed by the natural evaporation of the solvent at room temperature.

2.2.7 Fourier Transform Infrared (FTIR) Spectrometer

Fourier Transform Infrared (FTIR) spectrometer is an important technique that provides an easy way to identify the presence of certain functional groups in an organic molecule. FTIR spectrometers are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. FTIR can be a single purpose tool or a highly flexible research instrument. FTIR spectrometer offer speed and sensitivity that was impossible to achieve with earlier wavelength – dispersive instrument [6].

FTIR is a technique based on the vibrations of the atoms within a molecule. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelength which causes the change of dipole movement of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The intensity of absorption peak is related to the change of dipole movement and the possibility of the transition of energy level. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structure information of a molecule.

The commonly used region for infrared absorption spectroscopy is 4000 ˜ 400 cm $^{-1}$ because the absorption radiation of most organic compound and inorganic ions is with in this region.

A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D converter and a computer [7]. The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal

by the amplifier and analog –to – digital converter, respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out **[Fig. 2.3]**.

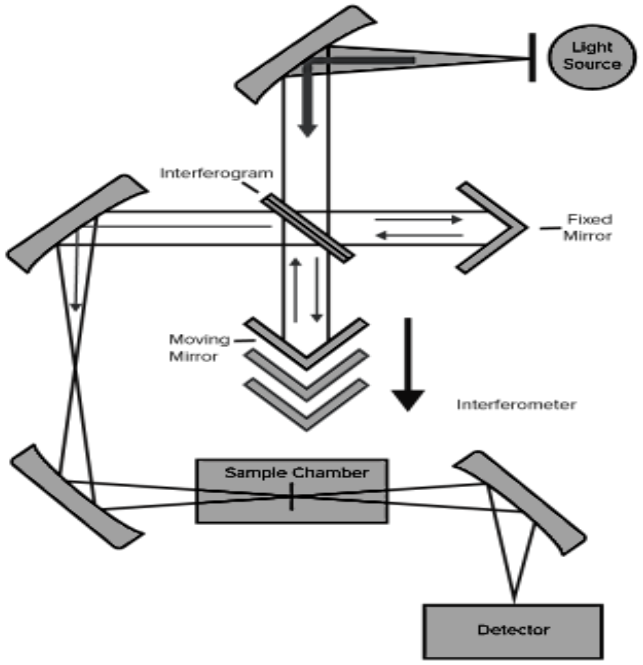

Figure 2.3: Block diagram of a Fourier Transform Infrared (FTIR) Spectrometer

2.2.8 Ultraviolet –Visible Spectrometer

UV-Vis spectroscopy, also known as ultraviolet-visible spectroscopy, is a subtype of absorption spectroscopy that specifically deals with the absorption of ultraviolet (UV) and visible range of the electromagnetic radiation spectrum. The absorption wavelength mainly ranges from 100-700 nm. Ultraviolet-visible spectroscopy is considered an important tool in analytical chemistry. In fact, this is one of the most used techniques in clinical as well as chemical laboratories. This tool is used for the qualitative analysis and identification of chemicals.

Ultraviolet–visible spectroscopy offers a relatively straight forward and effective way for qualitatively characterizing both organic and inorganic compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds. UV-Vis spectrophotometer is a laboratory technique used in the measurement of absorbance of light across ultraviolet and visible regions.

When the incident light strikes the sample, it is usually reflected, transmitted or absorbed. Absorbance of light causes the transition of molecules from ground state to excited state.

Molecules having π-electrons or non-bonding electrons (n-electrons) which are excited to higher anti-bonding molecular orbitals may absorb the energy in the form of ultraviolet or visible light. There are four possible types of transitions (π-π*, n-π*, σ-σ*, and n-σ*) which can be ordered as follows: σ-σ* > n-σ* > π-π* > n-π*.

This technique is used to detect the presence or absence of a functional group in the compound. The absence of a band at a particular wavelength is regarded as evidence of the absence of particular group. Kinetics of reaction can also be studied using UV-Vis spectroscopy. UV/Vis radiation is passed through the reaction cell, and the absorbance changes can be observed.

The design of the UV-Visible spectrophotometer includes both the parts of the spectrometer and photometer [**Fig. 2.4**]. The spectrometer contains a light source, sample cell, monochromator and slits. The microcontroller controls grating in the monochromator, whereas the photometer part consists of a photo diode, preamplifier, and data acquisition system.

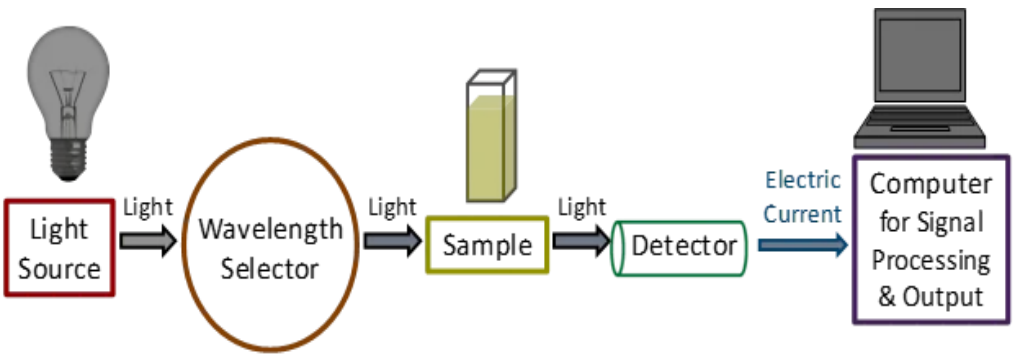

Figure 2.4: A simplified schematic diagram of the main components in a UV-Vis spectrophotometer

UV spectrophotometer principle follows the Beer-Lambert Law. This law states that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is proportional to the concentration of the solution and the incident radiation.

This law is expressed through this equation:

$$\mathbf{A = \log (I_0/I) = \varepsilon cl}$$

A stand for the absorbance, I_0 refers to the intensity of light upon a sample cell, I refer to the intensity of light departing the sample cell, c stands for the concentration of the solute, l stands for the length of the sample cell and ε refers to the molar absorptivity. Based on the Beer-Lambert law, it has been established that the greater the number of the molecules that are capable of absorbing light at a certain wavelength, the greater the extent of the absorption of light.

Visible (Systronics-166) and Double beam spectrophotometer (Systronics-2203) were used for spectrophotometric measurements. The spectrum range was set from 200 nm to 800 nm in double beam spectrophotometer. Spectrophotometer can be used to determine kinetics and the rate constant of a chemical reaction and optical characterization of the synthesized metallic nanoparticles. The rate constant of a particular reaction can be determined by measuring visible absorbance at specific time intervals. It also helps to study growth of metal nanoparticles in polymeric network or growth of polymeric network around metal nanoparticle core. The obtained UV spectra of our sample were first done baseline by reference to nullify other reagent peaks, after the spectra of reaction mixture was obtained. Spectra were plotted between wavelength v/s absorbance.

All other reagents were either of Anala R or guaranteed reagent grade and used as supplied. Further details regarding their preparations etc. are mentioned in the respective chapters. Doubly distilled water, prepared from ultrapure water purification system (Millipore Elix Model), was employed in all the preparations and kinetic studies. The glass vessels employed for storing the solutions and for kinetic studies were either of Corning or Borosil make. The instruments discussed earlier were frequently used as and when desired in kinetic studies. Kinetic procedure methodology [8] adopted for the monitoring of kinetics and analysis of the kinetic results is given in concerned chapters.

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CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF PALLADIUM NANOPARTICLE

ABSTRACT

This chapter gives an overview of the development and involvement of nanoparticles synthesis, which is a rapidly developing area of research that covers a wide range of applications. It plays a very important role in developing novel methods for creating new products that are compatible with existing production equipment, restructuring materials and chemicals to elevate performance, minimizing energy, material consumption and reduce environmental impact. Nanoparticles are considered one of the most promising areas of recent research and can be synthesized using various techniques, broadly classified into bottom-up and top-down approaches, as documented in the literature. The properties of palladium nanoparticles are highly dependent on the synthesis methods employed. This chapter presents the experimental procedures involved in the synthesis of palladium nanoparticles using the chemical reduction method. The synthesized nanoparticles are subjected to morphological and structural characterization using various techniques, including UV-Visible Spectroscopy, FT-IR Spectroscopy and Transmission Electron Microscopy (TEM).

3.1 INTRODUCTION

Nanotechnology represents one of the major breakthroughs of modern science, enabling materials of distinctive size, structure and composition to be formed. Nanotechnology is the science of the small; the very small. It is the use and manipulation of matter at a tiny scale. At this size, atoms and molecules work differently and provide a variety of surprising and interesting uses in academic, research and industrial applications. Nanotechnology represents the design, production and application of atomic, molecular and macromolecular scales to produce new nanosized materials [1].

Nanoparticles form the foundation of Nanotechnology. Nanoparticles are extremely small particles, typically measuring between 1 and 100 nanometers, and are composed of materials such as carbon, metal, metal oxide or organic matter [2]. In this size range, the nanoparticles exhibit unique physical, chemical and biological properties [3]. This phenomenon arises from the relatively large surface area-to-volume ratio of nanoparticles, which gives rise to properties such as enhanced electrical and thermal conductivity, lowered melting points, stronger magnetism and distinctive optical characteristics [4].

3.1.1 Classification of Nanoparticles

The key element of nanotechnology are nanomaterials. Nanomaterials are defined as materials having one of their dimensions in the nanoscale, i.e less than 100 nm [5].

[1] **Zero – dimensional nanomaterials (0-D) -** All the three dimensions are in the nanoscale range. Example- Quantum dots, Fullerenes and nanoparticles.

[2] **One – dimensional nanomaterials (1-D**) -They have one dimensions outside the nanoscale range. Example- Nanotubes, nanofibers, nanorods, nanowires and nano horns.

[3] **Two – dimensional nanomaterials (2-D**) - They have plate–like shapes and include graphene, nanofilms, nanolayers and nanocoating's.

[4] **Three–dimensional nanomaterials (3-D**) - These materials are not restricted to the nanoscale in any dimension. They contain bulk powders, dispersion of nanoparticles, arrays of nanowires and nanotubes etc.

The nanoparticles are generally classified as organic, inorganic and carbon based.

3.1.1.1 Organic nanoparticles- Few known organic nanoparticles are dendrimers, micelles, liposomes, ferritin and polymeric nanoparticles. These are biodegradable, non-toxic and some particles such as micelles and liposomes have a void core. **[Fig. 3.1]**. They are also referred to as nano capsules that are sensitive to thermal and electromagnetic radiation including heat and light [6].

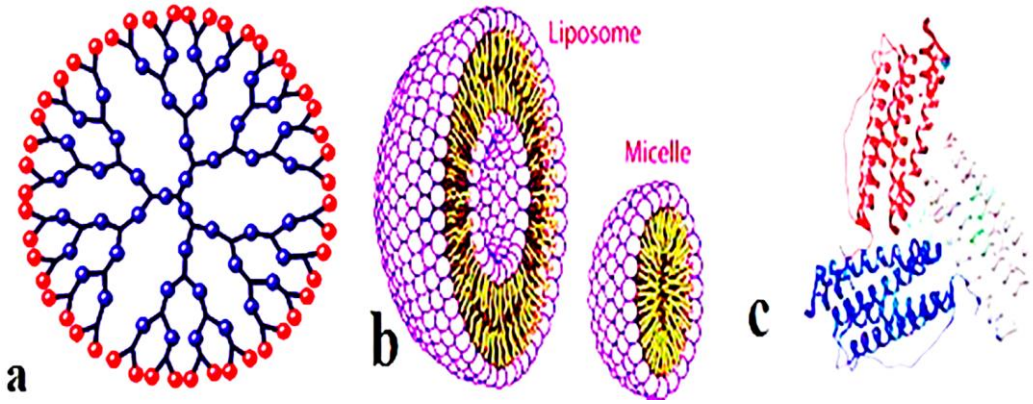

Figure 3.1: Organic nanoparticles (a) Dendrimers (b) Liposomes and Micelles (c) Ferritin.

3.1.1.2 Inorganic nanoparticles- Particles which are not made up of carbon. Metal and metal oxide-based nanoparticles are classified as inorganic nanoparticles.

(a) Metal NPs- Metal nanoparticles are prepared from metal precursors and can be synthesized by chemical, electrochemical or photochemical methods. The resultant nanomaterials can adsorb small molecules and have high surface energy. Metal nanoparticles are utilized across several research fields, including detection and imaging of biomolecules and in environmental and bioanalytical applications.

Nanoparticles can be synthesized from almost all metals. [7]. The widely used metals for nanoparticles synthesis include Aluminium (Al), Cadmium (Cd), Cobalt (Co), Copper (Cu), Gold (Au), Iron (Fe), Lead (Pb), Silver (Ag) and Zinc (Zn). Nanoparticles can have spherical or cylindrical shapes and show distinct properties such as color, reactivity and sensitivity to environmental factors like air, moisture, heat and sunlight.

(b) Metal oxide based- The metal oxide-based nanoparticles are synthesized to change the property of their respective metal-based nanoparticles. Metal oxide nanoparticles are prepared mainly due to their increased reactivity and efficacy

[8]. The commonly synthesized nanoparticles are Aluminum oxide (Al_2O_3), Iron oxide (Fe_2O_3), Silicon oxide (SiO_2), Titanium oxide (TiO_2) and Zinc oxide (ZnO).

3.1.1.3 Carbon based- This comprises nanoparticles that are prepared only from carbon atoms [9]. Famous examples include fullerenes, carbon black nanoparticles and quantum dots **[Fig. 3.2]**.

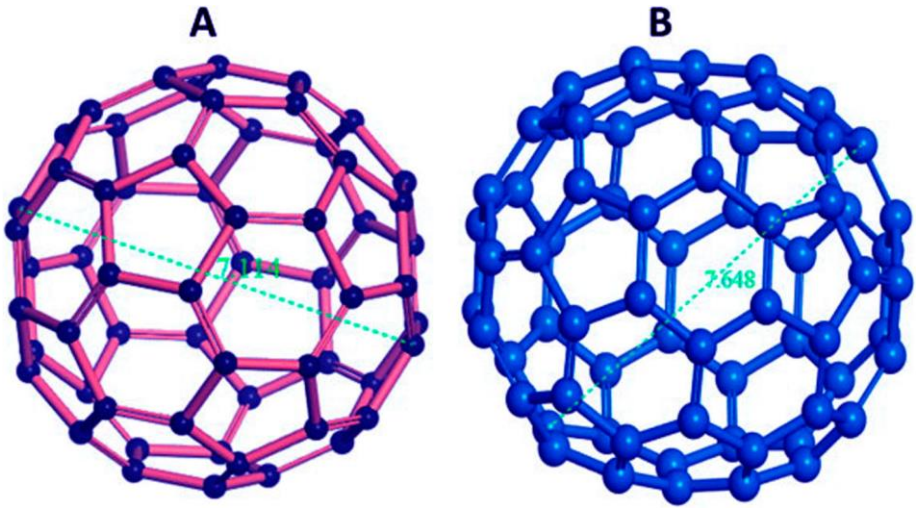

Figure 3.2: Different form of Fullerenes (A) C60 and (B) C70.

Carbon-based nanoparticles (NPs) combine the unique properties of sp_2-hybridized carbon bonds with the exceptional physicochemical characteristics observed at the nanoscale. Owing to their remarkable electrical conductivity, high mechanical strength, electron affinity and distinctive optical and thermal properties [10, 11], carbon – based NPs are utilized in a wide range of applications such as drug delivery [12], energy storage [13], bioimaging [14], photovoltaic devices and environmental sensing to monitor microbial ecology.

3.1.2 Classification of Techniques for synthesis of Nanoparticles

The synthesis of nanomaterials and nanostructures is an important aspect of nanoscience and nanotechnology. New physical properties and application of nanomaterials are only possible when nanostructured materials are made available with desired size, shape, morphology, crystal structure and chemical composition. Nanoparticles can be synthesized using two general approaches, as illustrated in **[Fig. 3.3 & 3.4]**.

(a) Top - down approach

(b) Bottom - up approach

3.1.2.1 Top-down approach

The methods begin with larger particles which are reduced to nanoparticles after a sequence of operations performed over them. The methods are quite expensive and not suitable for large-scale production. This method is suitable for laboratory experimentation. The approach is based upon the grinding of materials. A diagrammatic representation of this method is given in **[Fig. 3.3]** [15, 16].

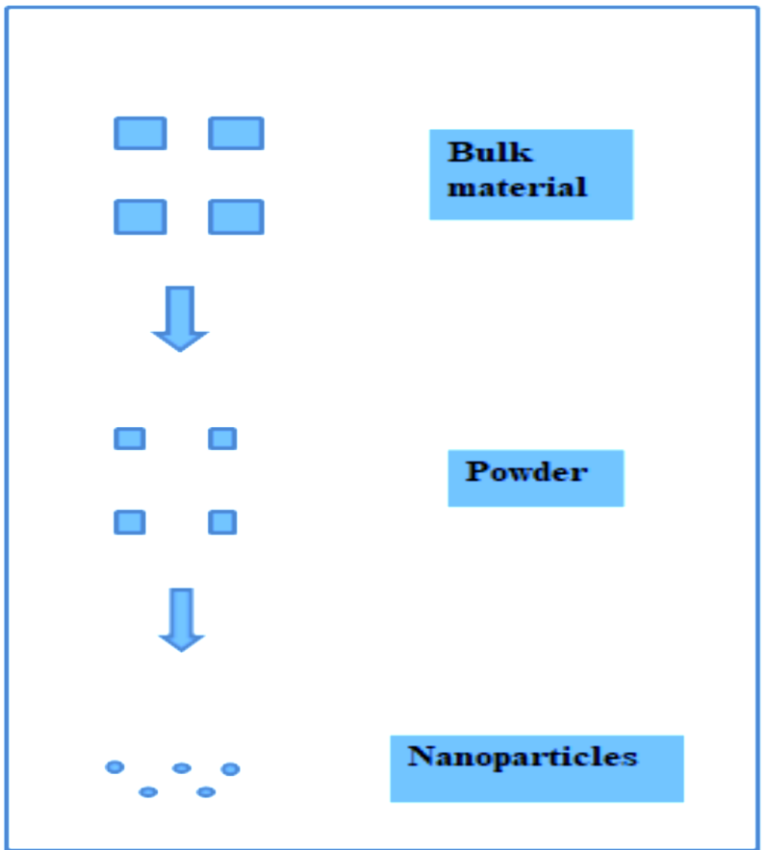

Figure 3.3: Top – down approach

Methods in Top-down approach:

- Physical vapour deposition
- Chemical vapour deposition
- Ion implantation
- Electron beam lithography
- X-ray lithography

3.1.2.2 Bottom-up approach

Bottom-up approaches of production of nanomaterials comprise the miniaturization of materials constituents to the atomic level with the additional procedure that leads to the development of nanostructures. This methodology fundamentally relies on the concept of molecular recognition. A diagrammatic representation of this approach is given in **[Fig. 3.4]** [17, 18].

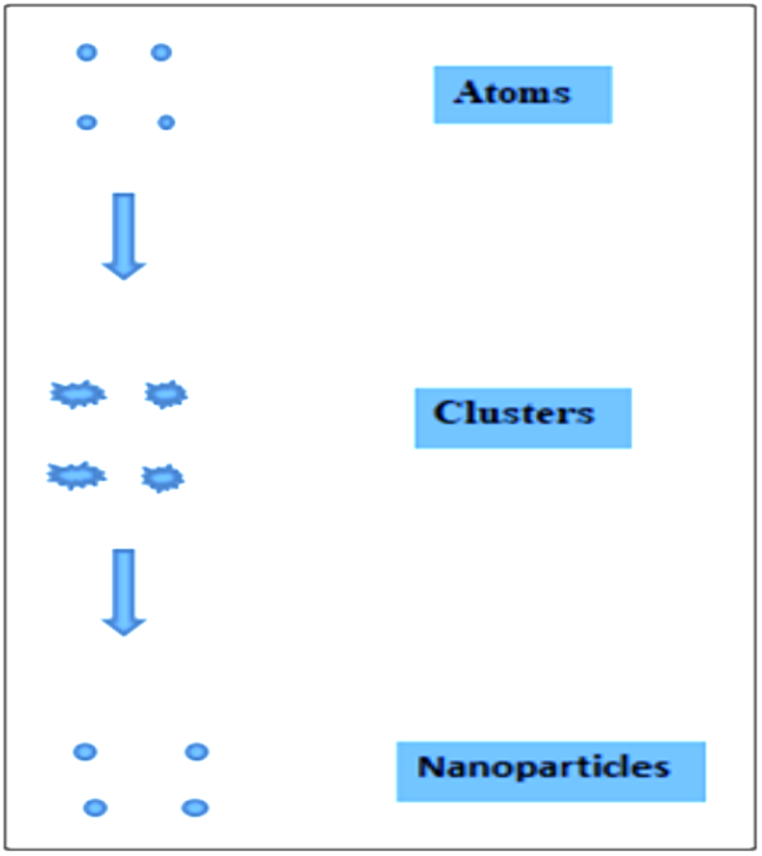

Figure 3.4: Bottom –up approach

Methods in a Bottom-up approach:

- Sol-gel synthesis
- Colloidal precipitation
- Hydrothermal synthesis
- Organometallic chemical route
- Electrodeposition

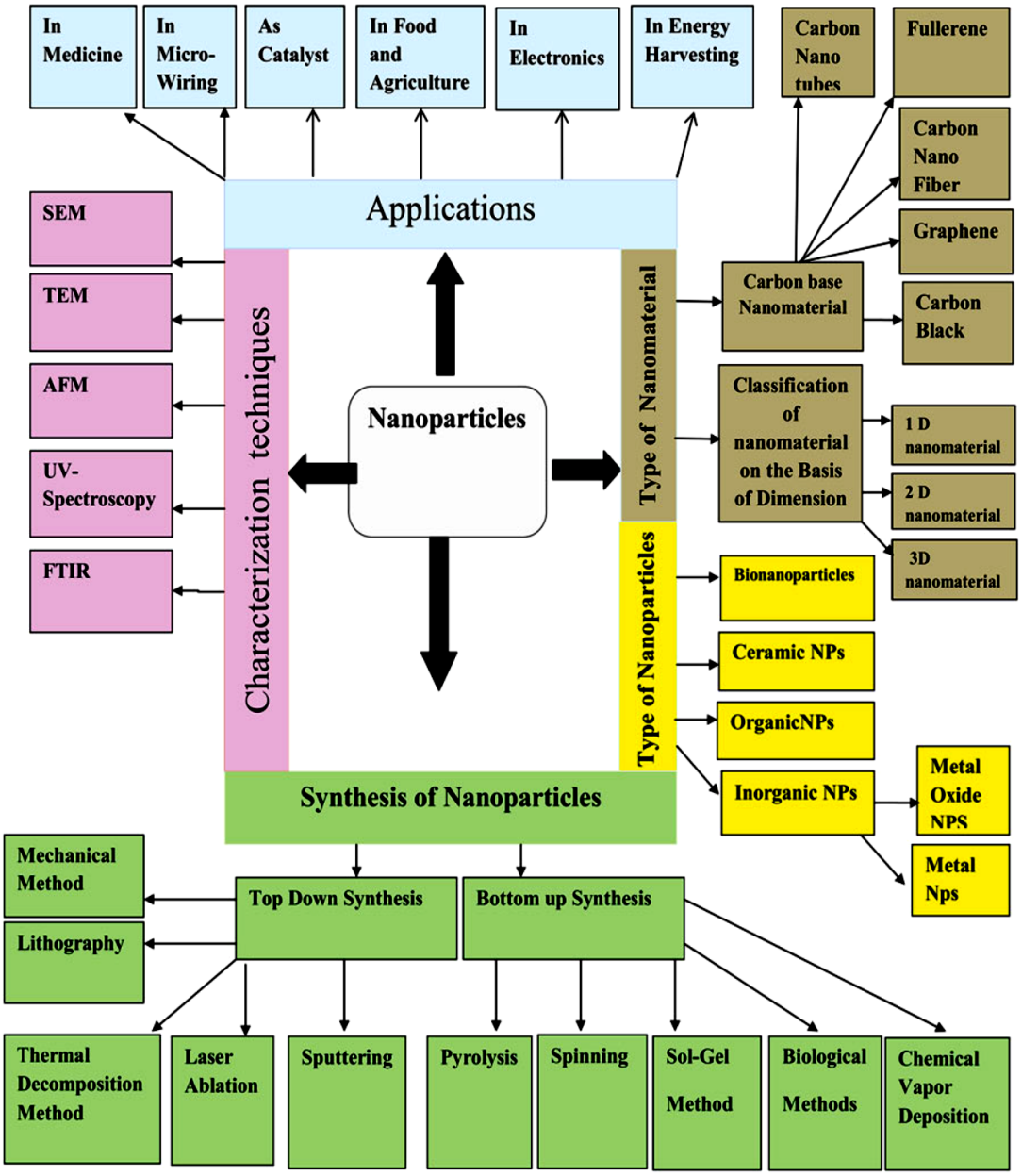

Figure 3.5: Application Hierarchy

3.1.3 Synthesis of nanoparticles

There are three kinds of approaches to produce nanoparticles. These methods are listed in **[Table 1]**.

1. Physical Methods
2. Chemical Methods
3. Biological Methods

Table 3.1: Synthesis of Nanoparticles

Physical methods	**Chemical methods**	**Biological methods**
1. Mechanical Method 2. Pulse Laser Ablation 3.Pulsed Wire Discharge Method 4.Chemical Vapor Deposition 5. Laser Pyrolysis 6.Ionized Cluster Beam Deposition	1. Sol-gel Method 2.Sonochemical Synthesis 3.Co-precipitationMethod 4. Inert Gas Condensation Method 5.Hydrothermal Synthesis	1.Synthesis Using Microorganisms 2. Synthesis Using Plant Extracts 3. Synthesis Using Algae

3.2 PALLADIUM NANOPARTICLES (PdNPs)

Palladium (Pd) is a major constituent of many catalysts. Nanoparticles (NPs) provide a significantly larger surface area as compared to bulk materials. With the five-fold increase in Palladium costs in the last 10 years, Pd nanoparticles (Pd NPs) are in increasing demand due to their novel and enhanced physiochemical properties at the nanoscale. Pd NPs are widely applied not only in chemical catalysis, but also in fields such as hydrogen sensing and storage as well as in medicine—for photothermal therapy, antibacterial treatments, and anticancer applications. On an industrial scale, Pd NPs are currently synthesized using a variety of chemical and physical methods.

Pd nanoparticles have been widely studied and employed as highly efficient catalysts for the various catalytic reactions of different compounds [19-26]. The catalytic activity strongly depends on both particle size and shape. Pd nanoparticles with well-defined sharp shapes exhibit enhanced catalytic performance for organic reactions such as Suzuki, Heck and Stille coupling reactions [21,22]. Notably they retain their catalytic properties even in aqueous suspension, which makes it ideal to study the size dependence of catalytic behavior [23,24]. Currently, significant research is concentrated on controlling the size and shape of Pd nanoparticles using the polyol method, that aims to optimize their synthesis for catalytic applications.

3.2.1 Synthesis Method of Palladium nanoparticles (PdNPs)

Chemical Reduction method

The chemical reduction of metal salts is one of the most widely used methods for synthesizing transition metal nanoparticles [27, 28]. In this method, the metal salt dissociates into metal ions, which are subsequently reduced by a reducing agent to form metal nanoparticles. These nanoparticles are typically stabilized by a stabilizing agent. Frequently used reducing agents include solvents such as alcohols [29–31], salts such as sodium borohydride [32–35] and sodium citrate [36, 37] and gases such as carbon monoxide [38] and hydrogen [39, 40].The alcohols most commonly used for the reduction of metal salts include ethanol, methanol and isopropanol and they act both as a reducing agent and solvent. The transition metal nanoparticles are formed by the reduction of metal salts in refluxing alcohol, during which the alcohol is oxidized to its corresponding carbonyl compounds (e.g. methanol to formaldehyde and ethanol to acetaldehyde). The size distribution of resulting metal nanoparticles depends on the structure and quantity of the alcohol, the choice of stabilizing agent, the metallic precursor, the reaction temperature and the base employed [29-31].

3.2.2 Synthesis of PVP Stabilized Palladium nanoparticles

The Palladium nanoparticles were synthesized using the chemical reduction method described previously [41-44]. The Palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887g of $PdCl_2$ and 6 ml of 0.2 M HCl and diluting it to 250 ml using doubly distilled water to prepare H_2PdCl_4 solution having concentration of 2mM. The entire volume was transferred to a flask, refluxed for 3 hours, and then allowed to age for 2 days. The resulting product typically exhibited a pale-yellow colour. Then, 15 mL of 2 mM H_2PdCl_4 solution was mixed with 21 mL of doubly deionized water, 0.667 g of PVP and 4 drops of 1 M HCl. The mixture was heated at 100 °C. As soon as the solution began to reflux, 14 ml of ethanol was added. The solution was then refluxed for 3hours which resulted in a dark – brown suspension of Pd nanoparticles **[Fig. 3.6]**. Thus, the reduction of H_2PdCl_4 by ethanol, which acts both as a solvent and reducing agent occurred. As a result, palladium nanoparticles were formed and effectively stabilized by polyvinylpyrrolidone (PVP) that acted as a capping agent. To evaluate their characteristics, various volumes of Pd solution were centrifuged at 15000 rpm for 30 min by a Sigma 3K30C-Kubota centrifuge, separated and precipitated upon adding triple volume of acetone. The resulting mixture was centrifuged again and redispersed

in 3ml of ethanol using an ultrasound generator at 200W and 37 KHz for the generation to facilitate Pd nanoparticles formation. For washing Pd nanoparticles, 9ml of hexane was added followed by centrifugation at 15000 rpm for 5min. The product was then washed three times with ethanol and hexane to remove residual impurities.

Figure 3.6: Image shows the color change from palladium nanoparticle

3.2.3 Steric Stabilization

Stabilization of metal nanoparticles by high molecular compounds presents a major branch of modern polymer colloidal science. Capping agents are frequently used in colloidal dispersions to precisely control the growth, agglomeration, and physicochemical properties of nanoparticles [45].

The capping agent is an amphiphilic molecule consisting of a polar head group and a non-polar hydrocarbon tail **[Fig. 3.7]**.

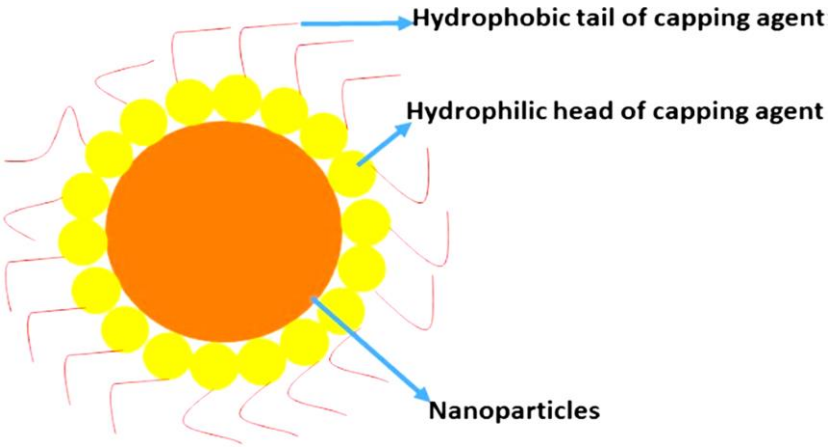

Figure 3.7: Nanoparticles covalently bound with capping agents

Various types of capping agents have been used in nanoparticles synthesis, including surfactants, small ligand, polymers, dendrimers, cyclodextrins and polysaccharides. All these agents have been successfully employed to induce subtle changes in nanoparticle properties contributing to significant therapeutic potential and environmental remediation effects [46]. [**Fig. 3.8]** illustrates the different types of capping agents.

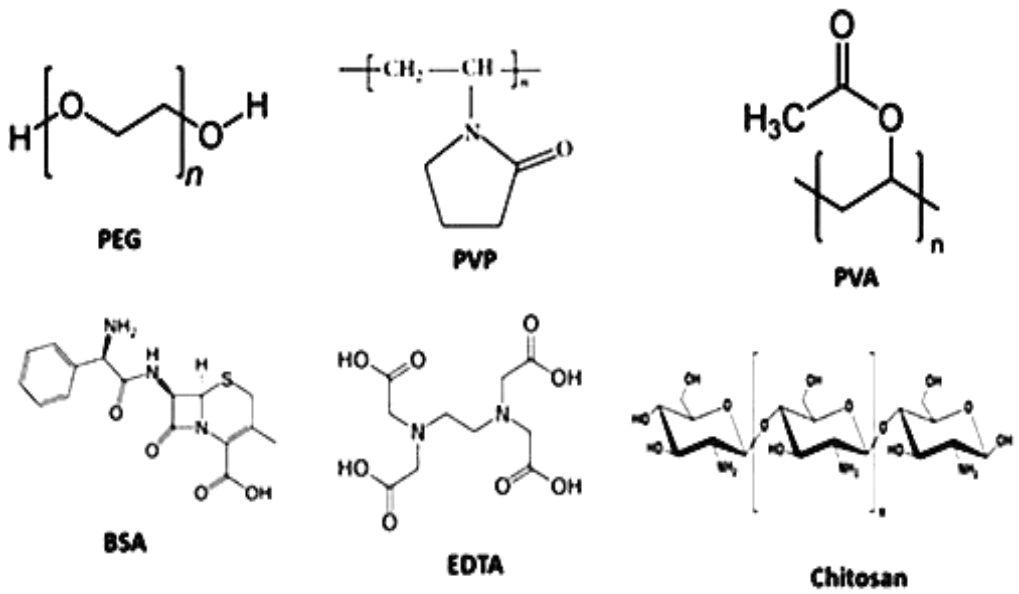

Figure 3.8: Different types of capping agents utilized in nanotechnology

The stabilization of metal nanoparticles can also be achieved using macromolecules such as polymers or oligomers [47, 48]. Most utilized polymers include PVP [49-52], polyacrylate [53, 54] etc. The bulky group of PVP will form a protective layer around the surface of nanoparticles there by preventing the aggregation of the particles.

3.2.4 PVP (Polyvinylpyrrolidene)

PVP, also known as povidone or polyvidone, is a water-soluble polymer $(C_6H_9NO)_n$. PVP is synthesized by the of polymerization of the monomer N- vinyl pyrrolidone. It appears as a light, flaky and hygroscopic powder that absorbs approximately 40% of water by its mass. PVP with its unique physico-chemical properties like solubility in both water and organic solvents, biocompatibility, chemical stability and non-toxicity makes it a promising biomaterial for a wide range of medical and non-medical applications.

PVP is extensively used in many medical products, cosmetics, and hair care formulations. Among available polymers, PVP is one of the most widely used due to

its low cost and its ability to stabilize nanoparticles with high surface areas in polar solvents such as water. However, PVP does not completely passivate the nanoparticle surface, allowing for catalytic activity to be retained.

It has been employed to stabilize spherical nanoparticles of platinum [53], palladium [49, 50, 55], and rhodium [56]. PVP-stabilized nanoparticles have shown effective catalytic activity in various chemical reactions.

PVP is one of the efficient capping agents that have been utilized in nanotechnology to mitigate the drawbacks linked with classical methods of synthesis of nanoparticles such as toxicity, size and agglomeration. Hence ecofriendly nano formulations are obtained using PVP having more applicability [57,58]. In various research, PVP has been used as a capping agent around metal nanoparticles such as Iron (Fe), Silver (Ag), Gold (Au), Zinc (Zn) etc. [59].

3.2.5 Application of Palladium nanoparticles

EI-Sayed and Co-workers reported that Palladium nanoparticles stabilized by PVP act as efficient catalysts for Suzuki Cross Coupling reactions [43]. They reported that by verifying the PVP / metal ratio, the size of the nanoparticle can be varied [60]. They have also shown that the decrease in palladium nanoparticle size down to 3 nm improved the catalytic activity in the Suzuki reaction [55, 43].

Miyake and Co-workers reported that the size of palladium nanoparticles can be controlled by altering the amount of the protective polymer, PVP and the kind or concentration of alcohol used [29,30]. The smaller sized palladium nanoparticles were prepared in case of reduction of H_2PdCl_4 with increase in the amount of the polymer. Also, the size of particles and standard deviation became smaller during the reduction of $PdCl_2$ in the presence of sodium hydroxide and methanol [31].

3.3 CHARACTERIZATION OF NANOPARTICLES

Nanoparticles are generally characterized by their size, morphology and surface charge, using advanced microscopic techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The average particle diameter, size distribution and surface charge significantly influence the physical stability and in vivo distribution of nanoparticles. Electron microscopy techniques are highly effective for determining the overall shape of polymeric

nanoparticles, which may determine their toxicity. The surface charge of the nanoparticles influences physical stability, dispersibility of the polymer dispersion and their vivo performance.

3.3.1 Transmission Electron Microscopy (TEM)

The Transmission electron microscope (TEM) is the perfect instrument for structural and chemical characterization at the nanoscale. Transmission electron microscopy (TEM) is one of the most suitable techniques for determining the size and shape of nanomaterials. TEM is a technique that uses an electron beam to image a nanoparticle sample, providing much higher resolution than is possible with light–based imaging technique. TEM gives information about internal structure, which SEM cannot provide.

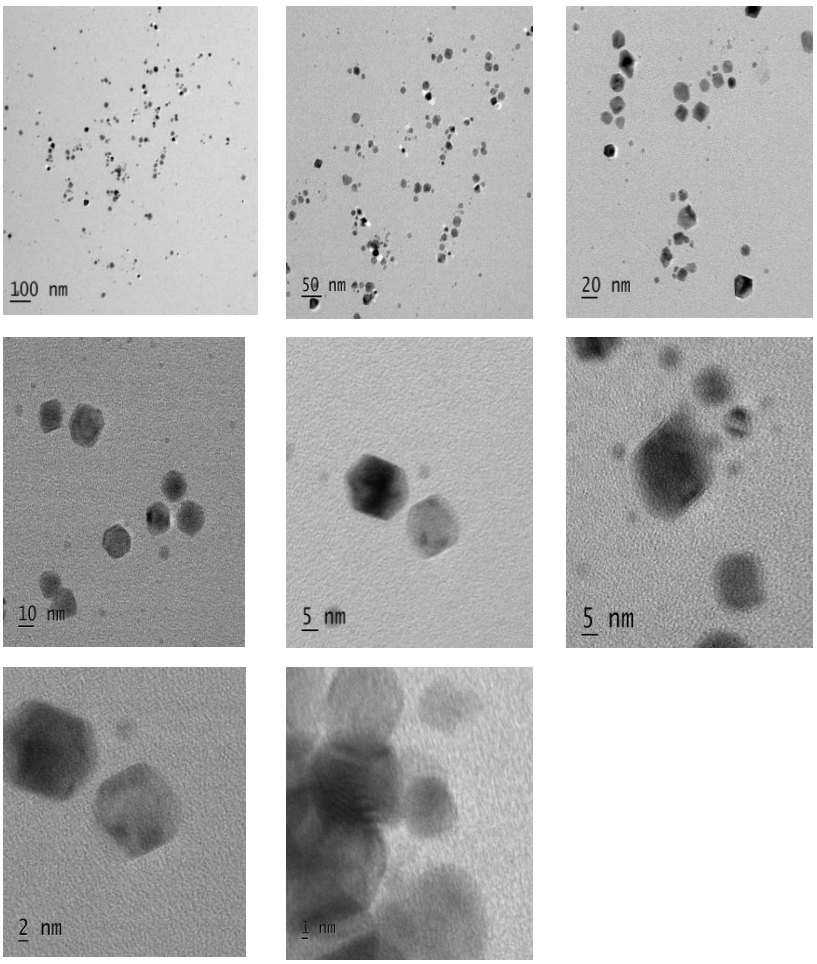

Figure 3.9: TEM images of major shapes and various sizes of Pd nanoparticles. TEM images of Pd nanoparticles with scale bars: (a) 100 nm (b) 50 nm (c) 20 nm (d) 10 nm (e, f) 5 nm (g) 2 nm and (h) 1 nm

The results show the electron microscopy characterization of palladium nanoparticles (NPs) obtained by the polyol [61,62] method at different temperatures [63] **[Fig. 3.9]**. The TEM images were obtained on JEOL JEM-2010 XII instruments operating at an accelerating voltage of 200 kv. Samples for TEM analysis were prepared by dispersing Pd nanoparticles in ethanol followed by drop-coating on a copper grid coated with carbon film. From the TEM images, we can infer the following:

1. Morphology

The nanoparticles are mostly polyhedral in shape (hexagonal, cubic and irregular faceted particles) but a few spherical particles are also present, but faceted shapes dominate suggesting crystalline nature.

2. Size

The Size distribution seems polydisperse (not uniform), some particles are as small as 1–20 nm while others are 20+ nm. Some particles are monodispersed (uniform in size) also.

3. Dispersion

The nanoparticles are quite well separated, with very less clustering which suggests nucleation followed by aggregation around a seed particle.

4. Crystallinity

The faceted morphology of the larger particle suggests crystalline growth with distinct planes, while the smaller ones are too small to see facets clearly but likely crystalline as well.

3.3.2 UV-Visible Spectrophotometer

UV-Vis spectrophotometer was used to record the optical absorption spectra of the Pd nanoparticles thin films. UV-Visible spectral analyses were carried out on a double beam spectrophotometer-2203(Systronics). The formation of Pdnps was monitored in 220-600 nm range. The reaction mixture changes gradually from pale yellow to dark brown due to surface plasmon vibrations. **[Fig. 3.10]** shows the absorption peaks at 310 and 410 nm that attribute to $[PdCl_4]^{2-}$, while the peak at 256 nm and 315 nm corresponds to PVP-stabilized PdNPs using ethanol as reductant. This is ascribed to ligand (Cl^-) → metal (Pd^{+2}) charge transfer transition of Pd (II) ions [29,64]. The disappearance of the absorption peak after 15 minutes is due to the complete reduction of metal ions Pd^{+2} to Pd^0. After 30 minutes, the colour intensity of the reaction mixture changes leading to an increase in the absorbance of the solution.

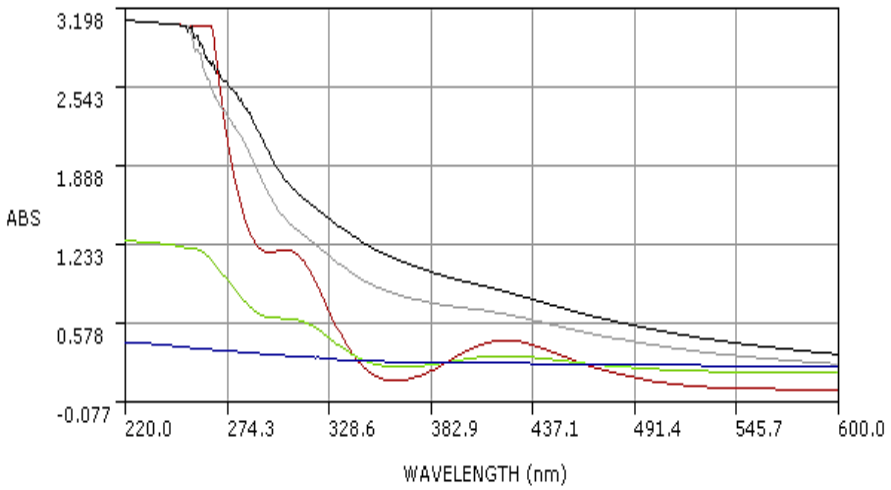

Figure 3.10: UV–Vis spectra of PVP-protected Pd NPs in the range 220–600 nm Red – H_2PdCl_4, Green - 0 min, Blue – 5 min., Grey - 15 min., Black – 30 min.

3.4 CONCLUSION

Pd nanoparticles with uniform shape were prepared by chemical reduction method at 45°C. The current results show that chemical reduction method is an easy and efficient method for synthesizing nanoparticles and modifying the kinetics of atoms to assemble, grow and generate particle shapes. The reduction of H_2PdCl_4 is done by ethanol, which acts both as a solvent and reducing agent. The TEM image shows ultra-small nanoparticles (mostly 2–5 nm) along with a few larger faceted particles (~10–20 nm), polydisperse, with some aggregation. The larger faceted particle proves crystalline nature, while clustering suggests possible secondary growth.

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CHAPTER 4

KINETICS AND MECHANISM OF PALLADIUM (II) CATALYSED OXIDATION OF VALINE BY N- BROMOSUCCINIMIDE IN PERCHLORIC ACID MEDIUM

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 35ºC. The rate of reaction decreased with an 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 change to zero order at its higher concentration. Variation in [Hg (II)], [NHS], $[Cl^-]$ and ionic strength has no effect on the rate of reaction. NBS itself and $[PdCl_4]^{2-}$ 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 iso-butyraldehyde and ammonia. A mechanism supported by kinetic and spectrophotometric data has been proposed. Various activation parameters have been calculated and based on these parameters, a suitable explanation of the reaction mechanism has been given.

4.1 INTRODUCTION

Oxidation reactions of amino acid are one of the most relevant biochemical reactions because such reactions serve as models for protein oxidations [1-3]**.** Several uncatalysed [4-10] and catalyzsed [11-16] kinetic studies have been reported on the oxidation of amino acids by different oxidants such as N-Bromosuccinimide, diperiodatoargentate (III), hexacyanoferrate (III) etc. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [17-19]. 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 medium [20-26]. Though there are several reports [27-29] 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 reactions [30-34] but the nature of its active form in such reactions remains obscure and 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 has been studied using various oxidants but catalyzed oxidation using transition metals as catalyst has not been studied in detail by using oxidants like N-bromosuccnimide. 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.

4.2 EXPERIMENTAL

4.2.1 Materials

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 (Hypo) using starch as an indicator [35-36]. The reaction mixture wasprepared 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 ion. $NaClO_4$ (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 the highest available purity.

4.2.2 Kinetic Procedure

The reaction was carried out in stoppered Erlenmeyer flasks immersed in a water bath thermostated at 35 ± 0.1°C unless where stated otherwise. Requisite volumes of all reagents except NBS were introduced into reaction vessel and equilibrated at 35ºC. 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.

4.2.3 Stoichiometry and Product Analysis

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

$$(CH_3)_2CHCH(NH_2)COOH + 2NBS + H_2O \xrightarrow{Pd(II)/H^+} 2NHS + CO_2 + Br_2 + NH_3 + (CH_3)_2CHCHO \quad (1)$$

The main reaction products were succinimide, iso-butyraldehyde, ammonia and CO_2. Liberated ammonia was identified by Nessler′ s reagent where a brownish colour was observed indicating a deamination reaction [35]**.** CO_2 was identified by freshly prepared lime water and the solution turned milky, indicating a decarboxylation reaction [36].

Iso-butyraldehyde was confirmed by the IR spectrum of the corresponding hydrazone [**Fig.4.1**]. The reaction mixture was treated with acidified 2,4 - DNP solution which yielded a hydrazone. An Iso-butyraldehyde hydrazone typically shows a strong C=N stretch at 1617 cm^{-1}, N–H stretch around ~3300 $cm^{-1}$and alkyl C–H stretch at 2970/2870 cm^{-1}. Further, aldehyde group was confirmed with qualitative test such as

Tollen′s reagent [37]. The product has also been confirmed by UV-Vis spectra [**Fig.4.2**]. The reaction was carried out and spectra taken at different time intervals. The formation of the complex was kinetically proven by Michaelis-Menten plot that is non-zero intercept of the plot of 1/rate v/s 1/ [Val]. The complex formation between oxidant and reductant is also reported in literature [38].

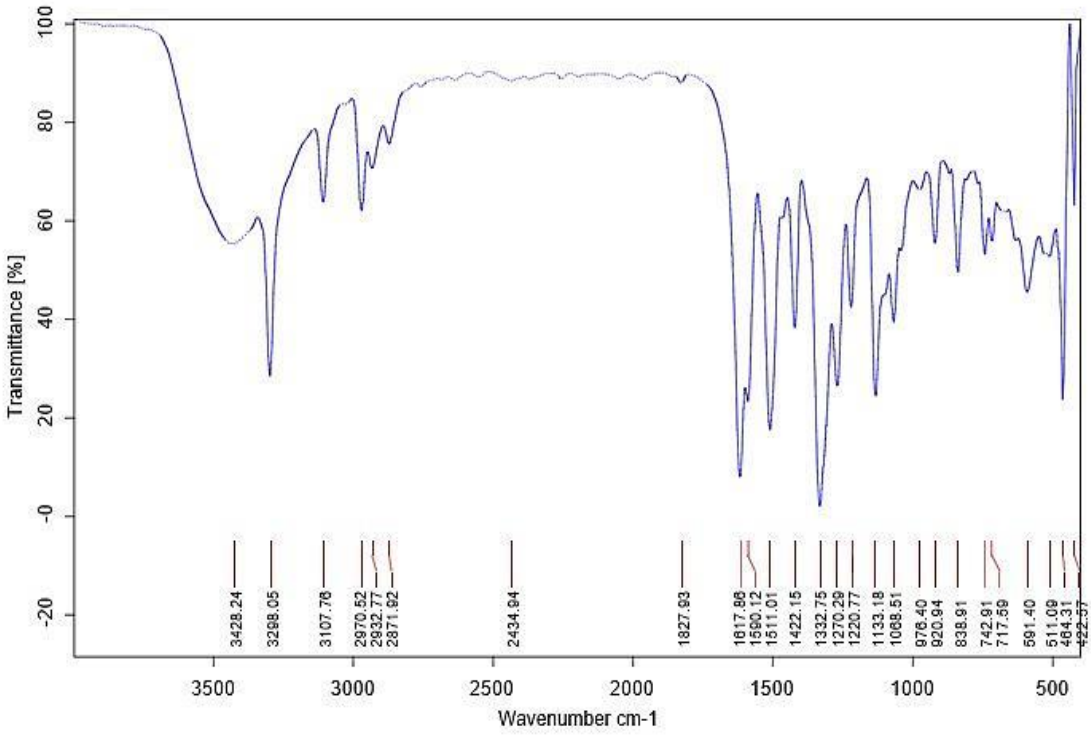

Figure 4.1: IR Spectrum of Iso-butyraldehyde Hydrazone

Kinetics of oxidation of valine using chloro complex of Pd (II) as homogeneous catalyst in acidic medium have been investigated at 35ºC. 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 is constant.

$$k_{obs} = \frac{-d[NBS]/dt}{[NBS]} \qquad (2)$$

4.2.4 Spectroscopic analysis

The spectrum [**Fig.4.2]** shows strong UV absorption around 220 nm due π→π* transitions of NBS and valine's far-UV intrinsic transitions. Pd (II) complexes can show charge-transfer transitions in the near-UV region (300–350 nm) when ligands with

donor atoms (like N from valine or NBS) coordinate. At 328 nm, this could be a ligand-to-metal charge transfer (LMCT) from N or O donor atoms of valine or NBS to the empty Pd (II) orbitals. After 5 min, the main UV band near 220–230 nm begins to decrease slightly and a small feature around 328 nm appears (very weak). This indicates consumption of NBS and the formation of a new Pd-containing complex. Around 15 min, 328 nm approaches a plateau, and the 220 nm band falls further. This suggests the intermediate is reaching a constant concentration and most of the NBS is consumed. After 55 min the 328 nm band decreases and 220 nm is low, showing the reaction moving towards completion.

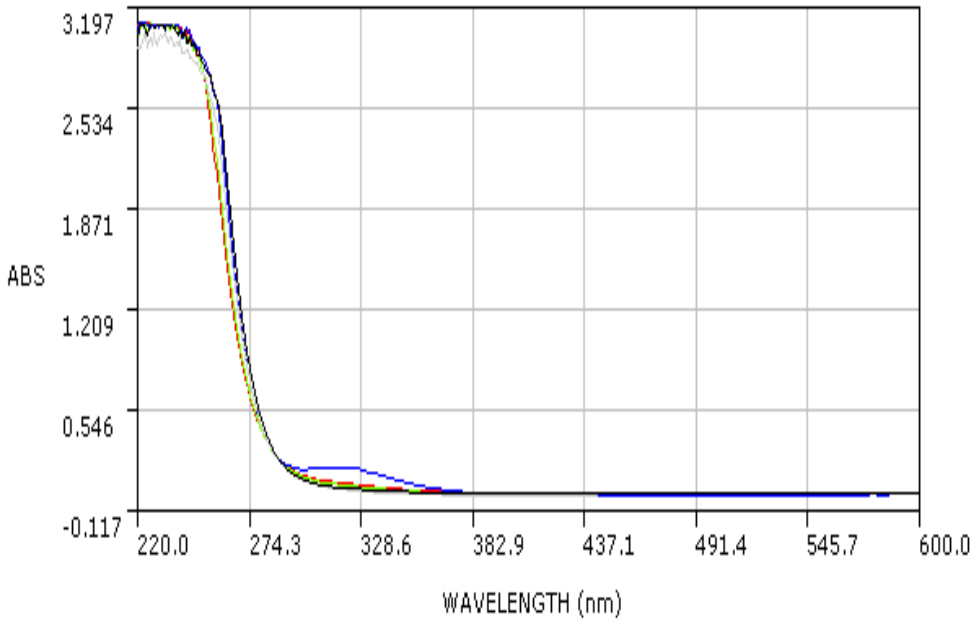

Figure 4.2: Spectral changes during the oxidation of Valine by NBS in aqueous perchloric acid medium at 35ºC

[NBS]=5 × 10^{-3} mol dm^{-3} [H^+] = 0.1 mol dm^{-3} [Val]= 5 × 10^{-2} mol dm^{-3}
[Pd (II)] =5 ×10^{-5} mol dm^{-3}, Time scan: Red – 0 min, Green -5 min,
Blue – 15 min, Grey – 30 min, Black – 55 min.

4.3 RESULTS

4.3.1 Effect of NBS concentration

The effect of NBS concentration on the reaction was studied between the concentration range of 0.75 $\times 10^{-3}$ to 5.0 $\times 10^{-3}$ mol dm^{-3} at fixed concentration of [Valine] = 2.0 $\times 10^{-2}$ mol dm^{-3}, [Pd(II)] = 2.0 $\times 10^{-5}$ mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3}, [I] = 0.25 mol dm^{-3} and temperature 308 K. Increase of concentration of NBS yields constant pseudo first order rate confirming the first order dependence on NBS in [**Table 4.1**]. When log $[NBS]_t$ was plotted against time, linear plots were obtained which also proves first order with respect to [NBS] [**Fig.4.3**]. Results are given in [**Tables 4.2].**

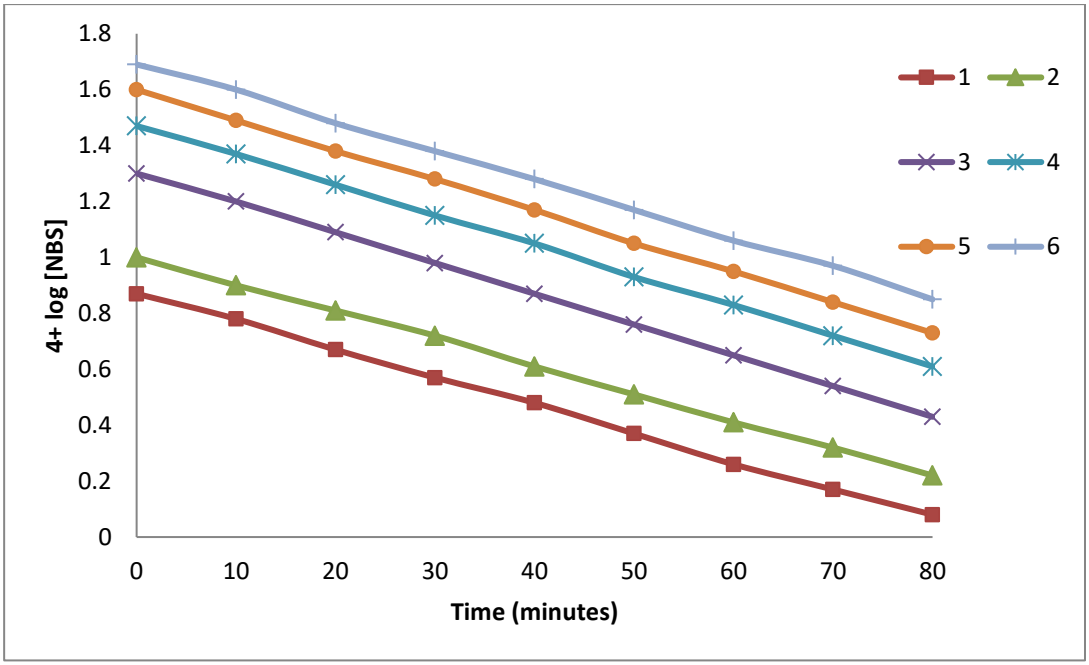

Figure 4.3: Pseudo first order plots for the variation of NBS at 35°C

[NBS] = (1) 0.75 × 10^{-3} mol dm^{-3} (2) 1.0 × 10^{-3} mol dm^{-3}
(3) 2.0 × 10^{-3} mol dm^{-3} (4) 3.0 × 10^{-3} mol dm^{-3}
(5) 4.0 × 10^{-3} mol dm^{-3} (6) 5.0 × 10^{-3} mol dm^{-3}
[Val] = 2.0 × 10^{-2} mol dm^{-3} $[H^+]$ = 0.10 mol dm^{-3}
[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3} [I] = 0.25 mol dm^{-3}

Table 4.1: 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

Table 4.2: Variation of NBS

[Pd (II)] = 2.0×10^{-5} mol dm^{-3} **[$Na_2S_2O_3$] = 2.0×10^{-3} mol dm^{-3}**

[Val] = 2.0×10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35°C**

10^3 [NBS], mol dm^{-3}	**0.75***	**1.0***	**2.0****	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**					
0	12.5	16.7	10.0	7.5	10.0	12.5
5	11.0	14.8	9.0	6.6	8.9	10.9
10	9.9	13.3	8.0	5.9	7.9	9.7
15	8.8	11.9	7.1	5.3	7.0	8.7
20	7.8	10.7	6.4	4.7	6.3	7.9
30	6.3	8.5	5.1	3.8	5.0	6.3
40	4.9	6.9	4.1	3.0	4.0	5.0
60	3.2	4.4	2.6	1.9	2.5	3.2
80	2.0	2.8	1.7	1.2	1.6	2.1
100	(95) 1.4	1.8	1.1	0.8	1.0	1.3
10^4 k_{obs} (sec^{-1})	**3.76**	**3.72**	**3.74**	**3.74**	**3.76**	**3.72**

[$Na_2S_2O_3$] * = 3.0×10^{-4} mol dm^{-3}

[$Na_2S_2O_3$] ** = 1.0×10^{-3} mol dm^{-3}

Figures in parenthesis denotes time in minutes.

4.3.2 Effect of [H^+]

Hydrogen ion concentration was varied from 0.05 to 0.50 mol dm^{-3} at fixed concentration of all other reactants. According to results it was found that the rate of reaction decreases with increase of perchloric acid concentration in Pd (II) catalysed oxidation. The rate constant k_{obs} decreased with the increase in [H^+] concentration [**Fig.4.4**]. The plot of log k_{obs} versus log [H^+] is linear with a fractional slope. Results are given in [**Tables 4.3].**

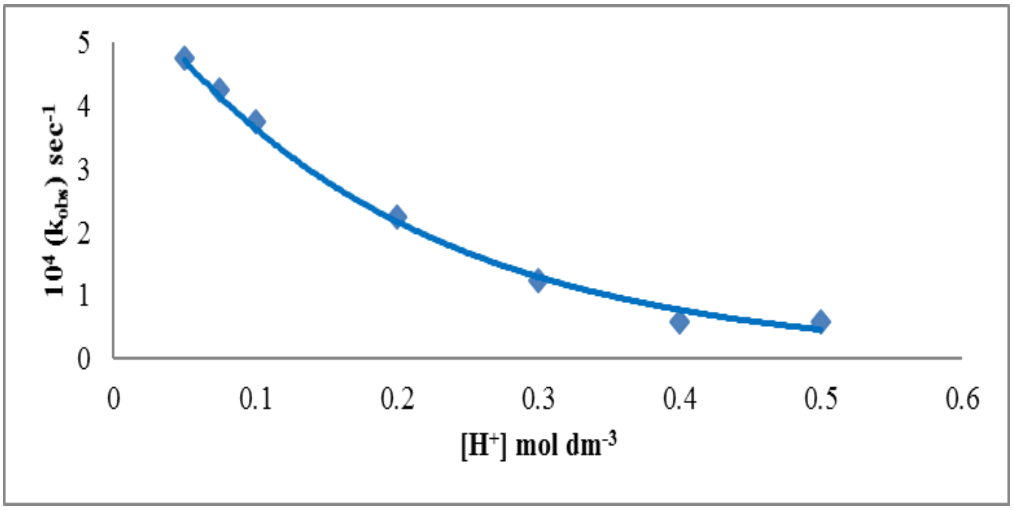

Figure 4.4: Variation of Hydrogen ion

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[Val] =2.0 × 10^{-2} mol dm^{-3}**

[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3} **[I] = 0.25 mol dm^{-3}** **Temp.= 35°C**

Table 4.3: Variation of [H^+]

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0 × 10^{-3} mol dm^{-3}**

[Val] = 2.0 × 10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3} **Temp. = 35°C**

[H^+], mol dm^{-3}	**0.05**	**0.075**	**0.10**	**0.20**	**0.30**	**0.40**	**0.50**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.8	8.7	9.0	9.4	9.6	9.7	9.8
10	7.6	7.7	8.0	8.7	9.3	9.6	9.7
15	6.7	6.8	7.1	8.1	8.9	9.3	9.5
20	5.9	6.0	6.4	7.6	8.6	9.1	9.3
30	4.4	4.7	5.1	6.6	7.9	8.9	9.1
40	3.3	3.6	4.1	5.7	7.4	8.7	8.8
60	1.9	2.2	2.6	4.4	6.4	8.1	8.3
80	1.1	1.3	1.7	3.4	5.5	7.5	7.7
100	0.6	0.7	1.1	2.6	4.7	7.0	7.3
10^4 k_{obs}(sec^{-1})	**4.75**	**4.25**	**3.74**	**2.25**	**1.25**	**0.58**	**0.50**

4.3.3 Effect of Valine

The concentration of valine acid was varied from 0.50 $\times 10^{-3}$ to 5.0 $\times 10^{-3}$ mol dm^{-3} at constant [NBS], [H^+], [Pd (II)] and mercuric acetate at different initial concentration of valine at three temperatures 30°C, 35°C and 40°C respectively The plot of log [k_{obs}] v/s log [Val] was a straight line with fractional slope **[Fig.4.5].** The results show first order dependence of the reaction on amino acid at low concentration, which shifts towards zero order at its higher concentration. Results are given in **[Tables 4.4].**

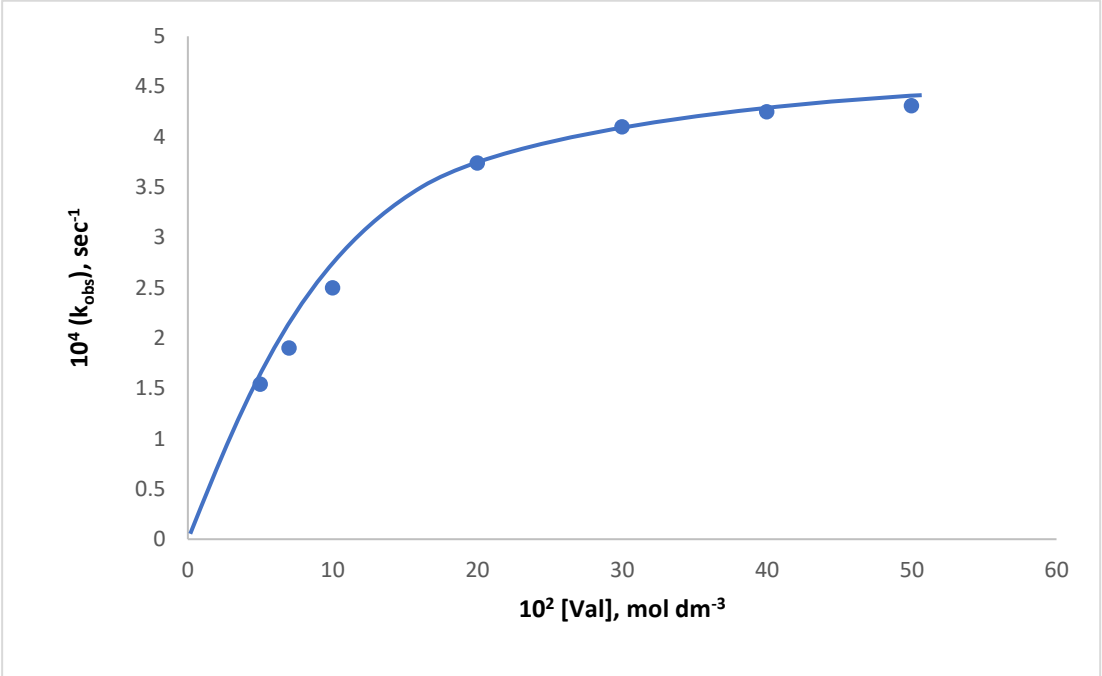

Figure 4.5: Variation of Valine

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

[Pd(II)] = 2.0 × 10^{-5} mol dm^{-3} **[I]= 0.25 mol dm^{-3}** **Temp.= 35 °C**

4.3.4 Effect of Palladium (II) catalyst

The reaction rates were measured by varying [Pd (II)] from 0.50 $\times 10^{-5}$ to 5.0 $\times 10^{-5}$ mol dm^{-3} at fixed concentration of all other reactants. 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.4.6].** The line does not pass through origin indicating the reaction proceed without catalyst also but at a very slow rate. The Results are given in **[Tables 4.5].**

Table 4.4: Variation of Valine

[NBS] = 2.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pd (II)] = 2.0×10^{-5} mol dm^{-3} **Temp. = 35°C**

10^2 [Val], mol dm^{-3}	**0.50**	**0.70**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.6	9.5	9.2	9.0	8.9	8.8	8.7
10	9.1	8.9	8.6	8.0	7.9	7.8	7.6
15	8.7	8.6	7.9	7.1	7.0	6.8	6.6
20	8.3	7.9	7.4	6.4	6.3	6.1	6.0
30	7.6	7.1	6.3	5.1	5.0	4.7	4.2
40	6.9	6.3	5.4	4.1	4.0	3.6	3.3
60	5.7	5.0	4.1	2.6	2.5	2.2	2.1
80	4.8	4.0	3.0	1.7	1.6	1.3	1.1
100	4.0	2.8	2.2	1.1	1.0	0.9	0.8
10^4 k_{obs}(sec^{-1})	**1.54**	**1.90**	**2.50**	**3.74**	**4.10**	**4.25**	**4.31**

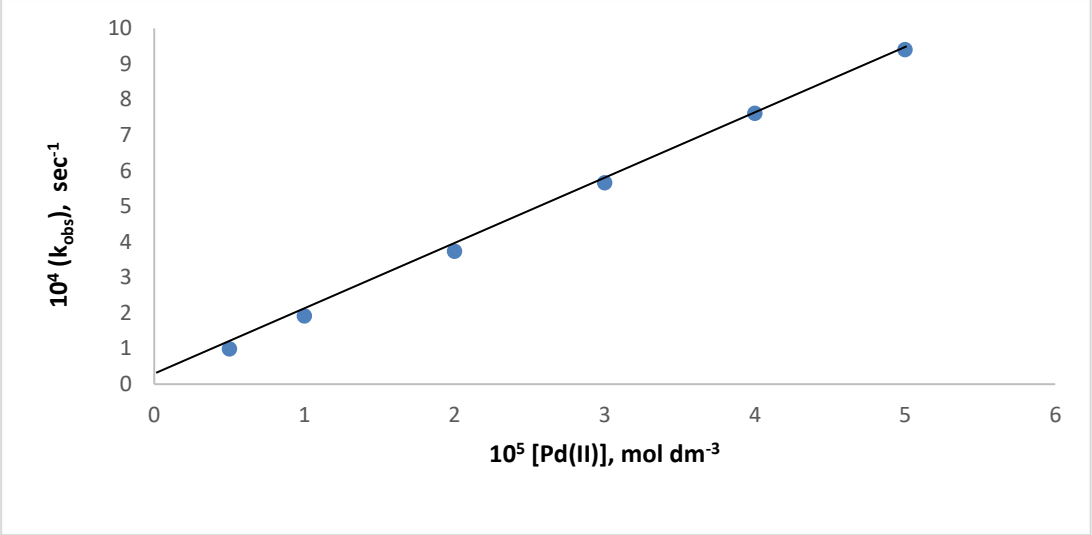

Figure 4.6: Variation of Palladium (II)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[Val] = 2.0 × 10^{-2} mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **[I] =0.25 mol dm^{-3}** **Temp. = 35°C**

Table 4.5: Variation of Palladium (II)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1 × 10^{-3} mol dm^{-3}**

[Val] = 2.0 × 10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35°C**

10^5[Pd (II)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.7	9.5	9.0	8.5	8.2	7.5
10	9.5	8.9	8.0	7.2	6.6	5.8
15	9.1	8.3	7.1	6.0	5.3	4.4
20	8.9	7.9	6.4	5.1	4.2	3.2
30	8.3	7.1	5.1	3.6	2.7	1.8
40	7.9	6.3	4.1	2.6	1.7	1.0
60	7.1	5.0	2.6	1.3	0.7	0.4
80	6.2	4.0	1.7	0.7	(65) 0.6	(65) 0.3
100	5.5	3.1	1.1	(90) 0.5	(75) 0.4	(70) 0.2
10^4 k_{obs}(sec^{-1})	**0.99**	**1.92**	**3.74**	**5.66**	**7.61**	**9.40**

Figures in parenthesis denotes time in minutes.

4.3.5 Effect of Ionic Strength

The effect of ionic strength on the rate of reaction was studied using sodium perchlorate (0.05 to 0.25 mol dm^{-3}) at fixed concentration of [NBS)] = 2.0×10^{-3} mol dm^{-3}, [Val] = 2.0×10^{-2} mol dm^{-3}, [Pd(II)] = 2.0×10^{-5} mol dm^{-3} and $[H^+]$ = 0.1 mol dm^{-3} at 35°C. Ionic strength had no effect on the rate of reaction**[Fig.4.7].** Results are shown in [**Table 4.6].**

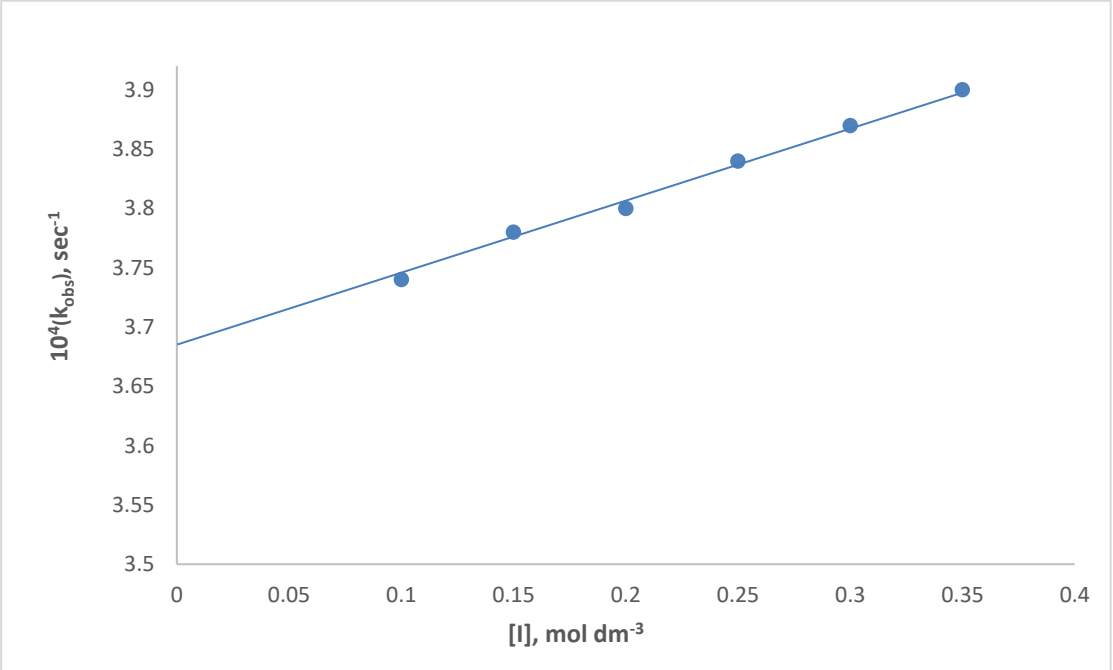

Figure 4.7: Variation of Ionic Strength

[NBS] = 2.0×10^{-3} mol dm^{-3} [Val] = 2.0×10^{-2} mol dm^{-3}

$[H^+]$ = 0.10 mol dm^{-3} [Pd (II)] = 2.0×10^{-5} mol dm^{-3} Temp. = 35°C

Table 4.6: Variation of Ionic Strength

[NBS] = 2.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[Val] = 2.0×10^{-2} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

[Pd (II)] = 2.0×10^{-5}mol dm^{-3} **Temp.= 35°C** **Aliquot = 5.0 ml**

[I], mol dm^{-3}	**0.10**	**0.15**	**0.20**	**0.25**	**0.30**	**0.35**
Time (minutes)	**Volume of the titrant (ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.0	8.9	8.9	8.8	8.8	8.7
10	8.0	8.0	7.9	7.9	7.8	7.7
15	7.1	7.0	7.0	6.9	6.9	6.8
20	6.4	6.3	6.3	6.2	6.2	6.1
30	5.1	5.0	5.0	4.9	4.9	4.8
40	4.1	4.1	4.0	4.0	3.9	3.9
60	2.6	2.6	2.5	2.5	2.4	2.4
80	1.7	1.6	1.6	1.5	1.5	1.4
100	1.1	1.1	1.0	1.0	0.9	0.9
10^4 k_{obs}(sec^{-1})	**3.74**	**3.78**	**3.80**	**3.84**	**3.87**	**3.90**

4.3.6 Effect of Temperature

The effect of temperature on the rate of reaction was studied in the range 303-313 K **[Table 2]** and various activation parameters computed. Activation energy is determined from the slope of a plot between 1/T and log k [**Fig. 4.8**]. Ea = 26.80 KJ mol^{-1}, $\Delta H^{\neq}$ = 24.24KJ mol^{-1}, $\Delta S^{\neq}$ = -147.20 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 69.57 KJ mol^{-1}.

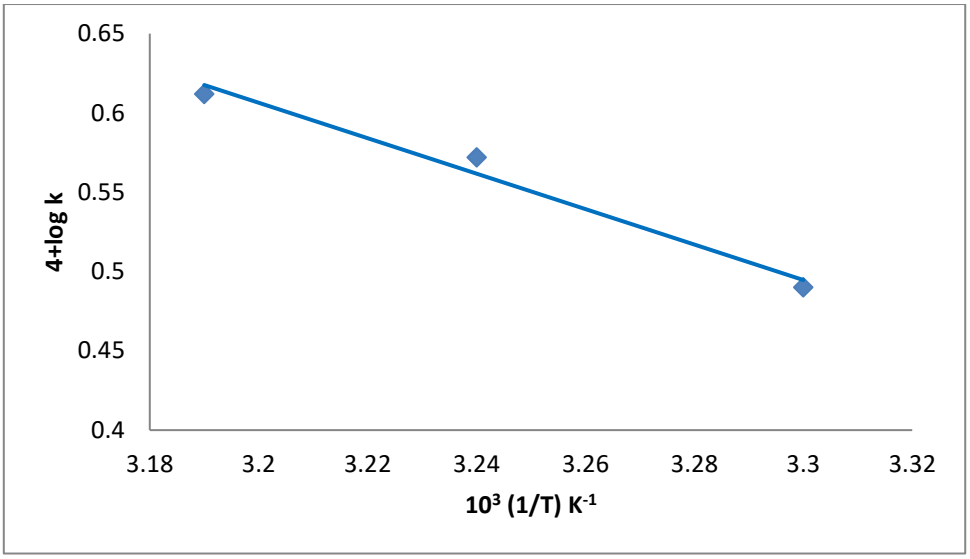

Figure 4.8: A Plot of log k versus 1/T

4.4 DISCUSSION

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.

4.4.1 Reactive species of NBS

It is reported that the nature of halogen atom, the groups attached to the nitrogen, pH of the medium and the reaction conditions play a very important role in knowing 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 forms [39-41] NBS itself, Br^+ or N^+BSH in the following way.

$$NBr + H^+ \rightleftharpoons N^+HBr \qquad (3)$$

(NBS) (N^+BSH)

$$NBr + H^+ \rightleftharpoons NH + Br^+ \qquad (4)$$

(NBS) (NHS)

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 remain as the reactive species of NBS. This conclusion finds support from UV-VIS spectra obtained for various solutions of NBS with different $[H^+]$ where a single peak was obtained at 220 nm.

4.4.2 Reactive species Pd (II) chloride in acidic medium

In most 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 as $[PdCl_4]^{2-}$ according to the equilibrium [42-44].

$$PdCl_2 + 2Cl^- \rightleftharpoons [PdCl_4]^{2-} \quad (5)$$

Such species using Pd (II) chloride has also been reported in the oxidation of amino acids by Cerium (IV) [45], Chloramine-T [46], N-bromophthalimide [47], acid bromate [48] and some sugars by N-Bromosuccinimide [49] and N-bromoacetamide [50] and oxidation of EDTA by NBS [51].

4.4.3 Reactive species amino acid in acidic medium

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

$$\underset{\text{Amino acid (S)}}{RCHNH_2COOH} \rightleftharpoons \underset{\text{Anion } (S^-)}{RCHNH_2COO^-} + H^+ \rightleftharpoons \underset{\text{Zwitterion } (S^0)}{RCH^+NH_3COO^-} \quad (6)$$

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

$$\underset{\text{Cation } (S^+H)}{RCH^+NH_3COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Zwitterion } (S^0)}{RCHN^+H_3COO^-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_2COO^- \quad (7)$$

Under the experimental conditions, the concentration of anion-form will be very low, and thepossible 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 showfirst 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.

4.4.4 Spectral study of various complexes formed during the studied reactions

To ascertain the formation of possible complexes during the course of reaction, spectra were obtained using Systronics UV-VIS Spectrophotometer-2203. Spectra for NBS solution with two different concentrations of $[H^+]$ such as 0.1 and 0.5 mol dm^{-3} was studied. 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 **[Fig.4.9].** This supports the inverse dependence of hydrogen ion concentration.

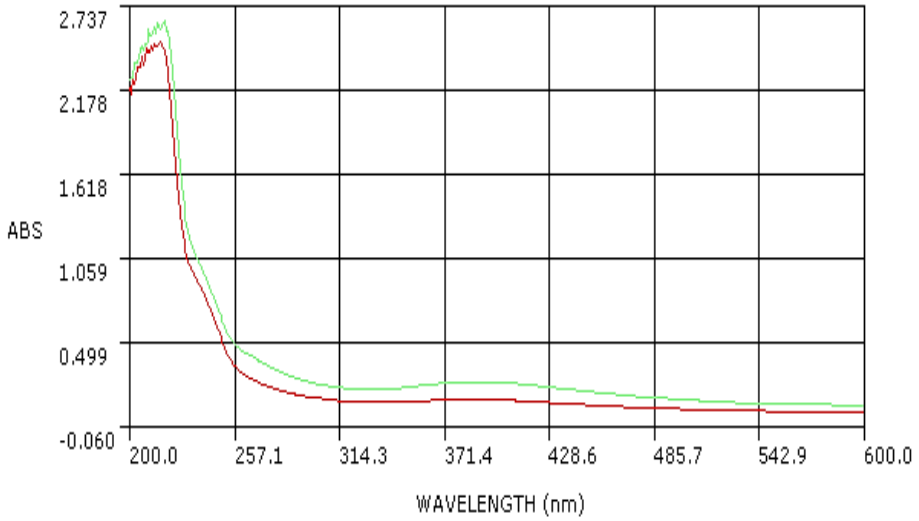

Figure 4.9: Spectral study of variation of Hydrogen ion

[NBS] = 5.0 × 10^{-3} mol dm^{-3} [Val] = 2.0 × 10^{-2} mol dm^{-3}
$[H^+]$ = 0.5 mol dm^{-3} (Red), 0.1 mol dm^{-3} (Green),
[Pd (II)] = 1.0 × 10^{-5} mol dm^{-3} Temp. = 35°C

UV-Vis spectra of NBS and H^+ solutions with three different concentrations of Pd (II) chloride shows an increase in absorption from 2.54, 2.71, 2.90 **[Fig. 4.10].** As [Pd] increases, UV absorption also increases. Higher Pd concentration produces more of the Pd-containing intermediate/complex that gives rise to the near-UV band. This confirms the formation ofcomplex(a) formed through equilibrium between $[PdCl_4]$ and a NBS molecule that 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.

$$NBS + [PdCl_4]^{2-} \rightleftharpoons [PdCl_4 . NBS]^{2-}$$

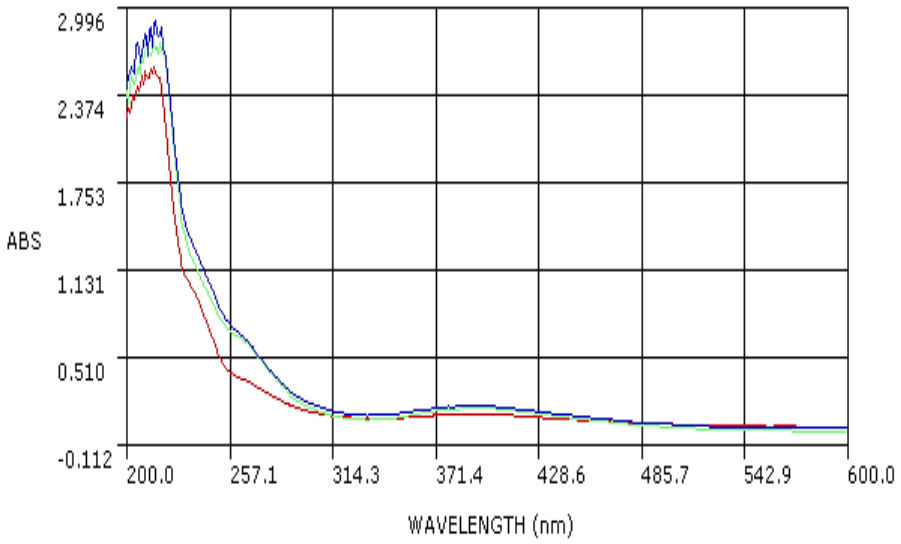

Figure 4.10: Spectral study of variation of catalyst [Pd (II)] variation

[NBS] = 5.0 × 10^{-3} mol dm^{-3} **[Val] = 2.0 × 10^{-2} mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35°C**

[Pd (II)] = 1.0 × 10^{-5} mol dm^{-3} (Red) **3.0 × 10^{-5} mol dm^{-3} (Green)**

5.0 × 10^{-5} mol dm^{-3} (Blue)

Further, when the spectrum of NBS, H^+ and $PdCl_2$ solution was compared with the spectrum of NBS, H^+ and Pd (II) chloride with three different concentrations of valine, an increase in absorbance from 2.48 to 2.60 and 2.65 was noted **[Fig. 4.11].** This indicates the formation of unstable activated complex.

$[\,NBS.PdCl_4.\,NH_3CHCH(CH_3)_2\,COOH\,]$

Further, the spectra of the reaction mixture at different time interval were studied at 35°C, NBS concentration decreased gradually with time **[Fig. 4.12]** 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 reaction with the increase in catalyst concentration.

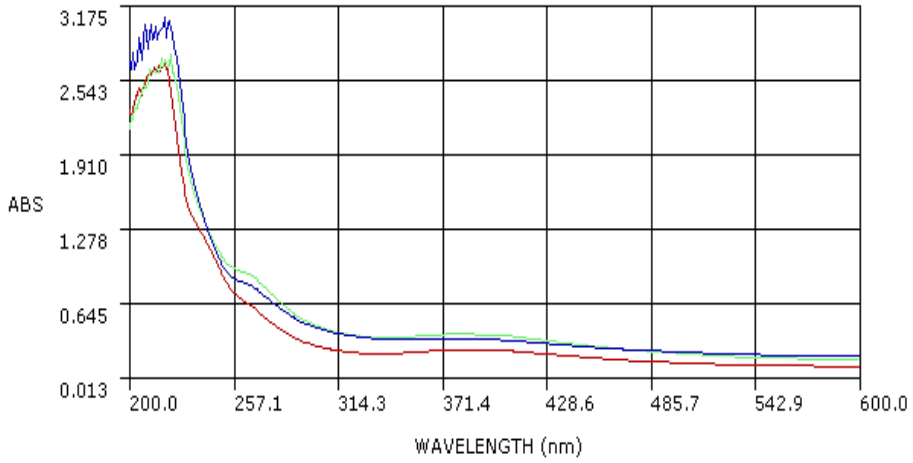

Figure 4.11: Spectral study of variation of Valine

[NBS] = 5.0 ×10^{-3} mol dm^{-3} [H^+] = 0.10 mol dm^{-3}

[Pd (II)] = 1.0 × 10^{-5} mol dm^{-3} Temp. = 35°C

[Val] = 1.0 × 10^{-2} mol dm^{-3} (Red), 3.0 × 10^{-5} mol dm^{-3} (Green),

5.0 × 10^{-5} mol dm^{-3} (Blue)

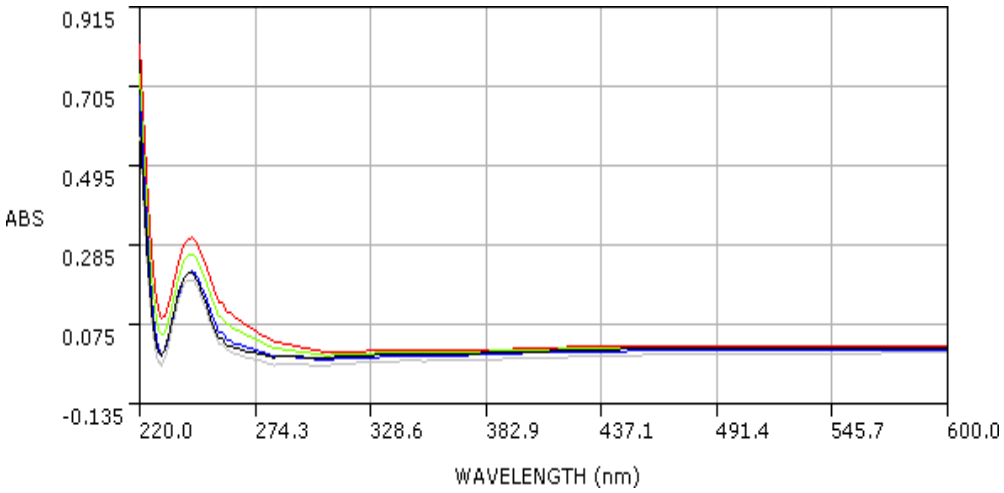

Figure 4.12: Spectral evidence for the formation of complexes during reaction at different time interval at 35°C

[NBS] = 5.0 × 10^{-3} mol dm^{-3} [H^+] = 0.10 mol dm^{-3}

[Pd (II)] = 1.0 × 10^{-5} mol dm^{-3} [Val] = 5.0 × 10^{-2} mol dm^{-3}

1. Red - 0 min. 2. Green-10 min. 3.Blue – 30 min.

4. Grey – 1 hour 5. Black – 2 hours

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

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

$$\underset{[AA]^+}{\overset{+}{NH_3}\text{-}CH(R)\text{-}COOH} \overset{K}{\rightleftharpoons} \underset{[AA]}{NH_2\text{-}CH(R)\text{-}COOH} + H^+ \qquad (8)$$

$$\underset{(C)}{[PdCl_4]^{2-}} + NBS \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \underset{(C_1)}{[PdCl_4.NBS]^{2-}} \qquad (9)$$

$$\underset{(C_1)}{[PdCl_4.NBS]^{2-}} + \underset{(AA)}{NH_2\text{-}CH(R)\text{-}COOH} \xrightarrow[slow]{k} \underset{(C_2)}{[Complex]} \qquad (10)$$

$$C_2 + 3H_2O \xrightarrow{fast} NHS + [PdCl_2(H_2O)_2] + NH_3 + RCHO + 2Cl^- + Br^- \qquad (11)$$

$$Br^- + NBS \rightarrow NHS + Br_2 \qquad (12)$$

Scheme-1

Since all the kinetic studies are conducted in the presence of mercuric acetate, the liberated Br_2 during the course of reaction can be removed in the form of $HgBr_4^{-2}$ or $HgBr_2$ complexes because $Hg(OAc)_2$ acts as a scavenger for Br^- formed in the reaction [53].

$$\text{rate} = \frac{-d[NBS]}{dt} = 2k[C_1][AA] \qquad (13)$$

On applying the law of chemical equilibrium, we get

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

$$\text{or} \quad [AA]^{+} = \frac{[AA][H^{+}]}{K} \tag{14}$$

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

$$\frac{d[C_1]}{dt} = K_1[NBS][C] - K_{-1}[C_1] - k[C_1][AA] = 0 \tag{15}$$

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

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

$$\text{or} \quad C_1 = \frac{K_1[NBS][C]}{K_{-1} + k[AA]} \tag{16}$$

Substituting the value of $[C_1]$ from Eq. (16) to Eq. (13) we get Eq. (17).

$$\text{rate} = \frac{-d[NBS]}{dt} = \frac{2kK_1[NBS][C][AA]}{K_{-1} + k[AA]} \tag{17}$$

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

$$[Pd(II)]_T = [C] + [C_1] \tag{18}$$

In reaction C >>> C_1, so concentration of [C] can be taken as equal to total concentration of [Pd (II)]. i.e. $[Pd(II)]_T$. Thus Eq. (17) can be written as:

$$\frac{-d[NBS]}{dt} = \frac{2kK_1[NBS][Pd(II)]_T[AA]}{K_{-1} + k[AA]} \tag{19}$$

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

$$[AA]_T = [AA] + [AA^{+}] \tag{20}$$

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

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

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

$$\text{or} \quad [AA] = \frac{K[AA]_T}{K + [H^{+}]} \tag{21}$$

Substituting [AA] from Eq. (21) to Eq. (19).

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

$$\text{rate} = \frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T[AA]_T}{KK_{-1} + K_{-1}[H^+] + kK[AA]_T} \quad (22)$$

$$\text{or rate} = \frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T[AA]_T}{K_{-1}[H^+] + K[K_{-1} + k[AA]_T]} \quad (23)$$

Under reaction conditions, the $k[AA]_T >> K_{-1}$, so Eq. (23) changes into Eq. (24).

$$\frac{-d[NBS]}{dt} = \frac{2kKK_1[NBS][Pd(II)]_T[AA]_T}{K_{-1}[H^+] + kK[AA]_T} \quad (24)$$

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 $[H^+]$.

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

$$k_{obs} = \frac{2kKK_1[Pd(II)]_T[AA]_T}{K_{-1}[H^+] + kK[AA]_T} \quad (25)$$

$$k' = \frac{2kKK_1[(AA)_T]}{K_{-1}[H^+] + kK[(AA)_T]} \quad (26)$$

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 **eqn. (13)** and a straight line with non-zero intercept **[Fig. 4.13]** was obtained yielding the value of K_1 to be 12.5×10^{-4},14.7×10^{-4} and 17.2×10^{-4} $mol^{-1}dm^3$ sec^{-1}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 Ea=24.12 KJ mol^{-1}, $\Delta H^{\neq}$ = 21.56 KJ mol^{-1}, $\Delta S^{\neq}$ = -144.50 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 66.06 KJ mol^{-1}.

The kinetic data shows the increasing rate of reaction on increasing temperature. The fairly high value of negative $\Delta S^{\neq}$ suggest the formation of more ordered activation complex whereas the high positive value of the free energy of activation ($\Delta G^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) indicates that the transition state is highly solvated [54].

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.

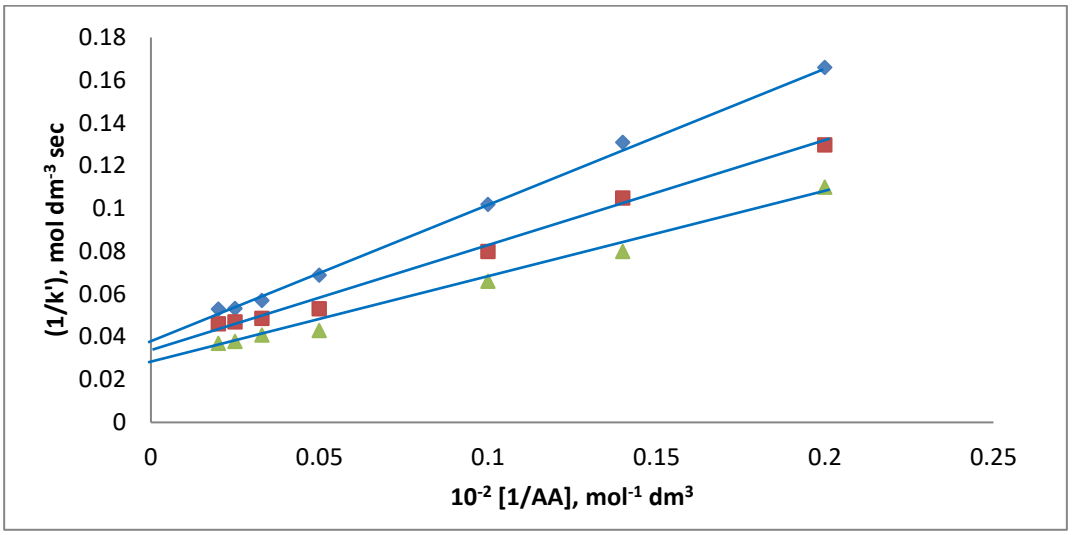

Figure 4.13: Variation of valine at three different temperatures

[NBS] = 2.0 × 10^{-3} mol dm^{-3} [H^+] = 0.10 mol dm^{-3}

Temp. (■) 30 °C, (▲) 35°C and (◆) 40°C

[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3} [I]= 0.25 mol dm^{-3}

Rate increases with increase in temperature indicating the reaction is endothermic which is consistent with ΔH >0. The moderate value of Δ H and ΔS favours electron transfer process. It is known fact [55] that for 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 an entropy decrease.

4.5 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, $PdCl_4^{2-}$. The decomposition of complex in the slow step followed by fast step leads to the products. The derived mechanism is consistent with all experimental results.

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CHAPTER 5

MECHANISTIC STUDY OF Pd (II) CATALYSED OXIDATION OF SERINE BY N-BROMOSUCCINIMIDE IN PERCHLORIC ACID MEDIUM

ABSTRACT

The Kinetics of Pd (II) catalysed and uncatalysed oxidation of serine by N-Bromosuccinimide (NBS) was studied in the presence of perchloric acid and Hg (II) at 35°C. In both Pd (II) catalysed and uncatalysed oxidations, the kinetic orders were first order in NBS and fractional order in substrate. The rate of reaction decreased with the increase in perchloric acid concentration and chloride ion. The reaction rate increases with the increase in Pd (II). However successive addition of mercuric acetate, succinimide (NHS) and variation of ionic strength of the medium did not bring about significant change in the rate of the reaction. $[PdCl4]^{2-}$ and NBS itself have been postulated as the reactive species of palladium (II) chloride and N-Bromosuccinimide in acidic medium respectively. 2-Hydroxyethanal was identified as the main oxidation product of the reaction. On the basis of the experimental findings, a suitable mechanism has been proposed. Activation parameters for the slow and rate determining step of the proposed mechanism have been obtained from the rate measurements at 30°C, 35°C and 40°C. The rate law conforming to the observed kinetic results has been derived as:

$$\text{Rate} = \frac{kK_2[NBS]_T[Ser]}{1 + K_1[H^+] + K_2[Ser]}$$

5.1 INTRODUCTION

Amino acid residues are the main constituents of proteins and the study of its sensitivity towards oxidation opens a new area to understand the mechanism involved in the protein and amino acid modifications [1]. Many uncatalyzed [2-8]and catalysed [9-14] kinetic studies have been reported on the oxidation of amino acid by different oxidants. Though there are several reports [15-18] on the oxidation of amino acid by N-halo compound, no information is available where the use of chloro complex of Pd (II) as catalyst has been made in the oxidation of amino acid by N- Bromosuccinimide in acidic medium.

Palladium (II) chloride is quite soluble in HCl and exists [19] primarily as $[PdCl_4]^{2-}$. Various mononuclear complexes, namely $[PdLCl_3]^-$, $[PdL_2Cl_2]$, $[PdLCl]^+$ and $[PdL_4]^{2+}$ (where L represent amine, phospine, thioether etc) are well known. Palladium (II) has shown a strong catalytic [20-24] as well as inhibitor [25-27] effect on the rate of various homogenous redox reactions but the nature of its active form in such reactions remain obscure.

The diverse nature of the chemistry of N-halocompounds [28-32] is due to their ability to act as a source of halogenonium cations, hypohalite and nitrogen anions species which act as both bases and nucleophiles. N-Bromosuccinimide (NBS) is a source of positive halogen and has been selectively used as an oxidant for a variety of substrates [33-38] in both acidic and alkaline solutions. This potent oxidising agent has been extensively used in the determination of number of pharmaceutical compounds [39-40]. The role of NBS as an oxidant in the oxidation of a large number of substrates has been probed using Ru (III)[41], Pd (II)[42-44], Pt (IV)[45] and Rh (III) [46,47] as homogeneous catalyst. However, little information is available in the literature on NBS reactions, particularly w.r.t the oxidation kinetics of bioactive compounds. This prompted us to undertake the present investigation which constitutes the studies of kinetics and mechanism of Pd (II) catalysed NBS oxidation of serine in perchloric acid media in presence of mercuric acetate.

5.2 EXPERIMENTAL

5.2.1 Materials

The reagents employed were N-Bromosuccinimide (G.R Merck), Palladium (II) chloride (Johnson Matthey, London), Mercuric acetate (G.R. Merck). $HClO_4$ (E. Merck) is used as a source of hydrogen ions and $NaClO_4$ (E. Merck) 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. Other reagents used were of analytical grade. All solutions were prepared with doubly distilled water. Stock solutions of N-Bromosuccinimide were prepared and standardized iodometrically [48].

5.2.2 Kinetic Measurements

A thermostatted water bath was used to maintain the desired temperature to within ± 0.1°C. All the Kinetic measurements were carried out at constant temperature 35°C under pseudo first order conditions with a large excess of amino acid over NBS. The reaction was initiated by rapid addition of NBS to the reaction mixture containing appropriate quantities of amino acid, Pd (II) chloride, perchloric acid, mercuric acetate and water and mixing them by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed NBS at regular time intervals iodometrically.

5.2.3 Stoichiometry and Product Analysis

The Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBS over amino acid (in varying ratios) at 35°C for 48 hours and estimations of residual NBS in different sets showed that 1 mole of amino acid consumes two moles of NBS according to the stoichiometric equation.

$$\text{Serine} + 2\,\text{NBS} + H_2O \xrightarrow{\text{Pd(II)}/H^+} 2\,\text{NHS} + CO_2 + Br_2 + NH_3 + 2-\text{Hydroxyethanal}$$

The product analysis was carried out under kinetic conditions. In a typical experiment, serine (0.05M) and NBS (0.01M) were made up to 100 ml and the reaction mixture was allowed to stay in the dark for about one day to ensure completion of the reaction. The main reaction products were succinimide, 2 hydroxyethanal, ammonia and carbon dioxide. Liberated ammonia was identified by Nessler's reagent. CO_2 was identified by freshly prepared lime water where the solution turned milky indicating a decaboxylation reaction [49].

The solution was then treated with an excess of saturated solution of 2,4 DNP in 2M HCl and kept overnight in a refrigerator. The precipitated 2,4 DNP was filtered off, dried, weighed, recrystallised from ethanol. The DNP was found to have identical melting point and spectral data as the DNP of 2- hydoxyethanal.

2-hydroxyethanal was confirmed by the IR spectrum of the corresponding hydrazone. The IR peaks at 3323.91 cm^{-1}, 3108.36, 2922.22 cm^{-1} and 1614.84 cm^{-1} are attributed to –OH, –NH, −CH and −C=N stretching respectively **[Fig. 5.1]**. Further the aldehyde group was confirmed with a qualitative test such as Tollen's reagent [50] and spot test [51].

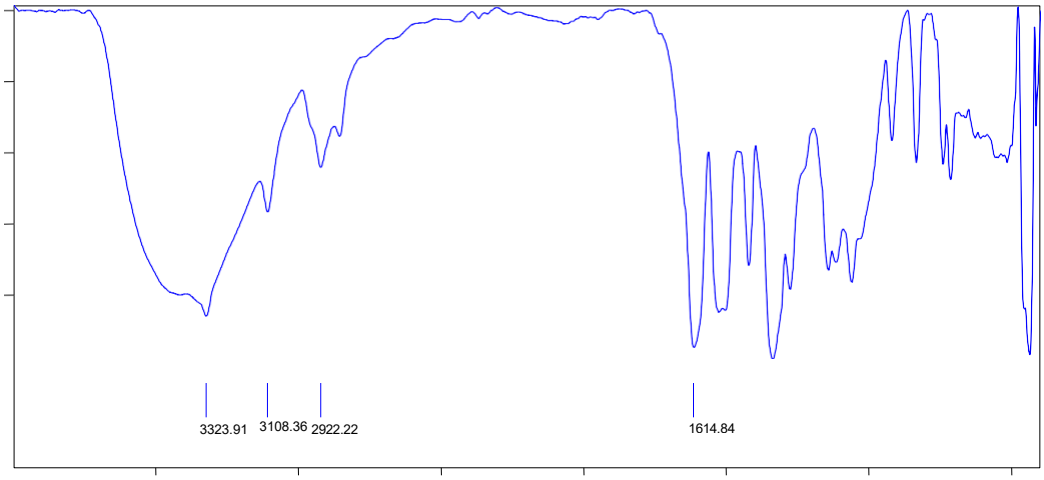

Figure 5.1: FT-IR Spectra of final product of Oxidation of Serine

5.3 RESULTS AND DISCUSSION (Uncatalysed Reactions)

5.3.1 Effect of NBS

For uncatalyzed reaction, the concentration of NBS was varied from 0.5×10^{-3} to 5.0×10^{-3} mol dm^{-3} at [Ser] = 2.0×10^{-2} mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3} and [I]= 0.25 mol dm^{-3} at temp.= 35°C. First order dependence in NBS was followed at all initial concentration of NBS. Pseudo first order rate constants (k_{obs}) were calculated from the slopes of log(a-x)-time plots [**Fig. 5.2**]. The first order kinetics w.r.t NBS are also verified by the constant values of k_{obs} obtained at various initial concentration of NBS [**Table 5.1].** Results are given in [**Table 5.2**].

Table-5.1: Effect of variation of [NBS], [Ser], [Pd (II)] and [H^+] on the Palladium (II) catalysed oxidation of Serine by NBS at 35°C

10^3[NBS] mol dm^{-3}	10^2 [Serine] mol dm^{-3}	10^5[Pd (II)] mol dm^{-3}	[H^+] mol dm^{-3}	Catalysed (10^4 k_{obs} sec^{-1})	Uncatalysed (10^4 k_{obs} sec^{-1})
0.5	2.0	2.0	0.10	3.78	2.89
0.75	2.0	2.0	0.10	3.76	2.84
1.0	2.0	2.0	0.10	3.74	2.82
2.0	2.0	2.0	0.10	3.78	2.80
3.0	2.0	2.0	0.10	3.72	2.83
4.0	2.0	2.0	0.10	3.79	2.86
5.0	2.0	2.0	0.10	3.76	2.88
2.0	0.5	2.0	0.10	1.74	1.28
2.0	0.75	2.0	0.10	2.18	1.62
2.0	1.0	2.0	0.10	2.61	1.90
2.0	2.0	2.0	0.10	3.78	2.80
2.0	3.0	2.0	0.10	4.76	2.88
2.0	4.0	2.0	0.10	5.15	3.01
2.0	5.0	2.0	0.10	5.25	3.10
2.0	2.0	0.0	0.10	2.87	2.80
2.0	2.0	0.50	0.10	3.00	-
2.0	2.0	1.0	0.10	3.25	-
2.0	2.0	2.0	0.10	3.78	-
2.0	2.0	3.0	0.10	4.26	-
2.0	2.0	4.0	0.10	4.70	-
2.0	2.0	5.0	0.10	5.20	-
2.0	2.0	2.0	0.05	5.00	4.00
2.0	2.0	2.0	0.075	4.26	3.45
2.0	2.0	2.0	0.1	3.78	2.80
2.0	2.0	2.0	0.2	2.45	2.44
2.0	2.0	2.0	0.3	1.93	1.96
2.0	2.0	2.0	0.4	1.65	1.61
2.0	2.0	2.0	0.5	1.41	1.42

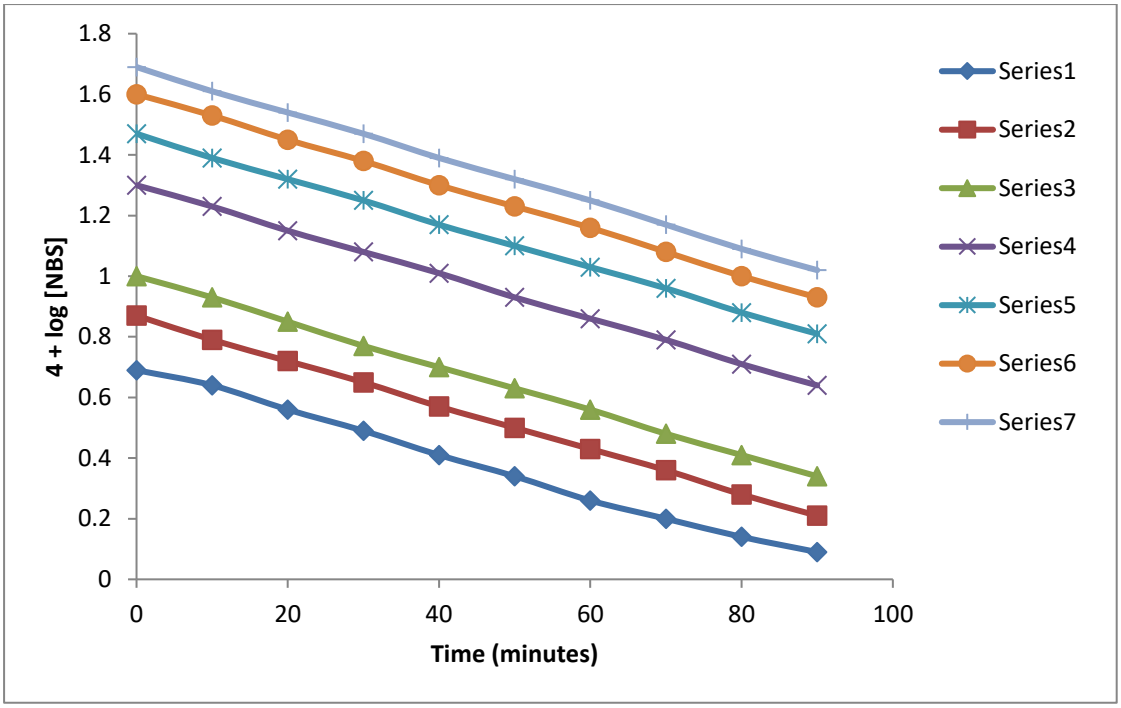

Figure 5.2: Psuedo first order plots for the Variation of Uncatalysed NBS

[Ser] = 2.0 × 10^{-2} mol dm^{-3} **[H^+] = 0 .10 mol dm^{-3}**

[I]= 0.25 mol dm^{-3} **Temp. = 35°C**

[NBS] = (1) 0.50 × 10^{-3} mol dm^{-3} **(2) 0.75 × 10^{-3} mol dm^{-3}**

(3) 1.0 × 10^{-3} mol dm^{-3} **(4) 2.0 × 10^{-3} mol dm^{-3}**

(5) 3.0 × 10^{-3} mol dm^{-3} **(6) 4.0 × 10^{-3} mol dm^{-3}**

(7) 5.0 × 10^{-3} mol dm^{-3}

Table 5.2: Variation of NBS (uncatalysed)

[Ser] = 2.0 × 10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[$Na_2S_2O_3$] = 2.0 × 10^{-3} mol dm^{-3} **[H^+] =0.10 mol dm^{-3}**

Temp. =35 °C

10^3 [NBS], mol dm^{-3}	**0.50***	**0.75***	**1.0***	**2.0****	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant(ml)**						
0	8.3	12.5	16.7	10.0	7.5	10.0	12.5
5	7.5	11.7	15.5	9.1	6.9	9.1	11.3
10	6.8	10.5	14.2	8.5	6.2	8.4	10.4
15	6.2	9.6	12.9	7.7	6.0	7.7	9.5
20	5.8	8.9	12.0	7.1	5.3	7.1	8.8
30	4.8	7.4	10.0	6.0	4.5	6.0	7.4
40	4.0	6.2	8.4	5.1	3.8	5.0	6.2
60	2.9	4.5	6.0	3.6	2.7	3.5	4.3
80	2.0	3.1	4.3	2.6	1.9	2.5	3.0
100	1.4	2.2	3.0	1.8	1.3	1.8	2.2
10^4 k_{obs}(sec^{-1})	**2.89**	**2.84**	**2.82**	**2.80**	**2.83**	**2.86**	**2.88**

[$Na_2S_2O_3$]* = 3.0 × 10^{-4} mol dm^{-3}

[$Na_2S_2O_3$] **= 1.0 × 10^{-3} mol dm^{-3}

5.3.2 Effect of Serine

The concentration of serine in uncatalyzed reaction was varied from 0.5×10^{-2} to 5.0×10^{-2} mol dm^{-3} at [NBS] = 2.0×10^{-3}, $[H^+]$ = 0.1 mol dm^{-3} [I]= 0.25 mol dm^{-3} at 35°C. A plot of –dc/dt versus serine shows first order dependence of the reaction on amino acid at low concentration, which shifts towards zero order at its higher concentration [**Fig. 5.3**]. The plot of log k_{obs} versus log [Ser] was a straight line with fractional slope confirming fractional order w.r.t serine. Results are given in [**Tables 5.3].**

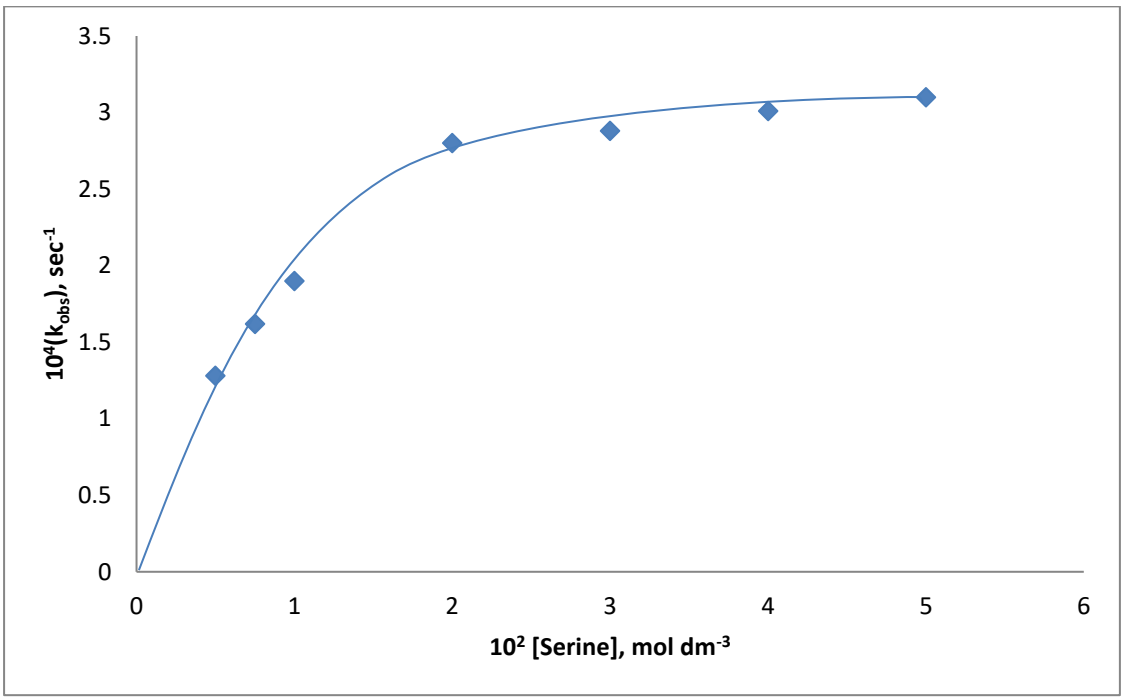

Figure 5.3: Variation of Serine (uncatalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} $[H^+]$ = 0.10 mol dm^{-3}

[I] = 0.25 mol dm^{-3} Temp. = 35°C

Table 5.3: Variation of Serine (uncatalysed)

[NBS]= 2.0×10^{-2} mol dm^{-3} [I] = 0.25 mol dm^{-3}

$[H^+]$ = 0.1 mol dm^{-3} $[Na_2S_2O_3] = 1.0 \times 10^{-3}$ mol dm^{-3}

Temp. =35°C

10^2 [Ser], mol dm^{-3}	0.50	0.75	1.0	2.0	3.0	4.0	5.0
Time (minutes)	**Volume of the titrant(ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.5	9.3	9.2	9.1	9.0	8.9	8.7
10	9.1	8.9	8.7	8.5	8.1	7.9	7.5
15	8.9	8.5	8.3	7.7	7.4	7.2	7.0
20	8.5	8.1	7.9	7.1	6.7	6.5	6.4
30	7.9	7.6	6.9	6.0	5.5	5.3	5.7
40	7.4	6.9	6.1	5.1	4.7	4.6	4.4
60	6.4	5.6	4.9	3.6	3.2	3.1	3.0
80	5.6	4.8	4.0	2.6	2.3	2.1	1.9
100	4.9	4.0	3.1	1.8	1.7	1.4	1.3
10^4 k_{obs}(sec^{-1})	1.28	1.62	1.90	2.80	2.88	3.01	3.10

5.3.3 Effect of Acid

The hydrogen ion concentration was varied from 0.05 to 0.5 mol dm^{-3} employing perchloric acid at fixed concentration of [NBS] = 2.0×10^{-3} mol dm^{-3}, [Ser] = 2.0×10^{-2} mol dm^{-3}, [I] = 0.25 mol dm^{-3} at 35°C. The first order rate constants decreased with the increase in perchloric acid concentration [**Fig.5.4**]. The order of reaction w.r.t hydrogen ions was determined as 0.63 from the slope of the plot of log k_{obs} and log $[H^+]$. Results are given in **[Tables 5.4].**

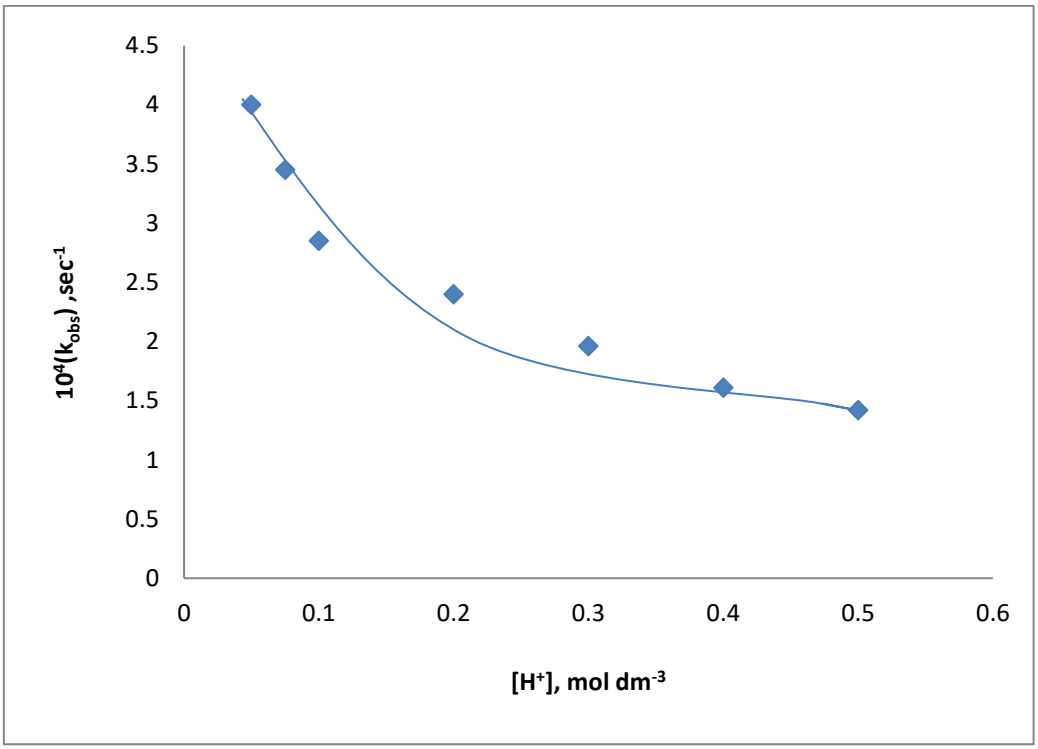

Figure 5.4: Variation of Hydrogen ion (uncatalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} **[Ser] = 2.0×10^{-2} mol dm^{-3}**

[I] = 0.25 mol dm^{-3} **Temp. = 35°C**

Table 5.4: Variation of $[H^+]$ (uncatalysed)

[NBS] = 2.0×10^{-2} mol dm^{-3} **[Ser] = 2.0×10^{-2} mol dm^{-3}**

[I] = 0.25 mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

Temp. = 35 °C

$[H^+]$, mol dm^{-3}	**0.05**	**0.075**	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
Time (minutes)	**Volume of the titrant(ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.7	8.9	9.1	9.3	9.5	9.7	9.8
10	7.9	8.0	8.5	8.7	8.9	9.1	9.3
15	7.1	7.4	7.7	7.9	8.5	8.7	8.7
20	6.4	6.6	7.1	7.4	7.9	8.3	8.5
30	5.1	5.4	6.0	6.4	7.1	7.6	7.7
40	4.1	4.2	5.1	5.5	6.1	6.7	7.1
60	2.6	2.8	3.6	4.1	4.9	5.6	6.0
80	1.7	1.8	2.6	3.1	3.8	4.7	5.0
100	1.1	1.2	1.8	2.3	2.9	3.8	4.9
10^4 k_{obs}(sec^{-1})	**4.00**	**3.45**	**2.80**	**2.44**	**1.96**	**1.61**	**1.42**

5.3.4 Effect of Ionic Strength

The effect of ionic strength on the rate of reaction was studied using sodium perchlorate (0.05 to 0.25 mol dm^{-3}) at fixed concentration of [NBS)]= 2.0×10^{-3} mol dm^{-3}, [Ser] = 2.0×10^{-2} mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3} at 35°C. Ionic strength had no marginal effect on the rate of reaction **[Fig.5.5].** Results are shown in **[Table 5.5].**

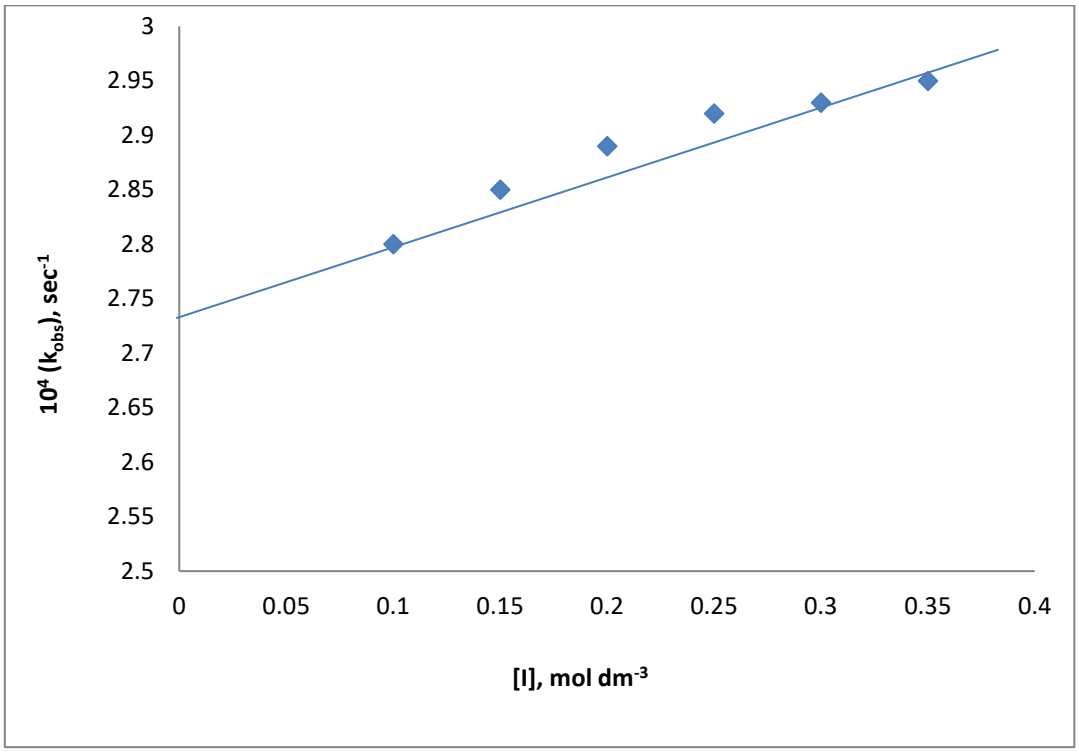

Figure 5.5: Variation of Ionic Strength (uncatalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} **[Ser] = 2.0×10^{-2} mol dm^{-3}**

$[H^+]$ = 0.10 mol dm^{-3} **Temp. = 35°C**

Table 5.5: Variation of Ionic Strength (uncatalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[Ser] = 2.0×10^{-2} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

Temp. = 35°C **Aliquot = 5.0 ml**

[I] , mol dm^{-3}	**0.10**	**0.15**	**0.20**	**0.25**	**0.30**	**0.35**
Time (minutes)	**Volume of the titrant (ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.1	9.0	9.0	9.0	8.9	8.9
10	8.5	8.4	8.3	8.2	8.2	8.1
15	7.7	7.6	7.6	7.5	7.4	7.4
20	7.1	7.0	7.0	7.0	7.0	7.0
30	6.0	6.0	5.9	5.8	5.7	5.6
40	5.1	5.0	5.0	5.0	5.0	5.0
60	3.6	3.5	3.4	3.3	3.2	3.2
80	2.6	2.5	2.4	2.3	2.2	2.1
100	1.8	1.7	1.6	1.5	1.4	1.4
10^4 k_{obs}(sec^{-1})	**2.80**	**2.85**	**2.89**	**2.92**	**2.93**	**2.95**

5.3.5 Effect of Added Salt

The effect of Cl^- was studied by successive addition of KCl in the reaction mixture. Addition of Cl^- showed a decrease in the rate constant [**Fig.5.6**].

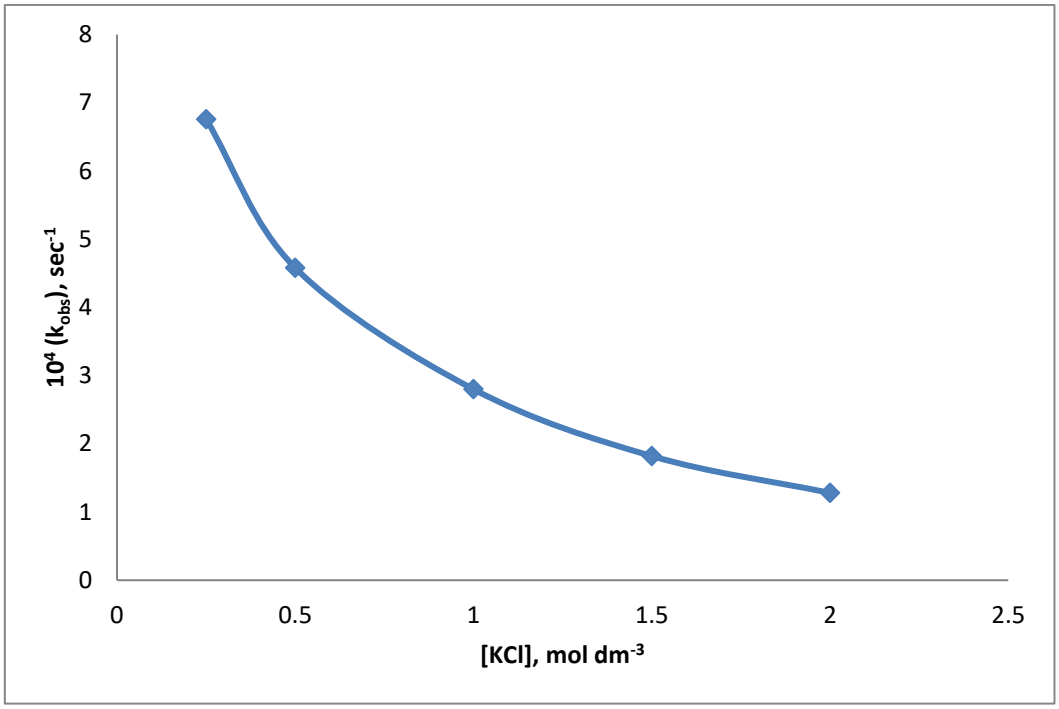

Figure 5.6: Variation of Chloride ion (uncatalysed)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[Ser] = 2.0 × 10^{-2} mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35°C**

It was observed that the change in the concentration of added mercuric acetate had a negligible effect on the rate [52]. The function of added mercuric acetate is to fix up Br^- formed in the course of the reaction as $HgBr_2$ or $HgBr_4^{2-}$. It suppresses completely the oxidation by Br_2, which would have been formed by the interaction of HBr and NBS. Mercuric acetate thus ensures oxidation purely through NBS.

5.3.6 Rate and activation parameters

The reaction was studied at different temperatures (30-40°C) at fixed concentration of [NBS] = 2.0 × 10^{-3}, [Ser] = 2.0 × 10^{-2} mol dm^{-3}, [H^+] = 0.1and I = 0.25 mol dm^{-3}. From the linear Arrhenius plot of log k_{obs} vs 1/T **[Fig.5.7]** values of activation parameters, energy of activation (E_a)**,** enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) for the composite reaction were calculated.

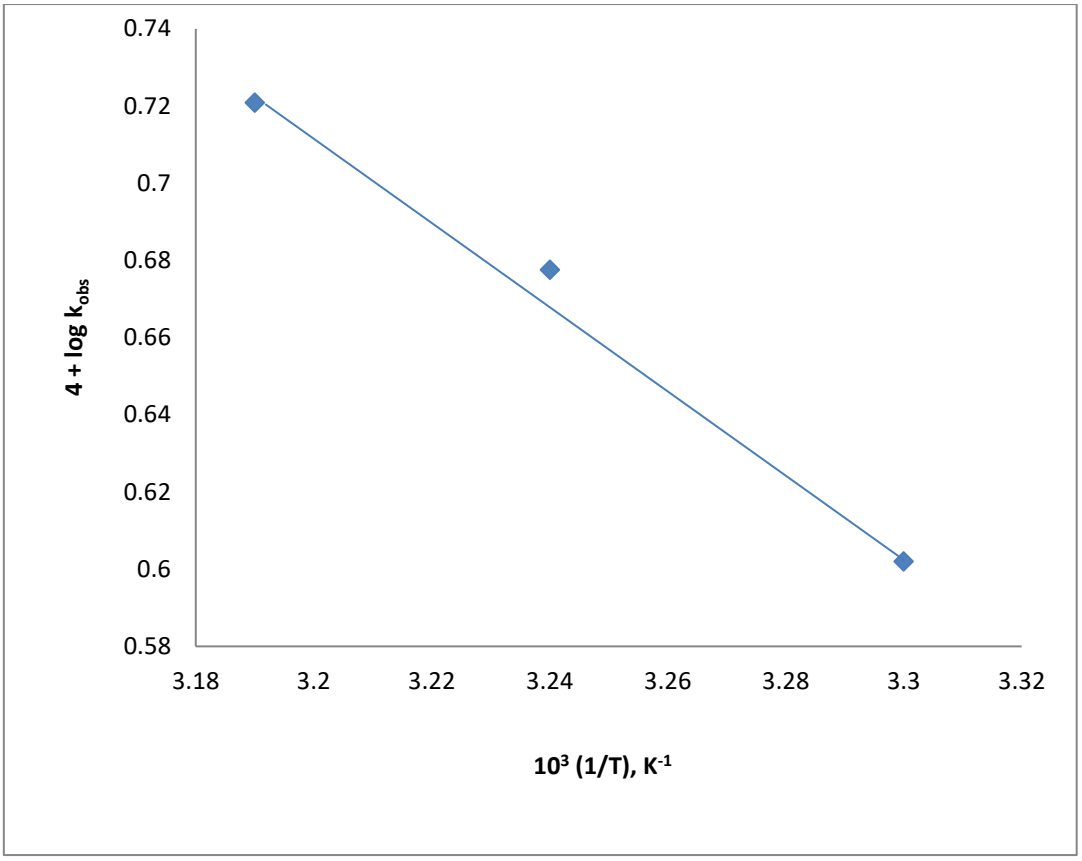

Figure 5.7: Arrhenius plot of log k_{obs} vs 1/T

5.3.7 Mechanism

$$NBS + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} NBSH^+$$

$$NBS + Serine \overset{K_2}{\rightleftharpoons} Complex(C_1)$$

$$Complex(C_1) \xrightarrow[slow]{k} CH_2(OH)C(COOH) = NH + Br^- + Succinimide$$

$$\downarrow$$

$$CH_2(OH)C(COOH) = N \xrightarrow{H_2O} CH_2(OH)CHO$$

$$Rate = k\ Complex(C_1) \quad (1)$$

$$= k\ K_2\ [NBS]\ [Ser] \quad (2)$$

$$[NBS]_T = NBS + [NBSH^+] + complex(C_1) \quad (3)$$

$$= NBS + K_1 [NBS] [H^+] + K_2 [NBS] [Ser] \quad (4)$$

$$= NBS\left[1 + K_1 [H^+] + K_2[Ser]\right] \quad (5)$$

$$NBS = \frac{[NBS]_T}{1 + K_1[H^+] + K_2[Ser]} \quad (6)$$

From (2) and (6)

$$Rate = \frac{kK_2[NBS]_T[Ser]}{1 + K_1[H^+] + K_2[Ser]} \quad (7)$$

The above rate law explains the first order in oxidant, fractional order in substrate and inverse order in acid. Further

$$\frac{Rate}{[NBS]} = k_{obs} = \frac{kK_2[Ser]}{1 + K_1[H^+] + K_2[Ser]} \quad (8)$$

The mechanism of scheme 1 and the rate law may be verified by rearranging it in the form

$$\frac{1}{k_{obs}} = \frac{1}{kK_2[Ser]} + \frac{K_1[H^+]}{kK_2[Ser]} + \frac{1}{k} \quad (9)$$

According to equation (9) the plots of $1/k_{obs}$ versus $1/[Ser]$ and $1/k_{obs}$ versus $[H^+]$ are linear with non-zero intercepts which are verified in **[Fig.5.8 & 5.9] .** From the slopes and intercepts of such plots k, K_1 and K_2 values are obtained at 35°C as 4.76×10^{-4} s^{-1}, 193.92 mol^{-1} dm^3 and 2100 $mol^{-1}dm^3$. This not only proves the validity of rate law but also gives support to the proposed reaction scheme-I. The fair degree of closeness in k values 4.76×10^{-4} sec^{-1} obtained from **[Fig.5.8]** and 4.74×10^{-4} sec^{-1} from plot **[Fig.5.9]** also supports the validity of proposed mechanism. The values of k in s^{-1} are were found to be 4.0×10^{-4}, 4.76×10^{-4}, 5.26×10^{-4} at 30°C, 35°C and 40°C respectively. The activation parameters were evaluated from the plot of log k versus 1/T which are as follows, Ea = 20.87 KJ mol^{-1}, $\Delta H^{\neq}$ =18.30 KJ mol^{-1}, $\Delta S^{\neq}$ = -240.50 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 92.22 KJ mol^{-1}.

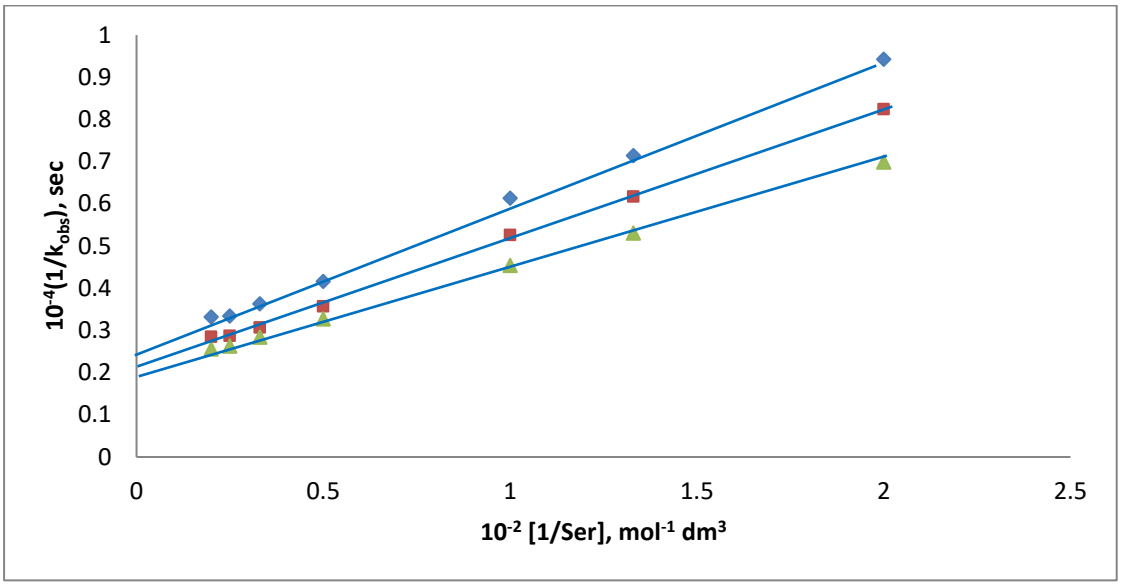

Figure 5.8: Plot of $1/k_{obs}$ versus 1/Ser

[NBS] = 2.0×10^{-3} mol dm^{-3} $[H^+] = 0.10$ mol dm^{-3}

[I] = 0.25 mol dm^{-3} Temp. = 35°C

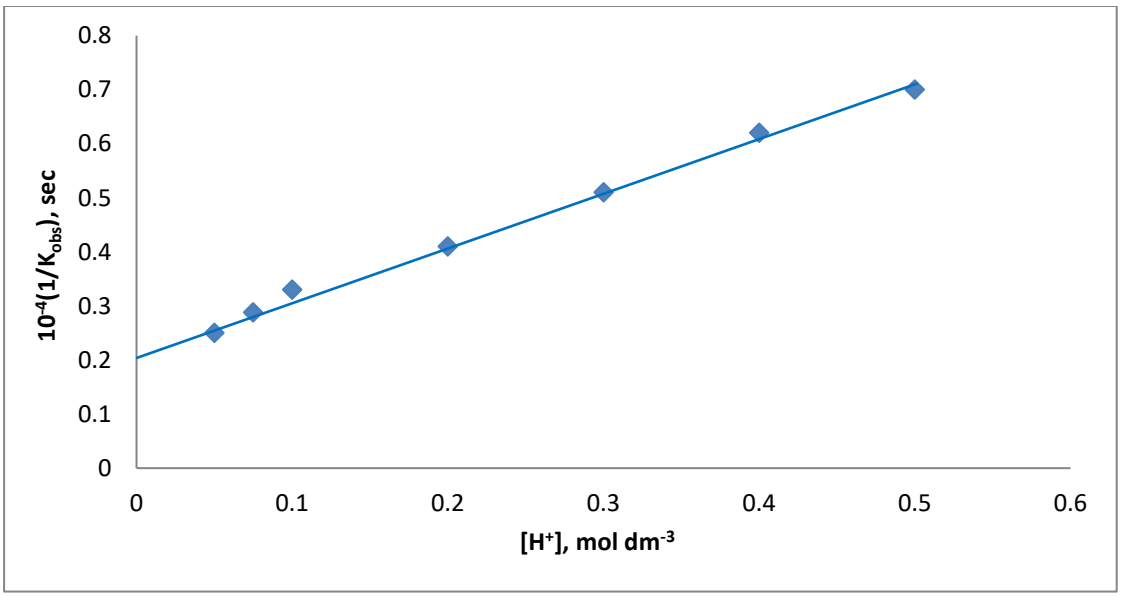

Figure 5.9: Plot of $1/k_{obs}$ versus $[H^+]$

[NBS] = 2.0×10^{-3} mol dm^{-3} [Ser] = 2.0×10^{-2} mol dm^{-3}

[I] = 0.25 mol dm^{-3} Temp. = 35°C

An insignificant effect of ionic strength on the rate is also in the favour of rate determining step in which a neutral species is involved [53]. The entropy of activation

in each case was found to be negative (reduction of the entropy of system), suggesting the compactness of the transition stateas compared to the ground state.

5.4 RESULTS AND DISCUSSION (Catalysed Reactions)

5.4.1 Effect of variation of concentration of NBS

For catalyzed reaction, the concentration of NBS was varied from 0.5×10^{-3} to 5.0×10^{-3} mol dm^{-3} at [Ser] = 2.0×10^{-2}, [H^+] = 0.1mol dm^{-3} and [Pd(II)]= 2.0×10^{-5} mol dm^{-3} and [I] = 0.25 mol dm^{-3} at temp.= 35°C.The reaction is first order in NBS as evidenced by the linear plots of log(a-x) versus time **[Fig 5.10].** Increase in concentration of NBS yields constant first order rate constants confirming the first order dependence on NBS **[Table 5.1]**. Results are given in **[Table 5.6].**

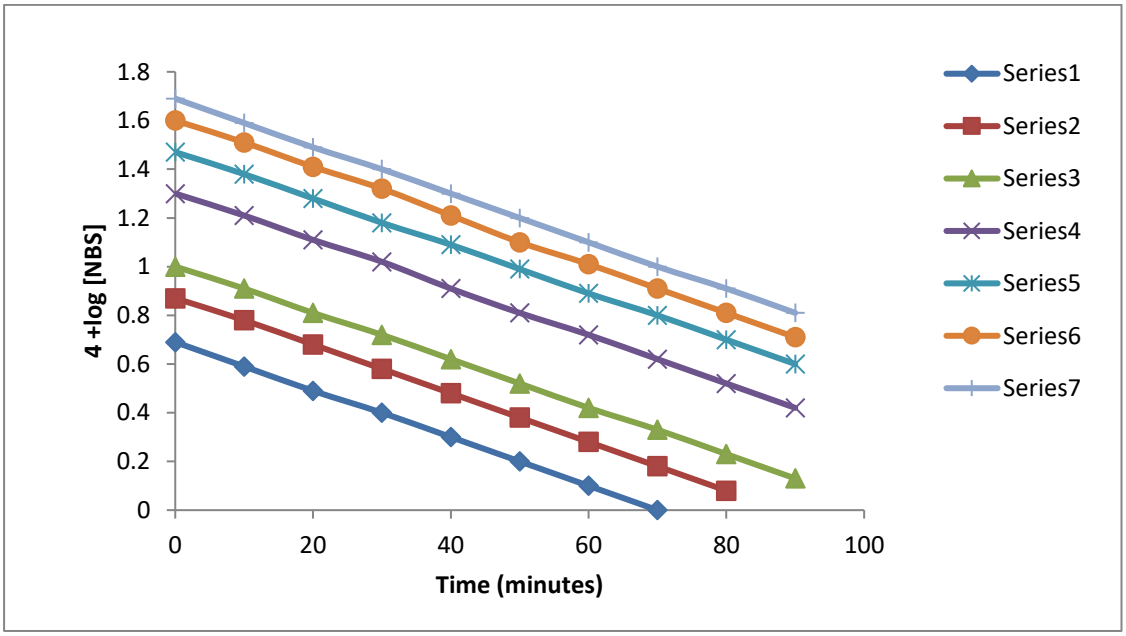

Figure 5.10: Psuedo first order plots for the Variation of Catalysed NBS

[Ser] = 2.0×10^{-2} mol dm^{-3} [H^+] = 0 .10 mol dm^{-3}

[I] = 0.25 mol dm^{-3} Temp. = 35°C

[NBS] = (1) 0.50×10^{-3} mol dm^{-3} (2) 0.75×10^{-3} mol dm^{-3}

(3) 1.0×10^{-3} mol dm^{-3} (4) 2.0×10^{-3} mol dm^{-3} (5) 3.0×10^{-3} mol dm^{-3}

(6) 4.0×10^{-3} mol dm^{-3} (7) 5.0×10^{-3} mol dm^{-3}.

Table 5.6: Variation of NBS (catalysed)

[Ser] = 2.0 × 10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[$Na_2S_2O_3$] = 2.0 × 10^{-3} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

Temp. = 35°C **[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3}**

10^3 [NBS], mol dm^{-3}	**0.50***	**0.75***	**1.0***	**2.0****	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant(ml)**						
0	8.3	12.5	16.7	10.0	7.5	10.0	12.5
5	7.4	11.0	14.8	8.7	6.6	9.0	10.9
10	6.6	9.8	13.2	7.7	6.0	8.1	9.9
15	5.8	8.7	12.0	7.1	5.3	7.1	8.6
20	5.3	7.8	10.6	6.3	4.7	6.3	7.7
30	4.2	6.3	8.5	5.1	3.8	5.1	6.2
40	3.3	5.0	6.8	4.1	3.0	4.0	4.9
60	2.1	3.2	4.4	2.7	1.9	2.5	3.0
80	1.4	2.0	2.8	1.7	1.2	1.6	1.9
100	0.8	1.3	1.8	1.1	0.8	1.0	1.2
10^4 k_{obs} (sec^{-1})	**3.78**	**3.76**	**3.74**	**3.78**	**3.72**	**3.79**	**3.76**

[$Na_2S_2O_3$] * = 3.0 × 10^{-4} mol dm^{-3}

[$Na_2S_2O_3$] ** = 1.0× 10^{-3} mol dm^{-3}

5.4.2 Effect of variation of concentration of Serine

The concentration of serine in palladium (II) catalyzed reaction was varied from 0.5 × 10^{-2} to 5.0 × 10^{-2} mol dm^{-3} at fixed concentration of [NBS]= 2.0 × 10^{-3} mol dm^{-3}, [H^+] = 0.1 mol dm^{-3}, [Pd(II)] =2.0×10^{-5} mol dm^{-3} and [I] = 0.25 mol dm^{-3} at 35°C.The rate of reaction increased with the increase concentration of serine **[Fig 5.11].** The order in substrate was computed from the slopes of log k_{obs} versus log (substrate) which indicated a fractional order dependence on serine. Results are given in **[Table 5.7].**

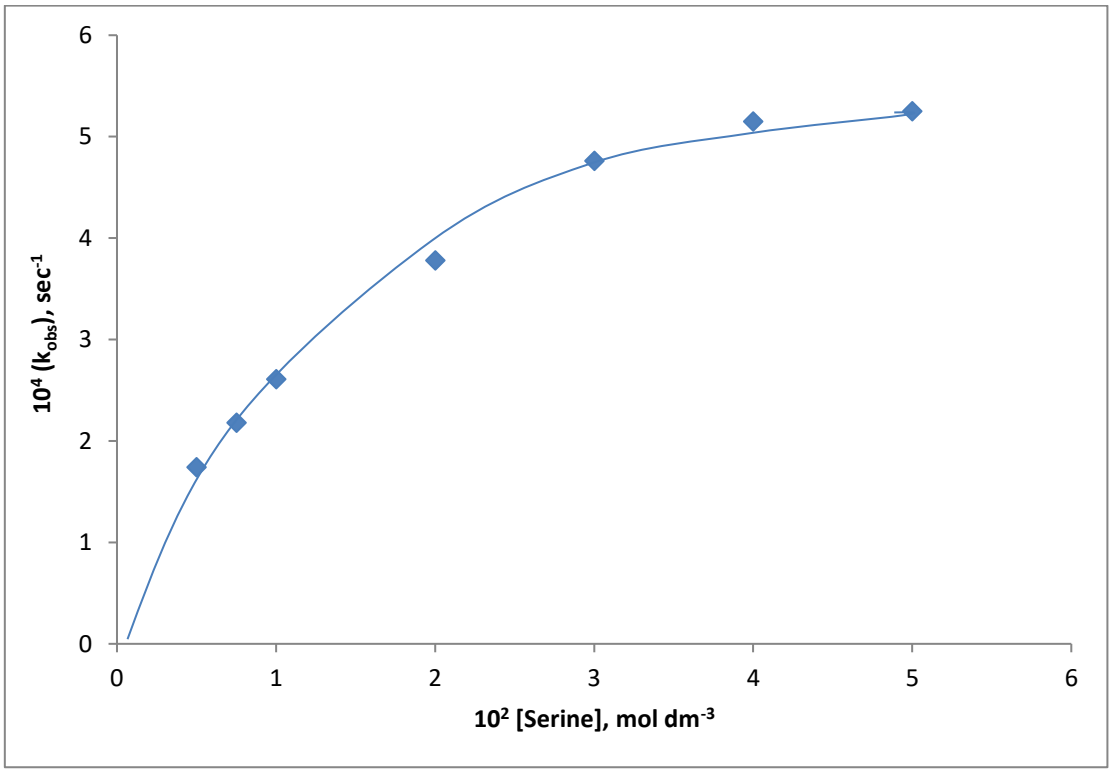

Figure 5.11: Variation of Serine (catalysed)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} [H^+] = 0.10 mol dm^{-3}

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

Table 5.7: Variation of Serine(catalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pd (II)] = 2.0×10^{-5} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. =35°C**

10^2 [Ser], mol dm^{-3}	**0.50**	**0.75**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant(ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.3	9.1	8.9	8.7	8.3	8.5	8.3
10	8.9	8.7	8.5	7.7	7.2	7.2	7.1
15	8.5	8.1	7.7	7.1	6.4	6.3	6.0
20	8.1	7.6	7.2	6.3	5.6	5.4	5.2
30	7.2	6.7	6.1	5.1	4.2	4.0	3.6
40	6.6	5.9	5.4	4.1	3.2	2.9	2.7
60	5.4	4.6	3.9	2.7	1.9	1.6	1.4
80	4.4	3.4	2.9	1.7	1.1	0.9	0.7
100	3.5	2.7	2.1	1.1	(85) 0.9	(85) 0.7	(85) 0.61
10^4 k_{obs}(sec^{-1})	**1.74**	**2.18**	**2.61**	**3.78**	**4.76**	**5.15**	**5.25**

Figures in parenthesis denotes time in minutes.

5.4.3 Pd(II) Catalysed Reactions

The concentration of palladium (II) varied from 0.5×10^{-5} to 5.0×10^{-5} mol dm^{-3} at [NBS] = 2.0×10^{-3} mol dm^{-3}, [Ser] = 2.0×10^{-2} mol dm^{-3} and [H^+] = 0.10 mol dm^{-3} and [I] = 0.25 mol dm^{-3} at 35°C**.** It was observed that with increasing Pd (II) concentration, the first order rate constant in NBS increased linearly. The plot of k_{obs} versus [$PdCl_2$] was linear with an intercept **[Fig. 5.12]** indicating uncatalysed reaction along with catalysed one. The value of k_{obs} obtained in absence of palladium chloride i.e. [$PdCl_2$=0], was matching with the intercept of the plot of k_{obs} versus [$PdCl_2$]. Results are given in **[Table 5.8].**

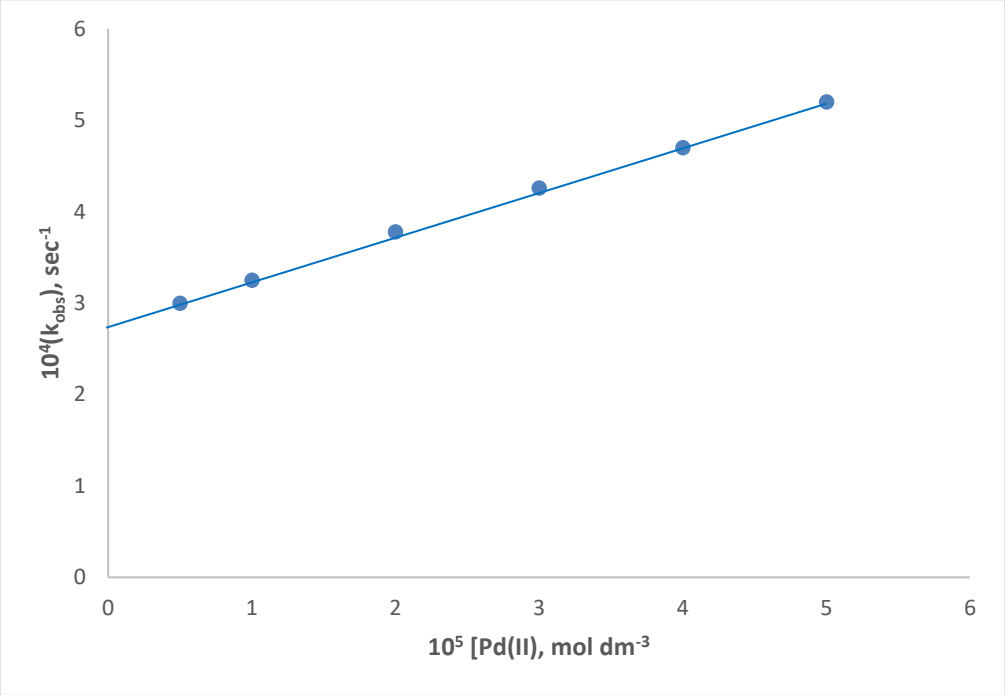

Figure 5.12: Variation of Palladium (II) (catalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} [Ser] = 2.0×10^{-2} mol dm^{-3}

[H^+] = 0 .10 mol dm^{-3} [I] = 0.25 mol dm^{-3} Temp. = 35°C

Table 5.8: Variation of Pd (II) (catalysed)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] =1.0 × 10^{-3} mol dm^{-3}**

[Ser] = 2.0 × 10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35°C**

10^5 Pd [II], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant(ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.1	8.9	8.7	8.7	8.3	8.2
10	8.3	8.1	7.7	7.6	7.2	7.1
15	7.6	7.4	7.1	6.7	6.3	6.0
20	6.9	6.7	6.3	5.9	5.5	5.4
30	5.7	5.6	5.1	4.6	4.1	4.0
40	4.8	4.7	4.1	3.4	3.1	3.0
60	3.3	3.1	2.7	2.1	1.8	1.7
80	2.3	2.2	1.7	3.1	1.1	0.9
100	1.6	1.5	1.1	0.8	0.6	0.8
10^4 k_{obs}(sec^{-1})	**3.00**	**3.25**	**3.78**	**4.26**	**4.70**	**5.20**

5.4.4 Effect of variation of concentration of Hydrogen ion

The hydrogen ion concentration was varied from 0.05 to 0.5 mol dm^{-3} employing perchloric acid at fixed concentration of [NBS]= 2.0×10^{-3} $moldm^{-3}$, [Ser] = 2.0×10^{-2} mol dm^{-3} [Pd(II)] = 2.0×10^{-5} mol dm^{-3} and I = 0.25 mol dm^{-3} at 35°C.The rate constant decreases with the increase in the concentration of perchloric acid **[Fig. 5.13]**. The plot of log k_{obs} versus log $[H^+]$ is linear and yields a fractional slope (- 0. 63) conforming inverse dependence on $[H^+]$. This inverse effect of hydrogen ion indicates free serine molecules as the predominant species. Results are given in **[Table 5.9].**

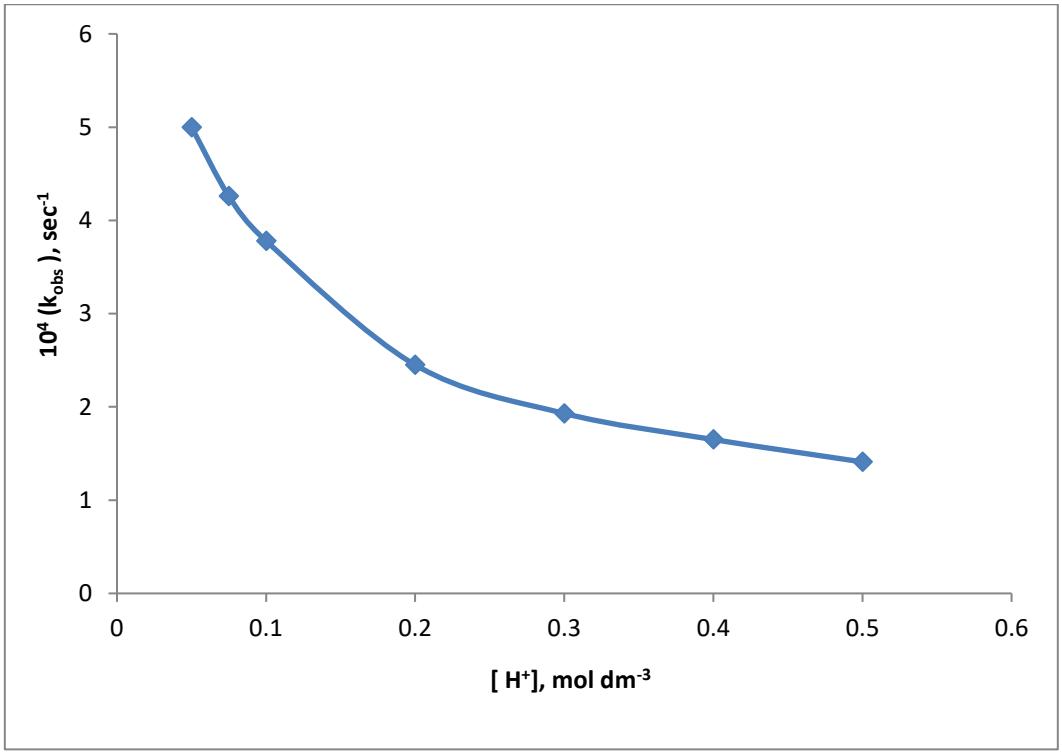

Figure 5.13: Variation of Hydrogen ion (catalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} [Ser] = 2.0×10^{-2} mol dm^{-3}

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

Table 5.9: Variation of $[H^+]$ (catalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pd (II)] = 2.0×10^{-5} mol dm^{-3} **[Ser] = 2.0×10^{-2} mol dm^{-3}**

[$Na_2S_2O_3$] =1.0×10^{-3} mol dm^{-3} **Temp. =35°C**

$[H^+]$, mol dm^{-3}	**0.05**	**0.075**	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
Time (minutes)	**Volume of the titrant(ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.5	8.6	8.7	9.1	9.2	9.3	9.5
10	7.2	7.4	7.7	8.5	8.7	8.9	9.1
15	6.4	6.7	7.1	7.7	8.3	8.5	8.7
20	5.5	5.9	6.3	7.4	7.9	8.1	8.3
30	4.1	4.6	5.1	6.4	7.1	7.4	7.6
40	3.1	3.5	4.1	5.5	6.3	6.6	7.1
60	1.7	2.2	2.7	4.1	5.0	5.5	6.1
80	0.9	1.3	1.7	3.1	4.0	4.7	5.1
100	0.5	0.79	1.1	2.3	3.2	3.6	4.3
10^4 k_{obs}(sec^{-1})	**5.00**	**4.26**	**3.78**	**2.45**	**1.93**	**1.65**	**1.41**

5.4.5 Effect of variation of Ionic Strength

The effect of ionic strength on the rate of reaction was studied using sodium perchlorate (0.05 to 0.30 mol dm^{-3}) at fixed concentration of [NBS)]= 2.0×10^{-3} mol dm^{-3}, [Ser] = 2.0×10^{-2} mol dm^{-3}, [Pd(II)] = 2.0×10^{-5} mol dm^{-3} and $[H^+]$ = 0.1 mol dm^{-3} at 35°C. Ionic strength had no effect on the rate of reaction **[Fig. 5.14]** . Results are shown in **[Table 5.10].**

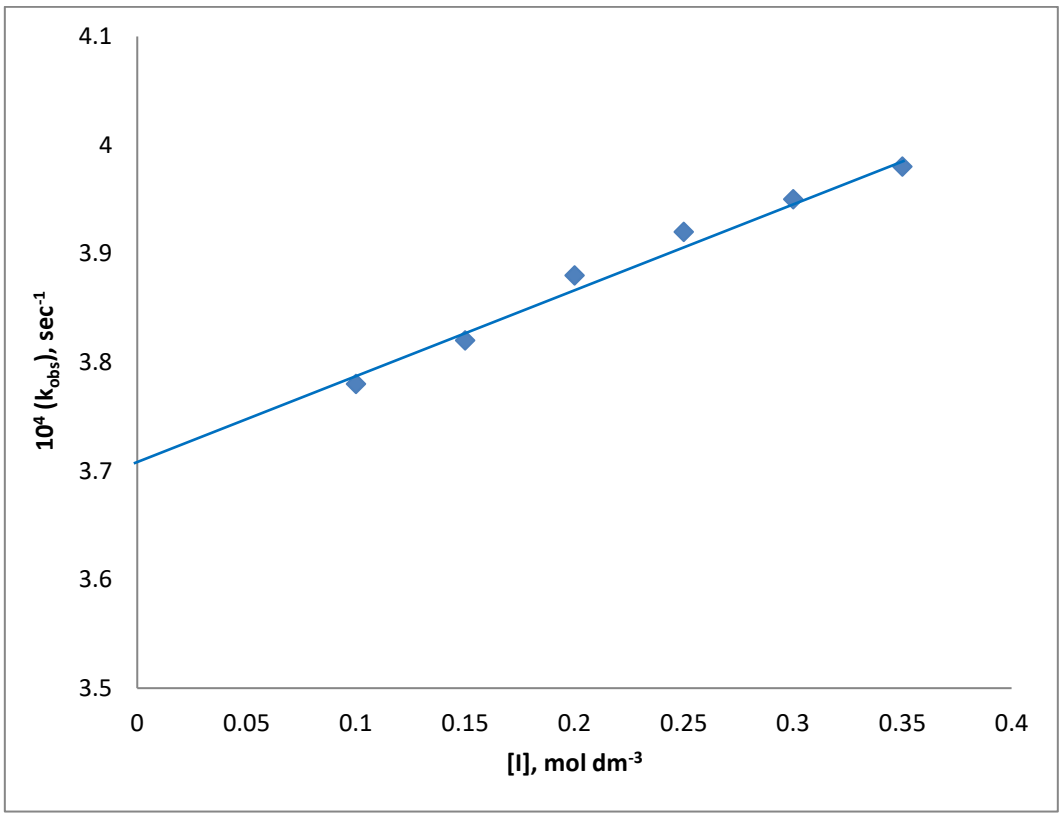

Figure 5.14: Variation of Ionic Strength (catalysed)

[NBS] = 2.0×10^{-3} mol dm^{-3} [Ser] = 2.0×10^{-2} mol dm^{-3},

[Pd (II)] = 2.0×10^{-5} mol dm^{-3} $[H^+]$ = 0 .10 mol dm^{-3} Temp. = 35°C

Table 5.10: Variation of Ionic Strength (catalysed)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0 × 10^{-3} mol dm^{-3}**

[Ser] = 2.0 × 10^{-2} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

[Pd (II)] = 2.0 × 10^{-5}mol dm^{-3} **Temp. = 35°C** **Aliquot = 5.0 ml**

[I] , mol dm^{-3}	**0.10**	**0.15**	**0.20**	**0.25**	**0.30**	**0.35**
Time (minutes)	**Volume of the titrant (ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.7	8.6	8.5	8.4	8.4	8.3
10	7.7	7.6	7.6	7.5	7.5	7.4
15	7.1	7.0	7.0	6.9	6.9	6.8
20	6.3	6.2	6.2	6.1	6.1	6.0
30	5.1	5.0	5.0	4.9	4.8	4.7
40	4.1	4.1	4.0	4.0	3.9	3.9
60	2.7	2.7	2.6	2.6	2.5	2.5
80	1.7	1.6	1.6	1.5	1.5	1.4
100	1.1	1.1	1.0	1.0	0.9	0.9
10^4 k_{obs}(sec^{-1})	**3.78**	**3.82**	**3.88**	**3.92**	**3.95**	**3.98**

5.4.6 Effect of Chloride ion

The effect of chloride on the rate of reaction was studied by the successive addition of sodium chloride; the observed rate constants decreased with [Cl^-] [**Fig.5.15**].

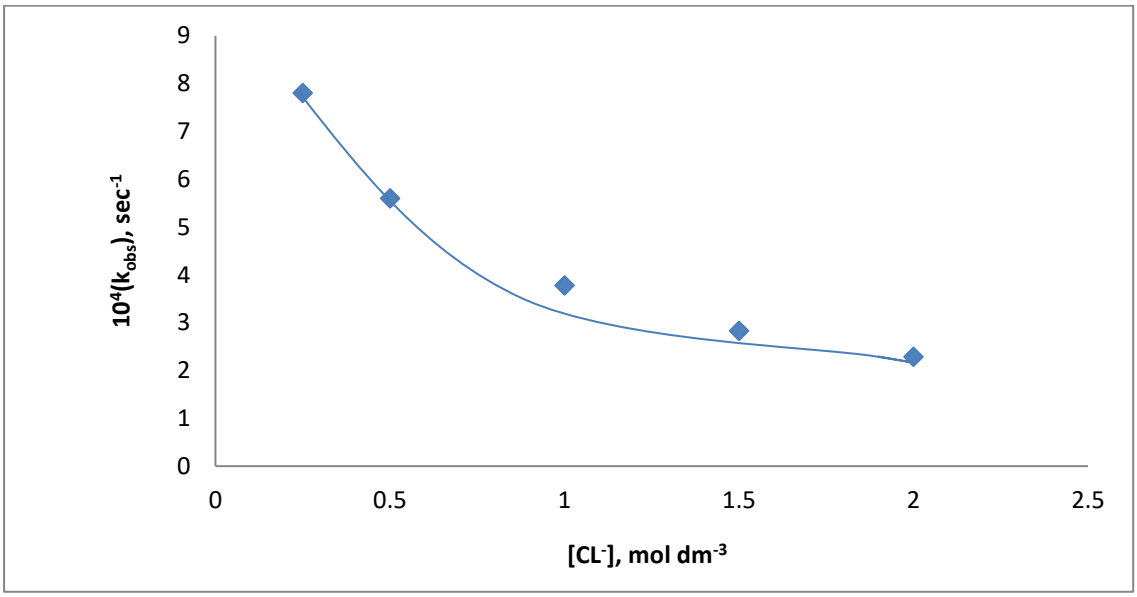

Figure 5.15: Variation of Chloride ion (catalysed)

[NBS] = 2.0 × 10^{-3} mol dm^{-3} **[Ser] = 2.0 × 10^{-2} mol dm^{-3}**

[Pd (II)] = 2.0 × 10^{-5} mol dm^{-3} **[I] = 0.25 mol dm^{-3}** **Temp. = 35°C**

Table 5.11-Variation of Chloride ion

10^2[NaCl] mol dm^{-3}	**10^4 (K_{obs}) sec^{-1}**
0.25	7.80
0.5	5.60
1.0	3.78
1.5	2.83
2.0	2.29

5.4.7 Various complexes formed during the course of reaction

To ascertain the formation of possible complex or complexes during the course of reaction, spectra were obtained by using systronics UV-Vis Spectrophotometer-2203 for different acidic solutions of NBS, Pd (II) and serine separately and in the form of mixture. In the first case NBS concentration was fixed and acid conc. varied, and the spectra recorded indicates decrease in absorption with increase in acid concentration where a single peak was obtained at 227nm.[53] **[Fig. 5.16]**.

Further, Pd (II)chloride solution of three different concentrations such as 5.0×10^{-5}, 7.0×10^{-5} and 9.0×10^{-5} were added to the acidic solution of NBS, it was observed that there is an increase in absorbance which can be assigned to the existence of equilibrium step **(Eqn. 11)(**Complex C2) proposed in the reaction scheme **[Fig. 5.17].** Again keeping the conc. of NBS, Pd(II) and acid constant and varying the serine conc. indicates increase in absorption which shows that the complex formed between NBS, Pd(II) and serine increases with the increase in conc. of serine **[Fig. 5.18]**.This indicates the formation of an unstable activated complex C3 in the reaction under investigation as shown in the rate determining step **(Eqn. 12)** of reaction **[Scheme 1]**.

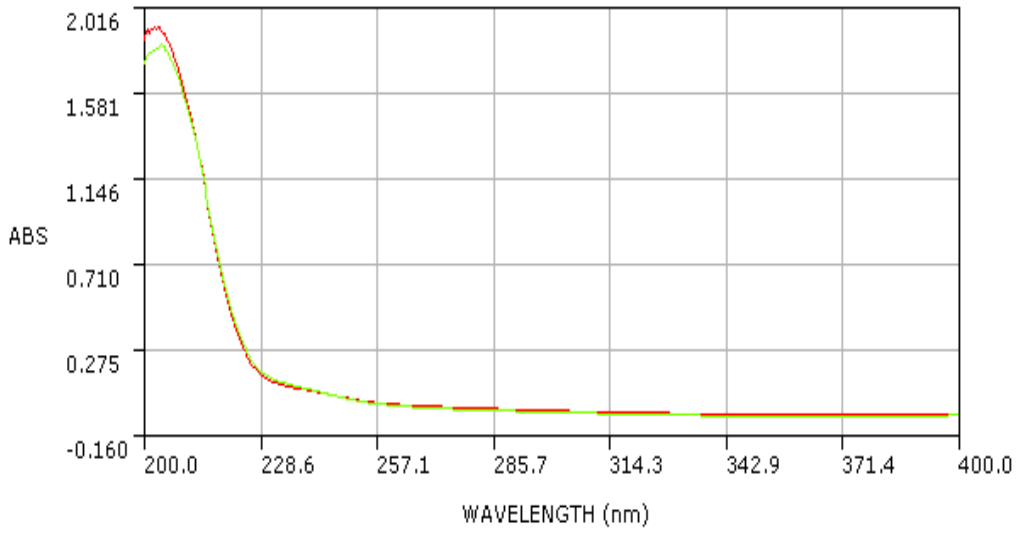

Figure 5.16: Spectra study of Variation of Acid

[NBS] = 2.0×10^{-3} mol dm^{-3} $[H^+]$ = 0.1 mol dm^{-3} (Red), 0.5 mol dm^{-3} (Green)

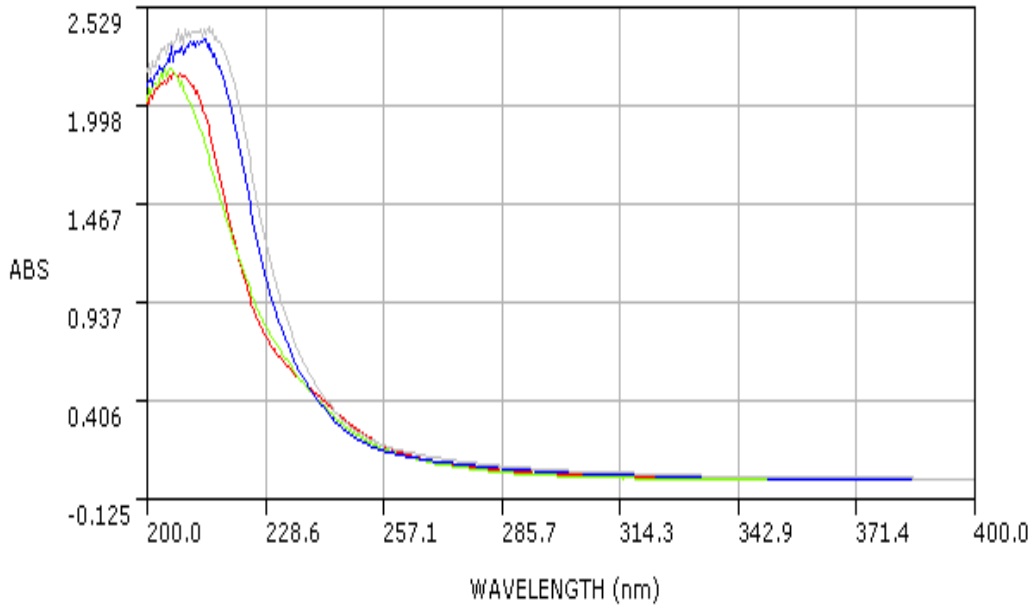

Figure 5.17: Spectra study of Variation of Serine

[NBS] = 5.0 × 10^{-4} mol dm^{-3}, [Pd (II)] = 5.0 × 10^{-5} mol dm^{-3}, Temp. = 35°C

[Serine] = 2.0 ×10^{-2} mol dm^{-3} (Red), 3.0 × 10^{-2} mol dm^{-3} (Green), 4.0 × 10^{-2} mol dm^{-3} (Blue), 5.0 × 10^{-2} mol dm^{-3} (Grey)

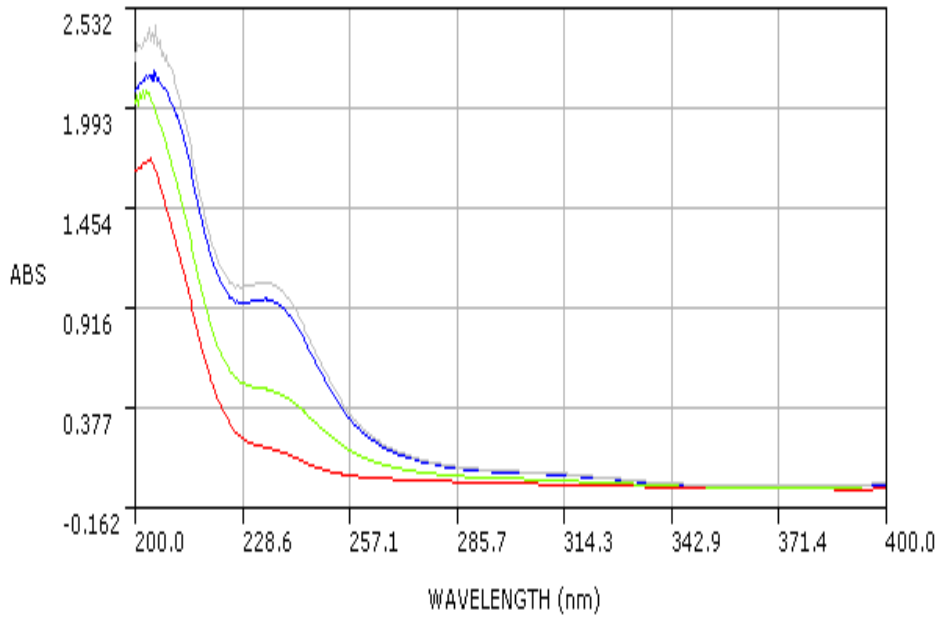

Figure 5.18: Spectra study of Variation of [Pd(II)]

[NBS]=5 × 10^{-4} mol dm^{-3}, [H^+] =0.1 mol dm^{-3}, Temp. = 35°C, [Pd (II)] = 5 × 10^{-5} mol dm^{-3}(Green), 7 × 10^{-5} mol dm^{-3}(Blue), 9 × 10^{-5} mol dm^{-3}(Grey)

On the basis of observed kinetic orders, spectroscopic information collected for the possible formation of complex or complexes in the reaction, a probable reaction path can be proposed.

$$\underset{[AA]}{Ser} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{[AA]^+}{Ser \cdot H^+} \tag{10}$$

$$\underset{C_1}{[PdCl_4]^{2-}} + NBS \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} \underset{C_2}{[PdCl_3.NBS]^{-1}} + Cl^- \tag{11}$$

$$HOCH_2CH(NH_2)COOH + \underset{C_3}{C_2} \xrightarrow{k} Complex[C] \tag{12}$$

$$Complex[C] \xrightarrow{2H_2O} [PdCl_2(OH)_2]^{2-} + NH_2CH(R)C(=O)OBr + NHS + Cl^- + 2H^+ \tag{13}$$

$$NH_2CH(R)C(=O)OBr \xrightarrow{2H_2O} \overset{+}{N}H_2=CH(R) + CO_2 + Br^- \tag{14}$$

$$\overset{+}{N}H_2=CH(R) \xrightarrow{H_2O} NH_3 + RCHO + H^+ \tag{15}$$

$$[PdCl_2(OH)_2] + 2Cl^- \longrightarrow [PdCl_4]^{2-} + 2OH^- \tag{16}$$

$$2OH^- + 2H^+ \longrightarrow 2H_2O \tag{17}$$

$$H^+ + Br^- \longrightarrow HBr \tag{18}$$

$$Br^- + NBS \xrightarrow{H^+} NHS + Br_2 \tag{19}$$

Scheme 1

The negligible effect of succinimide concentration on the rate of reaction is obvious, as it does not appear in the rate law.

The above rate law explains the first order in oxidant, fractional order in substrate and inverse order in acid.

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

$$\frac{-d[C_2]}{dt} = K_2[NBS][C_1] - K_{-2}[C_2][Cl^-] - k[AA][C_2] = 0$$

(20)

$$K_2[NBS][C_1] = K_{-2}[C_2][Cl^-] + k[AA][C_2] \tag{21}$$

$$= C_2\left[K_{-2}[Cl^-] + k[AA]\right] \tag{22}$$

$$C_2 = \frac{K_2[NBS][C_1]}{K_{-2}[Cl^-] + k[AA]} \tag{23}$$

$$\frac{-d[NBS]}{dt} = 2k[C_2][AA] = \frac{2kK_2[NBS][C_1][AA]}{K_{-2}[Cl^-] + k[AA]} \tag{24}$$

$$= \frac{2kK_2[NBS][Pd(II)][AA]}{K_{-2}[Cl^-] + k[AA]} \tag{25}$$

Pd(II) =C1

$[AA]_T = [AA] + [AA]^+$

$= [AA] + K1\ [AA]\ [H^+]$

$[AA]_T = [AA]\ \{1+K_1[H^+]\}$

$$[AA] = \frac{[AA]_T}{1 + K_1[H]^+}$$

$$\frac{-d[NBS]}{dt} = \frac{2kK_2[NBS][Pd(II)][AA]_T}{K_{-2}[Cl^-] + \frac{k[AA]_T}{1 + K_1\left[H^+\right]}} \tag{26}$$

$$1 + K_1[H^+] = \frac{\frac{2kK_2[NBS][Pd(II)][AA]_T}{K_{-2}[Cl^-]\left[1 + K_1[H^+]\right] + k[AA]_T}}{1 + K_1[H^+]} \tag{27}$$

$$= \frac{2kK_2[NBS][Pd(II)][AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (28)$$

$$-\frac{d(NBS)/dt}{(NBS)} = \frac{2kK_2[Pd(II)][AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (29)$$

$$\frac{K_{obs}}{Pd(II)} = k' = \frac{2kK_2[AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (30)$$

$$\frac{1}{k'} = \frac{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]}{2kK_2[AA]_T} + \frac{k[AA]_T}{2kK_2[AA]_T} \quad (31)$$

$$= \frac{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]}{2kK_2[AA]_T} + \frac{1}{2K_2} \quad (32)$$

$$\frac{1}{k'} = \frac{K_{-2}[Cl^-]}{2kK_2[AA]_T} + \frac{K_{-2}K_1[H^+][Cl^-]}{2kK_2[AA]_T} + \frac{1}{2K_2} \quad (33)$$

Equation (32) suggests that 1/k′ versus $1/[AA]_T$ at constant $[H^+]$ and $[Cl^-]$ should be linear plots with positive intercept as shown in **[Fig.5.19].** The value of K_2 comes out to be 18.52 mol^{-1} dm^3 from the intercept equal to 0.027. **Equation (33)** suggests that 1/k′versus $[H^+]$ at constant $[Cl^-]$ and $[AA_T]$ should yield good linear plots as shown in **[Fig.5.20].** A high positive value of free energy of activation indicates that the transition state is highly solvated while negative value of entropy of activation suggests formation of an activated complex with a reduction in the degree of freedom of reacting molecules.

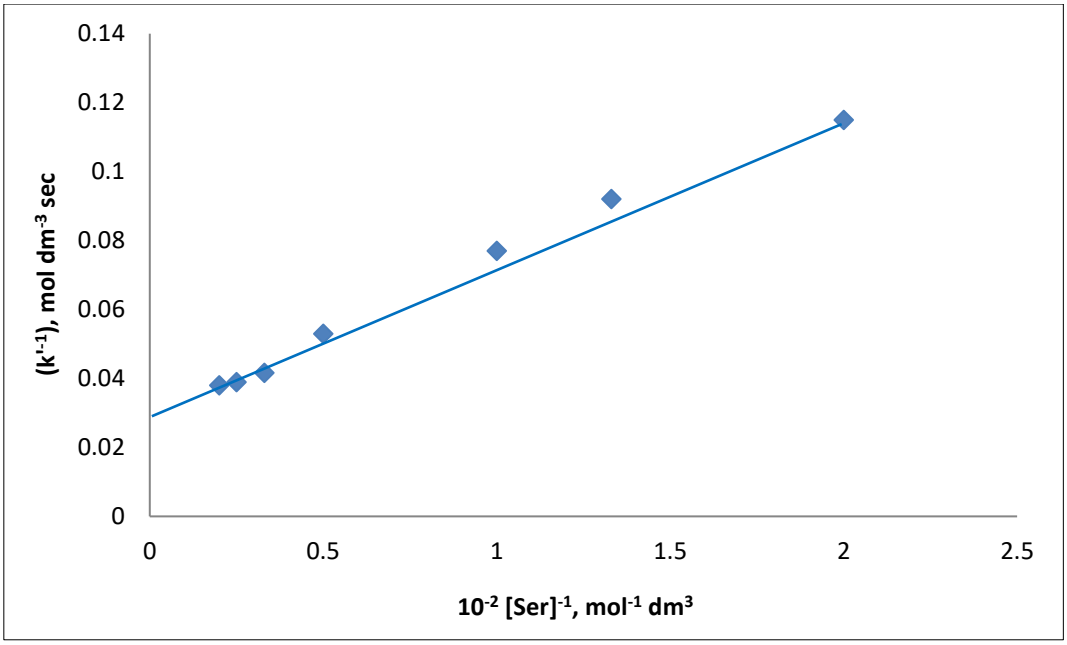

Figure 5.19: Variation of 1/k´ versus 1/[Ser]

[NBS] = 2.0 × 10^{-3} mol dm^{-3} [Pd (II)] = 2.0 × 10^{-5} mol dm^{-3},

[I] = 0.25 mol dm^{-3} [H^+] = 0.10 mol dm^{-3} Temp. = 35°C

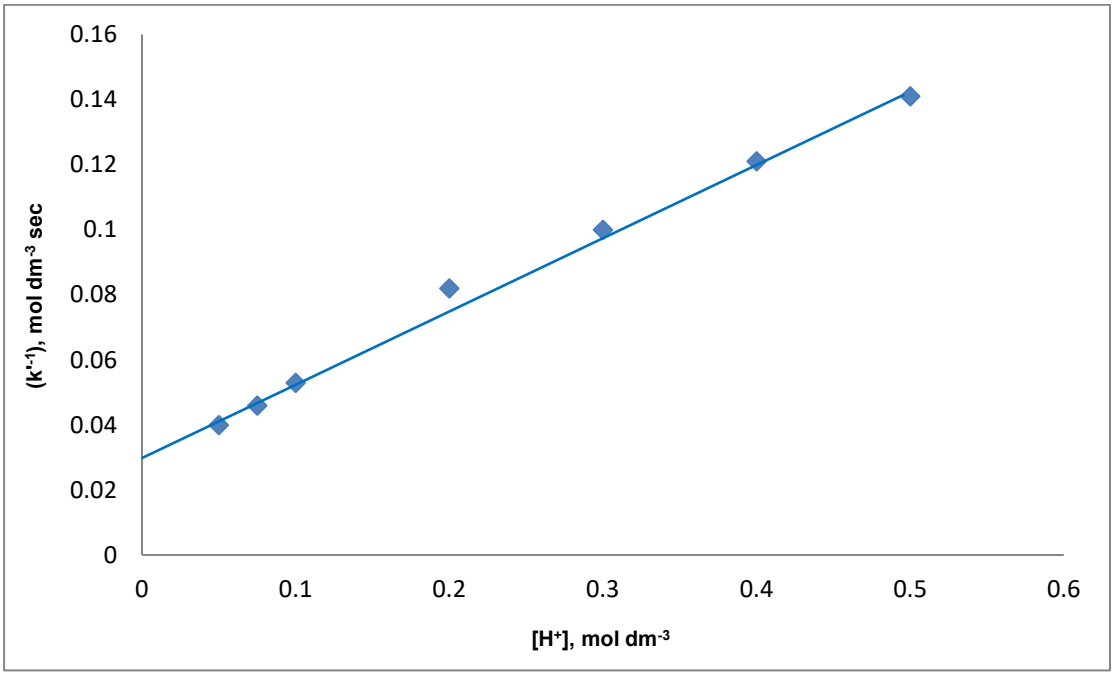

Figure 5.20: Variation of 1/k´ versus [H^+]

[NBS] = 2.0 × 10^{-3} mol dm^{-3} [Ser] =2.0 × 10^{-2}mol dm^{-3}

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

5.5 CONCLUSION

It is concluded that oxidation of serine by N-Bromosuccinimide in perchloric acid medium has the stoichiometry 2:1. The reaction is slow at room temperature but becomes fast in the presence of Pd (II) catalyst. The order with respect to NBS and Pd (II) is one and fractional order with respect to amino acid. The rate of reaction decreased with increase in perchloric acid and chloride ion concentration. The derived mechanism is consistent with all the experimental results.

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CHAPTER 6

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF PALLADIUM NANOPARTICLES ON OXIDATION OF ASPARTIC ACID IN ACIDIC AQUEOUS MEDIUM

ABSTRACT

Palladium nanoparticles are synthesized through a single route chemical reduction method using synthetic polymer such as poly N-vinyl pyrrolidone (PVP) stabilizer. The synthesized palladium nanoparticles (Pdnps) were characterized by UV-visible spectrophotometer and Transmission Electron Microscopy (TEM) analysis. The particle size of palladium nanoparticles was found to be 1nm to 50 nm and spherical in shape at the optimal experimental conditions. The synthesized palladium nanoparticles are used as a catalyst for the oxidation of Aspartic acid by N-Bromo succinimide in aqueous medium. The effect of palladium nanoparticles on the rate of oxidation has been studied at different temperatures. The palladium nanoparticles exhibited very good catalytic activity. The kinetics of the reaction was found to be first order with respect to [NBS]and Pdnp and fractional order with respect to Aspartic acid. Increase in $[H^+]$ decreased the reaction rate. The main oxidation product of Aspartic acid has been identified as the aldehyde which is confirmed by the FTIR spectrum of a corresponding hydrazone. The palladium nanoparticles catalyst exhibited better catalytic activity than equal amount of palladium precursor. Various activation parameters have been calculated and on the basis of these parameters, a suitable explanation of the reaction mechanism has been given.

6.1 INTRODUCTION

Amino acids play an important role in metabolism and in protein synthesis. Amino acids find a number of applications in biochemical research, metabolism, microbiology, nutrition, pharmaceuticals and fortification of foods and feeds. Generally, only the amino and carboxyl functional groups in $RCH(NH_2)$ COOH undergo chemical transformations while the hydrocarbon moiety remains intact. This property is attributed to the higher reactivity of the former compared to R. Aspartic acid is an amino acid useful in maintaining solubility and ionic character of proteins [1]. Aspartic acid facilitates normal cell function and increases endurance and resistance to fatigue by producing immune-globulins and antibodies and reportedly removes highly toxic ammonia from central nervous system [1]. Oxidation of aspartic acid has been reported with different oxidants like cerium (IV) [2], N chloro saccharin [3], dihydroxydiperiodato argentate [4], hexacyanoferrate [5], manganese (III) [6].

Potassium permanganate [7] hexacyanoferrate, peroxomonosulfate [8], N-bromobenzenesulphonamide [9], molybdenum-oxime-ligand [10], Gold [11].

N-Bromosuccinimide (NBS) is a mild and selective oxidant for many organic compounds. It is a source of positive halogen and has been used as oxidant for a variety of substrates in both acidic and alkaline medium [12]. The nature of active oxidizing species and the mechanism depends on the nature of the halogen atom; the groups attached to the nitrogen and the reaction condition. The active oxidizing species may be different depending on the pH of the medium. It has many applications in organic transformations [13-18], synthesis of drugs and pharmaceuticals. Although the NBS oxidation of a number of amino acids have been studied, there seems to be no report on oxidation in presence of Pd nanocatalyst.

Metal nanoparticles are gaining importance in fields of physics (quantum optics), chemistry (catalyst) and nanotechnology. Chemical and physical properties of nanoscale metal clusters are quite different from those of bulk metals. The field of nanocatalysis has undergone explosive growth during the past decades both in homogenous and heterogenous catalysis [19-20]. Since nanoparticles have a large volume ratio compared to bulk materials, they are attractive to use as catalysts [21-22]. Now it is possible to prepare soluble analogues of heterogenous catalysts which are intermediate between those of the bulk metal and single metal particle (homogenous) catalysts. The major difficulty in working with nanoparticles is their undesirable

agglomeration to form large particles. To prevent formation of such agglomerates, surfactants [23-24], ligand exchange materials [25-26] and polymeric carriers [27] are used extensively. Several studies on the uncatalysed and catalysed oxidation of amino acids have been reported [28-31] but with the emergence of metal nanoparticles processing appreciable stability and high surface area per particle, their potential use as catalyst for organic biochemical reactions stands well documented in recent years [32-33]. Nobel metals like Pt [34], Pd [35], Ru [36] and Au [37] nanoparticles have been used as a catalyst in electron transfer and oxidation reactions. Nobel metal nano crystals play an important role in different fields of science, such as catalysis, medicine, electronics etc. For most of these applications, the size, shape and size distribution of metal nanoparticles constitute the key factors. Not many studies on the oxidation of amino acids by Pd nano catalyst have been reported. So, the present study deals with the synthesis, characterization of palladium nanocatalyst and their application on oxidation of aspartic acid by NBS catalysed by palladium nanoparticle.

6.2 EXPERIMENTAL

6.2.1 Materials

Analytical grade chemicals such as $PdCl_2$, Aspartic acid, $HClO_4$, Mercuric acetate and NBS were obtained from E. Merck. Other reagents used were HCl, ethanol, and PVP. The mol. wt. of PVP is 40 KD. A fresh solution of NBS, KI, hypo and starch was prepared before starting the experiment. All chemicals were used as received without further purification. Double distilled water was used for the study. Stock solutions of N-Bromosuccinimide were prepared and standardized iodometrically

6.2.2 Synthesis of Pd Nanoparticles

The chemical reduction method

The metal salts dissociate to form metal ions. The metal ions are then reduced by a reducing agent to form metal nanoparticles that are stabilized by a stabilizer.

The palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887 gms of $PdCl_2$ and 6 ml of 0.2 M HCl and diluting it to 250 ml with doubly distilled water. A solution containing 15 ml of 2 mM of H_2PdCl_4. 21 ml of doubly deionized water, 0.0667 gms of PVP and 4 drops of 1M HCl was heated. When the solution began to reflux, 14 ml of ethanol was added. The solution was then refluxed for 3 hours, and this resulted

in a dark brown suspension of Pd nanoparticles **[Fig.6.1].** Thus, the reduction of H_2PdCl_4 by ethanol (as both solvent and reducing agent) occurred and Polyvinylpyrrolidone (PVP) stabilized Pd nanoparticles of various shapes.

6.2.3 Characterization

UV-Visible spectrum is an effective method to investigate whether the metal precursors are completely reduced or not [38]. Palladium concentration effects on the conversion of Pd^{+2} to nano Pd^0 and preliminary estimation of palladium nano particle synthesis were investigated by UV-Visible spectrophotometer (Double beam spectrophotometer-2203).

Figure 6.1: Photograph of Palladium nanoparticle formation

The morphology of palladium nanoparticles strongly depends on the reaction conditions like temperature, duration, pH and the type of metallic precursor and stabilizer. The palladium particle size distribution of the colloidal solution decreased with increasing pH has been reported by Thiebaut [39]. The morphological study of the palladium nano particle was carried out with scanning of Transmission electron microscope by employing JEOL-JEM-2010XII TEM at 200 kV. TEM images were recorded to confirm the size and shape of newly synthesized palladium nanoparticles. The oxidation product was monitored by FTIR (ALPHA-T Bruker).

6.2.4 Kinetic Measurements

In a typical experiment, glass stoppered Pyrex round bottom flask was used. Appropriate amount of the amino acid solution in acidic form, mercuric acetate, $NaClO_4$ (Ionic Strength) and water (to keep the volume constant) were taken in the

flask. The temperature was maintained at 35℃ by circulating thermostated water bath. An NBS solution kept in the thermostat separately was added to initiate the reaction. The progress of the solution was monitored by iodometric determination of the unreacted NBS in a measured weight of the reaction mixture at different intervals of time [40]. The rate constants were computed from the linear plots of log [NBS] against time.

6.3 RESULTS AND DISCUSSION

6.3.1 Pd Nanoparticles Characterization Results

The reduction of Pd^{+2} to Pd^{0} nanoparticles was monitored by UV-Visible spectroscopy in the range of 220 – 600 nm. **[Fig.6.2]** shows the absorption spectra of solutions at different times of reduction. The solution before the reduction is pale yellow colour showing the peak at 310 nm in the spectrum. This is due to a charge transfer transition of the $(PdCl_4)^{2-}$ ions [41-42]. During the reduction reaction, the consecutive disappearance of the absorption peak is attributed to the Pd^{+2} reduction completely reduced after 15 minutes. The colour intensity changes resulting in the increase in absorbance of the solution.

6.3.2 Stability of nanoparticles dispersion

The stabilization of metal nanoparticles is achieved using macromolecules such as polymers. PVP is mostly used because of its low cost and its ability to stabilize nanoparticles with accessible surface area in polar solvents such as water. One part of PVP chain absorbs to the surface of the nanoparticles and the other part suspends freely in solution forming a protective layer. The Pd nanoparticle solution remains stable for more than 2 months**.**

6.3.3 Spectra at different time of preparation

Show in **[Fig.6.2]** the absorption peaks at 310 and 410 nm that attribute to $[PdCl_4]^{2-}$, while the peak at 256 nm and 315 nm corresponds to PVP-stabilised Pd NPs using ethanol as reductant. These Pd NPs are stabilised by PVP polymer. Then, PVP polymer can bind preferentially to the {1 1 1} and {1 0 0} planes of metal Nanoparticles [43].

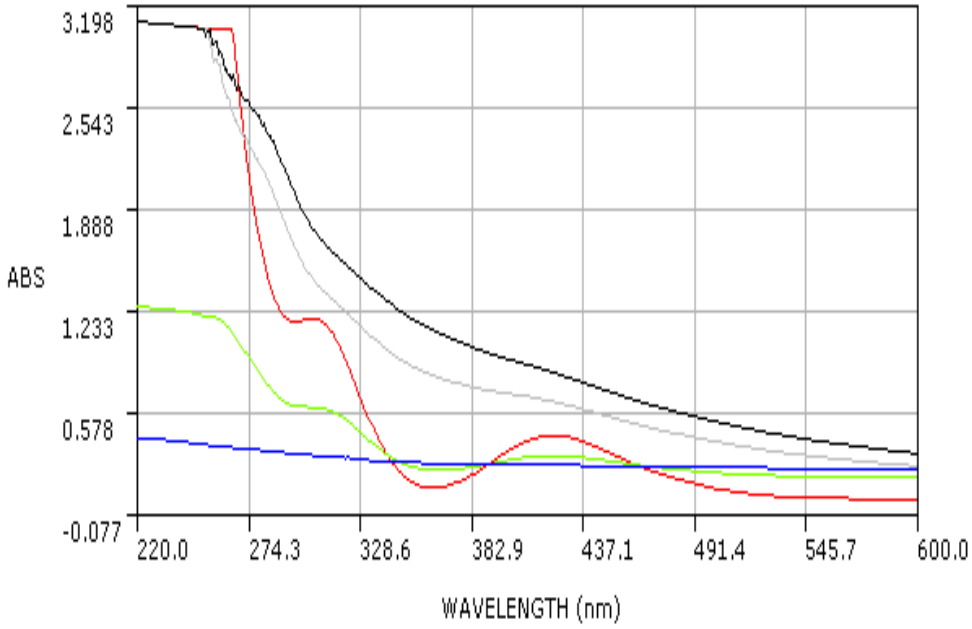


Figure 6.2: UV–Vis spectra of PVP-protected Pd NPs in the range 220–600 nm

The spectroscopic studies indicate that PVP–Pd interaction occurs through the carbonyl group of the pyrrolidone ring. In our synthesis process, Pd NPs in the size range 1–50 nm in diameter have been obtained from aqueous solutions of $PdCl_2$ in the presence of PVP. They exhibit the most typical characteristics of Pd NPs synthesized in alcohol reduction. In general, cubic and octahedral Pd NPs have {1 0 0} and {1 1 1} planes. It is seen that Pd NPs of big size and sharp shape were observed. The important conclusion is that most of the large sized Pd NPs with tetrahedral, octahedral and cubic shapes have been found due to the aggregation of the smaller seeds of spherical Pd NPs that are formed. It is clear that their sizes and shapes are not controlled, and their sizes are large. There is a lot of aggregation and clustering of small Pd NPs possibly leading to the big Pd NPs. It has been known that the major shapes of nanoparticles include cube, octahedron, tetrahedron, decahedron and icosahedrons, and structural variations from cubic to octahedral through cubo-octahedral nanocrystals. Noble metals have a face-centred cubic (fcc) lattice with different surface energies for different crystal planes, such as the combinations of the low-index and/or high-index {1 1 1, 1 0 0} and {1 1 0} planes [44-46].

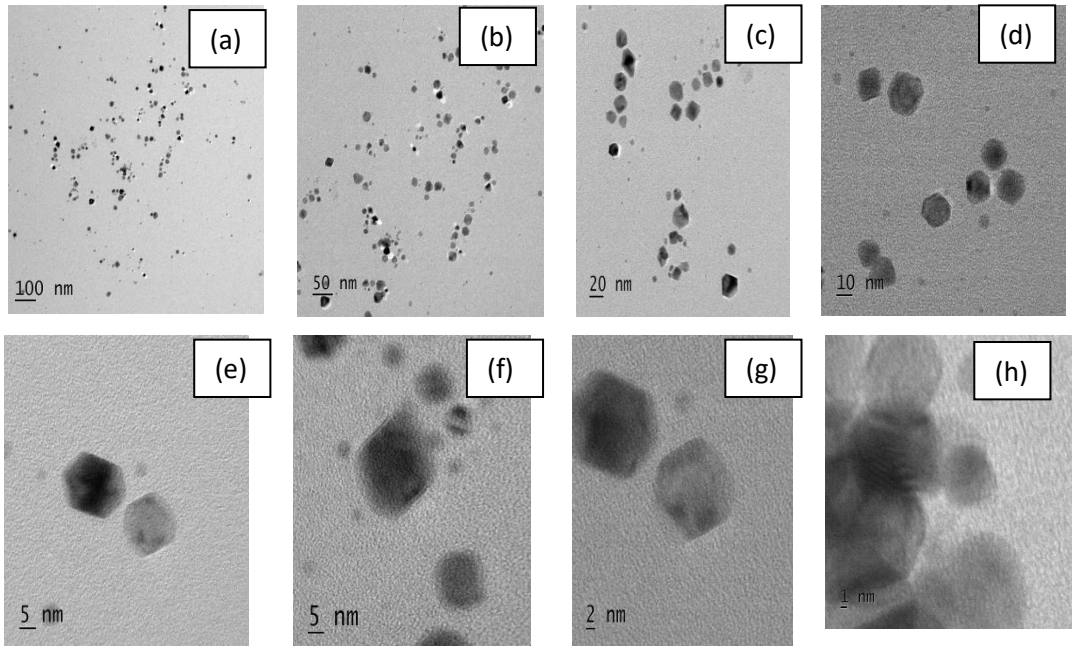


Figure 6.3: TEM images of major shapes and various sizes of Pd nanoparticles. TEM images of Pd nanoparticles with scale bars: (a) 100 nm (b) 50 nm (c) 20 nm (d) 10 nm (e, f) 5 nm (g) 2 nm and (h) 1 nm

In **[Fig.6.3]** (a)–(h), various shapes of Pd nanoparticles are spheres, cubes, tetrahedrons, octahedrons, twinned nanoparticles of twinned decahedral and icosahedral shapes, and other irregular shapes that are characterized by the formation of Pd nanoparticles by alcohol reduction [47].

6.3.4 Stoichiometry and Product Analysis

The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBS over amino acid (in varying ratios) at 35℃ for 48 hours and estimations of residual NBS in different sets showed that 1 mole of amino acid consumes two moles of NBS according to the stoichiometric equation. The main reaction product was identified 3-oxopropanoic acid which was confirmed by quantitative test and further 2,4-dinitrophenyl hydrazone derivates were also obtained which is confirmed by FTIR spectrum **[Fig.6.4]**. The IR Spectra shows the band at 1632.07 cm^{-1} due to C=N stretching frequency of the carboxylic group and the band at 3449.28 cm^{-1} due to –OH stretching frequency of the carboxylic OH group. Ammonia identified by Nessler's reagent, brownish colour was observed indicating deamination

reaction, CO_2 was identified by freshly prepared lime water and the solution turned milky indicating decarboxylation reaction.

$$RCH(NH_2)COOH + 2NBS + H_2O \xrightarrow{Pd(II)/H^+} RCHO + 2NHS + CO_2 + Br_2 + NH_3 \quad (1)$$

Where R= $-CH_2-COOH$

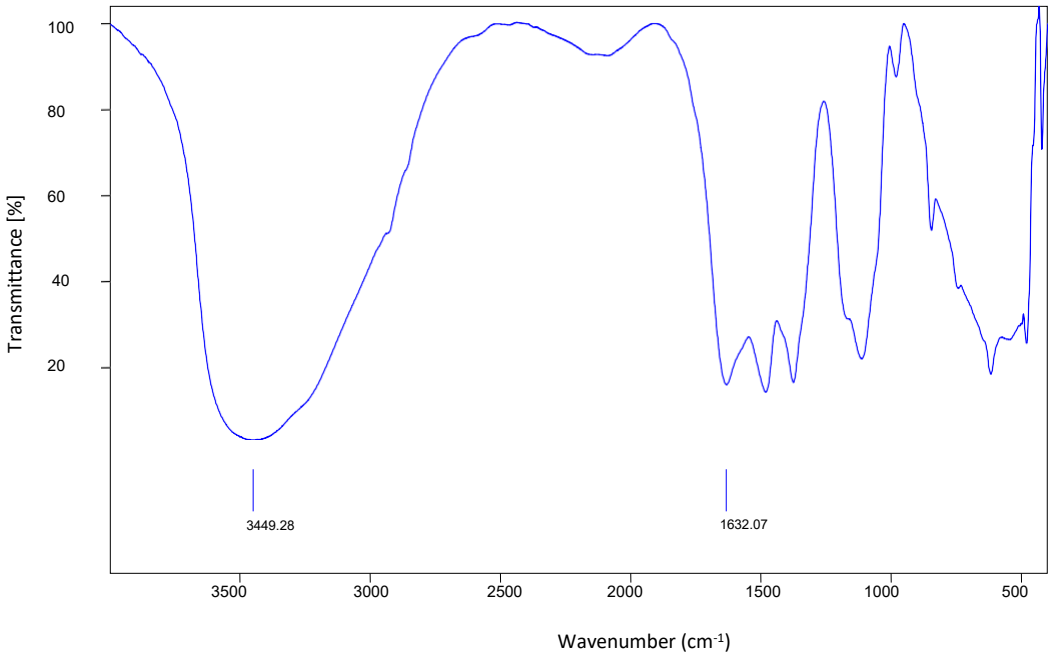


Figure 6.4: FT-IR spectra of the hydrazone derivative from the reaction mixture of Aspartic acid and NBS in the presence of palladium nanoparticles

6.3.5 Effect of NBS concentration

The Palladium nanoparticle catalysed oxidation of aspartic acid was studied at different concentration of NBS varying from 1×10^{-3} to 5×10^{-3} mol dm^{-3} at fixed concentration of [Aspartic Acid] = 2×10^{-2} mol dm^{-3}, [Pdnps] = 2×10^{-6}mol dm^{-1}, $[H^+]$ = 0.1 M, [I] = 0.25 mol dm^{-3} and temperature 35 °C. First order dependence in NBS was followed at all initial concentration of NBS **[Table 6.1]**. Pseudo first order rate constants (k_{obs}) were calculated from the slope of log (a-x) versus time plots **[Fig.6.5]** The first order kinetics with respect to NBS are also verified by the constant values of k_{obs} obtained at various initial concentrations of NBS. Results are given in **[Table 6.2].**

Table 6.1: Effect of [NBS], [Asp], [Pdnps] and [H^+] on oxidation of Aspartic acid by NBS in perchloric acid medium in the presence of Pd nanocatalyst at 35°C

10^3 [NBS] mol dm^{-3}	10^2 [Aspartic Acid] mol dm^{-3}	10^6 [Pd nano catalyst] mol dm^{-3}	[H^+] mol dm^{-3}	10^4 k_{obs} sec^{-1}
1.0	2.0	2.0	0.10	6.06
2.0	2.0	2.0	0.10	6.70
3.0	2.0	2.0	0.10	6.25
4.0	2.0	2.0	0.10	6.64
5.0	2.0	2.0	0.10	6.10
2.0	0.50	2.0	0.10	2.01
2.0	0.75	2.0	0.10	2.80
2.0	1.0	2.0	0.10	3.61
2.0	2.0	2.0	0.10	6.70
2.0	3.0	2.0	0.10	8.60
2.0	4.0	2.0	0.10	9.81
2.0	5.0	2.0	0.10	10.0
2.0	2.0	0.5	0.10	4.30
2.0	2.0	0.75	0.10	4.70
2.0	2.0	1.0	0.10	5.12
2.0	2.0	2.0	0.10	6.70
2.0	2.0	3.0	0.10	8.21
2.0	2.0	4.0	0.10	9.82
2.0	2.0	5.0	0.10	11.40
2.0	2.0	2.0	0.05	8.12
2.0	2.0	2.0	.075	7.31
2.0	2.0	2.0	0.10	6.70
2.0	2.0	2.0	0.20	5.50
2.0	2.0	2.0	0.30	4.32
2.0	2.0	2.0	0.40	3.21
2.0	2.0	2.0	0.50	2.40

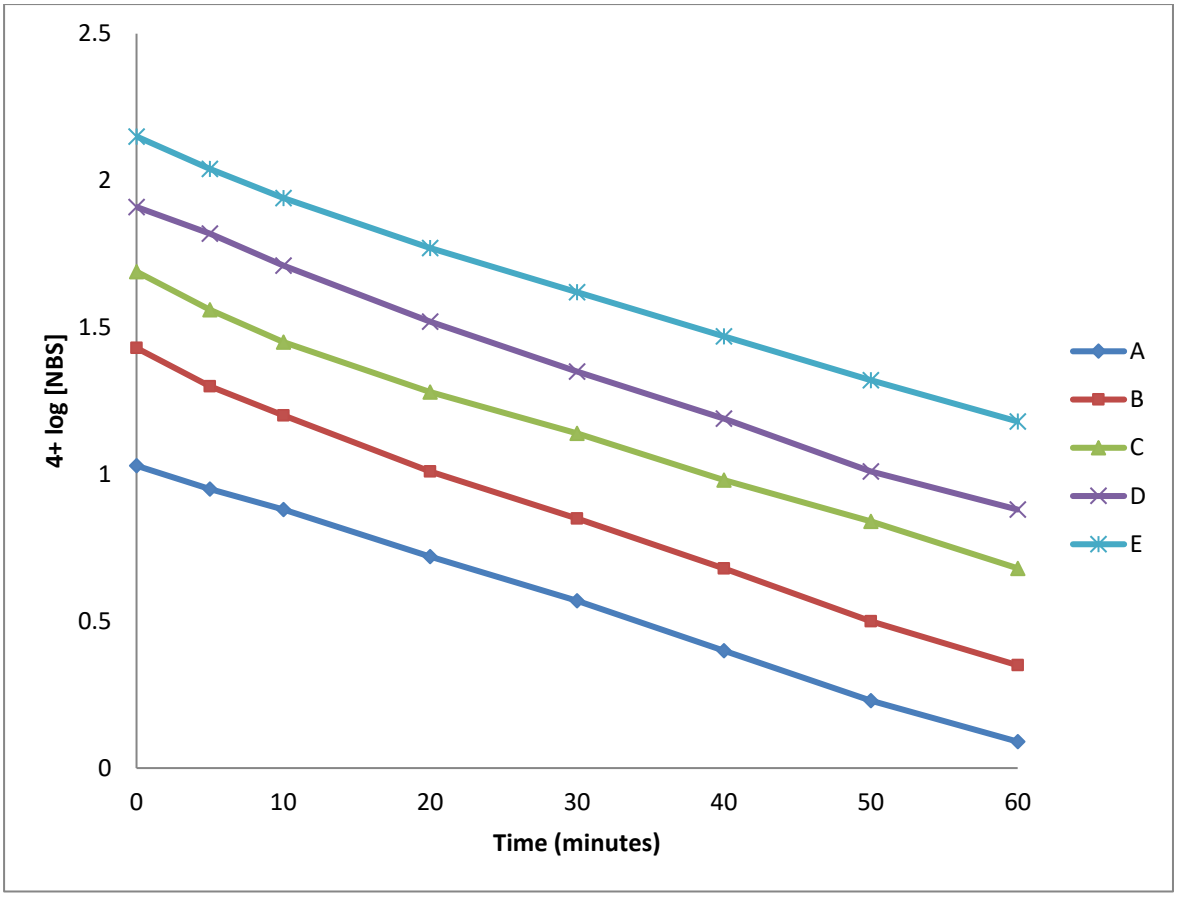


Figure 6.5: Variation of NBS

[Asp] = 2 ×10^{-2} mol dm^{-3} **[Pdnps] = 2 ×10^{-6} mol dm^{-3}**

[H^{+}] = 0.10 mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

Temp. = 35°C

[NBS] = (A) 1 × 10^{-3} mol dm^{-3} **(B) 2 × 10^{-3} mol dm^{-3}**

(C) 3 × 10^{-3} mol dm^{-3} **(D) 4 × 10^{-3} mol dm^{-3}**

(E) 5 × 10^{-3} mol dm^{-3}

Table 6.2: Variation of NBS

[Pdnps] = 2.0×10^{-6} mol dm^{-3} **[$Na_2S_2O_3$] = 2.0×10^{-3} mol dm^{-3}**

[Asp] = 2.0×10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35 °C**

10^3 [NBS], mol dm^{-3}	**1.0***	**2.0****	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**				
0	16.7	10.0	7.5	10.0	12.5
5	14.8	8.1	6.3	8.3	10.4
10	14.3	6.7	5.2	6.6	8.7
15	9.8	5.5	4.3	5.5	7.2
20	8.3	4.5	3.5	4.6	6.1
30	5.6	3.1	2.5	3.0	4.2
40	3.8	2.1	1.7	2.0	3.0
50	2.6	1.4	1.1	1.4	2.1
60	1.8	0.9	0.8	0.9	1.4
70	(65) 0.4	(65) 0.8	(65) 0.6	(65) 0.7	(65) 1.2
10^4 k_{obs}(sec^{-1})	**6.06**	**6.70**	**6.25**	**6.64**	**6.10**

[$Na_2S_2O_3$]* = 3.0×10^{-4} mol dm^{-3}

[$Na_2S_2O_3$] **= 1.0×10^{-3} mol dm^{-3}

Figures in parenthesis denotes time in minutes.

6.3.6 Effect of Aspartic Acid

The effect of aspartic acid concentration was studied by varying concentration from 0.5×10^{-3} to 5×10^{-3} mol dm^{-3} at constant [NBS], [H^+], [Pdnps], [I] and temp. The kinetic runs were carried out with initial concentration of aspartic acid. A plot of k_{obs} versus [Aspartic acid] shows first order dependence of the reaction on aspartic acid at low concentration, which shifts towards zero order at its higher concentration **[Fig.6.6].** The plot of log k_{obs} versus log [aspartic acid] was straight line with fractional slope confirming fractional order with respect to aspartic acid. Results are given in **[Table 6.3].**

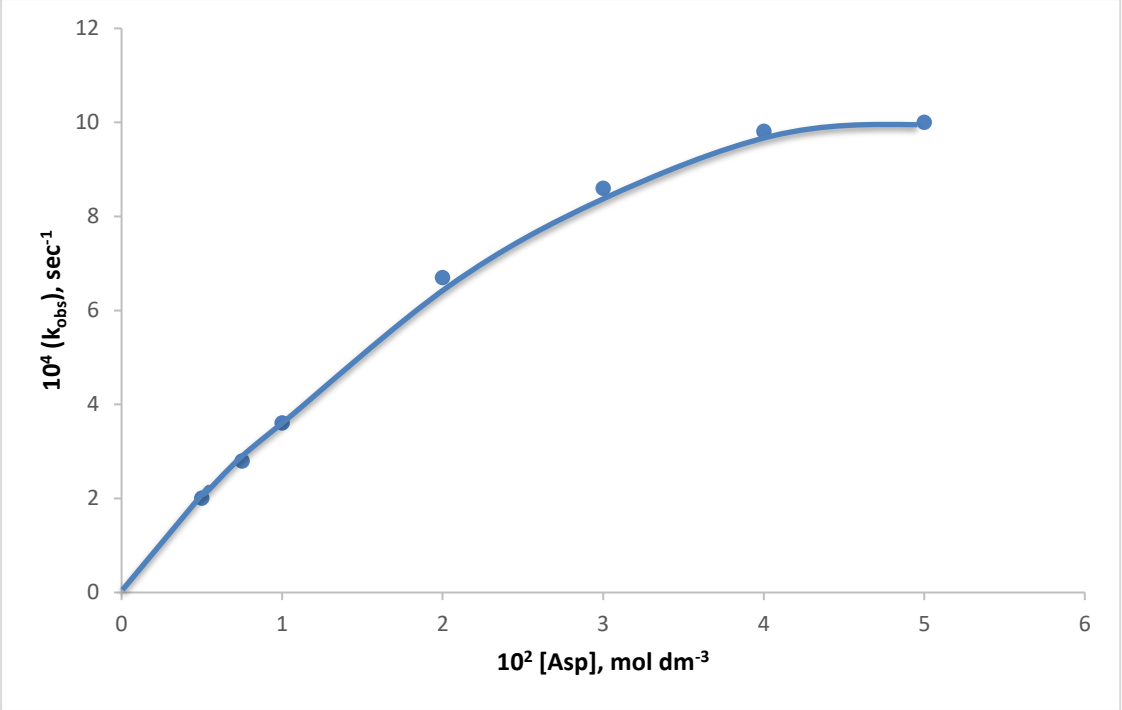


Figure 6. 6: Variation of Aspartic acid

[NBS] = 2 ×10^{-3} mol dm^{-3} [Pdnps] = 2 ×10^{-6} mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

Table 6.3: Variation of Aspartic acid

[NBS] = 2.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[Pdnps] = 2.0×10^{-6} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[H^+] = 0.10 mol dm^{-3} **Temp. = 35 °C**

10^2 [Asp], mol dm^{-3}	**0.5**	**0.75**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.5	9.2	9.1	8.1	7.9	7.7	7.4
10	8.9	8.5	8.3	6.6	6.0	5.6	5.6
15	8.1	7.7	7.6	5.4	4.6	4.1	4.1
20	7.8	7.2	7.0	4.0	3.7	3.2	3.1
30	6.9	6.0	6.0	3.0	2.2	1.7	1.8
40	6.1	5.6	5.0	2.0	1.3	0.9	(35) 1.3
60	4.7	3.6	3.6	(50) 1.3	(50) 0.8	(45) 0.7	(40) 1.0
80	3.7	2.6	2.5	(60) 0.9	(60) 0.5	(50) 0.5	(45) 0.6
100	2.9	1.9	1.8	(65) 0.7	(65) 0.4	(60) 0.3	(50) 0.5
10^4 k_{obs} (sec^{-1})	**2.01**	**2.80**	**3.61**	**6.70**	**8.60**	**9.81**	**10.0**

Figures in parenthesis denotes time in minutes.

6.3.7 Effect of Pd nano catalyst

The effect of Pd nano catalyst was studied by varying the concentration from 0.5 to 5 $\times 10^{-6}$ mol dm^{-1} at fixed concentration of all reactants [NBS] = 2 $\times 10^{-3}$ mol dm^{-3}, [Aspartic acid] = 2 $\times 10^{-2}$ mol dm^{-3}, [H^+]= 0.10 mol dm^{-3}, [I] = 0.25 mol dm^{-3} at three temperature (30°C, 35°C, 40°C). The rate of reaction increases with increasing concentration of palladium nanoparticles **[Table 6.1]**. The catalytic activity of palladium nanoparticles is shown by plotting a graph of k_{obs} versus palladium nanoparticles. The straight line indicated that the rate of reaction directly depends on concentration of palladium nanoparticles **[Fig.6.7]**. Results are given in **[Table 6.4].** So, it is evident that the uncatalysed oxidation of aspartic acid by NBS is also possible.

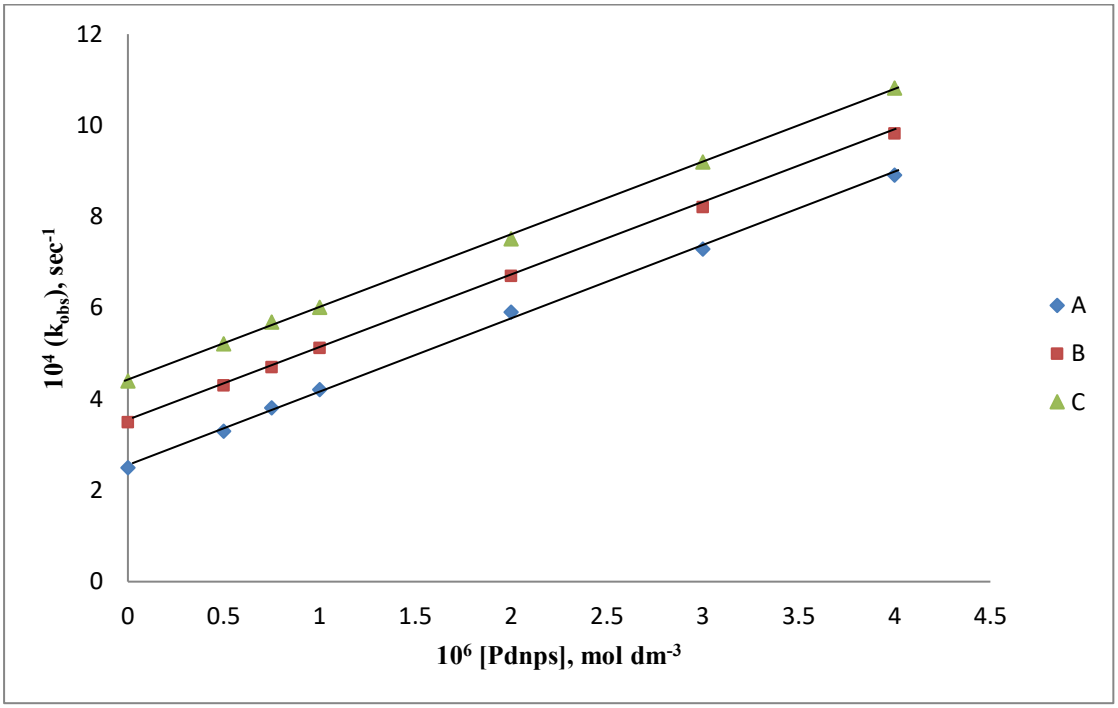


Figure 6.7: Variation of [Pdnps] at Different Temperature

Temp. = (A) 30°C (B) 35°C (C) 40°C

[NBS] = 2 ×10^{-3} mol dm^{-3} [Asp] = 2 × 10^{-2} mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

Table 6.4: Variation of Palladium nanoparticle

[NBS] = 2.0 × 10^{-3} mol dm^{-3} [$Na_2S_2O_3$] = 1.0 × 10^{-3} mol dm^{-3}

[Asp] = 2.0 × 10^{-2} mol dm^{-3} [I] = 0.25 mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} Temp. = 35 °C

10^6 [Pdnps], mol dm^{-3}	**0.5**	**0.75**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.9	8.7	8.5	8.4	7.9	7.4	7.0
10	7.9	7.5	7.2	7.2	6.2	5.7	5.0
15	6.9	6.1	6.3	6.3	5.0	4.2	3.4
20	6.0	5.7	5.5	5.4	3.8	3.1	2.5
25	5.2	4.9	4.6	4.5	3.0	2.4	1.7
30	4.5	4.2	4.0	3.9	2.4	1.8	1.2
40	3.4	3.1	3.0	2.8	(35) 1.8	(35) 1.4	(35) 0.9
60	2.0	1.8	1.6	1.5	(40) 1.4	(40) 1.0	(40) 0.6
80	1.2	1.0	0.9	0.8	(50) 0.9	(45) 0.7	(45) 0.5
10^4 k_{obs}(sec^{-1})	**4.30**	**4.70**	**5.12**	**6.70**	**8.21**	**9.82**	**11.40**

Figures in parenthesis denotes time in minutes.

6.3.8 Comparison of rate between Palladium Nanoparticles and Palladium(II) Species

The comparison of Pd nano particles and Pd (II) rates was studied by varying the concentration of palladium nanoparticles from 0.5 to 5 ×10^{-6} mol dm^{-3} and Palladium (II) from 0.5 to 5 ×10^{-5} mol dm^{-3} at fixed concentration of all reactants [NBS]= 2×10^{-3} mol dm^{-3}, [Aspartic acid] = 2 ×10^{-2} mol dm^{-3}, [H^+]= 0.10 mol dm^{-3}, [I] = 0.25 mol dm^{-3}

The results show that palladium nanoparticles catalyst exhibited better catalytic activity than palladium precursor **[Fig.6.8]**.

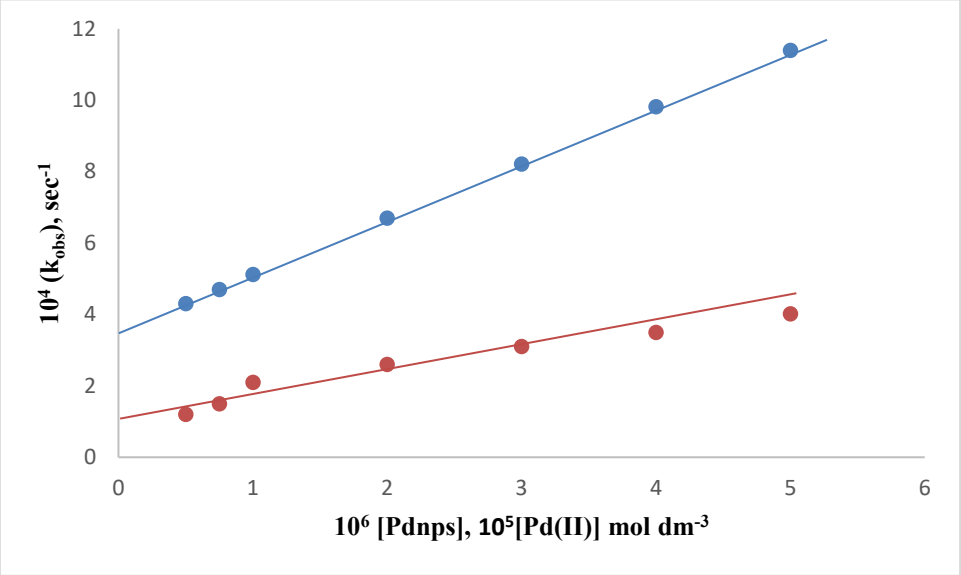


Figure 6.8: Comparison of [Pdnps] and [Pd (II)] catalytic activity

[NBS] = 2 ×10^{-3} mol dm^{-3} [Asp] = 2 ×10^{-2} mol dm^{-3} [H^{+}] = 0.10 mol dm^{-3}

[I] = 0.25 mol dm^{-3} [Pdnps] = Blue Pd (II) = Red

6.3.9 Effect of Temperature

The effect of temperature on the rate of reaction was studied at three temperature 30°C, 35°C, 40°C respectively keeping concentration of other reaction ingredients constant viz. [Asp] = 2.0 × 10^{-2} mol dm^{-3}, [NBS] =2.0 × 10^{-3} mol dm^{-3}, [Pdnps] = 2.0×10^{-6} mol dm^{-3}, [H^{+}] = 0.10 mol dm^{-3}, I = 0.25 mol dm^{-3}. The observed rate constants increased with an increase in temperature **[Table-6.4]**.

By applying Arrhenius equation, logk = logA –Ea/2.303RT, (2)

the logarithm of observed rate constant (k_{obs}, sec^{-1}) was plotted against 1/T in Kelvin^{-1} that yielded a straight line **[Fig.6.9]**. From the slope of the graph–Ea/2.303R, the energy of activation (E_a) for oxidation of aspartic acid by NBS was calculated to be 26.48 ± 2 kJ mol^{-1}. From the activation energy, various activation parameters were calculated **[Table -6.5].**

Table-6.5: Activation parameters of the reaction

[NBS] = 2 × 10^{-3} mol dm^{-3} [Asp] = 2 ×10^{-2} mol dm^{-3}

[Pdnps] = 2 × 10^{-6} mol dm^{-3} [H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

Temperature (K)	10^4 k_{obs} (sec^{-1})	E_a (KJ mol^{-1})	$\Delta H^{\neq}$ (KJmol^{-1})	$\Delta S^{\neq}$(J$K^{-1}$$mol^{-1}$)	$\Delta G^{\neq}$ (KJ mol^{-1})
303	5.91	26.48	23.92	-220.01	91.68
308	6.70				
313	7.51				

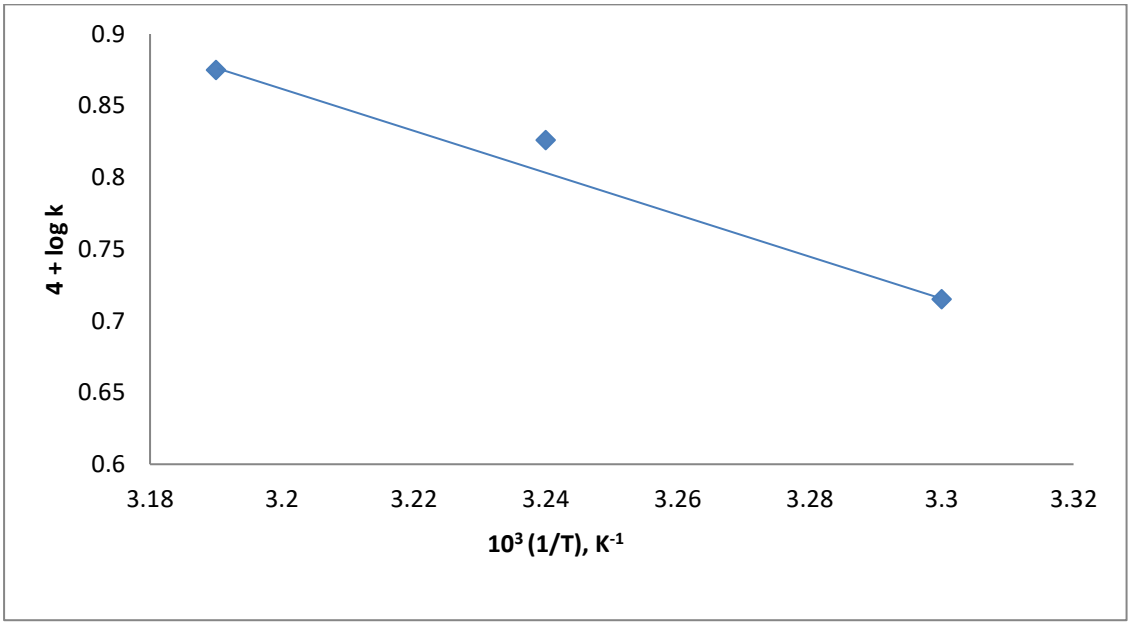


Figure 6.9: Variation of Temperature

[NBS] = 2 ×10^{-3} mol dm^{-3} [Asp] = 2 ×10^{-2} mol dm^{-3}

[Pdnps] = 2 ×10^{-6} mol dm^{-3} [H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

6.3.10 Effect of $[H^+]$

A change in the rate of the reaction with the change in the concentration of $[H^+]$ was observed in the present investigation at constant concentration of all other reactants. The rate constant k_{obs} decreased with the increase in $[H^+]$ concentration **[Fig.6.10].** The plot of log k_{obs} versus log $[H^+]$ is linear with a fractional slope. Results are given in **[Table 6.6]**.

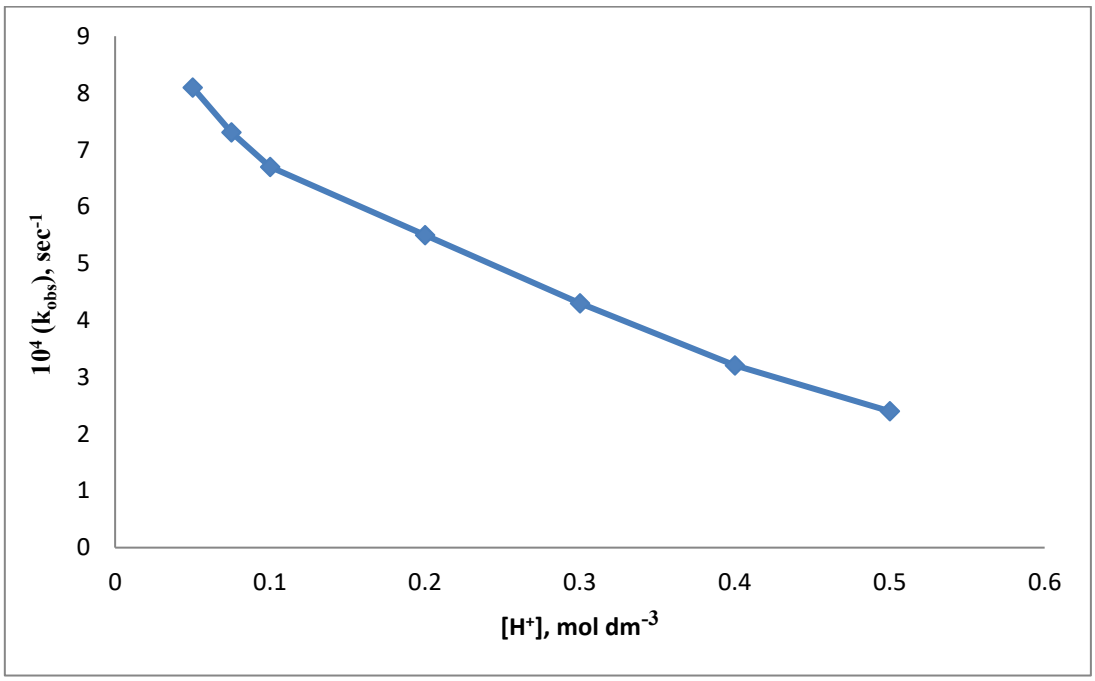


Figure 6.10: Variation of Hydrogen ion

[NBS] = 2 ×10^{-3} mol dm^{-3} [Asp] = 2 ×10^{-2} mol dm^{-3}

[Pdnps] = 2 ×10^{-6} mol dm^{-3} [I] = 0.25 mol dm^{-3} Temp.= 35°C

Table 6.6: Variation of $[H^+]$

[NBS] = 2.0×10^{-3} mol dm^{-3} **$[Na_2S_2O_3]$ = 1×10^{-3} mol dm^{-3}**

[Asp] = 2.0×10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pdnps] = 2.0×10^{-6} mol dm^{-3} **Temp. = 35 °C**

[H^+], mol dm^{-3}	**0.05**	**0.075**	**0.10**	**0.20**	**0.30**	**0.40**	**0.50**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	7.9	8.0	8.1	8.3	8.7	9.3	9.3
10	6.2	6.4	6.6	7.0	7.7	8.3	8.7
15	4.7	5.2	5.4	6.3	6.7	7.6	8.0
20	3.6	4.3	4.4	5.2	6.0	6.9	7.5
25	2.8	3.5	3.6	4.4	5.2	6.1	6.9
30	2.2	2.8	3.0	3.8	4.6	5.6	6.4
40	1.3	1.9	2.0	2.7	3.6	4.5	5.5
50	0.8	1.2	1.3	2.0	2.8	3.7	4.8
60	0.5	0.8	0.9	1.3	2.2	3.1	4.2
10^4 k_{obs}(sec^{-1})	**8.12**	**7.31**	**6.70**	**5.50**	**4.32**	**3.21**	**2.40**

6.3.11 Effect of Ionic strength

The variation of ionic strength on the reaction rate was studied using $NaClO_4$ (0.05 to 0.25 mol dm^{-3}) at fixed concentration of [NBS)]= 2.0×10^{-3} mol dm^{-3}, [Asp] = 2.0×10^{-2} mol dm^{-3}, $[H^+]$ = 0.1 mol dm^{-3} at 35°C. Ionic strength had no effect on the rate of reaction **[Fig.6.11].** Results are shown in **[Table 6.7].**

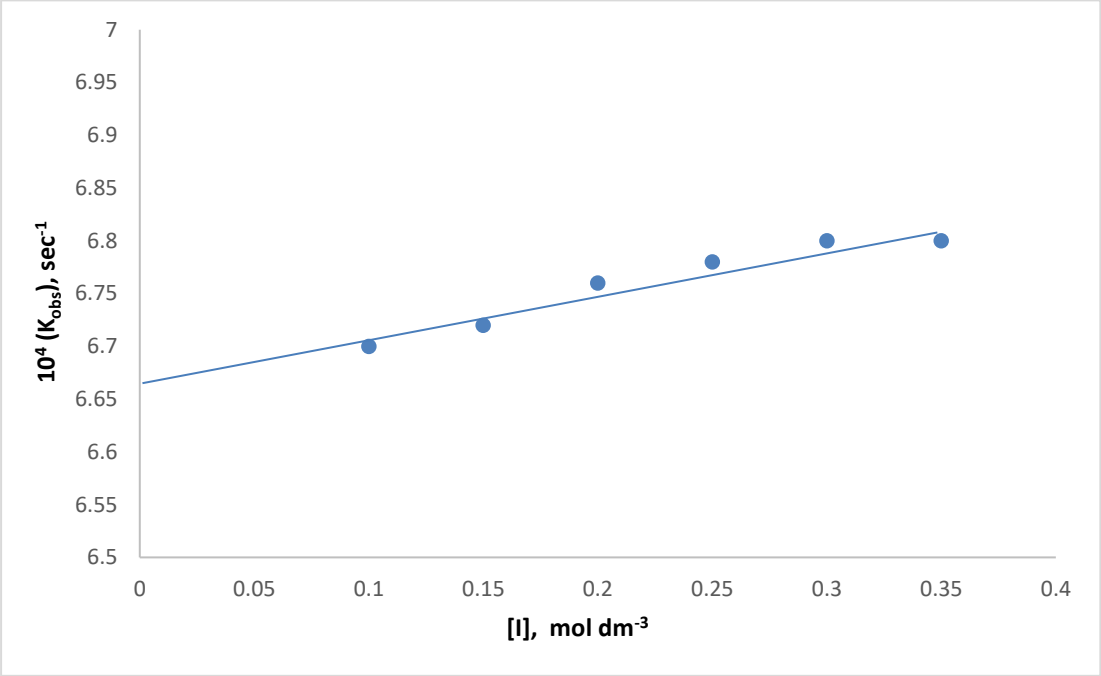


Figure 6.11: Variation of Ionic Strength

[NBS] = 2.0 x 10^{-3} mol dm^{-3} **[Asp] = 2.0 x 10^{-2} mol dm^{-3}**

$[H^+]$ = 0.10 mol dm^{-3} **Temp. = 35°C**

Table 6.7: Variation of Ionic Strength

[NBS] = 2.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[Asp] = 2.0×10^{-2} mol dm^{-3} **[H^+] = 0.10 mol dm^{-3}**

Temp. = 35°C **Aliquot = 5.0 ml**

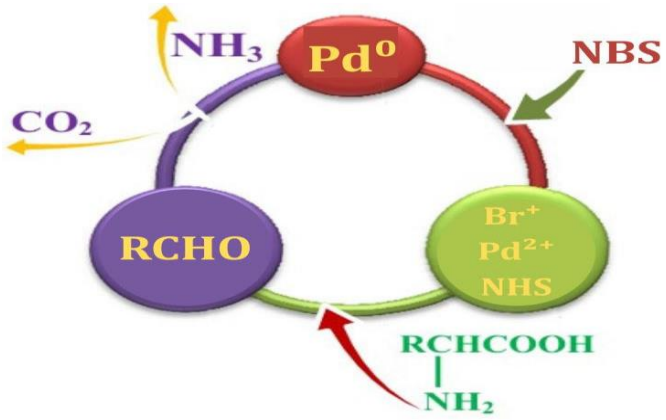
[I] , mol dm^{-3}	**0.10**	**0.15**	**0.20**	**0.25**	**0.30**	**0.35**
Time (minutes)	**Volume of the titrant (ml)**					
0	10.0	10.0	10.0	10.0	10.0	10.0
5	8.4	8.4	8.3	8.3	8.3	8.3
10	7.2	7.2	7.1	7.1	7.1	7.1
15	6.3	6.3	6.2	6.2	6.2	6.1
20	5.4	5.4	5.3	5.3	5.2	5.2
30	4.5	4.4	4.4	4.4	4.3	4.3
40	3.9	3.9	3.8	3.8	3.7	3.7
60	2.8	2.8	2.7	2.7	2.7	2.7
80	1.5	1.5	1.4	1.3	1.3	1.3
100	0.8	0.7	0.7	0.6	0.6	0.5
10^4 k_{obs}(sec^{-1})	**6.70**	**6.72**	**6.76**	**6.78**	**6.80**	**6.80**

6.3.12 Mechanism

Catalysis by metal nanoparticles can be regarded as a form of semi-heterogeneous or quasi-homogeneous catalysis, placed at the interface between homogeneous and heterogeneous catalytic processes [48]. We have used Palladium nanoparticles in solution medium which has advantage of high dispersion that leads to maximum surface accessibility and better interaction with NBS, and substrate compared to heterogeneous systems. [49]. Due to the high surface area and elevated surface energy, metal nanoparticles readily adsorb other molecules on their surfaces. Pd^0 nanoparticles act as

electron mediators, transferring electrons from the amino acid (reductant) to NBS (oxidant). This facilitates electron flow and lowers activation energy [50]. The remarkable increase in the rate of oxidation of amino acids by N-Bromosuccinimide (NBS) in the presence of palladium (Pd) nanocatalysts in homogeneous medium may be linked to various synergistic mechanistic effects. Firstly, Pd nanoparticles increase the activation of NBS by promoting the cleavage of the N–Br bond, rapidly producing reactive electrophilic bromine species (Br^+) that serve as the primary oxidants. Simultaneously, amino acids—due to their zwitterionic nature—readily coordinate to the Pd surface through their carboxylate or amino groups. This surface adsorption aligns the substrate optimally for oxidation, weakens adjacent C–H or N–H bonds through coordination, facilitating H-abstraction or electron transfer.

The system effectively works as a dual-component oxidative relay: with Pd acting as an electron-transfer mediator and structural activator, while NBS functions as the terminal oxidant **[Scheme 1].** The deamination of the amino group in aspartic acid to NH_3 occurs in the presence of palladium nanoparticles by NBS yielding aldehyde (2-Formylacetic acid) while NBS changes to succinimide.



Step 1: Activation of NBS by Pdnp

Pd^0 (on nanoparticle surface) + NBS → $[Br^+]$ + Succinimide

active oxidant

Step 2: Substrate Binding

Aspartic acid (COOH CH_2–$CH(NH_2)$–COOH) adsorbs onto Pdnp surface

→ through NH_2 lone pair coordination

Step 3: Oxidation of Aspartic acid

Br^+ attacks α-carbon or functional group of amino acid → forms oxidized intermediate (imine)

Pd^{2+} accepts electrons from aspartic acid → Pd^0 regenerated

Step 4: Product Release and Catalyst regeneration

Oxidized amino acid, 2-Formylacetic acid ($COOH\text{-}CH_2\text{-}CHO$) released from Pd surface and Pd^0 surface restored

Net Reaction:

$$COOH\ CH_2\text{–}CH(NH_2)\text{–}COOH + NBS + Pdnps \rightarrow COOH\text{-}CH_2\text{-}CHO + Succinimide + NH_3 + CO_2 + Pdnps\ (Recycled)$$

Scheme 1

6.4 CONCLUSION

Pd nanoparticles were successfully synthesized by the reduction of H_2PdCl_4 using ethanol as a reductant in the presence of PVP polymer. It was seen that the parameters of the supply rate of the precursor, temperature and time of synthesis reactions have been employed to make Pd nanoparticles by the chemical reduction method. In addition, the homogeneity of the solvent for the preparation of the stock solutions to synthesize and control the size and morphology of the Pd nanoparticles is very important in our preparation method. The catalytic activity of palladium nanoparticles was investigated through the oxidation of aspartic acid in aqueous acidic medium that drastically reduces the activation energy of the reaction and explains and the observed catalytic acceleration. The results of the study indicate first order dependence with respect to NBS and palladium nanoparticle and fractional order with respect to aspartic acid. Comparing the rates of Pdnp and Pd (II), we find the reactions proceed at a much faster rate with Pdnp than Pd (II). The study will be helpful for biochemical labeling or studying oxidative stress effects.

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CHAPTER 7

PALLADIUM NANOPARTICLES SYNTHESIS AND THEIR CATALYTIC APPLICATION ON OXIDATION OF ARGININE IN AQUEOUS ACIDIC MEDIUM

ABSTRACT

The paper describes the preparation of Palladium nanoparticle (Pdnp) through chemical reduction method using palladium chloride ($PdCl_2$) and stabilizer PVP (Poly vinyl pyrrolidone). Characterization of the palladium nanoparticle was done by UV-VIS Spectrometer and TEM. The range of the particle size was from 1 to 100 nm. Palladium nanoparticles of various shapes and sizes have been obtained by reduction in ethanol with HCl catalyst addition. The synthesized palladium nanoparticles are used as a catalyst for the oxidation of basic amino acid, Arginine by N-Bromosuccinimide in aqueous medium. The reaction shows first order kinetics with respect to NBS and fractional with respect to arginine. The rate increases with the increase in Pdnps and retarding effect of perchloric acid was observed. Various activation parameters have been calculated and on the basis of these parameters, a suitable explanation of the reaction mechanism has been given.

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7.1 INTRODUCTION

Nanoparticles prepared from noble metal have valuable importance due their distinctive physical–chemical properties such as catalytic, electronic, magnetic and optical properties and uses in the different fields of catalysts, medicine, electronics, chemical synthesis, fuel cell and oil refining processes. The size, shape and size distribution of metal nanoparticles constitute the major role. So concentration is focused on the preparation of noble metal nanoparticles with well-controlled morphology [1-6]. Compared to PGM (Platinum group metals), Palladium is attractive because of its lower cost and high activity towards oxygen reduction reactions [7]. Palladium (Pd) is interesting material for research due to its hydrogen storage preparation [8] .

The role of nanoparticles has increased in the fields of chemical, nanotechnology and physics. Their properties are different when compared with those of bulk metals. Both homogenous and heterogenous catalysis have grown during the last many years. The major property that makes it very efficient is the excess surface to volume ratio.

Many studies about the Pd catalysed oxidation of amino acid have been reported [9-11] but with the development of metal nanoparticles having high stability, their use as catalyst for biochemical reactions are well documented in recent years [12-14].

Palladium nanoparticles can be prepared through different method such as ion exchange/ adsorbtion [15], microwave plasma [16], sonochemical reduction [17], sol–gel process [18] etc. All these methods are complex and costly, so metal nanoparticles can be made by simply loading some liquid polymeric matrices.

Amino acids are the building blocks of essential biomolecules such as proteins, hormones, enzymes [19-20] etc. Amino acids are basically derived from proteins in diet or degradation in intracellular proteins. They lose their amino group through transamination or oxidative deamination. L-Arginine plays an important role in metabolism of any organism as it is precursor for synthesis of protein and other important biological molecules. For young organisms, it should be provided for optimal growth and proper development. For adults it is essential in case of trauma, burn injury and renal failure. L-Arginine improves immune and digestive functions and plays a crucial role in carcinogenesis and tumour growth.

In this manuscript, we present a one–step polyol method for synthesis of Pd monodispersed and good-shaped nanoparticles using ethanol as reducing agent and

PVP (Poly vinyl pyrrolidone) as the capping agent and their application on the oxidation of amino acid Arginine by N- Bromosuccinimide in aqueous medium.

7.2 EXPERIMENTAL

7.2.1 Materials

Palladium (II) chloride **(**$PdCl_2$ 99.9%) were purchased from Johnson Matthey and PVP (Poly vinyl pyrrolidone), Mw- 400000 used as stabilizer. NBS (E. Merck), Arginine (E. Merck) and ethanol were of AR grade used as solvent and reducing agent and was used as received without further purification. All glassware was cleaned using aqua regia, subsequently rinsed with double distilled water and dried before use. Fresh solutions of NBS, KI, Hypo and Starch were prepared before the experimental set up. For Palladium nanoparticles synthesis, chemical reduction method was used.

7.2.2 Synthesis of Palladium nanoparticle

Typically, 0.0887 gm of $PdCl_2$, 6 ml of 0.2 M HCl and 250 ml of distilled water were mixed to get 2mM concentration of H_2PdCl_4 solution. Then 15 ml of 2mM H_2PdCl_4, 21 ml of doubly deionized water, 0.0667 gm of PVP and 4 drops of 1 M HCL were mixed in a reflux condenser assembly. As the solution begins to reflux, add 14 ml of ethanol. Reflux the solution for 3 hours which results in a dark brown solution, so H_2PdCl_4 reduction occurs by ethanol which acts as solvent and reducing agent both.

7.2.3 UV-Visible spectrum of palladium nanoparticles and TEM Analysis

UV-Visible spectral analyses were carried out on a double beam spectrophotometer-2203(Systronics). The formation of Pdnps was monitored in 220-600 nm range. The reaction mixture changes gradually from pale yellow to dark brown due to surface plasmon vibrations. **[Fig.7.1]** shows the absorption peaks at 310 and 410 nm that attribute to $[PdCl_4]^{2-}$, while the peak at 256 nm and 315 nm corresponds to PVP-stabilised Pd NPs using ethanol as reductant. This is ascribed to ligand (Cl^-) → metal (Pd^{+2}) charge transfer transition of Pd (II) ions [21-22]. The disappearance of the absorption peak after 15 minutes is due to the complete reduction of metal ions (Pd^{+2}). The colour intensity of the reaction mixture changes leading to an increase in the absorbance of the solution.

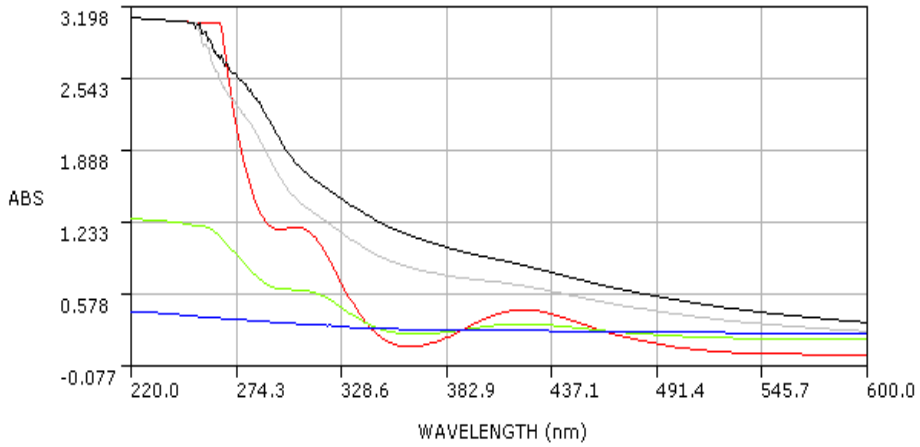


Figure 7.1: UV–vis spectra of PVP-protected Pd NPs in the range 220–600 nm

The morphological study of the palladium nano particle was carried out with scanning of Transmission electron microscope by employing JEOL-JEM-2010XII TEM at 200 kV. TEM images were recorded to confirm the size and shape of newly synthesized palladium nanoparticles.

7.2.4 The influence of precursor concentration and metal/ PVP ratio.

At a given temperature, the size of the palladium nanoparticles (Pd np) can be arranged optimally by changing the H_2PdCl_4 concentration from 1 to 4 mM. Similarly, the PVP amount added was changed from 1: 5 (metal / PVP) to 1:20. So the size of nanoparticles could be changed by changing the metal precursor concentration and PVP/ metal ratio. PVP acts as an efficient stabilizer and protecting agent which prevents the aggregation of particles. The optical precursor concentration taken was 2mM and PVP / metal ratio 1:10.

PVP also helps in the reduction of metal in ethanol speeding up the rate of particle formation. PVP and Palladium nanoparticles (Pd np) complexes by coordinate bond between N and O atoms of PVP and surface sites of Palladium nanoparticle (Pdnp) which causes reduction in the free metal nanoparticles concentration decreasing the electrode reduction potential of Pd ion and then increased the rate of reduction of metal ions during process of the growth of particle [23]. The increase in concentration of PVP minimizes the diffusion of Palladium nanoparticles leading to aggregation, ie increasing the Pdnp size.

According to spectroscopic studies, PVP–Pd interaction occurs through the carbonyl group of the pyrrolidone ring. In our synthesis process, Pd NPs in the size range 1–100 nm in diameter have been obtained from aqueous solutions of $PdCl_2$ in the presence of PVP. The major outcome is that most of the large sized Pd NPs with spherical, tetrahedral, octahedral twinned decahedral icosahedral and cubic shapes have been found due to the aggregation of the smaller seeds of spherical Pd NPs that are proved. Noble metals have a face-centred cubic (fcc) lattice with different surface energies for different crystal planes, such as the combinations of the low-index and/or high-index {1 1 1, 1 0 0} and {1 1 0} planes [24-26].

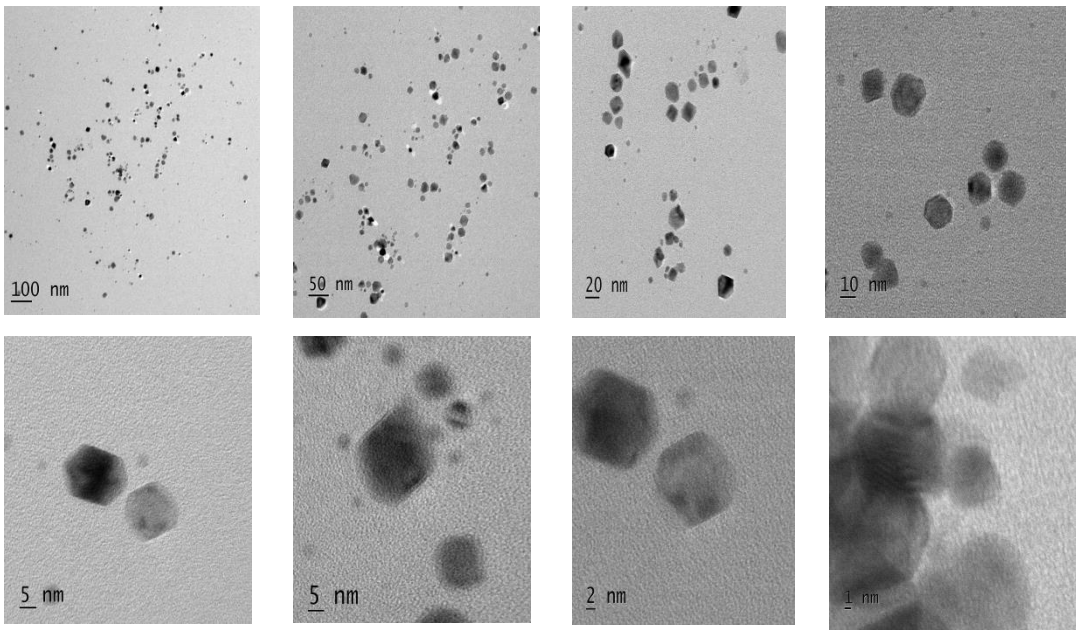


Figure 7.2: TEM images of major shapes and various sizes of Pd nanoparticles. TEM images of Pd nanoparticles with scale bars: (a) 100 nm (b) 50 nm (c) 20 nm (d) 10 nm (e, f) 5 nm (g) 2 nm and (h) 1 nm

7.2.5 Kinetic Measurements

Appropriate amount of Arginine in acidic form, mercuric acetate, $NaClO_4$ (Ionic Strength), Pdnp and water (to keep the volume constant) were taken in the Erlenmeyer flask. Mercuric acetate [$Hg(OAc)_2$] acts as a bromide ion scavenger. The temperature was maintained at 35°C by circulating thermostated water bath. NBS solution kept in the thermostat separately was added to start the reaction. The progress of the solution was monitored by iodometric determination of the unreacted NBS in a measured weight

of the reaction mixture at different intervals of time [27]. The rate constants were computed from the linear plots of log [NBS] against time. The order of reaction with respect to any reactant can be obtained from a plot of log k_{obs} versus log [Reactant] utilizing the following equation: log k_{obs} = log k + m log [Reactant]. The plot exhibits a straight line with positive slope which represents the order of reaction.

7.2.6 Stoichiometry of the reaction

Different sets of reaction mixtures containing amino acid (arginine) and an excess of NBS were left to stand for 48 hours at 308K. After completion of reaction, it showed that one mole of amino acid (arginine) consumes two moles of NBS as shown in stoichiometry **(Eqn.1)** given below. The oxidation reaction product was identified by qualitative test. Ammonia was identified by Nessler's reagent and carbon dioxide was qualitatively detected by passing the gas into lime water.

$$RCH(NH_2)COOH + 2NBS + H_2O \xrightarrow{Pd(II)/H^+} RCHO + 2NHS + CO_2 + Br_2 + NH_3 \quad (1)$$

R= $-CH_2-$ CH_2- CH_2-NH-C (NH_2) =NH

7.3 RESULTS AND DISCUSSION

7.3.1 Effect of NBS concentration

The concentration of NBS varied from 1×10^{-3} to 5×10^{-3} mol dm^{-3} at fixed concentration of [Arginine] = 3×10^{-2} mol dm^{-3}, [Pdnps] = 3×10^{-6} mol dm^{-3}, $[H^+]$ = 0.10 mol dm^{-3}, [I] = 0.25 mol dm^{-3} and temperature 35°C. Pseudo first order rate constants (k_{obs}) were calculated from the slope of log (a-x) versus time plots and were found to be independent of initial concentration of NBS indicating first order w.r.t NBS **[Fig. 7.3, Table -7.1].** Results are given in **[Table 7.2].**

Table-7.1: Effect of [NBS], [Arg], [Pdnps] and [H^+] on oxidation of Arginine by [NBS] in perchloric acid medium in the presence of Pd nano catalyst at 35°C

10^3[NBS] mol dm^{-3}	10^2[Arginine] mol dm^{-3}	10^6[Pdnp] mol dm^{-3}	[H^+] mol dm^{-3}	10^4 (k_{obs}) sec^{-1}
1.0	3.0	3.0	0.1	5.17
2.0	3.0	3.0	0.1	5.12
3.0	3.0	3.0	0.1	5.10
4.0	3.0	3.0	0.1	5.16
5.0	3.0	3.0	0.1	5.13
3.0	1.0	3.0	0.1	2.20
3.0	2.0	3.0	0.1	3.40
3.0	3.0	3.0	0.1	5.10
3.0	4.0	3.0	0.1	6.30
3.0	5.0	3.0	0.1	7.60
3.0	6.0	3.0	0.1	7.85
3.0	7.0	3.0	0.1	7.95
3.0	3.0	1.0	0.1	1.67
3.0	3.0	2.0	0.1	3.24
3.0	3.0	3.0	0.1	5.10
3.0	3.0	4.0	0.1	6.25
3.0	3.0	5.0	0.1	7.78
3.0	3.0	6.0	0.1	9.63
3.0	3.0	7.0	0.1	11.58
3.0	3.0	3.0	0.1	5.10
3.0	3.0	3.0	0.2	3.59
3.0	3.0	3.0	0.3	2.78
3.0	3.0	3.0	0.4	2.26
3.0	3.0	3.0	0.5	1.97

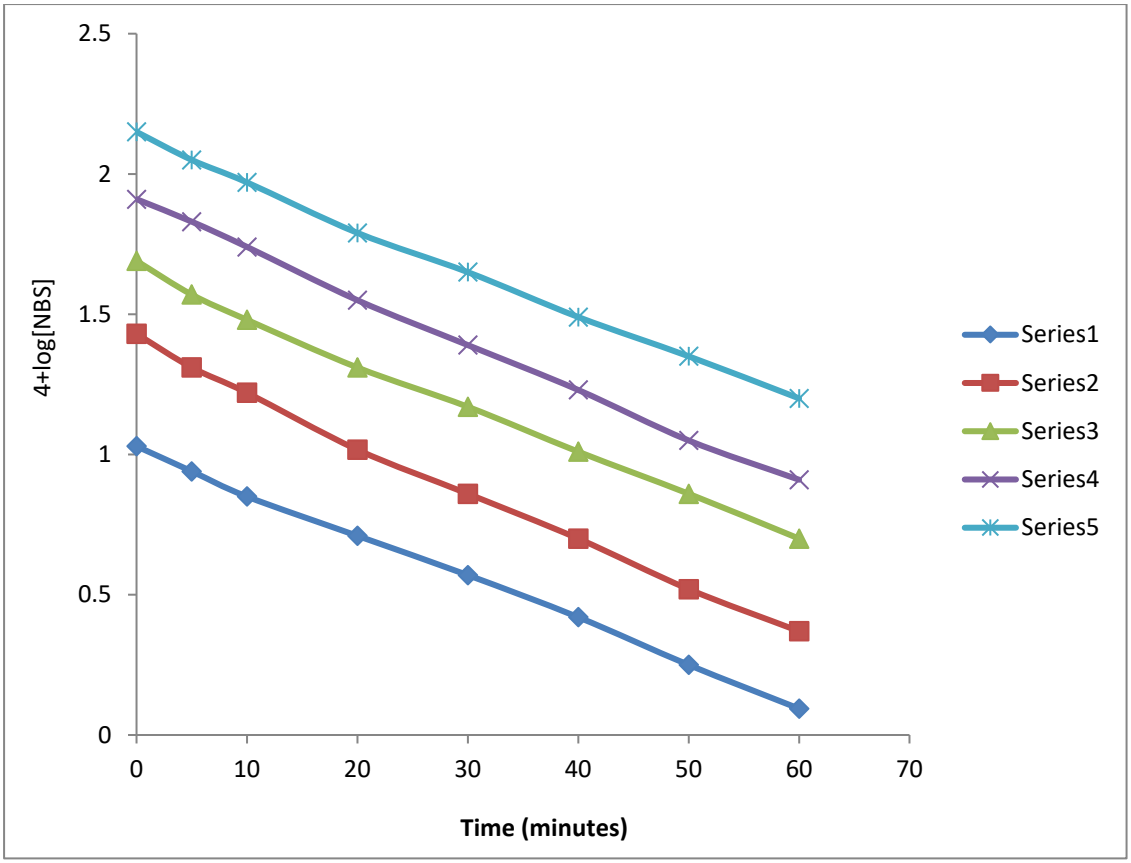


Figure 7.3: Variation of NBS

[NBS] = (1) 1 ×10^{-3} mol dm^{-3} (2) 2 ×10^{-3} mol dm^{-3}

(3) 3 ×10^{-3} mol dm^{-3} (4) 4 ×10^{-3} mol dm^{-3}

(5) 5 ×10^{-3} mol dm^{-3}

[Arg] = 3 ×10^{-2} mol dm^{-3} [Pdnps] = 3×10^{-6} mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3} Temp. = 35°C.

Table 7.2: Variation of NBS

[Pdnps] = 3.0×10^{-6} mol dm^{-3} [$Na_2S_2O_3$] = 2×10^{-3} mol dm^{-3}

[Arg] = 3.0×10^{-2} mol dm^{-3} [I] = 0.25 mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} Temp. = 35°C Aliquot = 5.0 ml

10^3 [NBS], mol dm^{-3}	1.0*	2.0**	3.0	4.0	5.0
Time (minutes)	**Volume of the titrant (ml)**				
0	16.7	10.0	7.5	10.0	12.5
5	14.1	8.3	6.7	8.7	10.7
10	12.1	7.2	5.7	7.4	9.3
15	10.3	6.1	4.9	6.3	7.9
20	8.7	5.4	4.2	5.5	6.7
30	6.5	3.9	3.1	4.1	5.0
40	4.8	2.9	2.4	3.0	3.6
60	2.6	1.6	1.3	1.6	2.0
80	1.4	0.9	0.7	0.9	1.1
100	0.8	0.5	0.4	0.5	0.6
10^4 k_{obs}(sec^{-1})	**5.17**	**5.12**	**5.10**	**5.16**	**5.13**

[$Na_2S_2O_3$] * = 3.0×10^{-4} mol dm^{-3}

[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

7.3.2 Effect of Pd nano catalyst

The concentration of Pd nano catalyst varied from 1×10^{-6} to 7×10^{-6} mol dm^{-3} at fixed concentration of all reactants [NBS] = 3×10^{-3} mol dm^{-3}, [Arginine] = 3×10^{-2} mol dm^{-3}, $[H^+]$ = 0.10 mol dm^{-3} and, [I] = 0.25 mol dm^{-3} at 35°C. A plot of concentration of Pd nano catalyst versus rate constant shows the catalytic activity of palladium nano catalyst. The straight line indicated that the rate of reaction directly depends on concentration of palladium nanoparticles [**Fig.7.4]**. The straight line does not pass through the origin, so it is evident that the uncatalyzed oxidation of arginine by NBS is also possible. The plot of log k_{obs} versus log [Pdnps] is linear with a slope of .81 **[Fig.7.5]**. Results are given in **[Table 7.3].**

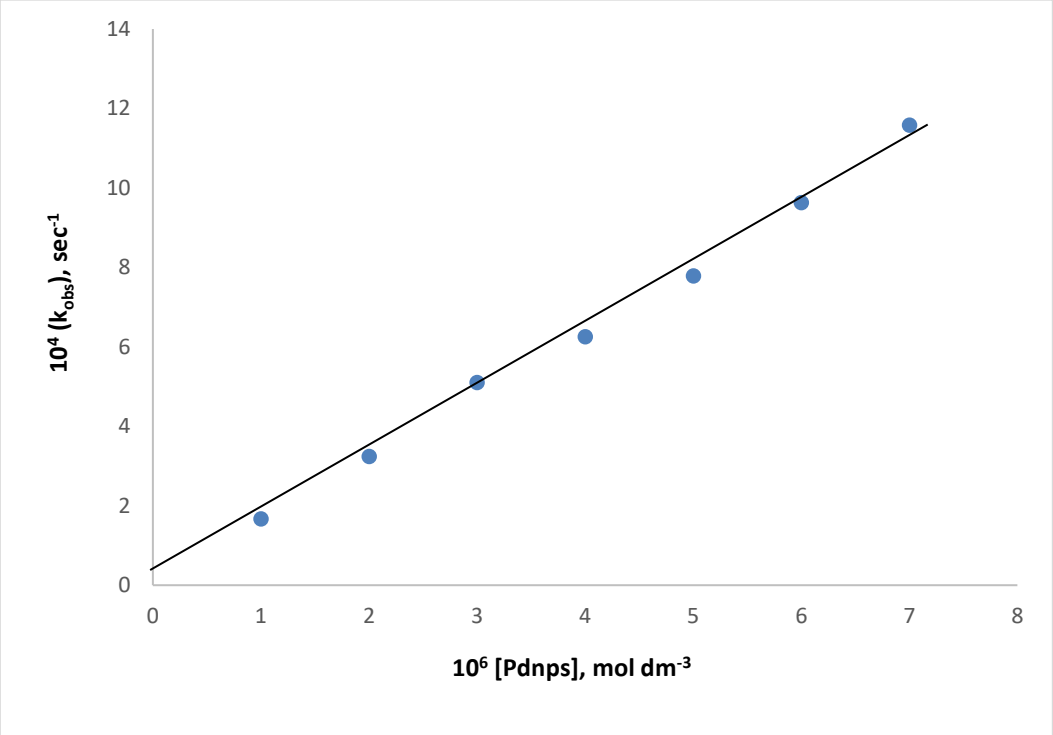


Figure 7.4: Variation of [Pdnps]

[NBS] = 3×10^{-3} mol dm^{-3} [Arg] = 3×10^{-2} mol dm^{-3}

$[H^+]$ = 0.10 mol dm^{-3} [I]= 0.25 mol dm^{-3} Temp. = 35°C

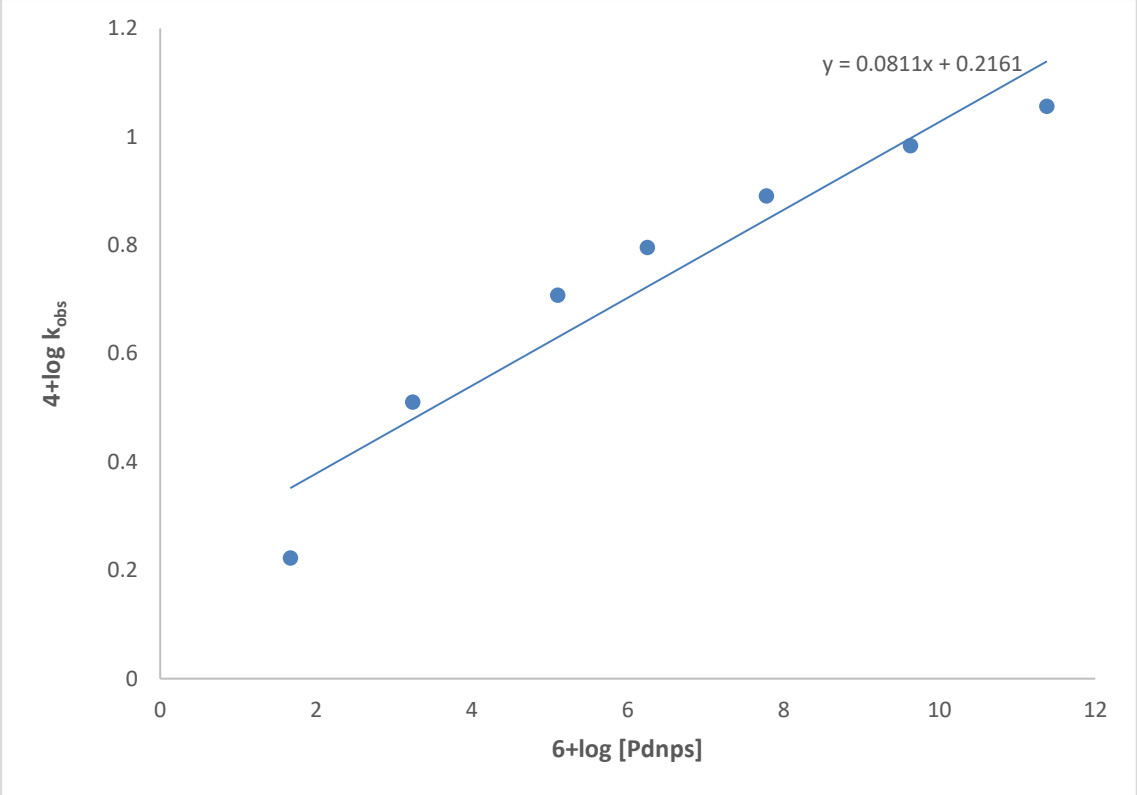


Figure 7.5: A plot to find out the order of the reaction with respect to Palladium nanoparticles concentration at 35°C.

Table 7.3: Variation of Palladium Nanoparticle (Pdnp)

[NBS] = 3.0×10^{-3} mol dm^{-3} [$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}

[H^+] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

[Arg] = 3.0×10^{-2} mol dm^{-3} Temp. = 35 °C Aliquot = 5.0 ml

10^6 [Pdnps], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.5	9.1	8.5	8.3	7.9	7.6	6.3
10	9.1	8.3	7.4	6.9	6.3	5.6	5.1
15	8.5	7.6	6.3	6.0	5.1	4.3	3.5
20	8.1	6.7	5.6	4.8	4.2	3.1	2.6
30	7.4	5.6	4.2	3.4	2.7	1.8	1.6
40	6.6	4.6	3.2	2.3	1.8	1.0	(35) 1.2
60	5.6	3.1	1.8	1.2	(45) 1.4	(45) 0.8	(40) 0.8
80	4.4	2.1	1.1	0.5	(50) 1.2	(50) 0.4	(45) 0.6
100	3.7	1.4	0.6	0.3	(60) 0.8	(55) 0.3	(50) 0.4
10^4 k_{obs}(sec^{-1})	**1.67**	**3.24**	**5.10**	**6.25**	**7.78**	**9.63**	**11.58**

Figures in parenthesis denotes time in minutes.

7.3.3 Rate comparison between Palladium Nanoparticles and Palladium (II) Species

The comparison of Pd nanoparticles and Pd (II) rates was studied by varying the concentration of palladium nanoparticles from 0.5 to 5 $\times 10^{-6}$ mol dm^{-3} and Palladium (II) from 0.5 to 5 $\times 10^{-5}$ mol dm^{-3} at fixed concentration of all reactants [NBS] = 3 $\times 10^{-3}$ mol dm^{-3}, [Arginine] = 3 $\times 10^{-2}$ mol dm^{-3}, $[H^+]$= 0.10 mol dm^{-3}, [I] = 0.25 mol dm^{-3}. The results show that palladium nanoparticles catalyst exhibited better catalytic activity than palladium precursor **[Fig.7.6]**.

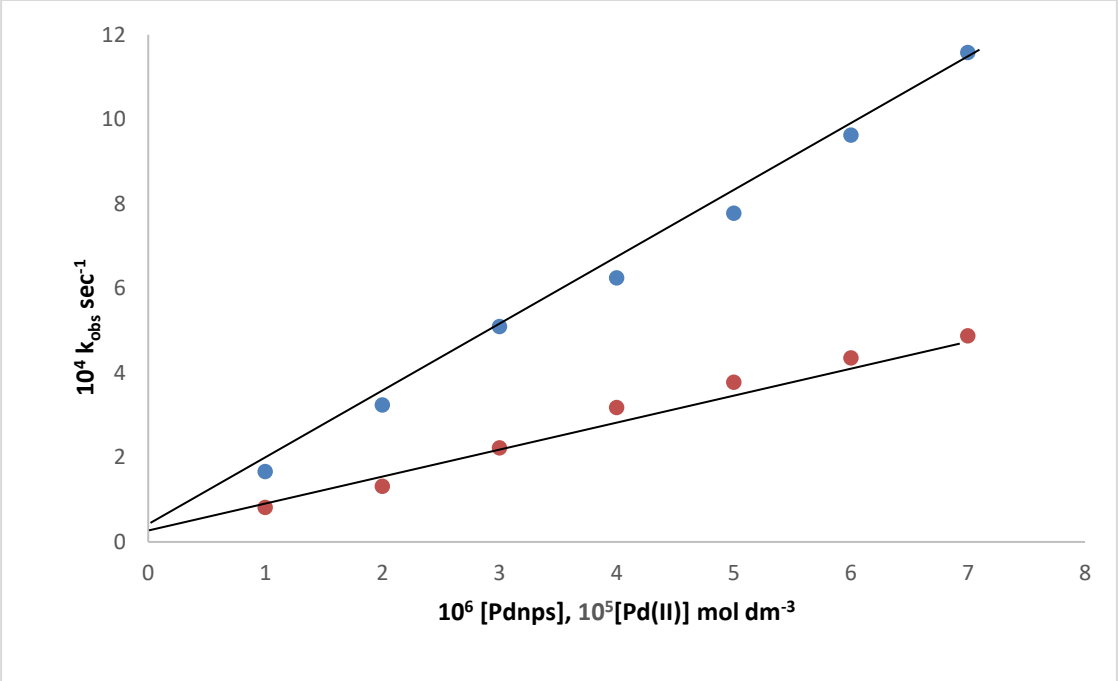


Figure 7.6: Comparison of [Pdnps] and [Pd (II)] on reaction rate

[NBS] = 3 $\times 10^{-3}$ mol dm^{-3} [Arg] = 3$\times 10^{-2}$ mol dm^{-3} $[H^+]$ = 0.10 mol dm^{-3}
[I]= 0.25 mol dm^{-3} Temp. = 35°C [Pdnps] – Blue [Pd (II)] - Red

7.3.4 Effect of $[H^+]$

Hydrogen ion concentration was varied from 0.1 to 0.5 mol dm^{-3} at fixed concentration of all other reactants. The rate constant k_{obs} decreased with the increase in $[H^+]$ concentration **[Fig.7.7].** The plot of log k_{obs} versus log $[H^+]$ is linear with a fractional slope **[Fig.7.8]**. Results are given in **[Table 7.4].**

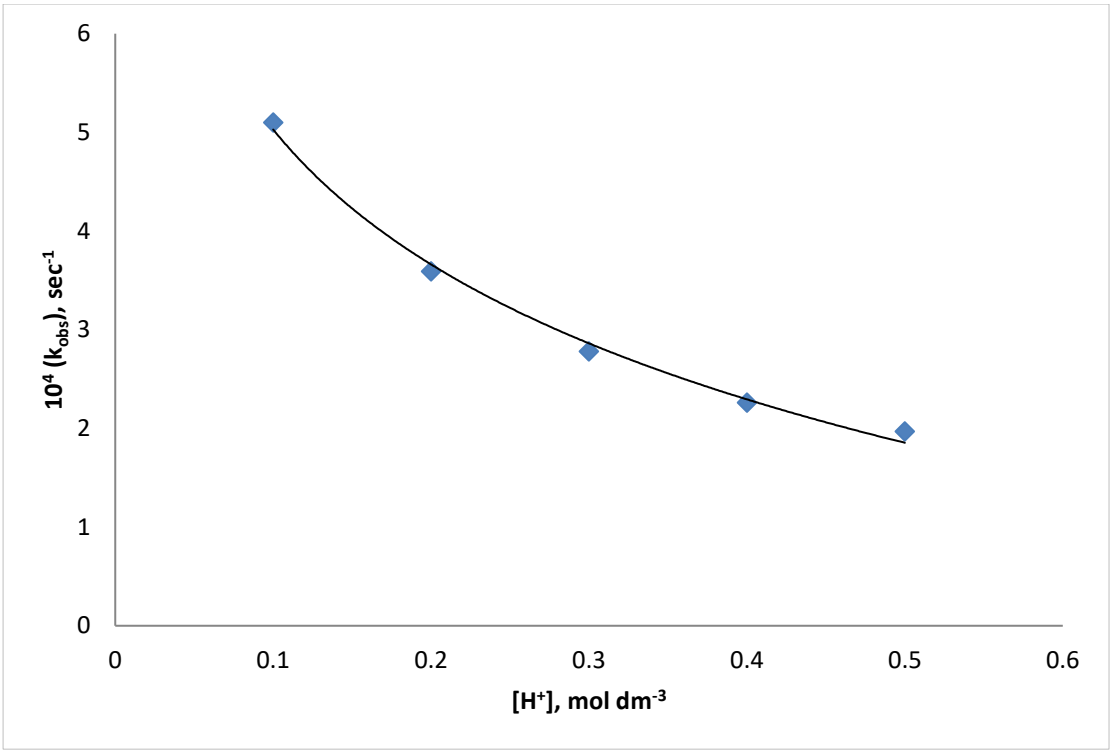


Figure 7.7: Variation of Hydrogen ion

[NBS] = 3 ×10^{-3} mol dm^{-3} [Arg] = 3 ×10^{-2} mol dm^{-3}

[Pdnps] = 3 ×10^{-6} mol dm^{-3} [I]= 0.25 mol dm^{-3} Temp. = 35°C.

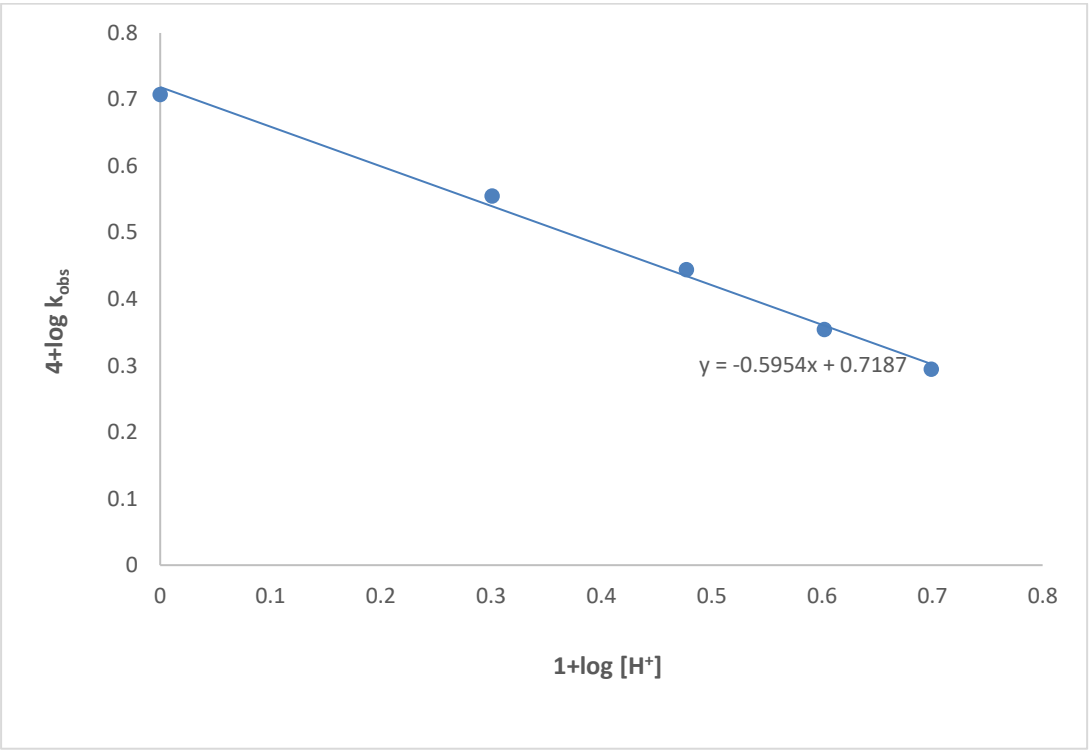


Figure 7.8: A plot to find out the order of the reaction with respect to Hydrogen ion concentration at 35°C.

Table 7.4: Variation of $[H^+]$

[NBS] = 3.0×10^{-3} mol dm^{-3} **[$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}**

[Arg] = 3.0×10^{-2} mol dm^{-3} **[I] = 0.25 mol dm^{-3}**

[Pdnp] = 3.0×10^{-6}mol dm^{-3} **Temp. = 35°C** **Aliquot = 5.0 ml**

$[H^+]$, mol dm^{-3}	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**
Time (minutes)	**Volume of the titrant (ml)**				
0	10.0	10.0	10.0	10.0	10.0
5	8.5	8.7	8.9	9.1	9.3
10	7.4	8.1	8.3	8.5	8.7
15	6.3	7.4	7.5	7.7	8.3
20	5.6	6.6	6.9	7.2	7.7
30	4.2	5.4	5.6	6.0	6.9
40	3.2	4.3	4.7	5.1	6.1
60	1.8	2.8	3.1	3.6	4.9
80	1.1	1.8	2.1	2.6	3.9
100	0.6	1.2	1.4	1.9	3.0
10^4 k_{obs}(sec^{-1})	**5.10**	**3.59**	**2.78**	**2.26**	**1.97**

7.3.5 Effect of Arginine

The concentration of arginine was altered from 1×10^{-3} to 7×10^{-3} mol dm^{-3} at constant [NBS], $[H^+]$, [Pdnps] and temperature. The kinetic runs were carried out with initial concentration of arginine. A plot of k_{obs} versus [Arginine] shows first order dependence of the reaction on arginine at low concentration, which shifts towards zero order at its higher concentration **[Fig.7.9].** The plot of log k_{obs} versus log [Arginine] was straight line with fractional slope confirming fractional order with respect to arginine **[Fig.7.10].**. Results are given in **[Table 7.5].**

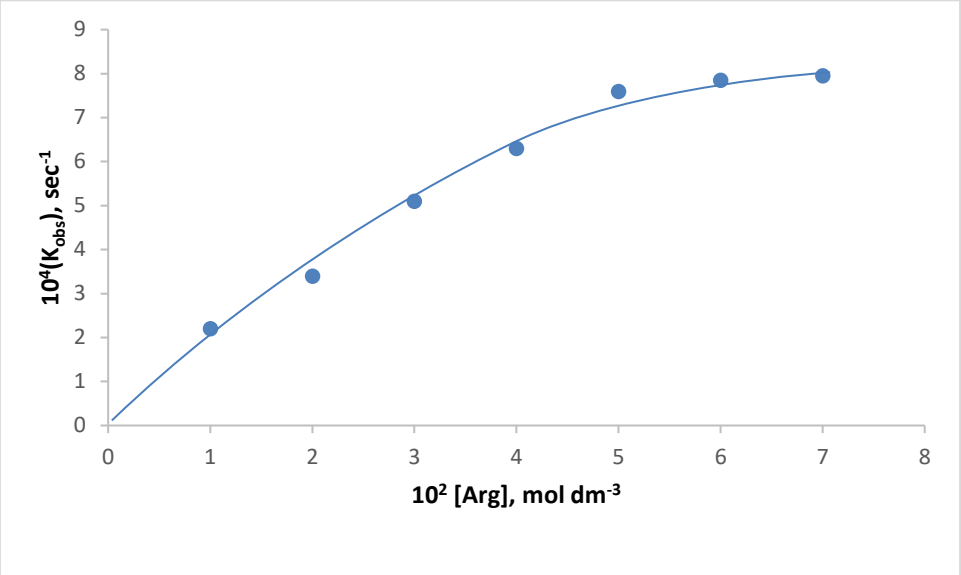


Figure 7.9: Variation of Arginine

[NBS] = 3 ×10^{-3} mol dm^{-3} [Pdnps] = 3 ×10^{-6} mol dm^{-3}

[H^+] =0.10 mol dm^{-3} [I]= 0.25 mol dm^{-3} Temp. = 35°C

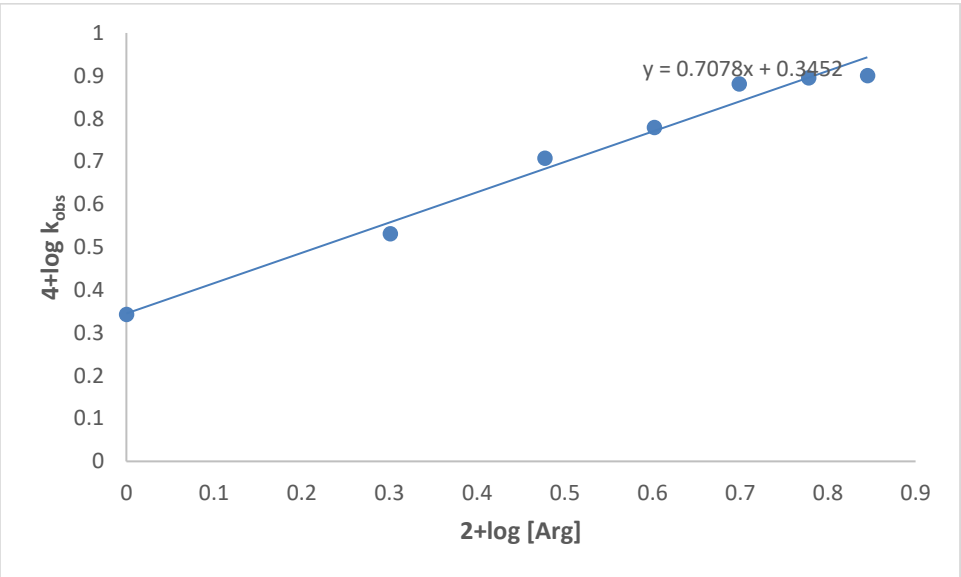


Figure 7.10: A plot to find out the order of the reaction with respect to Arginine concentration at 35°C.

Table 7.5: Variation of Arginine

[NBS] = 3.0×10^{-3} mol dm^{-3} [$Na_2S_2O_3$] = 1.0×10^{-3} mol dm^{-3}

[H^+] = 0.10mol dm^{-3} [I] = 0.25 mol dm^{-3}

[Pdnp] = 3.0×10^{-6} mol dm^{-3} Temp. = 35°C Aliquot = 5.0 ml

10^2 [Arg], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
Time (minutes)	**Volume of the titrant (ml)**						
0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5	9.3	9.1	8.5	8.3	8.1	7.7	7.6
10	8.7	8.1	7.4	6.7	6.6	6.1	6.0
15	8.1	7.4	6.3	5.7	5.2	4.9	4.7
20	7.6	6.6	5.6	4.8	4.2	3.9	3.6
30	6.6	5.5	4.2	3.3	2.8	2.4	2.2
40	5.9	4.3	3.2	2.3	1.8	1.4	1.3
60	4.4	2.9	1.8	1.1	0.8	0.6	0.5
80	3.4	1.9	1.1	0.6	(75) 0.4	(65) 0.4	0.3
100	2.6	1.3	0.6	(95) 0.3	(80) 0.4	(70) 0.3	(70) 0.2
10^4 k_{obs}(sec^{-1})	**2.20**	**3.40**	**5.10**	**6.30**	**7.60**	**7.85**	**7.95**

Figures in parenthesis denotes time in minutes.

7.3.6 Effect of Temperature

The temperature variation on the reaction rate was studied at three temperature 30°C, 35°C, 40°C respectively at constant concentration of other reactants viz. [NBS] = 3.0×10^{-3} mol dm^{-3}, [Arg] = 3×10^{-2} mol dm^{-3}, [Pdnp] = 3×10^{-6} mol dm^{-3}, [H^+] = 0.10 mol dm^{-3}, I = 0.25 mol dm^{-3}. From the linear Arrhenius plot of log k_{obs} vs 1/T **[Fig.7.11],** various activation parameters viz. energy of activation (E_a)**,** enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) for the composite reaction were calculated by the following formulae **(Eqn. 2-4) [Table 7.6].**

$\Delta H^{\neq} = Ea - RT$ (2)

$\ln A = \ln kT/h + \ln \Delta S^{\neq}/R$ (3)

$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ (4)

Where:

k: Boltzmann constant

h: Planck constant

Table 7.6: Activation parameters of the reaction

[NBS] = 3 ×10^{-3} mol dm^{-3} [Arg] = 3 ×10^{-2} mol dm^{-3}

[Pdnps] = 3 ×10^{-6} mol dm^{-3} [H^{+}] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

Temperature (K)	10^4 k_{obs} (sec^{-1})	E_a(KJ mol^{-1})	$\Delta H^{\neq}$ ($KJmol^{-1}$)	$\Delta S^{\neq}$($JK^{-1}mol^{-1}$)	$\Delta G^{\neq}$ (KJ mol^{-1})
303	4.12	20.85	18.28.	-248.51	94.82
308	5.10				
313	6.32				

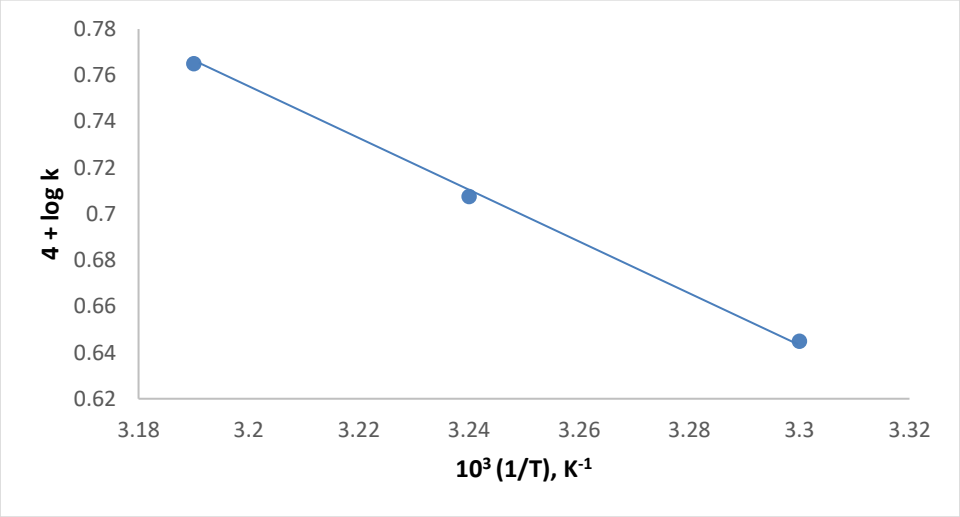


Figure 7.11: Variation of temperature

[NBS] = 3 ×10^{-3} mol dm^{-3} [Arg] = 3 ×10^{-2} mol dm^{-3} [Pdnps] = 3 ×10^{-6} mol dm^{-3}

[H^{+}] = 0.10 mol dm^{-3} [I] = 0.25 mol dm^{-3}

The enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) were also obtained 18.28 kJ mol^{-1}, -248.51 $JK^{-1}mol^{-1}$ and 94.82 kJ mol^{-1} respectively. Moderate values of both favoured the electron transfer process. The high positive values of free energy of activation ($\Delta G^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) depict the highly solvated transition state [28] while the negative values of entropy of activation (ΔS) indicates the formation of more ordered transition state that decreases the degree of freedom of the molecules.

7.3.7 Mechanism

NBS is a positive source of positive halogen. It remains as the reactive species for the oxidation of amino acid in acidic medium and explains the inverse fractional order in H^+ and nil effect in NHS [29]. NBS initiates the reaction by electrophilic bromination of the amino nitrogen group forming an N-bromamine. The N-bromination of the aminoacid as reported by Ramachandran et al. [30]

Palladium nanoparticles are prepared in homogenous medium and remain in zero oxidation state, so the definite mechanism of metal nanoparticles catalyzed oxidation of arginine is not clear. Although we identify the formation of transition species through certain physical measurements, it is rather difficult to isolate and characterize from homogeneous mixture. The proposed scheme for the oxidation of arginine by NBS in the presence of palladium nano particles is shown **[Scheme-1].** The deamination of the amino group to NH_3 occurs, while NBS changes to succinimide. The plausible mechanism in support of the observed kinetics is given in scheme-1. Various Steps involved in oxidation of Arginine by NBS in the presence of Palladium nanoparticles:

Step 1: Activation of NBS

Pd^0 donates electrons to N-Bromosuccinimide (NBS), cleaving the N–Br bond and generating Br^+ (or Br•) and succinimide, while Pd is transiently oxidized.

Step 2: Substrate Adsorption

The amino acid binds to the Pd surface via carboxylate or amine coordination, positioning reactive sites close to the activated bromine species.

Step 3: Process of Oxidation

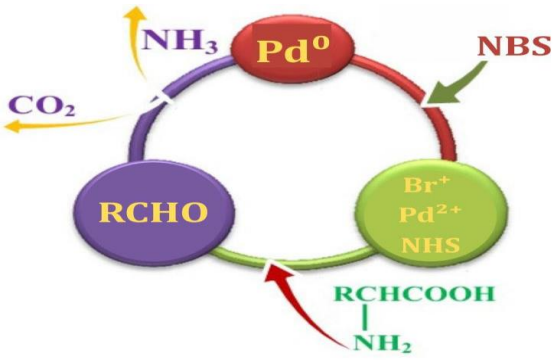
Br^+ abstracts hydrogen or electrons from the amino acid, forming the oxidized product (imine, aldehyde).

Step 4: Redox Regeneration

Electrons from the oxidation step reduce Pd^{2+} back to Pd^0, restoring the active catalytic surface.

Step 5: Reuse of Catalyst

Pd^0 is available again to activate another NBS molecule and continue the cycle, maintaining high turnover and reaction rates.



Scheme 1: The plausible route of palladium nanoparticles catalysed oxidation of arginine by NBS in aqueous medium

$2NBS + Pd^0 + H_2O \rightarrow 2NHS + Pd^{+2} + Br^+$

$Pd^{+2} + Br^+ + R\text{-}CH(NH_2)\,COOH \rightarrow RCHO + NH_3 + CO_2 + Br_2 + Pd^0$

$2NBS + R\text{-}CH(NH_2)\,COOH + H_2O \rightarrow RCHO + 2NHS + NH_3 + CO_2 + Br_2$

Where $R = -CH_2\text{-}\,CH_2\text{-}\,CH_2\text{-}NH\text{-}C(NH_2) = NH$

Scheme-1

7.4 CONCLUSION

In this paper we investigated the catalytic effect of synthesized palladium nano catalyst through the oxidation of arginine in aqueous acidic medium. The results of the study showed first order with NBS, inverse fractional order with hydrogen ion, fractional first order kinetics with respect to Arginine and first order with respect to palladium nano particles. The catalytic rates of Pdnp and Pd (II) were compared, and it was found that palladium nanoparticle increased the reaction rate many times in comparison to Pd (II). Activation energy was calculated by studying the temperature variation at 30, 35 and 40°C and using this other thermodynamic parameter were studied.

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CONCLUSION

CONCLUSION

The reaction of oxidation of amino acids using N-Bromosuccinimide in presence of Pd (II) catalyst and palladium nanoparticles in aqueous acid medium proceed smoothly and demonstrates significant advantages in terms of reaction efficiency. We have used Pd (II) and Palladium nanoparticles as catalysts. For this we synthesised Pd nanoparticle by chemical reduction method and characterised it by UV-Visible Spectrophotometer and Transmission Electron Microscopy (TEM) analysis and used it for studying the kinetics of oxidation of four amino acids viz. Valine, Serine, Aspartic acid and Arginine by NBS in acidic medium. TheTEM image shows ultra-small nanoparticles (mostly 2–5 nm) along with a few larger faceted particles (10–20 nm), polydisperse, with some aggregation. The larger faceted particle confirms crystalline nature, while clustering suggests possible secondary growth.

The results indicate that the oxidation reaction follows first order kinetics with respect to NBS and catalyst, fractional and negative order w.r.t amino acid and acid respectively and the observed rate constants significantly increase in the presence of catalyst as compared to aqueous medium. It was found that Pd nanoparticles increased the rate at a much faster speed than Pd (II). The prepared nanoparticles remained stable for a long period. The main products are aldehydes, succinimide, ammonia and carbon dioxide characterized by FT-IR and other tests.

SUMMARY

SUMMARY

The oxidations of amino acids particularly α-amino acids have been a subject of interest for the last four decades and the oxidants of varied thermodynamic potentialities have been employed both in acid and alkaline medium. The metal complexes of amino acids play very important role in many biological systems.

The interactions between transition metals and various amino acids have been extensively investigated, with the stability of the resulting complexes determined using various electrometric techniques. The oxidation of amino acids has prominent importance, both chemically and in understanding the mechanisms underlying amino acid metabolism. Some studies have reported the formation of aldehydes via hydrolysis of an imine intermediate, while others suggest that the imine undergoes further oxidation to yield nitriles. In addition to aldehydes and nitriles, the formation of α-keto acids has also been reported as a product of amino acid oxidation"

NBS are sources of positive halogens, and these reagents have been used as oxidant for a variety of substrates in solution and mechanistic details are also available in many cases. This reagent has been selectively used as an oxidant for a variety of substrates in both acid and alkaline media. This compound also serves as a key oxidizing agent in the oxidation of various coordination complexes and biochemical substances. Its strong oxidative properties have been effectively utilized in the transformation of esters, alcohols, and ketones.

Palladium is a soft silver white metal. It is least dense and has the lowest melting point of the platinum group metals. Common oxidation states of Pd are (0), (+1), (+2) and (+4). The field of nano catalyst has sustained an accelerated surge during the past decades, both in homogeneous and heterogeneous catalysis. Nanoscale inorganic materials have received much more attention because of their high chemical inertness, non-swelling effect, high purity and rigidity. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are compelling to be used as catalyst. With the improved developments in nano chemistry, we can prepare soluble analogues of heterogeneous catalyst that might have properties intermediate between those of the bulk metal particle (homogeneous) catalysts. Pd nanoparticles have been used as a catalyst in electron transfer and oxidation reaction.

This thesis comprises seven chapters. The summary of work embodied in chapters is given below.

CHAPTER 1: INTRODUCTION

The first chapter briefly gives an overview of chemical Kinetics, NBS (N-Bromo succinimide), Kinetics studies of NBS with different Compounds, Amino acids, Palladium (II), Review of Pd (II) studies, Metal nanoparticles, Nano catalysis, Role of the Transition Metal Nanoparticles in Catalysis, Palladium nanoparticles and Oxidation of Amino Acids.

CHAPTER 2: MATERIALS AND METHODS

This chapter describes the details of various chemicals and reagents, equipment's, preparation of various solutions, kinetic measurements used for analysis of the products and determination of stoichiometry. It also describes various spectral techniques for identification of intermediates which include UV-Visible Spectroscopy, Transmission Electron Microscopy (TEM) and FT-IR Spectroscopy.

CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF PALLADIUM NANOPARTICLES

This chapter gives an overview of the development and involvement of nanoparticles synthesis, which is a rapidly developing area of research that covers a wide range of applications. It plays a very important role in developing novel methods for creating new products that are compatible with existing production equipment, restructuring materials and chemicals to elevate performance, minimize energy, material consumption and reduce environmental impact. "Nanoparticles are considered one of the most promising areas of recent research and can be synthesized using various techniques, broadly classified into bottom-up and top-down approaches, as documented in the literature. The properties of palladium nanoparticles are highly dependent on the synthesis methods employed. This chapter presents the experimental procedures involved in the synthesis of palladium nanoparticles using the chemical reduction method. The synthesized nanoparticles are subjected to morphological and structural characterization using various techniques, including UV-Visible spectroscopy, FT-IR spectroscopy, and Transmission Electron Microscopy (TEM).

CHAPTER 4: KINETICS AND MECHANISM OF PALLADIUM (II) CATALYSED OXIDATION OF VALINE BY N-BROMOSUCCINIMIDE IN PERCHLORIC ACID MEDIUM

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 35ºC. 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 $[PdCl_4]^{2-}$ 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 iso-butyraldehyde 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.

CHAPTER 5: MECHANISTIC STUDY OF PD(II) CATALYSED OXIDATION OF SERINE BY N-BROMOSUCCINIMIDE IN PERCHLORIC ACID MEDIUM

The Kinetics of Pd (II) catalysed and uncatalysed oxidation of Serine by N-Bromo succinimide (NBS) was studied in the presence of perchloric acid and Hg (II) at 35°C. In both Pd (II) catalysed and uncatalysed oxidations, the kinetic orders were first order in NBS and fractional order in substrate. The rate of reaction decreased with the increase in perchloric acid concentration and chloride ion. The reaction rate increases with the increase in Pd (II). However successive addition of mercuric acetate, succinimide (NHS) and variation of ionic strength of the medium did not bring about significant change in the rate of the reaction. $[PdCl_4]^{2-}$ and NBS itself have been postulated as the reactive species of palladium (II) chloride and N-Bromo succinimide in acidic medium respectively. 2-Hydroxyethanal was identified as the main oxidation product of the reaction. On the basis of the experimental findings, a suitable mechanism has been proposed. Activation parameters for the slow and rate determining step of the proposed mechanism have been obtained from the rate measurements at 30, 35 and 40°C. The rate law conforming to the observed kinetic results
has been derived as:

$$\text{Rate} = \frac{kK_2[NBS]_T[Ser]}{1 + K_1[H^+] + K_2[Ser]}$$

CHAPTER 6: SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF PALLADIUM NANOPARTICLES ON OXIDATION OF ASPARTIC ACID IN ACIDIC AQUEOUS MEDIUM

Palladium nanoparticles are synthesized through a single route chemical reduction method using synthetic polymer such as poly N-vinyl pyrrolidone (PVP) stabilizer. The synthesized palladium nanoparticles (Pdnps) were characterized by UV-visible spectrophotometer and Transmission Electron Microscopy (TEM) analysis. The particle size of palladium nanoparticles was found to be 1nm to 50 nm and spherical in shape at the optimal experimental conditions. The synthesized palladium nanoparticles are used as a catalyst for the oxidation of Aspartic acid by N-Bromo succinimide in aqueous medium. The effect of palladium nanoparticles on the rate of oxidation has been studied at different temperature. The palladium nanoparticles exhibited very good catalytic activity. The kinetics of the reaction was found to be first order with respect to [NBS]and Pdnp and fractional order with respect to Aspartic acid. Increase in $[H^+]$ decreased the reaction rate. The main oxidation product of Aspartic acid has been identified as the aldehyde which is confirmed by the FTIR spectrum of a corresponding hydrazone. The palladium nanoparticles catalyst exhibited better catalytic activity than equal amount of palladium precursor. Various activation parameters have been calculated and on the basis of these parameters, a suitable explanation of the reaction mechanism has been given.

CHAPTER 7: PALLADIUM NANOPARTICLES SYNTHESIS AND THEIR CATALYTIC APPLICATION ON OXIDATION OF ARGININE IN AQUEOUS ACIDIC MEDIUM

The paper describes the preparation of Palladium nanoparticle (Pdnp) through chemical reduction method using palladium chloride ($PdCl_2$) and stabilizer PVP (Poly vinyl pyrrolidone). Characterization of the palladium nanoparticle was done by UV-VIS Spectrometer and TEM. The range of the particle size was from 1 to 100 nm. Palladium nanoparticles of various shapes and sizes have been obtained by reduction in ethanol with HCl catalyst addition. The synthesized palladium nanoparticles are

used as a catalyst for the oxidation of basic amino acid, Arginine by N-Bromosuccinimide in aqueous medium. The reaction shows first order kinetics with respect to NBS and fractional with respect to arginine. The rate increases with the increase in Pdnps and retarding effect of perchloric acid was observed. Various activation parameters have been calculated and on the basis of these parameters, a suitable explanation of the reaction mechanism has been given.

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RESEARCH PUBLICATIONS
IN UGC REFEREED JOURNALS

LIST OF RESEARCH PUBLICATIONS

1. *Kinetics and Mechanism of Palladium (II) Catalysed Oxidation of Valine by N Bromo succinimide in Perchloric Acid Medium, Manju Bala Yadav,* ***Rashmi Gupta****, Dhan Raj, Int. J. Science and Research Methodology (IJSRM), Vol. 10, Issue 3, Sept 2018*, *131-147.*

2. *Mechanistic study of Pd (II) catalysed oxidation of serine by NBS in perchloric acid medium, Dhan Raj,* ***Rashmi Gupta****, Manju Bala Yadav, International Journal of Research and Analytical Reviews (IJRAR), Jan 2021, Vol 8, Issue 1, 571-582.*

3. *Synthesis, Characterization and Catalytic Application of Palladium Nanoparticles on Oxidation of Aspartic Acid in Acidic Aqueous Medium, Dhan Raj,* ***Rashmi Gupta****, Manju Meena, Manju Bala Yadav, The Journal of Oriental Research Madras, [Vol. MMXXII-XCIII-IV], Feb 2022.*

4. *Palladium Nanoparticles Synthesis and Their Catalytic Application on Oxidation of Arginine in Aqueous Acidic Medium, Dhanraj,* ***Rashmi Gupta****, M. B. Yadav, Greener Living, 978-1-989416-12-9, Pustak Bharati Publishers and Distributors, Varanasi, U.P, India, 2023.*

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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 $[PdCl_4]^{2-}$ 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 oxidations[1-3]. A number of uncatalyzed[4-10] and catalyzed[11-16] 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 oxidants[17-19] 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 medium[20-26]. Though there are several reports[27-29] 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 reactions[30-34] 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-bromosuccnimide. 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.

$NaClO_4$ (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 ±10°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-

$$(CH_3)_2CHCH(NH_2)COOH + 2NBS + H_2O \xrightarrow{Pd(II)/H^+} 2NHS + CO_2 + Br_2 + NH_3\uparrow + (CH_3)_2CHCHO$$

The main reaction products were succinimide, iso-butylaldehyde, ammonia and CO_2. Liberated ammonia was identified by Nessler' s reagent where a brownish colour was observed indicating a deamination reaction[35]. CO_2 was identified by freshly prepared lime water and the solution turned milky, indicating a decarboxylation reaction[36].

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 reagent [37]. 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.

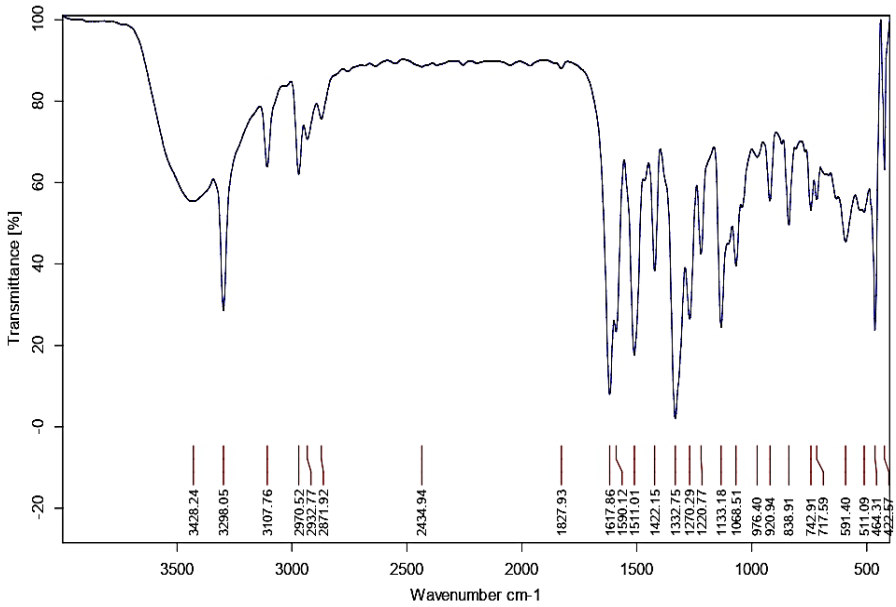

Fig. 1- IR Spectra of hydrazone of Iso-butylaldehyde

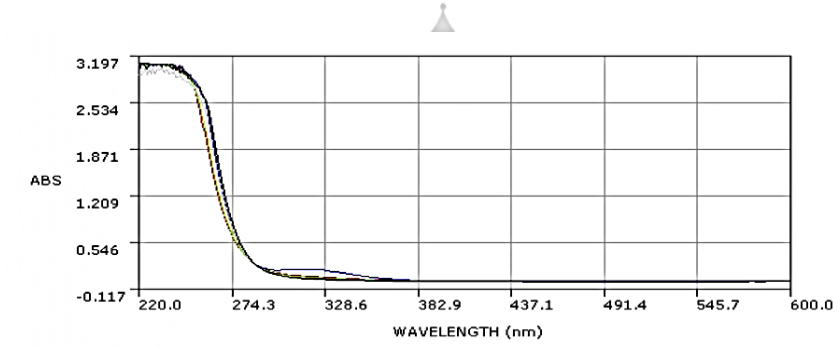

Fig. 2-UV-spectra of NBS in acid medium and [Pd(II).NBS] complex

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

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

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 $[NBS]_t$ was plotted against time, very good linear plots were obtained which also proves first order with respect to [NBS] (Fig. 3). At constant [NBS], $[H^+]$, [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_{obs} vs log[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/rate vs 1/ [val]. The complex formation between oxidant and reductant was also reported in literature [38]. Keeping concentration of all reactants fixed, perchloric acid concentration was varied and kinetic runs were taken at fixed ionic strength (I = 0.5 mol dm^{-3}). The result showed a negative effect with respect to $[H^+]$ (Fig. 4). The plot of log k_{obs} vs log $[H^+]$

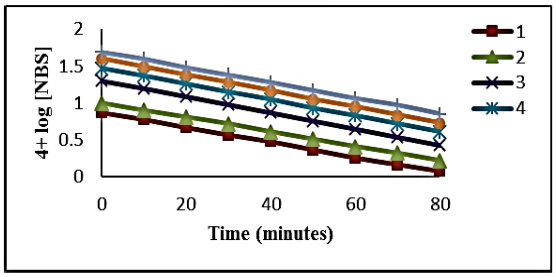

Fig. 3-Psuedo first order plots for the variation of NBS

[Val] = 2.0×10^{-2} mol dm^{-3}, $[H^+]$ = .10 mol dm^{-3},

[Pd(II)] = 2.0×10^{-5} mol dm^{-3}, I = .25 mol dm^{-3}, Temp. =

[NBS] = (1) 0.75×10^{-3} mol dm^{-3}, (2) 1.0×10^{-3} mol dm^{-3},

(3) 2.0×10^{-3} mol dm^{-3}, (4) 3.0×10^{-3} mol dm^{-3},

(5) 4.0×10^{-3} mol dm^{-3}, (6) 5.0×10^{-3} 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. Ea = 26.80 KJ mol^{-1}, $\Delta H^{\neq}$ = 24.24KJ mol^{-1}, $\Delta S^{\neq}$ = -147.20 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 69.57 KJ mol^{-1}

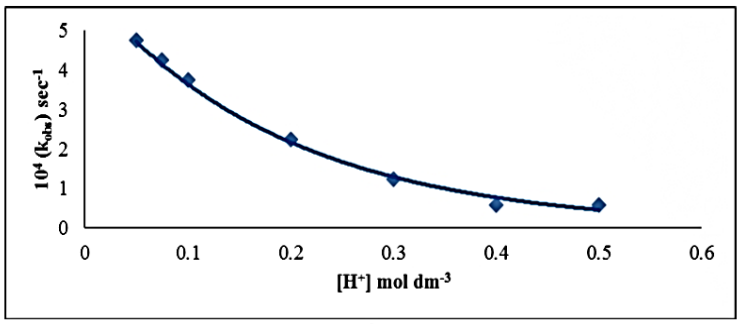

Fig. 4- Variation of hydrogen ion

[NBS] = 2.0 × 10^{-3} mol dm^{-3}; [Val] = 2.0 × 10^{-2} mol dm

[Pd(II)] = 2.0 × 10^{-5} 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. Ea = 26.80 KJ mol^{-1}, $\Delta H^{\neq}$ = 24.24KJ mol^{-1}, $\Delta S^{\neq}$ = -147.20 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 69.57 KJ mol^{-1}.

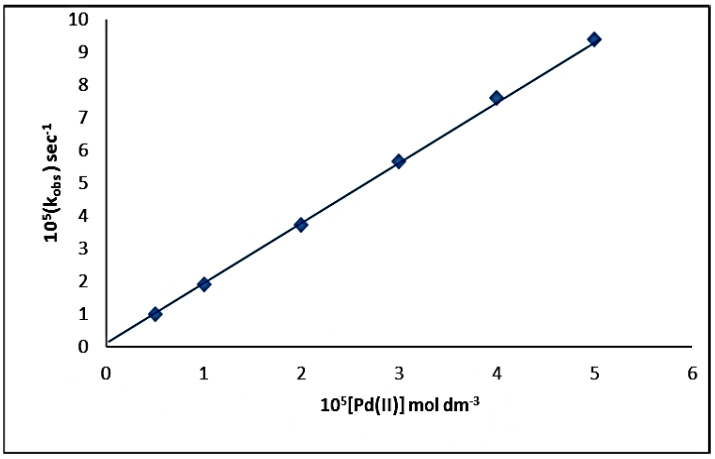

Fig. 5- Variation of palladium(II)

[NBS] = 2.0×10^{-3} mol dm^{-3}; [Val] = 2.0×10^{-2} mol dm^{-3}; [H^+] = 0.10 mol dm^{-3};

I =0 .25 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 forms[39-41]. NBS itself, Br^+ or N^+BSH in the following way

$$NBr + H^+ \rightleftharpoons N^+HBr \qquad (A)$$

(NBS) (N^+BSH)

$$NBr + H^+ \rightleftharpoons NH + Br^+ \qquad (B)$$

(NBS) (NHS)

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 $[H^+]$ 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 as[42-43] $[PdCl_4]^{2-}$ according to the equlibrium[44].

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

Such species using Pd(II) chloride has also been reported in the oxidation of amino acids by Cerium(IV)[45], Chloramine-T[46], N-bromophthalimide[47], acid bromate[48] and some sugars by N-bromosuccinimide[49] and N-bromoacetamide[50] and oxidation of EDTA by NBS[51].

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.

$$RCHNH_2COOH \rightleftharpoons RCHNH_2COO^- + H^+ \rightleftharpoons RCH^+NH_3COO^-$$

Amino acid (S) Anion (S^-) Zwitterion (S^0)

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:

$$RCH^+NH_3COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHN^+H_3COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_2COO^-$$

Cation (S^+H) Zwitterion (S^0)

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 $NBS + [PdCl_4]^{2-} \rightarrow [PdCl_4.NBS]^{2-}$

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°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 $5x10^{-4}$ 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.

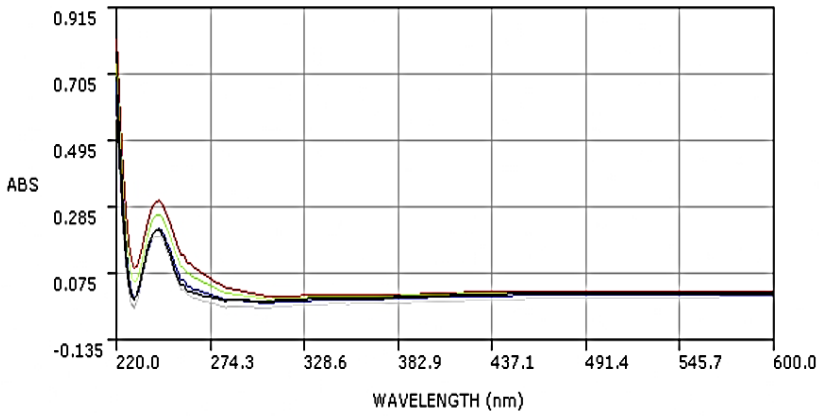

Fig. 6- Spectra of the reaction mixture at time interval

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.

$$\underset{[AA]^+}{{}^{+}NH_3\text{-}CH(R)\text{-}COOH} \overset{K}{\rightleftharpoons} \underset{[AA]}{NH_2\text{-}CH(R)\text{-}COOH} + H^+$$

$$[PdCl_4]^{2-} + NBS \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [PdCl_4.NBS]^{2-}$$

$$(C) \qquad\qquad (C_1)$$

$$\underset{(C_1)}{[PdCl_4.NBS]^{2-}} + \underset{(AA)}{NH_2\text{-}CH(R)\text{-}COOH} \xrightarrow[slow]{k} \underset{(C_2)}{[Complex]}$$

$$C_2 + 3H_2O \xrightarrow{fast} NHS + [PdCl_2(H_2O)_2] + NH_3 + RCHO + 2Cl^- + Br^-$$

$$Br^- + NBS \rightarrow NHS + Br_2$$

Scheme-1

Since all the kinetic studies are conducted in the presence of mercuric acetate, the liberated Br_2 during the course of reaction can be removed in the form of $HgBr_4^{-2}$ or $HgBr_2$ complexes because $Hg(OAc)_2$ acts as a scavenger for Br^- formed in the reaction.

$$\text{rate} = \frac{-d[NBS]}{dt} = 2k[C_1][AA] \qquad \text{-------- (1)}$$

On applying the law of chemical equilibrium, we get

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

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

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

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

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

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

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

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

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

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

$$[Pd(II)]_T = [C] + [C_1] \qquad \ldots\ldots (5)$$

In reaction C >>> 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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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 $[H^+]$.

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

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

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

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 Ea = 24.12 KJ mol^{-1},$\Delta H^{\neq}$ = 21.56 KJ mol^{-1}, $\Delta S^{\neq}$ = -144.50 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 66.06 KJ mol^{-1}. The kinetic data shows the increasing rate

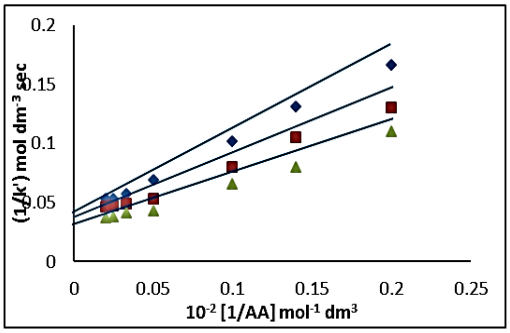

Fig.7- Variation of valine at three different temperatures

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

[Pd(II)] = 2.0×10^{-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 $\Delta S^{\neq}$ suggest the formation of more ordered activation complex whereas the high positive value of the free energy of activation ($\Delta G^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) 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 fact[55] 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, $PdCl_4^{-2}$. 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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Mechanistic study of Pd (II) Catalysed Oxidation of Serine by N-bromosuccinimide in Perchloric Acid Medium

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ABSTRACT

The Kinetics of Pd(II) catalysed and uncatalysed oxidation of serine by N-bromosuccinimide (NBS) was studied in the presence of perchloric acid and Hg(II) at 35°C. In both Pd (II) catalysed and uncatalysed oxidations, the kinetic orders were first order in NBS and fractional order in substrate. The rate of reaction decreased with the increase in perchloric acid concentration and chloride ion. The reaction rate increases with the increase in Pd(II). However successive addition of mercuric acetate, succinimide (NHS) and variation of ionic strength of the medium did not bring about significant change in the rate of the reaction. $[PdCl_4]^{2-}$ and NBS itself have been postulated as the reactive species of palladium (II) chloride and N-bromosuccinimide in acidic medium respectively. 2-Hydroxyethanal was identified as the main oxidation product of the reaction. On the basis of the experimental findings, a suitable mechanism has been proposed. Activation parameters for the slow and rate determining step of the proposed mechanism have been obtained from the rate measurements at 30, 35 and 40°C. The rate law conforming to the observed kinetic results has been derived as:

$$\text{Rate} = \frac{kK_2[NBS]_T[Ser]}{1+K_1[H^+]+K_2[Ser]}$$

Keywords: Mechanism, Pd(II) catalysis, Oxidation, Amino acid, N-bromosuccinimide.

INTRODUCTION

Amino acid residues are the main constituents of proteins and the study of its sensitivity towards oxidation opens up a new area to understand the mechanism involved in the protein and amino acid modifications[1]. Many Uncatalysed[2-8] and Catalysed[9-14] kinetic studies have been reported on the oxidation of amino acid by different oxidants. Though there are several reports[15-18] on the oxidation of amino acid by N-halo compound, no information is available where the use of chloro complex of Pd(II) as catalyst has been made in the oxidation of amino acid by N- bromosuccinimide in acidic medium.

Palladium (II) chloride is quite soluble in HCl and exists[19] primarily as $[PdCl_4]^{2-}$.Various mononuclear complexes, namely $[PdLCl_3]^-$, $[PdL_2Cl_2]$, $[PdLCl]^+$ and $[PdL_4]^{2+}$ (where L represent amine, phospine, thioether etc.) are well known. Palladium(II) has shown a strong catalytic[20-24] as well as inhibitor[25-27] effect on the rate of various homogenous redox reactions but the nature of its active form in such reactions remain obscure.

The diverse nature of the chemistry of N-halocompounds[28-32] is due to their ability to act as a source of halogenonium cations, hypohalite and nitrogen anions species which act as both bases and nucleophiles. N-bromosuccinimide (NBS) is a source of positive halogen and has been selectively used as an oxidant for a variety of substrates[33-38] in both acidic and alkaline solutions. This potent oxidising agent has been extensively used in the determination of number of pharmaceutical compounds[39-40]. The role of NBS as an oxidant in the oxidation of a large number of substrates has been probed using Ru (III)[41], Pd (II)[42-44], Pt(IV)[45] and Rh(III)[46-47] as homogeneous catalyst. However, little information is available in the literature on NBS reactions, particularly with respect to the oxidation kinetics of bioactive compounds .This prompted us to undertake the present investigation which constitutes the studies of kinetics and mechanism of Pd(II) catalysed NBS oxidation of serine in perchloric acid media in presence of mercuric acetate.

MATERIALS AND METHODS

Experimental

The reagents employed were N-bromosuccinimide (G.R Merck), Palladium (II) chloride (Johnson Matthey, London), Mercuric acetate (G.R. Merck). $HClO_4$ (E.Merck) used as a source of hydrogen ions and $NaClO_4$ (E.Merck) 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. Other reagents used were of analytical grade. All solutions were

prepared with doubly distilled water. Stock solutions of N-bromosuccinimide were prepared and standardized iodometrically[48].

Kinetic Measurements

A thermostatted water bath was used to maintain the desired temperature to within ± 0.1°C. All the kinetic measurement were carried out at constant temperature 35°C under pseudo first order conditions with a large excess of amino acid over NBS. The reaction was initiated by rapid addition of NBS to the reaction mixture containing appropriate quantities of amino acid, Pd (II) chloride, perchloric acid, mercuric acetate and water and mixing them by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed NBS at regular time intervals iodometrically.

RESULTS AND DISSCUSSION (UNCATALYSED REACTIONS)

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBS over amino acid (in varying ratios) at 35°C for 48 hours and estimations of residual NBS in different sets showed that 1 mole of amino acid consumes two moles of NBS according to the stoichiometric equation.

$$\text{Serine} + 2\,\text{NBS} + H_2O \xrightarrow{Pd(II)/H^+} 2\,\text{NHS} + CO_2 + Br_2 + NH_3 + 2-\text{Hydroxyethanal}$$

Effect of NBS

The kinetics of the oxidation of serine was investigated under pseudo first order conditions keeping the concentration of serine in large excess (nearly tenfold) over that of NBS keeping all other concentrations constant(**Table 1)** First order dependence in NBS was followed at all initial concentration of NBS. Pseudo first order rate constants (k_{obs}) were calculated from the slopes of log-time plots (**Figure 1**). The first order kinetics with respect to NBS are also verified by the constant values of k_{obs} obtained at various initial concentration of NBS.

Table-1 Effect of [NBS], [Serine], [Pd(II)] and [H^+] on uncatalysed and Pd(II) catalysed oxidation of serine by NBS in perchloric acid medium.

10^3[NBS] mol dm^{-3}	10^2 [Serine] mol dm^{-3}	10^5Pd(II) moldm^{-3}	H^+ mol dm^{-3}	Catalysed 10^4 K_{obs} sec^{-1}	Uncatalysed 10^4 K_{obs} sec^{-1}
0.5	2.0	2.0	.10	3.78	2.89
0.75	2.0	2.0	.10	3.76	2.84
1.0	2.0	2.0	.10	3.74	2.82
2.0	2.0	2.0	.10	3.78	2.80
3.0	2.0	2.0	.10	3.72	2.83
4.0	2.0	2.0	.10	3.79	2.86
5.0	2.0	2.0	.10	3.76	2.88
2.0	0.5	2.0	.10	1.74	1.28
2.0	0.75	2.0	.10	2.18	1.62
2.0	1.0	2.0	.10	2.61	1.90
2.0	2.0	2.0	.10	3.78	2.80
2.0	3.0	2.0	.10	4.76	2.88
2.0	4.0	2.0	.10	5.15	3.01
2.0	5.0	2.0	.10	5.25	3.10
2.0	2.0	0.0	.10	---	2.80
2.0	2.0	0.50	.10	3.00	---
2.0	2.0	1.0	.10	3.25	---
2.0	2.0	2.0	.10	3.78	---
2.0	2.0	3.0	.10	4.26	---
2.0	2.0	4.0	.10	4.70	---
2.0	2.0	5.0	.10	5.20	---
2.0	2.0	2.0	0.05	5.00	4.00
2.0	2.0	2.0	0.075	4.26	3.45
2.0	2.0	2.0	.1	3.78	2.80
2.0	2.0	2.0	.2	2.45	2.44
2.0	2.0	2.0	.3	1.93	1.96
2.0	2.0	2.0	.4	1.65	1.61
2.0	2.0	2.0	.5	1.41	1.42

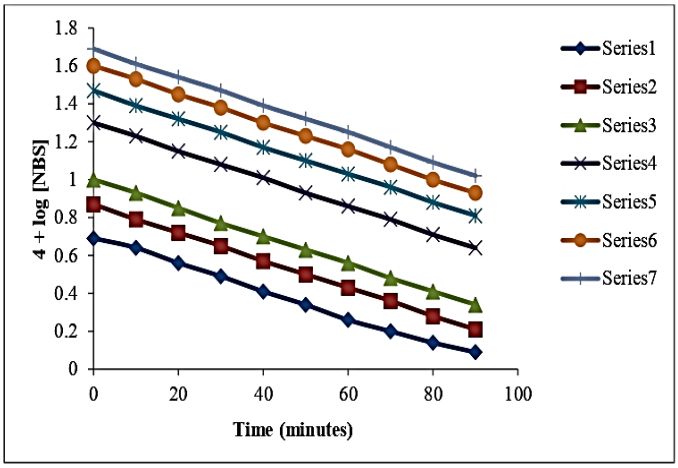

Figure 1 Psuedo first order plots for the variation of Uncatalysed NBS
[Ser] = 2.0 x 10^{-2} mol dm^{-3}, [H^+] = .10 mol dm^{-3},
I = 0.25 mol dm^{-3}, Temp. = 35°C
[NBS] = (1) 0.50 x 10^{-3} mol dm^{-3}, (2) 0.75 x 10^{-3} mol dm^{-3},
(3) 1.0 x 10^{-3} mol dm^{-3}, (4) 2.0 x 10^{-3} mol dm^{-3},
(5) 3.0 x 10^{-3} mol dm^{-3}, (6) 4.0 x 10^{-3} mol dm^{-3},
(7) 5.0 x 10^{-3} mol dm^{-3}.

Effect of Serine

At constant [NBS], [H^+], [Pd(II)], mercuric acetate and temperature, the kinetic runs were carried out with initial concentration of serine. A plot of –dc/dt versus serine shows first order dependence of the reaction on amino acid at low concentration, which shifts towards zero order at its higher concentration. The plot of log k_{obs} versus log [Ser] was a straight line with fractional slope confirming fractional order with respect to serine.

Effect of acid

The first order rate constants decreased with the increase in perchloric acid concentration (**Figure 2**). The order of reaction with respect to hydrogen ions was determined as 0.63 from the slope of the plot of log k_{obs} and log H^+.

Effect of added salt

The effect of Cl^- was studied by successive addition of KCl in the reaction mixture. Addition of Cl^- showed a decrease in the rate constant.

It was observed that the change in the concentration of added mercuric acetate had negligible effect on the rate. The function of added mercuric acetate is to fix up Br^- formed in the course of the reaction as $HgBr_2$ or $HgBr_4^{2-}$.It suppresses completely the oxidation by Br_2, which would have been formed by the interaction of HBr and NBS .Mercuric acetate thus ensures the oxidation purely through NBS.

Rate and activation parameters

The effect of temperature on the rate of reaction was studied in the range 303-323K under varying (L-Serine) and various activation parameters computed.

Product Analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, serine (0.05M) and NBS (0.01M) were made upto 100 ml and the reaction mixture was allowed to stay in the dark for about one day to ensure completion of the reaction. The main reaction products were succinimide, 2-hydroxyethanal, ammonia and carbon dioxide. Liberated ammonia was identified by Nesselers reagent. CO_2 was identified by freshly prepared lime water where the solution turned milky indicating a decaboxylation reaction[49].

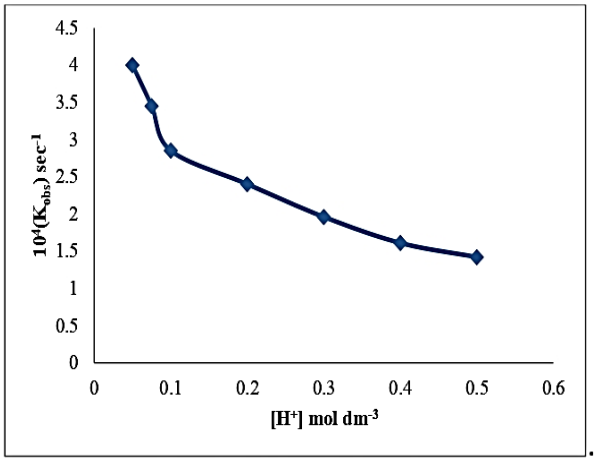

Figure 2 Variation of hydrogen ion
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Ser] = 2.0 x 10^{-2} mol dm^{-3},
I = 0.25 mol dm^{-3}, Temp. = 35 °C

The solution was then treated with an excess of saturated solution of 2,4 DNP in 2M HCl and kept overnight in a refrigerator. The precipitated 2,4 DNP was filtered off, dried, weighed, recrystallised from ethanol. The DNP was found to have identical melting point and spectral data as the DNP of 2-Hdroxyethanal. Further the aldehyde group was confirmed with qualitative test such as Tollens reagent[50] and spot test[51].

$$NBS + H^+ \overset{K_1}{\rightleftharpoons} NBSH^+$$

$$NBS + Serine \overset{K_2}{\rightleftharpoons} Complex\ (C_1)$$

$$Complex\ (C_1) \xrightarrow[slow]{k} CH_2(OH)C(COOH)=NH + Br^- + Succinimide$$

$$\downarrow$$

$$CH_2(OH)C(COOH)=N \xrightarrow{H_2O} CH_2(OH)CHO$$

Scheme-1

$$Rate = k\ Complex(C_1) \quad (1)$$

$$= k\ K_2\ [NBS]\ [Ser] \quad (2)$$

$$[NBS]_T = NBS + [NBSH^+] + complex(C_1) \quad (3)$$

$$= NBS + K_1\ [NBS]\ [H^+] + K_2\ [NBS]\ [Ser] \quad (4)$$

$$= NBS\left[1 + K_1\ [H^+] + K_2[Ser]\right] \quad (5)$$

$$NBS = \frac{[NBS]_T}{1 + K_1[H^+] + K_2[Ser]} \quad (6)$$

From (2) and (6)

$$Rate = \frac{kK_2[NBS]_T[Ser]}{1 + K_1[H^+] + K_2[Ser]} \quad (7)$$

The above rate law explains the first order in oxidant, fractional order in substrate and inverse order in acid. Further

$$\frac{Rate}{[NBS]} = K_{obs} = \frac{kK_2[Ser]}{1 + K_1[H^+] + K_2[Ser]} \quad (8)$$

The mechanism of scheme 1 and the rate law may be verified by rearranging it in the form

$$\frac{1}{K_{obs}} = \frac{1}{kK_2[Ser]} + \frac{K_1[H^+]}{kK_2[Ser]} + \frac{1}{k} \quad (9)$$

According to equation (9) the plots of $1/K_{obs}$ versus 1/[Ser] and $1/K_{obs}$ versus $[H^+]$ are linear with non-zero intercepts which are verified in **(Figure 3 and 4)**. From the slopes and intercepts of such plots k, K_1 and K_2

values are obtained at 35 as $4.76 \times 10^{-4}\ s^{-1}$, 193.92 $moldm^{-3}$ and 2100 $dm^3\ mol^{-1}$. This not only proves the validity of rate law but also gives support to the proposed reaction scheme-1. The fair degree of closeness in k values (4.76×10^{-4}) sec^{-1} obtained from plot-A and $4.74 \times 10^{-4}\ sec^{-1}$ from plot B) also supports the validity of proposed mechanism. The values of k in s^{-1} are were found to be 4.0×10^{-4}, 4.76×10^{-4}, 5.26×10^{-4} at 30, 35 and 40 respectively. The activation parameters were evaluated from the plot of log k versus 1/T which are as follows Ea = 20.87 KJ mol^{-1}, $\Delta H^{\neq}$ =18.30 KJ mol^{-1}, $\Delta S^{\neq}$ = 240.50 J K^{-1} mol^{-1} and $\Delta G^{\neq}$ = 92.22 KJ mol^{-1}.

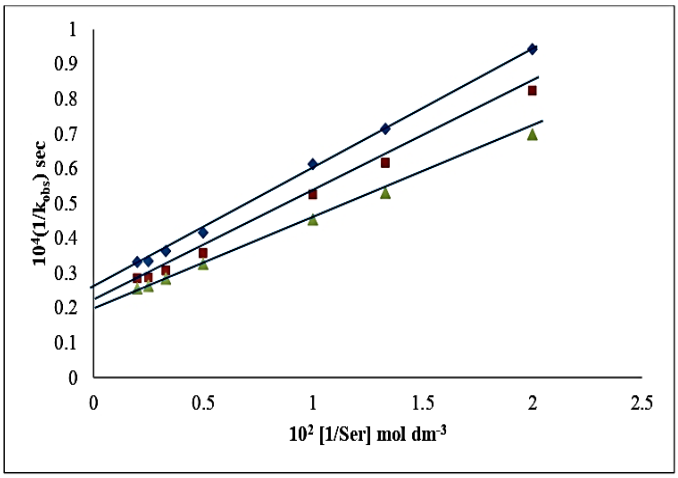

Figure 3: Plot of $1/k_{obs}$ versus 1/ Ser
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, $[H^+]$ = .10 mol dm^{-3},
I = 0.25 mol dm^{-3}, Temp. = 30℃, 35 ℃, 40℃.

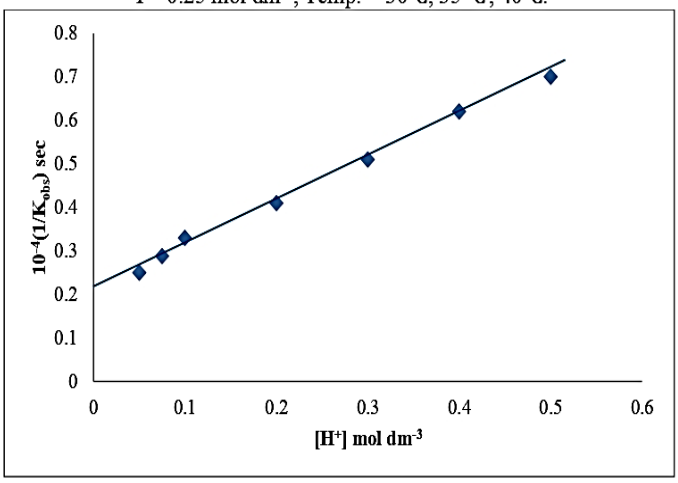

Figure 4 Uncatalysed hydrogen ion
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Ser] = 2.0 x 10^{-2} mol dm^{-3},
I = 0.25 mol dm^{-3}, Temp. = 35 ℃

An insignificant effect of ionic strength on the rate is also in the favour of rate determining step in which a neutral species is involved. The entropy of activation in each case was found to be negative(reduction of the entropy of system), suggesting the compactness of the transition stateas compared to the ground state.

Pd(II) Catalysed Reactions

Palladium (II) chloride accelerates the oxidation of serine by NBS in perchloric acid medium **(Table 1)**.

Effect of variation of concentration of NBS

The reaction is first order in NBS as evidenced by the linear plots of log(a-x) versus time .Increase in concentration of NBS yields constant first order rate constants confirming the first order dependence on NBS(**Table 1**).

Effect of variation of concentration of Serine

The rate of reaction increased with the increase in concentration of serine.The order in substrate was computed from the slopes of log k_{obs} versus log(substrate) and was found to be 0.62 indicating a fractional order dependence on serine.

Effect of variation of concentration of Pd(II)

The rate of reaction was found to be highly influenced by Pd(II). It was observed that with increasing Pd(II) concentration, the first order rate constants in NBS increased linearly. The plot of k_{obs} versus [$PdCl_2$] was linear with an intercept (**Figure 5**) indicating uncatalysed reaction along with catalysed one. The value of k_{obs} obtained in absence of palladium chloride i.e.[$PdCl_2$=0], was matching with the intercept of the plot of k_{obs} versus [$PdCl_2$].

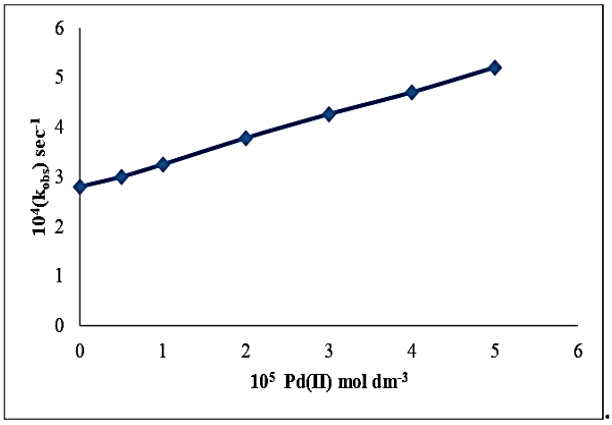

Figure 5 Variation of Palladium(II)
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Ser] = 2.0 x 10^{-2} mol dm^{-3},
[H^+] = 10 mol dm^{-3}, I = 0.25 mol dm^{-3}, Temp. = 35°C

Effect of variation of concentration of Hydrogen ion

The effect of (H^+) on the reaction rate was studied at fixed ionic strength(I =0.25 mol dm^{-3}) maintained with $NaClO_4$.The rate constant decreases with the increase in the concentration of perchloric acid. The plot of log k_{obs} versus log (H^+) is linear and yields a fractional slope (- 0. 63) conforming inverse dependence on (H^+). This inverse effect of hydrogen ion indicates free serine molecules as the predominant species.

The effects of adding mercury(I) acetate and perchlorate(ionic strength variation) on the rate constant were negligible. Successive addition of succinimide (the reaction product of NBS) has no effect on the rate constant. The effect of chloride on the rate of reaction was studied by the successive addition of sodium chloride, the observed rate constants decreased with [Cl^-] (**Table 2**) and a plot of 1/k_{obs} versus [Cl^-] was linear with an intercept (**Figure 6**).

Table-2. Variation of chloride ion

10^2[NaCl] mol dm^{-3}	10^4 (K_{obs}) sec^{-1}
0.25	7.80
0.5	5.60
1.0	3.78
1.5	2.83
2.0	2.29

Various complexes formed during the course of reaction

To ascertain the formation of possible complex or complexes during the course of reaction, spectra were obtained by using systronics UV-VIS Spectrophotometer 2203 for different acidic solutions of NBS, Pd(II) and serine either alone or in the form of mixture. In the first case NBS concentration was fixed and acid conc. varied and the spectra recorded indicates decrease in absorption with increase in acid concentration (**Figure 7**). Further, Pd(II)chloride solution of three different concentrations such as 5.0×10^{-5}, 7.0×10^{-5} and 9.0×10^{-5} were added to the acidic solution of NBS,

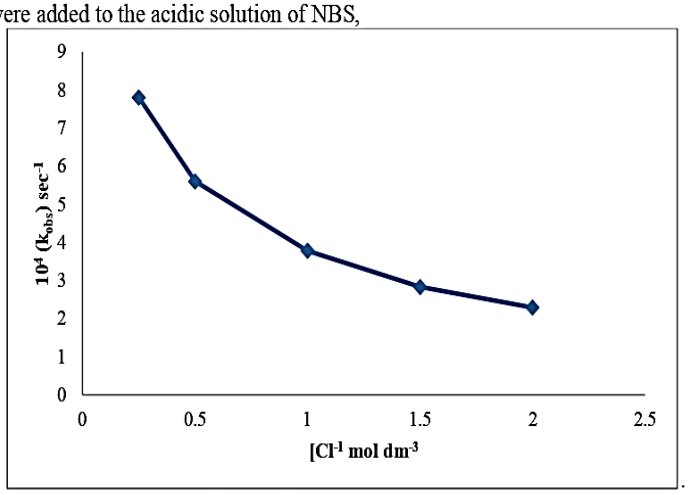

Figure 6 Variation of chloride ion

[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Ser] = 2.0 x 10^{-2} mol dm^{-3}, I = 0.25 mol dm^{-3}, [H^+] = .10 mol dm^{-3}, Temp. = 35 °C

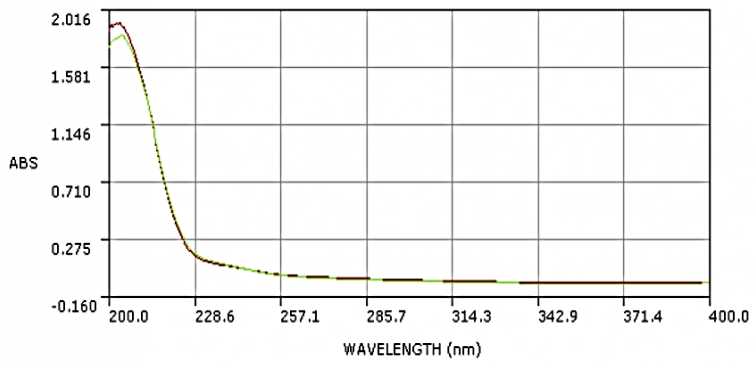

Figure 7 Acid variation

it was observed that there is an increase in absorbance which can be assigned to the existence of equilibrium step (11)(Complex C_2)proposed in the reaction scheme 2. (**Figure 8)** Again keeping the concentration of NBS, Pd(II) and acid constant and varying the serine concentration indicates increase in absorption which shows that the complex formed between NBS, Pd(II) and serine increases with the increase in concentration of serine (**Figure 9**).This indicates the formation of an unstable activated complex C_3 in the reaction under investigation as shown in the rate determining step (12) of reaction scheme 2.

On the basis of observed kinetic orders, spectroscopic information collected for the possible formation of complex or complexes in the reaction, a probable reaction path in the form of Scheme 2 can be proposed.

$$Ser + H^+ \overset{K_1}{\rightleftharpoons} Ser \cdot H^+ \quad (10)$$

[AA] [AA]$^+$

$$[PdCl_4]^{2-} + NBS \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} [PdCl_3.NBS]^{-1} + Cl^- \quad (11)$$

C_1 C_2

$$HOCH_2CHNH_2COOH + C_2 \xrightarrow{k} Complex[C] \quad (12)$$

C_3

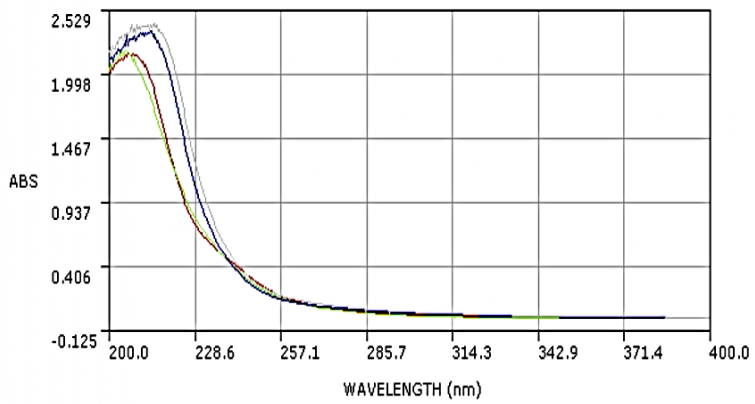

Figure 8 Serine concentration variation

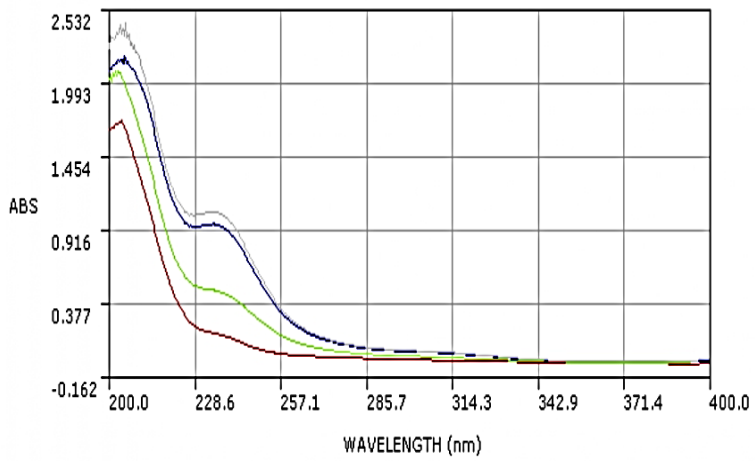

Figure 9 Pd(II) concentration variation

$$HOCH_2CHNH_2COOH + C_2 \xrightarrow{k} Complex[C] \quad (12)$$

C_3

$$Complex[C] \xrightarrow{2H_2O} [PdCl_2(OH)_2]^{2-} + NH_2\underset{\underset{R}{|}}{CH}\overset{\overset{O}{\|}}{C}OBr + NHS + Cl^- + 2H^+ \quad (13)$$

$$NH_2\underset{\underset{R}{|}}{CH}\overset{\overset{O}{\|}}{C}OBr \xrightarrow{2H_2O} \overset{+}{N}H_2=\underset{\underset{R}{|}}{CH}+CO_2+Br^- \qquad (14)$$

$$\overset{+}{N}H_2=\underset{\underset{R}{|}}{CH}\xrightarrow{H_2O}NH_3+RCHO+H^+ \qquad (15)$$

$$[PdCl_2(OH)_2]+2Cl^- \longrightarrow [PdCl_4]^{2-}+2OH^-$$

$$2OH^-+2H^+ \longrightarrow 2H_2O$$

$$H^++Br^- \longrightarrow HBr$$

$$Br^-+NBS \xrightarrow{H^+} NHS+Br_2$$

Scheme 2

The negligible effect of succinimide concentration on the rate of reaction is obvious, as it does not appear in the rate law.

The above rate law explains the first order in oxidant, fractional order in substrate and invert order in acid.

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

$$\frac{-d[C_2]}{dt}=K_2[NBS][C_1]-K_{-2}[C_2][Cl^-]-k[AA][C_2]=0 \qquad (16)$$

$$K_2[NBS][C_1]=K_{-2}[C_2][Cl^-]+k[AA][C_2]$$

$$=C_2\left[K_{-2}[Cl^-]+k[AA]\right]$$

$$C_2=\frac{K_2[NBS][C_1]}{K_{-2}[Cl^-]+k[AA]} \qquad (17)$$

$$\frac{-d[NBS]}{dt}=2k[C_2][AA]=\frac{2kK_2[NBS][C_1][AA]}{K_{-2}[Cl^-]+k[AA]} \qquad (18)$$

$$Pd(II)=C_1+C_2$$

$$=\frac{2kK_2[NBS][Pd(II)][AA]}{K_{-2}[Cl^-]+k[AA]}$$

$$Pd(II)=C_1$$

$$[AA]_T=[AA]+[AA]^+$$

$$=[AA]+K1\,[AA]\,[H^+]$$

$$[AA]_T=[AA]\,\{1+K_1[H^+]\}$$

$$[AA]=\frac{[AA]_T}{1+K_1[H]^+}$$

$$\frac{-d[NBS]}{dt}=\frac{2kK_2[NBS][Pd(II)][AA]_T}{K_{-2}[Cl^-]+\dfrac{k[AA]_T}{1+K_1\left[H^+\right]}} \qquad (19)$$

$$1+K_1[H^+]=\frac{2kK_2[NBS][Pd(II)][AA]_T}{\frac{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T}{1+K_1[H^+]}} \quad (20)$$

$$=\frac{2kK_2[NBS][Pd(II)][AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (21)$$

$$-\frac{d(NBS)/dt}{(NBS)}=\frac{2kK_2[Pd(II)][AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (22)$$

$$\frac{K_{obs}}{Pd(II)}=k'=\frac{2kK_2[AA]_T}{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]+k[AA]_T} \quad (23)$$

$$\frac{1}{k'}=\frac{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]}{2kK_2[AA]_T}+\frac{k[AA]_T}{2kK_2[AA]_T} \quad (24)$$

$$\frac{1}{k'}=\frac{K_{-2}[Cl^-]\left[1+K_1[H^+]\right]}{2kK_2[AA]_T}+\frac{1}{2K_2} \quad (25)$$

$$\frac{1}{k'}=\frac{K_{-2}[Cl^-]}{2kK_2[AA]_T}+\frac{K_{-2}K_1[H^+][Cl^-]}{2kK_2[AA]_T}+\frac{1}{2K_2} \quad (26)$$

Equation (25) suggests that plot of 1/k' versus $1/[AA]_T$ at constant $[H^+]$ and $[Cl^-]$ should be linear with positive intercept as shown in figure **(Figure 10)**. The value of K_2 comes out to be 18.52 mol^{-1} dm^3 sec^{-1} from the intercept equal to 0.027. Equation (26) suggests that 1/k'versus $[H^+]$ at constant $[Cl^-]$ and $[AA_T]$ should yield good linear plots passing through origin as shown in **(Figure 11)**. A high positive value of free energy of activation indicates that the transition state is highly solvated.

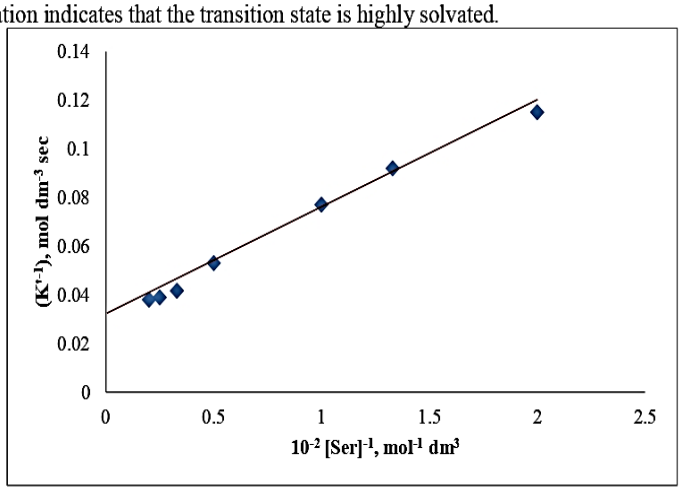

Figure 10 variation of 1/k' versus 1/[ser]
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Pd(II)] = 2.0 x 10^{-5} mol dm^{-3},
I = 0.25 mol dm^{-3}, $[H^+]$ = .10 mol $dm^{-}3$, Temp. = 35 ℃

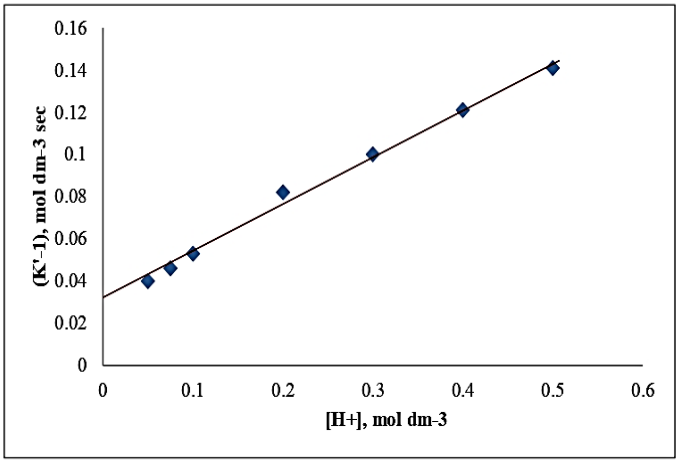

Figure 11 variation of 1/k' versus [H$^+$]
[NBS] = 2.0 x 10^{-3} mol dm^{-3}, [Ser] =2.0 x 10^{-2}mol dm^{-3},
[Pd(II)] = 2.0 x 10^{-5} mol dm^{-3}, I = 0.25 mol dm^{-3}, Temp. = 35 ºC

while negative value of entropy of activation suggests formation of an activated complex with a reduction in the degree of freedom of reacting molecules.

CONCLUSION

It is concluded that oxidation of serine by N-Bromosuccinimide in perchloric acid medium has the stoichiometry 2:1. The reaction is slow at room temperature but becomes fast in the presence of Pd(II) catalyst. The order with respect to NBS and Pd(II) is one and fractional order with respect to amino acid. The rate of reaction decreased with increase in perchloric acid and chloride ion concentration. The derived mechanism is consistent with all the experimental results.

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SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF PALLADIUM NANOPARTICLES ON OXIDATION OF ASPARTIC ACID IN ACIDIC AQUEOUS MEDIUM*

BY

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ABSTRACT

Palladium nanoparticles are synthesized through a single route chemical reduction method using synthetic polymer such as poly N-vinyl pyrollidone (PVP) stabilizer. The synthesized palladium nanoparticles were characterized by UV-visible spectrophotometer and Transmission Electron Microscopy (TEM) analysis. The particle size of palladium nanoparticles was found to be 1nm to 50 nm and spherical in shape at the optimal experimental conditions. The synthesized palladium nanoparticles are used as a catalyst for the oxidation of aspartic acid by N-bromosuccinimide in aqueous medium. The palladium nanoparticles catalyst exhibited better catalytic activity than equal amount of palladium precursor.

KEYWORDS

Oxidation, Palladium, Nanoparticles, Acidic Medium, Aspartic Acid.

Introduction

Metal nanoparticles are gaining importance in fields of physics (quantum optics), chemistry (catalyst) and nanotechnology. Chemical and physical properties of nanoscale metal clusters are quite different from those of bulk metals. The field of nanocatalysis has undergone an explosive growth during the past decades both in homogenous and heterogenous catalysis [1-2]. Since nanoparticles have a large surface to volume ratio compared to bulk materials, they are attractive to use as catalysts [3-4]. Now it is possible to prepare soluble analogues of heterogenous catalysts which are intermediate between those of the bulk metal and single metal particle (homogenous) catalysts. The major difficulty in working with nanoparticles is their undesirable agglomeration to form large particles. To prevent formation of such agglomerates, surfactants [5-6], ligand exchange materials [7-8] and polymeric carriers [9] are used extensively. Several studies on the uncatalysed and catalysed oxidation of amino acids have

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been reported [10-13] but with the emergence of metal nanoparticles processing appreciable stability and high surface area per particle, their potential use as catalyst for organic biochemical reactions stands well documented in recent years [14-15]. Noble metals like Pt [16], Pd [17], Ru [18] and Au [19] nanoparticles have been used as a catalyst in electron transfer and oxidation reactions. Noble metal nano crystals play an important role in different fields of science, such as catalysis, medicine, electronics etc. For most of these applications, the size, shape and size distribution of metal nanoparticles constitute the key factors. Not many studies on the oxidation of amino acids by Pd nano catalyst have been reported. So the present study deals with the synthesis, characterization of palladium nanocatalyst and their application on oxidation of aspartic acid by NBS catalysed by palladium nanoparticle.

Experimental

Reagents- Analytical grade chemicals such as $PdCl_2$, aspartic acid and NBS were obtained from E. Merck. Other reagents used were HCl, $HClO_4$, ethanol and PVP. The mol. wt. of PVP is 40 KD. A fresh solution of NBS, KI, hypo and starch was prepared before starting the experiment. All chemicals were used as received without further purification. Double distilled water was used for the study.

Synthesis of Pd nanoparticles

The chemical reduction method

The metal salts dissociate to form metal ions. The metal ions are then reduced by a reducing agent to form metal nanoparticles that are stabilized by a stabilizer.

The palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887 gms of $PdCl_2$ and 6 ml of 0.2 M HCl and diluting it to 250 ml with doubly distilled water. A solution containing 15 ml of 2 mm of H_2PdCl_4 , 21 ml of doubly deionized water, 0.0667 gms of PVP and 4 drops of 1M HCl was heated. When the solution began to reflux, 14 ml of ethanol was added. The solution was then refluxed for 3 hrs and this resulted in a dark brown suspension of Pd nanoparticles (Fig. 1). Thus, the reduction of H_2PdCl_4 by ethanol (as both solvent and reducing agent) occurred and Polyvinylpyrrolidone (PVP) stabilized Pd nanoparticles of various shapes.

Characterization

UV-visible spectrum is an effective method to investigate whether the metal precursors are completely reduced or not [20]. Palladium concentration effects on the conversion of Pd^{+2} to nano Pd^0 and preliminary estimation of palladium nano particle synthesis were investigated by UV-Visible spectrophotometer (double beam spectrophotometer-2203).

Figure-1. Photograph of palladium nanoparticle formation

The morphology of palladium nanoparticles strongly depend on the reaction conditions like temperature, duration, pH and the type of metallic precursor and stabilizer. The palladium particle size distribution of the colloidal solution decreased with increasing pH has been reported by Thiebaut [21]. The morphological study of the palladium nano particle was carried out with scanning of Transmission electron microscope by employing JEOL-JEM-2010XII TEM at 200 kV. TEM images were recorded to confirm size and shape of newly synthesized palladium nanoparticles. The oxidation product was monitored by FTIR (ALPHA-T Bruker).

Kinetic Measurements

In a typical experiment, glass stoppered Pyrex round bottom flask was used. Appropriate amount of the amino acid solution in acidic form, catalyst mercuric acetate, $NaClO_4$ (Ionic Strength) and water (to keep the volume constant) were taken in the flask. The temperature was maintained at 30° C by circulating thermostated water. An NBS solution kept in the thermostat separately was added to initiate the reaction. The progress of the solution was monitored by iodometric determination of the unreacted NBS in a measured weight of the reaction mixture at different intervals of time [22]. The rate constants were computed from the linear plots of log (NBS) against time.

Results and Discussion

(a) Pd nanoparticles Characterization Results

The reduction of Pd^{+2} to Pd^0 nanoparticles was monitored by UV visible spectroscopy in the range of 220 – 600 nm. Fig.-2 shows the absorption spectra of solutions at different times of reduction. The solution before the reduction is of pale yellow colour showing the peak at 310 nm in the spectrum. This is due to a charge transfer transition of the $(PdCl_4)^{2-}$ ions [23-24]. During

the reduction reaction, the consecutive disappearance of the absorption peak is attributed to the Pd^{+2} reduction completely reduced after 15 minutes. The colour intensity changes resulting in the increase in absorbance of the solution.

(b) Stability of nanoparticles dispersion

The stabilization of metal nanoparticles is achieved by the use of macromolecules such as polymers. PVP is mostly used because of its low cost and its ability to stabilize nanoparticles with accessible surface area in polar solvents such as water. One part of PVP chain adsorbs to the surface of the nanoparticles and the other part suspends freely in solution forming a protective layer. The Pd nanoparticle solution remains stable for more than 2 months.

Spectra at different time of preparation

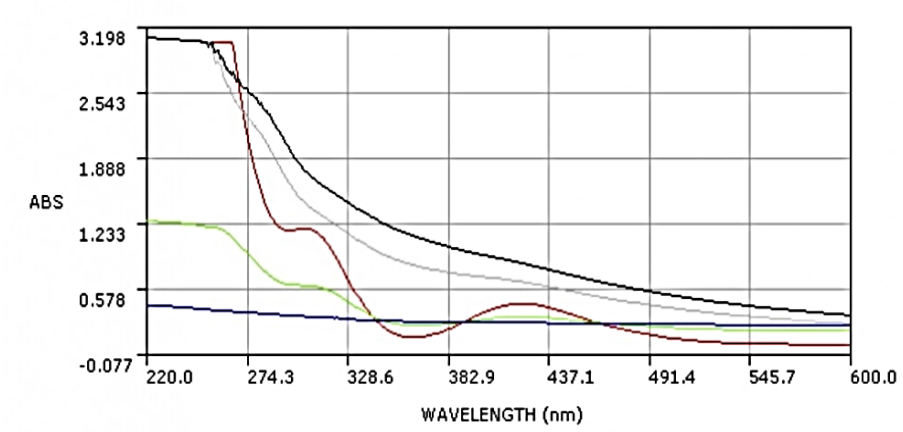

Figure 2. UV–vis spectra of PVP-protected Pd NPs in the range 220–600 nm

Results and discussion

Fig.-2 shows the absorption peaks at 310 and 410 nm that attribute to $[PdCl_4]^{2-}$, while the peak at 256 nm and 315 nm corresponds to PVP-stabilised Pd NPs using ethanol as reductant. These Pd NPs are stabilised by PVP polymer. Then, PVP polymer can bind preferentially to the {1 1 1} and {1 0 0} planes of metal Nanoparticles [25].

The spectroscopic studies indicate that PVP–Pd interaction occurs through the carbonyl group of the pyrrolidone ring. In our synthesis process, Pd NPs in the size range 1–50 nm in diameter have been obtained from aqueous solutions of $PdCl_2$ in the presence of PVP. They exhibit the most typical characteristics of Pd NPs synthesized in alcohol reduction. In general, cubic and octahedral Pd NPs have {1 0 0} and {1 1 1} planes. It is seen that Pd NPs of big size and sharp shape were observed. The important conclusion is that most of the large sized Pd NPs with

tetrahedral, octahedral and cubic shapes have been found due to the aggregation of the smaller seeds of spherical Pd NPs that are proved. It is clear that their sizes and the shapes are not controlled, and their sizes are large. There are a lot of aggregation and clustering of small Pd NPs possibly leading to form the big Pd NPs. It has been known that the major shapes of nanoparticles include cube, octahedron, tetrahedron, decahedron and icosahedrons, and structural variations from cubic to octahedral through cubo-octahedral nanocrystals. Noble metals have a face-centred cubic (fcc) lattice with different surface energies for different crystal planes, such as the combinations of the low-index and/or high-index {1 1 1}, {1 0 0} and {1 1 0} planes [26-28].

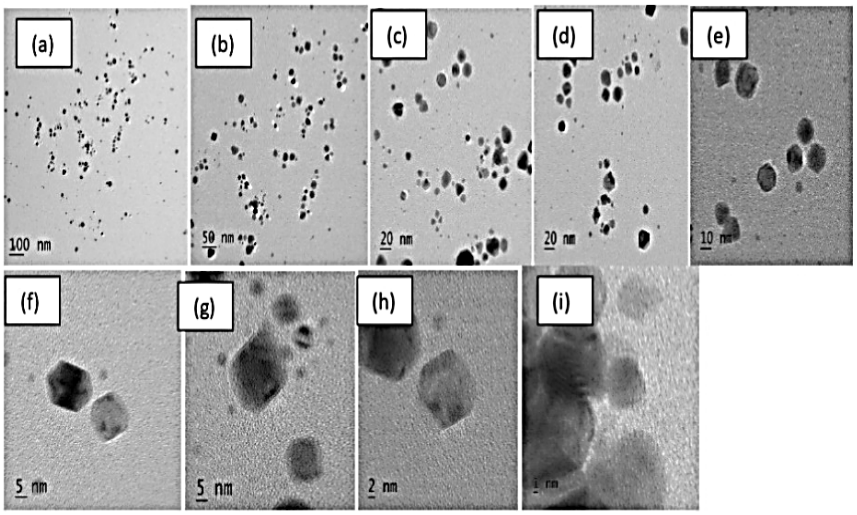

Figure-3. TEM images of major shapes and various sizes of Pd nanoparticles. TEM images of Pd nanoparticles with scale bars: (a) 100 nm, (b) 50 nm, (c, d) 20 nm, (e) 10 nm, (f, g) 5 nm, (h) 2 nm and (i) 1 nm

In fig.-3 (a)–(i), various shapes of Pd nanoparticles are spheres, cubes, tetrahedrons, octahedrons, twinned nanoparticles of twinned decahedral and icosahedral shapes, and other irregular shapes that are characterized by the formation of Pd nanoparticles by alcohol reduction [29].

Stoichiometry

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBS over amino acid (in varying ratios) at 35^0C for 48 hours and estimations of residual NBS in different sets showed that 1 mole of amino acid consumes two moles of NBS according to the stoichiometric equation. The reaction product was identified by qualitative test

and confirmed by FTIR spectrum in Fig.-4. Ammonia identified by Nessler's reagent, brownish colour was observed indicating deamination reaction, CO_2 was identified by freshly prepared lime water and the solution turned milky indicating decarboxylation reaction.

$$RCH(NH_2)COOH + 2NBS + H_2O \xrightarrow{Pd(II)/H^+} RCHO + 2NHS + CO_2 + Br_2 + NH_3$$

Where R= $-CH_2-COOH$

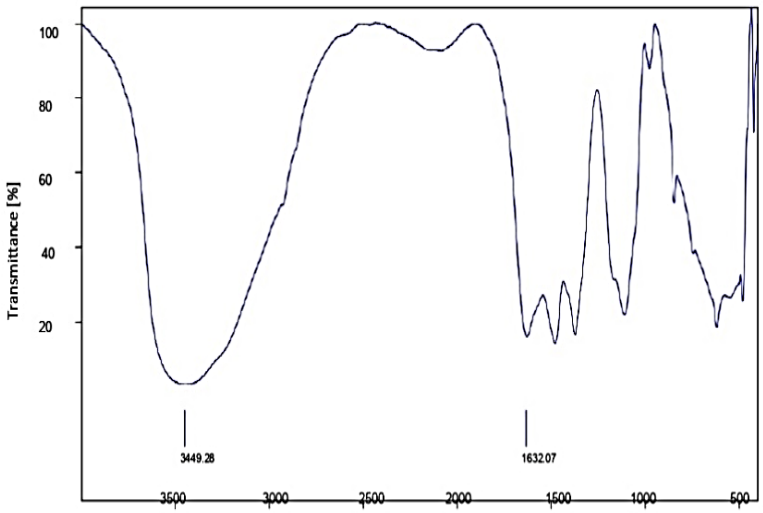

Figure-4. The FT-IR Spectra of the oxidation product of oxidation of Aspartic acid

Effect of NBS concentration

The Palladium nanoparticle catalysed oxidation of aspartic acid was studied at different concentration of NBS varying from 1×10^{-3} to 5×10^{-3} mol dm^{-1} at fixed concentration of [Aspartic Acid] = 2×10^{-2} mol dm^{-1}, $[Pd_{nps}] = 2\times10^{-5}$ mol dm^{-1}, $[H^+]$ = 0.1 M, [I] = 0.25 mol dm^{-3} and temperature 308 K. First order dependence in NBS was followed at all initial concentration of NBS. Psuedo first order rate constants (k_{obs}) were calculated from the slope of log (a-x) versus time plots (fig.-5). The first order kinetics with respect to NBS is also verified by the constant values of k_{obs} obtained at various initial concentrations of NBS.

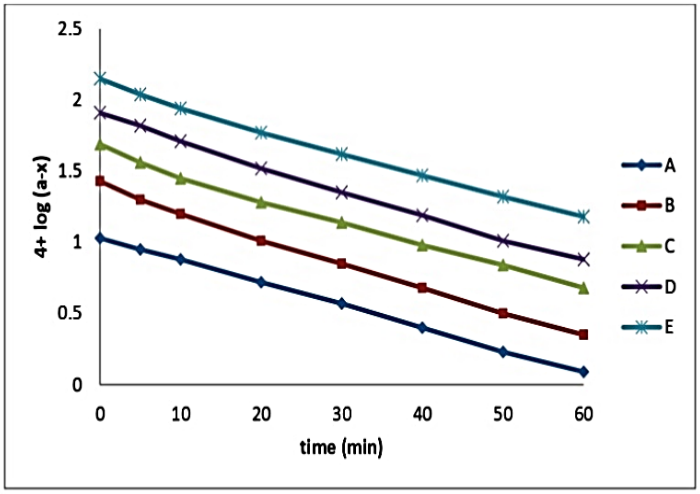

Figure-5 Variation of NBS

[NBS] = (A) 1 $\times 10^{-3}$ mol dm^{-3}, (B) 2 $\times 10^{-3}$ mol dm^{-3}, (C) 3 $\times 10^{-3}$ mol dm^{-3}, (D) 4 $\times 10^{-3}$ mol dm^{-3}, (E) 5 $\times 10^{-3}$ mol dm^{-3}

[Aspartic acid] = 2 $\times 10^{-2}$ mol dm^{-3}, [Pdnps] = 2 $\times 10^{-5}$ mol dm^{-1}, $[H^+]$ = 0.1 M, [I] = 0.25 moldm^{-3}, Temp.= 308 K.

Effect of Aspartic Acid

The effect of aspartic acid concentration was studied by varying concentration from 0.5$\times 10^{-3}$ to 5 $\times 10^{-3}$ mol dm^{-1} at constant [NBS], $[H^+]$, $[Pd_{nps}]$, [I] and temp., the kinetic runs were carried out with initial concentration of aspartic acid. A plot of (a-x) versus aspartic acid shows first order dependence of the reaction on aspartic acid at low concentration, which shifts towards zero order

at its higher concentration (table -1). The plot of log k_{obs} versus log [aspartic acid] was straight line with fractional slope confirming fractional order with respect to aspartic acid.

Effect of Pd nano catalyst

The effect of Pd nano catalyst was studied by varying the concentration from 0.5 to 5 $\times 10^{-3}$ mol dm^{-3} at fixed concentration of all reactants [NBS] = 2 $\times 10^{-3}$ mol dm^{-1}, [Aspartic acid] = 2 $\times 10^{-2}$ mol dm^{-3}, $[H^+]$= 0.1 M, [I] = 0.25 mol dm^{-3} at three temperature (303 K, 308 K, 313 K). The rate of reaction increases with increasing concentration of palladium nanoparticles (Table -1). The catalytic activity of palladium nanoparticles is shown by plotting a graph of k_{obs} versus palladium nanoparticles. The straight line indicated that the rate of reaction directly depends on concentration of palladium nanoparticles (fig.-6). The straight lines do not pass through the

Table-1 Effect of [NBS], Aspartic Acid, Pd nano catalyst and H^+ on oxidation of aspartic acid by NBS in perchloric acid medium in the presence of Pd nano catalyst

10^3 [NBS] mol dm^{-3}	10^2 [Aspartic Acid] mol dm^{-3}	10^5 [Pd nano catalyst] mol dm^{-3}	$[H^+]$ mol dm^{-3}	10^4 k_{obs} sec^{-1}
1.0	2.0	2.0	0.10	6.06
2.0	2.0	2.0	0.10	6.70
3.0	2.0	2.0	0.10	6.25
4.0	2.0	2.0	0.10	6.64
5.0	2.0	2.0	0.10	6.10
2.0	0.50	2.0	0.10	2.01
2.0	0.75	2.0	0.10	2.80
2.0	1.0	2.0	0.10	3.61
2.0	2.0	2.0	0.10	6.70
2.0	3.0	2.0	0.10	8.60
2.0	4.0	2.0	0.10	9.81
2.0	5.0	2.0	0.10	10.0
2.0	2.0	0.5	0.10	4.30
2.0	2.0	0.75	0.10	4.70
2.0	2.0	1.0	0.10	5.12
2.0	2.0	2.0	0.10	6.70
2.0	2.0	3.0	0.10	8.21
2.0	2.0	4.0	0.10	9.82
2.0	2.0	5.0	0.10	11.40
2.0	2.0	2.0	0.05	8.12
2.0	2.0	2.0	.075	7.31
2.0	2.0	2.0	0.10	6.70
2.0	2.0	2.0	0.20	5.50
2.0	2.0	2.0	0.30	4.32
2.0	2.0	2.0	0.40	3.21
2.0	2.0	2.0	0.50	2.40

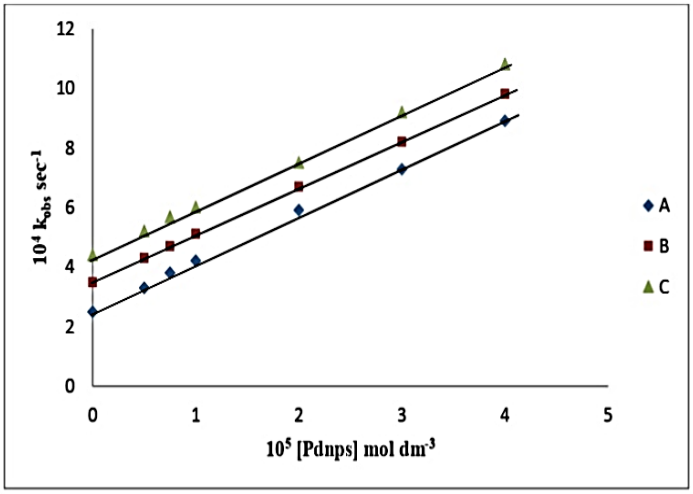

Figure- 6 Effect of [Pdnps] at different temperature

Temp. = (A) 303 K, (B) 308 K, (C) 313 K at fixed [NBS] = 2×10^{-3} mol dm^{-3}, [Aspartic acid] = 2×10^{-2} mol dm^{-3}, $[H^+]$ = 0.1 M, [I] = 0.25 mol dm^{-3}

origin, so it is evident that the uncatalysed oxidation of aspartic acid by NBS is also possible. The activation parameters of the reaction were calculated from the observed constants at three temperatures, 303 K, 308 K, 313 K (Table -2).

Table-2 Activation parameters of the reaction

[NBS] = 2×10^{-3} mol dm^{-3}, [Aspartic acid] = 2×10^{-2} mol dm^{-3}, [Pdnps] = 2×10^{-5} mol dm^{-3}, $[H^+]$ = 0.1 M, [I] = 0.25 mol dm^{-3}.

Temperature (K)	10^4 k_{obs} (sec^{-1})	E_a (KJ mol^{-1})	$\Delta H^{\neq}$ ($KJmol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	$\Delta G^{\neq}$ (KJ mol^{-1})
303	5.91	26.48	23.92	-220.01	91.68
308	6.70				
313	7.51				

Effect of $[H^+]$

A change in the rate of the reaction with the change in the concentration of $[H^+]$ was observed in the present investigation at constant concentration of all other reactants. The rate constants k_{obs} decreased with the increase in $[H^+]$ concentration (Fig.-7). The plot of log k_{obs} versus log $[H^+]$ is linear with a fractional slope.

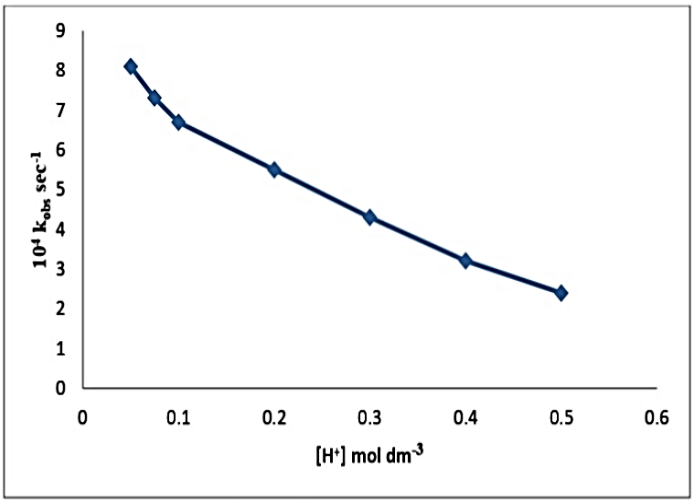

Figure-7 Variation of [H+]

[NBS] = 2 ×10^{-3} mol dm^{-3}, [Aspartic acid] = 2 ×10^{-2} mol dm^{-3}, [Pdnps] = 2 ×10^{-5} mol dm^{-3}, [I] = 0.25 mol dm^{-3}, Temp. 308 K

Mechanism

The definite mechanism of homogenous metal nanoparticles catalyzed oxidation is not clear. Although we identify the formation of transition species through certain physical measurements but it is very difficult to isolate and characterize from homogeneous mixture. The deamination of the amino group in aspartic acid to NH_3 occurs in the presence of palladium nanoparticles by NBS, while NBS changes to succinimide. The plausible mechanism in support of the observed kinetics is given in scheme-1.

$2NBS + Pd^0 + H_2O \rightarrow 2NHS + Pd^{+2} + O^{-2} + Br_2$

$Pd^{+2} + O^{-2} + R\text{-}CH(NH_2)COOH \rightarrow RCHO + NH_3 + CO_2 + Pd^0$

$2NBS + R\text{-}CH(NH_2)COOH + H_2O \rightarrow RCHO + 2NHS + NH_3 + CO_2 + Br_2$

Where R= $-CH_2-COOH$

Conclusion

Pd nanoparticles were successfully synthesized by the reduction of H_2PdCl_4 with the use of ethanol as a reductant in the existence of PVP polymer. It was seen that the parameters of the supply rate of the precursor, temperature and time of synthesis reactions have been used to make Pd nanoparticles by the soft chemical method. In addition, the homogeneity of the solvent for the preparation of the stock solutions to synthesize and control the size and morphology of the Pd nanoparticles is very important in our preparation procedure. The catalytic activity of

palladium nanoparticles was investigated through the oxidation of aspartic acid in aqueous acidic medium. The results of the study indicate the reaction between aspartic acid and N-bromo-succinimide in the presence of palladium Nanoparticles is fractional order. The study will be helpful in the biochemical and medical fields.

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Contents

10. Palladium Nanoparticles Synthesis and their Catalytic Application on Oxidation of Arginine in Aqueous Acidic Medium

Dhanraj[1]
Rashmi Gupta[2]
M. B. Yadav[3]

Abstract

The paper describes the preparation of Palladium nanoparticle (Pd np) through chemical reduction method using palladium chloride ($PdCl_2$) and stabilizer PVP (Poly vinyl pyrrolidone). Characterization of the palladium nanoparticle was done by UV-VIS Spectrometer and TEM. The range of the particle size was from 1 to 100 nm. Palladium nanoparticles of various shapes and sizes have been obtained by reduction in ethanol with HCl catalyst addition. The synthesized palladium nanoparticles are used as a catalyst for the oxidation of basic amino acid, arginine by N- bromosuccinimide in aqueous medium. These nanoparticles showed better catalytic activity as compared to equal amount of palladium precursor.

Keywords : Oxidation, Nanoparticle, Palladium, Arginine, Acidic medium.

Introduction

Nanoparticles prepared from noble metal have valuable importance due their distinctive physical–chemical properties such as catalytic, electronic, magnetic and optical properties and uses in the different fields of catalysts, medicine, electronics, chemical synthesis, fuel cell and oil refining processes. The size, shape and size distribution of metal nanoparticles constitute the major role. So concentration is focused on the preparation of noble metal nanoparticles with well-controlled morphology[1-6]. Compared to PGM (Platinum group metals), Palladium is attractive because of its lower cost and high activity towards oxygen reduction reactions[7]. Palladium(Pd) is interesting material for research due to its hydrogen storage preparation[8].

CONFERENCES/SEMINARS ATTENDED

LIST OF CONFERENCES ATTENDED

1. National Conference on “Recent Trends in Environmental Sustainability and Green Practices” (RTESGP-2019) organized by Dept. Of Botany, Government College Bundi, Rajasthan in collaboration with The Society of Life Science Satna (M.P.) Govt. College, Kota on 15-16 Nov. 2019. Presented paper on Kinetics of Isoamyl Alcohol inhibited uncatalysed on the Autoxidation of Sulphur Dioxide in Alkaline medium.
2. National Seminar on Environment: Problems, Solutions and Prospects organized by LBS Government College Kotputli, Jaipur on 13-14 December 2019. Presented paper on Mechanistic study of Uncatalyzed oxidation of Glycine by N-Bromosuccinimide in perchloric acid medium.
3. International Conference on “Multidisciplinary Approach Towards Sustainable Development and Climate Change for a Viable Future” (ICMSDC-2022), organized by Raj Rishi Govt. Autonomous College Alwar on 12th – 14th August 2022, Presented paper on Palladium Nanoparticles Synthesis and their Catalytic Application on Oxidation of Arginine in Aqueous Acidic Medium.
4. National Seminar on “Current Trends of Research in Biological Sciences” organized by Dept. Of Botany JDB Girls College, Kota on 27-28 Feb. 2023. Presented paper on Impact of heavy metals on biological activities of soil.
5. National Conference on “Recent Advances in Science and Technology” organized by Dept. Of Chemistry, Govt. College, Kota on 06-07 Oct. 2023. Presented paper on A Kinetic and Mechanistic Study of Oxidation of Arginine by QDC in Presence of SDS in Aqueous Perchloric Medium.

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