A Kinetic Study of Catalytic Oxidation of Amino Acids by Cerium (IV) in Aqueous Acid Medium

A Thesis

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Submitted by:

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Under the Supervision of

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Dedicated

To

My Parents

&

My Wife

University of Kota, Kota

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Certificate

It is to certify that,

(i) The thesis entitled ***"A Kinetic Study of Catalytic Oxidation of Amino Acids by Cerium(IV) in Aqueous Acid Medium"*** submitted by **Dhan Raj** is an original piece of research work carried out under my supervision.

(ii) Literary presentation is satisfactory and the thesis is in a form suitable for publication.

(iii) Work evidences the capacity of the candidate for critical examination and independent judgment.

(iv) Fulfills the requirement of the ordinance relating to the Ph.D. degree of the university.

(v) Candidate has put in at least 280 days of attendance every year.

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A Word of Gratitude

"Gratitude makes sense of our past, brings peace for today, and creates a vision for tomorrow."

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Chapter – 1

Introduction

Abstract

This chapter includes a brief review of chemical kinetics, reactive species of oxidant cerium(IV), catalyst manganese(II) and palladium(II). It also describes the importance of amino acids and discusses the oxidation studies of amino acids by different oxidants. This chapter also includes the application of chemical kinetics to study the complex chemistry of biological systems.

1.1 Chemical Kinetics

Chemical kinetics is a branch of physical chemistry which deals with the study of rate of reaction and the various factors which can hamper the yield of the overall reaction. It includes empirical studies of the effect of the concentration, temperature and hydrostatic pressure on reaction of various types. Such studies may be practically important in concentration with technical processes. A chemical reaction involve the breaking of existing bond which is present in the reactant and making of a new bond in respective product. A mechanism is a series of elementary steps by which the transformation might occur. Rates of chemical reactions are experimental findings. The rate of reaction always depends on the temperature at which it is run and usually depends on the concentrations of the reactants. Because of this latter fact, the rate of a reaction will usually change during the course of the reaction, the reactants get used up and their concentrations fall.

The rate of a reaction at a particular temperature often depends solely on the concentrations of the reactants present. For a reaction

$$A + B \rightarrow \text{Products}$$

such a dependence on concentration would be described by the rate law:

$$\text{Rate} = k\,[A]^{x}\,[B]^{y}$$

Where k is a constant called the rate constant, x and y are numbers, usually integers that give the order of the reaction. As written, the reaction would be x^{th} order in substance A, y^{th} order in the substance B and $(x + y)^{th}$ order overall. If one of the reacting species, for example A, has a concentration very much higher than the other species, then, during the course of the reaction, its concentration will not go down much. In other words, its concentration will be essentially a constant. In such a case, the rate law becomes rate ~ $k'[B]^{y}$, where $k' = k\,[A]^{x}$. By setting up an experiment this way, it is possible to determine specifically the effect of changing the concentration of B upon the rate of reaction. This amounts to determining the value of y. Likewise, if the concentration of B were deliberately made much larger than that of A, the exact effect of the concentration of A (the value of x) could be learned.

There are different types of chemical reactions and a wide variety of experimental techniques have been used to investigate them. A considerable amount of effort has been taken to study the kinetics and mechanism of the reaction in the gaseous phase. In many ways these investigations are useful for testing basic theories of reactions. Most of kinetic work has been done on reactions in liquid phase, especially since it is of greatest interest to the organic and inorganic chemist. A little amount of work has been done on the reactions in the solid phase. The reaction at the solid interfaces has received more attention. Though there are various types of reactions, but oxidation reactions are widely studied. Chemical kinetics is very useful to understand each step of the reaction and also it accounts the following different parameters- (1) the factors that affect the reaction rate (2) optimum condition which is very essential to obtain the desired product (3) the intermediate formed during the course of reaction (4) at what extent of time the reaction proceeds. Thus the mechanism of reaction can be easily understood with the help of chemical kinetics. The different factors which affect the rate of reaction are concentration of reactant, nature of solvents, temperature, catalyst, orientation of reacting species, surface area, ionic strength, intensity of light etc. A probable mechanism of reaction can be elucidated by using the information which is obtained by studying the rate of reaction.

The present research describes the application of chemical kinetics to study the complex chemistry of biological systems. Emphasis is given on extensive experimental data collection, determination of standard kinetic quantities relating to rate of reaction and development of the mechanism describing the chemical steps in solution phase. Product analysis and the stoichiometry under conditions as close as possible to those of the rate measurements are also explored.

The present research study broadly includes oxidation of amino acids, a biologically important reaction in the synthesis of polypeptides, proteins and nucleotides[1]. Oxidation of leucine and serine is studied by Ce(IV) in the presence of Mn (II) as catalyst and oxidation of valine and aspartic acid is studied by Ce(IV) in the presence of Pd (II) as catalyst.

A review of Ce(IV) as oxidant, Mn (II), Pd (II) as a catalyst and oxidation of amino acids is presented in this chapter.

1.2 Cerium (IV) – An Oxidant

Cerium has a property, unique among the lanthanides, which explain its ability to participate in one electron transfer reactions, its ability to exist in two stable adjacent oxidation states +3 and +4. Cerium in its ground state has an electronic configuration of $[Xe]4f^2 6s^2$, where Xe represents the xenon configuration. The electronic configuration of Ce^{3+} ion is $[Xe]4f^1$, while that of Ce^{4+} ion is $[Xe]4f^0$. The enhanced stability of the vacant f shell in Ce^{4+} accounts for the ability of cerium to exist in the +4 oxidation state. The large reduction potential value of 1.61V (vs NHE) make Ce(IV) a very efficient oxidizing reagent compared to other metal ions.

In acidic medium, cerium(IV) is a very strong one electron oxidant and its oxidizing power is comparable to that of lead(IV) oxide or that of manganese(III) salts. The first detailed study of the redox potential of the Ce^{4+}/Ce^{3+} couple under carefully controlled condition in sulphuric acid was published by Kunz (1931)**[2]**. Noyes and Garner (1936) studied**[3]** the redox potential of the same redox couple in nitric acid. The redox potential of the Ce^{4+}/Ce^{3+} couple depends very much on the nature and the concentration of the acid. For instance, the redox potential is +1.28V in 1M HCl, +1.44 V in 1M H_2SO_4, +1.61 V in 1M HNO_3, +1.70 V in 1M $HClO_4$ and it is as high as +1.87 V in 8M $HClO_4$**[4-5]**. The redox potential thus increases in the order hydrochloric acid < sulphuric acid < nitric acid < perchloric acid. Whereas the redox potential increases with increasing concentration of perchloric acid, it decreases with increasing concentration of nitric acid**[4]**. These variations in potential reflect the formation of ionic complexes and have been used to determine the nature and stability of these complexes. At a given acid concentration, the oxidation potential decreases as the ability of the anion to form stable complexes by association with the acid anion increases. Thus sulphate ion form very stable complexes with Ce(IV) whereas perchlorate ion probably does not make any complex at all.

The cerium(IV) species in perchloric acid[6-8] medium and sulphuric acid medium[9] have been established and equilibrium constants calculated. In aqueous H_2SO_4 media, Ce(IV) is both thermodynamically and kinetically weaker as an oxidising agent compared to Ce(IV) in aqueous $HClO_4$ media (cf. $E_0 = 1.7$ V in 1.0 mol dm^{-3} $HClO_4$; $E_0 = 1.4$ V in 1.0 mol dm^{-3} H_2SO_4). However Ce(IV) in aqueous H_2SO_4 media is highly stable and does not require any special precautions to prevent its photochemical decomposition[10] which occurs spontaneously in aqueous $HClO_4$ media.

Cerium(IV) is known to form several hydrolytic species depending on the pH of solution[11]. Hydrolytic forms of Ce(IV) are governed by following equilibria:

$$Ce^{4+} + H_2O \overset{K_h^1}{\rightleftharpoons} Ce(OH)^{3+} + H^+$$

$$Ce(OH)^{3+} + H_2O \overset{K_h^2}{\rightleftharpoons} Ce(OH)_2^{2+} + H^+$$

Hydrolysis of Ce(IV) in the absence of sulphate ion as a complexing ligand affects the kinetics of the oxidation reaction, this has been studied in detail[12]. However, the existence of hydrolytic species of Ce(IV) in the presence of SO_4^{2-} is still uncertain[12], and it is expected that complexation of this ion with sulphate in H_2SO_4 media suppresses the hydrolysis equilibria involving co-ordinated water ligands[13]. The possibility of such hydrolytic species however, can be ruled out in H_2SO_4 medium.

Cerium(IV) forms a number of complexes in sulphuric acid solution. Hardwick and Robertson[7] have reported the following equilibrium between various complexes in sulphuric acid solution of 2M ionic strength at 25°C.

$$Ce^{4+} + HSO_4^- \overset{K_1}{\rightleftharpoons} Ce(SO_4)^{2+} + H^+$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} HCe(SO_4)_3^-$$

The equilibrium constants K_1, K_2 and K_3 for above steps are reported[14] to be 3500, 200 and 20 at 25°C respectively spectrophotometrically. Since the species $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ are dominant forms of cerium(IV) in solution containing $[H_2SO_4] \leq 2.0$ mol dm^{-3}, the species $H_2Ce(SO_4)_4^{2-}$ governed by the following equilibrium is only formed in $[H_2SO_4] > 2.0$ mol dm^{-3}.

$$HCe(SO_4)_3^- + HSO_4^- \overset{K_4}{\rightleftharpoons} H_2Ce(SO_4)_4^{2-}$$

K_4 was determined to be 0.6 ± 0.1 at $20 \pm 2^{\circ}$C. Thus the species $H_2Ce(SO_4)_4^{2-}$ is ruled out to be reactive form of cerium (IV) under experimental conditions. In the oxidation of lactic[15] acid and mandelic[16] acid by cerium(IV) in sulphuric acid-sulphate media, $Ce(SO_4)_2$ had been identified as the active species.

1.2.1 Oxidation Studies with Cerium(IV)

The use of the ceric ion as an oxidant which reacts via a one electron step only is of substantial importance and is of interest in many fields in chemistry[17-20]. The oxidation of a variety of organic and inorganic compounds by cerium (IV) in acidic media has been the subject of several studies[21-28]. The mechanism suggested by various authors are not uniform, indicating that wide varieties of mechanism are possible depending upon the nature of cationic oxidant species as well as the various conditions for the reaction. In some cases, the mechanistic approach has been based on the intermediated complex formation, while in others the results have been interpreted by free radical mechanism. An intermediate complex between ceric ion and the organic species has been reported in perchloric acid, the coordination sites of the metal ion easily incorporates these species. However, in case of sulphuric acid, strong sulphate cerium(IV) complexes are formed and they block co-ordination sites of the oxidants to inhibit. Further the oxidation of organic compounds by Ce(IV) in sulphuric acid media in general seems to proceed through the intermediate complex formation[29-31]. Whereas, in the oxidation of the inorganic material As(III) and Sb(III) in perchloric or sulphuric acid media[32], oxidation of some amino acids, aldehyde and their derivatives in sulphuric acid media[33-35], evidence of free radical was observed and reduction of Ce(IV) to Ce(III) by one electron transfer was postulated.

S. T. Nandibewoor et al.[36] studied the kinetics of iodide catalysed oxidation of L-glutamic acid by cerium(IV) in aqueous sulphuric acid medium. The result suggest that L-glutamic acid combines with catalyst iodide to form a complex, which then reacts in a slow step with one mole of cerium(IV) to give the product cerium(III), a free radical derived from L-glutamic acid, carbon dioxide with regenerating the catalyst iodide. This free radical formed reacts with another mole of cerium(IV) in a further fast step to give the product cerium(III), succinic acid and ammonia. The results are accommodated in the scheme given below-

$$\mathrm{Ce^{4+} \cdot H^+ \overset{K_1}{\rightleftharpoons} Ce^{4+} + H^+}$$

$$\mathrm{HOOCCH_2CH_2CH(NH_2)COOH + I^- \overset{K_2}{\rightleftharpoons} Complex\ (C)}$$

$$\mathrm{Complex\ (C) + Ce^{4+} \xrightarrow[slow]{k} Ce^{3+} + HOOCCH_2CH_2\dot{C}H(NH_2) + H^+ + CO_2 + I^-}$$

$$\mathrm{HOOCCH_2CH_2\dot{C}H(NH_2) + Ce^{4+} \xrightarrow[H_2O]{fast} Ce^{3+} + HOOCCH_2CH_2CHO + H^+ + NH_3}$$

$$\mathrm{HOOCCH_2CH_2CHO + 2Ce^{4+} + H_2O \longrightarrow 2Ce^{3+} + HOOCCH_2CH_2COOH + 2H^+}$$

This scheme leads to rate law

$$(\mathrm{rate})_\mathrm{C} = \frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{kK_1K_2[\mathrm{Ce(IV)}][\mathrm{L-glu.acid}][\mathrm{I^-}]}{[\mathrm{H^+}] + K_1 + K_2[\mathrm{L-glu.acid}][\mathrm{H^+}] + K_1K_2[\mathrm{L-glu.acid}]}$$

Kinetics of oxidation of benzyl alcohol[37], vanillin[38], ketones[39], vicinal diols[40], chloramphenicol[41], serine[42] by cerium (IV) has been studied by various workers. The kinetics of oxidation of aspartic acid and glutamic acid[43] in nitric acid media by cerium(IV) and the oxidation of glycolic, malic, tartaric, and citric acid by cerium(IV) in nitric acid media were observed by N. Datt and co-workers[44].

A mechanism consisting of series of one electron steps has been reported in the reaction of Ce^{4+} with Hg(I)[45], H_2O[46], As(III)[47], Te(IV)[48]. An outer sphere electron transfer mechanism has been indicated in the oxidation of the one equivalent substrates be cerium(IV). Waters and Wilson[49] suggested the oxidation of hydroxyl amine by cerium(IV) in H_2SO_4 via inner sphere pathway to NH_2O which on further oxidation to HNO finally yielded N_2O.

Song et al.[50] studied the kinetics and mechanism of iridium(III) catalysed oxidation of ethylene glycol by cerium(IV) in sulphuric acid media. In the proposed mechanism, Ir(III) may bond to ethylene glycol to form an outer-sphere complex (Ir(III).EG), which is rapidly oxidized into an inner-sphere complex (Ir(IV).EG) by Ce(IV). As Ir(IV) is unstable, the free radicals can be generated through an inner-sphere electron transfer process between Ir(IV) and EG.

$$H^+ + HOCH_2CH_2OH \xleftrightarrow{K_1} HOCH_2CH_2OH_2^+$$

$$HOCH_2CH_2OH_2^+ + Ir(III) \xleftrightarrow{K_2} Ir(III).HOCH_2CH_2OH_2^+ \text{ (adduct)}$$

$$(Adduct) + Ce(SO_4)_2 \xrightarrow[slow]{k} Ir(IV).HOCH_2CHOH_2^+ + Ce(III) + 2SO_4^{2-}$$

$$Ir(IV).HOCH_2CHOH_2^+ \xrightarrow{fast} Ir(III) + HOCH_2\overset{\bullet}{C}HOH + 2H^+$$

$$HOCH_2\overset{\bullet}{C}HOH + Ce^*(IV) \xrightarrow{fast} Ce(III) + HOCH_2CHO + H^+$$

In the above equation Ce* represents any species of Ce(IV)

Kinetic investigations of the oxidation of oxalic acid by Cerium (IV) have been done in the sulphuric acid medium and results were analyzed in relation to inter molecular forces present in the medium[51]. The redox couple Ce(IV) / Ce(III) has been used to describe the fundamental processes involved in Belousov – Zhabotinsky Oscillating reactions [52].

Ce(IV) oxidation of different compounds in aqueous H_2SO_4 media in many cases kinetically highly sluggish and needs some metal ion catalyst. Some metal ions like Ruthenium(III)[53], Iridium (III)[54], Silver(I)[55], Rhodium(III)[56], Copper (II)[57], Osmium(VIII)[58], Mercury(II)[59], Chromium(III)[60] etc. have been used as catalyst in the oxidation by Ce (IV). Thus the use of suitable catalysts in Ce(IV) oxidation reaction in aqueous H_2SO_4 media is of much importance in cerate oxidimetry as well as in catalytic kinetic methods of analysis.

1.3 Metal Ion Catalysis

Transition metal ions have been extensively used as catalyst for effecting a number of reactions. The transition metal catalysed reactions are important for the chemical industry from both practical and economic point of view. Transition metal ions are found to be good catalysts and their complexes are also able to catalyse a wide variety of reactions like hydrogenation, oxidation and polymerization. In recent times, the studies on the use of transition metal ions either alone or as binary mixtures as catalysts in many redox reactions have been gaining interest. Their oxidizing and catalytic activities are due to the existence of variable oxidation states, as a consequence of partly filled d or f orbital. Their ability to form both sigma and pi bonds with other moieties or ligands is one of the chief factors for imparting catalytic properties of transition metals as well as their complexes. Most of the d-block elements show characteristics inter ligand migration reactions and such a process forms one of most important types of reaction in homogeneous catalysis.

The use of transition metals in catalysis has received considerable attention during the past century. Many of the properties of the transitions metals that make them useful in catalysis arise from their ability to exist in different oxidation states, allowing the metal to interact in a specific manner with a substrate depending on electron configuration. Transition metals in the higher oxidation state generally can be stabilized by chelation with suitable complex agent. Metal complexes are good oxidants in acid or alkaline media under appropriate reaction conditions.

The application of transition metal catalysts such as Ru (III)[61-62], Rh (III)[63-64], Cu (II)[65-66], Pd (II)[67-68] in kinetic studies of redox reactions involving organic substrates are reported in literature. It was found that these catalysts work efficiently in both acidic and alkaline media. Such studies become helpful for industrial growth as well as understanding of the biological properties of transition metal complexes.

1.3.1 Mn (II) – A Catalyst

Manganese is an essential microelement for the human body. In normal conditions, it plays an important role in bone and tissue formation (normal growth), normal reproductive functions and carbohydrate and lipid metabolism. Manganese (II) most probably acts as either catalyst or reductant, having the reduction potential[69] of the couple Mn^{VII}/Mn^{II} in dilute acid at 1.51V. Mn (II) has been widely used as a homogenous catalyst in various redox reactions[70-71]. The mechanism of catalysis is quite complicated due to the formation of different oxidizing states of the Mn (II). Although many complexes of Mn (II) with various organic and inorganic substances have been reported[72-74], the efficiency of Mn (II) as a homogenous catalyst can be visualised from the oxidation studies of organic substrates involving different oxidants such as Cr(VI)[75], V(V)[76], Ce(IV)[77] and Br(V)[78].

Manganese (II) has been used an efficient catalyst and reported in many kinetic studies[79-82]. In the oxidation of isopropyl alcohol by cerium(IV) in the presence of Mn(II) catalyst in aqueous H_2SO_4 media, the rate of reaction[79] increases with increase of Mn(II) concentration. Mn(II) oxidises the alcohol via 1:1 complex involving Mn(II) / Mn(III) catalytic cycle. The equilibrium $\mathrm{Ce(IV)} + \mathrm{Mn(II)} \rightleftharpoons \mathrm{Ce(III)} + \mathrm{Mn(III)}$ is rapidly attained. Similarly, oxidative decarboxylation and deamination of different amino acids by cerium(IV) mixed catalysed by Ir(III)-Mn(II) in aqueous H_2SO_4 medium has been reported[83], where the reactive intermediate is Mn(III). Whereas Radhakrishanmurti[84] and co-workers have reported that Mn(II) retard the oxidation of cyclohaxanol by Ce(IV) in acetic acid water mixture in the presence of perchloric acid. In the oxidation of As(III) by Ce(IV) in aqueous sulphuric acid medium catalysed by Mn(II), the participation of Mn(III) species was again reported[47].

A. S. Ogunja et al.[85] studied the kinetics and mechanism of Mn(II) catalysed oxidation of D-arabinose and D-xylose by chromium(VI) ions in perchloric acid medium. It is reported that in the presence of Mn(II), the reaction will proceed through the formation of a tri-molecular complex[86-87]. The positive catalytic effect of Mn(II) is due to a one step three electron reduction of Cr(VI) to Cr(III) in the rate determining step. One of the electrons transferred is donated by Mn(II) atom which transform Cr(IV) to Cr(III) and the other two electrons by the aldose sugar which is in accordance with Mohammed llyas[88]. The reaction mechanism was proposed as follows.

$$HCrO_4^- + H^+ \xrightleftharpoons{K_1} H_2CrO_4$$

$$H_2CrO_4 + RCH(OH)CHO \xrightleftharpoons{K_2} \underset{\text{ester}}{RCH(OH)CH - O - CrO_3H} + H_2O$$

$$H_2CrO_4 + Sugar + Mn(II) \xrightleftharpoons{K_3} \underset{\text{Complex (C)}}{(H_2CrO_4 - Sugar - Mn(II))}$$

$$\underset{\text{Complex (C)}}{(H_2\,CrO_4 - Sugar - Mn(II))} \xrightarrow[\text{slow}]{k_s} HCOOH + Cr(III) + RCHO + Mn(II)$$

$$H_2\,CrO_4 + RCHO \xrightarrow{Mn(II)/H^+} RCOOH + Cr(III) + Mn(III)$$

Where R = $C_3H_7O_3$

A similar complex formation was reported[89] in the oxidation of D-arabinose and D-xylose by vanadium(V) in the presence of manganese(II) homogeneous catalyst.

S. K. Rani et al.[90] reported the Mn(II) catalysed oxidation of α-amino acids by peroxomonosulphate in alkaline medium. The reaction proceed through formation of amino acid-Mn(II) complex. S. Mathur[91] and co-workers also reported the formation of such type a complex in the oxidation of alanine by cerium(IV) in presence of Mn(II) catalyst in sulphuric acid medium. In the kinetic study of Mn(II) catalysed oxidation of glycerol by Ce(IV) in aqueous sulphuric acid media[92], glycerol combines with Mn(II) to form a complex, which then reacts in a slow step with one mole of Ce(IV) to give Ce(III), a free radical derived from glycerol, and the regenerated Mn(II) catalyst. In a further fast step free radical then reacts with another mole of Ce(IV) to give Ce(III) and products. The proposed reaction mechanism is:

$$\mathrm{Ce^{4+}\cdot H^{+}} \xrightleftharpoons{\mathrm{K_1}} \mathrm{Ce^{4+} + H}$$

$$\mathrm{CH(OH)(CH_2OH)_2 + Mn^{2+}} \xrightleftharpoons{\mathrm{K_2}} \mathrm{Complex\ (C_1)}$$

$$\mathrm{Complex\ (C_1) + Ce^{4+}} \xrightarrow[\mathrm{slow}]{\mathrm{k}} \mathrm{Ce^{3+} + HOCH_2\dot{C}HOH + CH_2 = O + Mn^{2+} + H^{+}}$$

$$\mathrm{HOCH_2\dot{C}HOH + Ce^{4+}} \xrightarrow{\mathrm{fast}} \mathrm{Ce^{3+} + HOCH_2CHO + H^{+}}$$

The rate equation is:

$$\frac{-\mathrm{d[Ce(IV)]}}{\mathrm{dt}} = \frac{\mathrm{kK_1K_2[Ce(IV)][Glycerol][Mn(II)]}}{\mathrm{[H^{+}] + K_1 + K_2[Glycerol][H^{+}] + K_1K_2[Glycerol]}}$$

The oxidation of citric acid by acid bromate in presence of homogeneous catalyst Mn(II) has been reported by C. S. Reddy[93]. The proposed mechanism involves oxidation of the formed Mn(II)-citric acid binary complex to an intermediate by acid bromate which subsequently decomposes to the products.

1.3.2 Pd (II) – A Catalyst

One particular group of transition metals has been of special interest to chemists, namely the platinum group: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). The platinum group metals have shown outstanding catalytic activities in a broad range of chemical reactions ranging from oxidations, reductions, carbon-carbon couplings, carbon-heteroatom couplings and isomerizations[94-95]. Palladium redox chemistry seems to be essentially limited to organic compounds, only a few studies of redox reactions with inorganic species being available[96].

The versatility of palladium catalyst is directly related to some of its unique physical properties. First, palladium interconverts between the 0 and +2 oxidation state with relative ease ($d^{10}$and d^{8} respectively). As a rule of thumb, palladium in oxidation state 0 is considered nucleophilic while the +2 oxidation state is considered electrophilic. Until recently, the majority of research conducted on palladium catalysis has involved palladium in the 0 and +2 oxidation state. Nevertheless, species having oxidation states[97] +1, +3 and +4 do exist, and have recently found application in catalysis[98-99]. Palladium is moderately electronegative (2.2) and has a rather soft character. Properties like these make the metal center less prone to interact with electronegative hard groups (such as alcohols). Instead it has a higher affinity towards soft σ- and π-donors. Consequently, alkenes, alkynes and allenes readily form π-complexes with palladium[100].

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 dilute acid as 0.532V. Palladium chloride is the most important Pd (II) salt in the homogeneous catalytic chemistry of palladium. In acid media, as the chloride concentration increases the rate of the reaction also increases. In chloride media, palladium (II) forms several palladium (II) chloride complexes[101]. The utility of palladium (II) chloride as a non toxic and homogeneous catalyst has been reported by several workers[102-103].

The hydrolysis of palladium (II) chloride species in aqueous medium has received the attention of many investigators[104-107] and the formation constants for the mixed i.e. hydroxyl-chloride palladium species formed due to hydrolysis of palladium chloride complexes are reported[104-107]. The dominance of Pd(OH)Cl and $PdCl_3(OH)^{2-}$ species among various species in aqueous medium depending upon Cl^- concentration in solution has also been observed. The formation of these species may be considered as follows:

$$PdCl_2 + H_2O \rightleftharpoons PdCl(OH) + H^+ + Cl^- \qquad \text{(i)}$$

$$PdCl_4^{2-} + H_2O \rightleftharpoons PdCl_3(OH)^{2-} + H^+ + Cl^- \qquad \text{(ii)}$$

It has been observed that complex formation between amino acid and palladium (II) gets suppressed on increasing $[H^+]$ in the reaction mixture. Therefore, the complex formation may be proposed between amino acid and

PdCl(OH) (in the absence of Cl^-) and between amino acid and $PdCl_3(OH)^{2-}$ in the presence of Cl^-.

Palladium(II) is a well known catalyst for several organic transformations. Some interesting results in the homogeneous catalysis of successful commercial exploitation of the acetaldehyde in the presence of Pd(II) chloride have contributed to this interest. It is reported[108] that Pd(II) chloride is rather insoluble in aqueous solution but does dissolve in the presence of Cl^- ions as $PdCl_3(H_2O)^-$ and $PdCl_4^{2-}$.

$$Pd^{2+} + Cl^- \xrightleftharpoons{K_1} PdCl^+ \tag{iii}$$

$$PdCl^+ + Cl^- \xrightleftharpoons{K_2} PdCl_2 \tag{iv}$$

$$PdCl_2 + Cl^- \xrightleftharpoons{K_3} PdCl_3^- \tag{v}$$

$$PdCl_3^- + Cl^- \xrightleftharpoons{K_4} PdCl_4^{2-} \tag{vi}$$

Elding[104] has studies of both the stability constants and rates of reaction and determined values of log K_1 to log K_4 and also of log β_4. β_4 is the equilibrium constant for the following equilibrium:

$$Pd^{2+} + 4Cl^- \xrightleftharpoons{\beta_4} [PdCl_4]^{2-}$$

The equilibrium constants corresponding to the above equilibrium have been determined by several workers and all are in fair agreement with a value of log β_4 between 11 and 12 at 25°C[109].

In most of the studies using Pd(II) as the homogeneous catalyst, it has been employed in the form of Pd(II) Chloride. Pd(II) chloride, when dissolved in hydrochloric acid, exists in the form of $PdCl_4^{2-}$ as represent by equilibrium[110] (vi). The existence of $PdCl_4^{2-}$ is also supported by Ayres[111], who has observed that when a reaction ratio of 2:1 for sodium chloride (Cl^-ion) to palladium(II) chloride is maintained, the result is the formation of well known tetrachloropalladate(II), $PdCl_4^{2-}$.

M. K. Ghosh et al.[112] studied the kinetics and mechanism of palladium(II) catalysed oxidation of D-(+)galactose by cerium(IV) in aqueous medium. The kinetics of this reaction were studied and showed that the D-(+)galactose, Ce(IV) and catalyst Pd(II) ion interact in two equilibrium steps to form as intermediate complex[113-114] which is assumed to disproportionate forming a free radical and reduced to Ce^{3+} ion. Substrate is easily protonised in acid media in the presence of catalyst, indicating involvement of H^+ in the pre equilibrium step. Ce(IV) has been found kinetically active in this study with generation of free radicals in the reaction. Thus a mechanism consistent with the above kinetics is proposed in the given scheme.

$$Ce^{4+} + Pd^{2+} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \underset{\text{[Complex]}}{Pd^{3+} \cdots\cdots Ce^{3+}}$$

$$H^+ + D - \text{galactose[S]} + \underset{\text{[Complex]}}{Pd^{3+} \cdots\cdots Ce^{3+}} \xrightarrow{K_3} [\text{Complex}]_1$$

$$[\text{Complex}]_1 \xrightarrow[\text{slow}]{k_1} [\text{Free Radical}] + Pd^{2+} + 2H^+ + Ce^{3+}$$

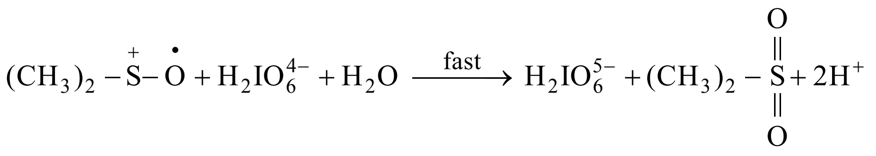
$$[\text{Free Radical}] + Ce^{4+} \xrightarrow[H_2O]{\text{fast}} \text{Arabinose} + HCOOH + H^+ + Ce^{3+}$$

Pushpanjali Singh[115] reported the 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 scavenger. The rate shows zero order kinetics in borate $[BrO_3^-]$ and order of reaction is one with respect to substrate and Pd(II) respectively. Increase in $[Cl^-]$ showed positive effect, while $[H^+]$ showed zero effect. A transient complex is formed between $[PdCl_2]$ and amino acid. Palladium chloride being reactive species of pallladium(II) chloride in 1:1 ratio, disproportionate in a slow and rate determining step. N. N. Halligudi et al.[116] studied the kinetics and mechanism of palladium(II) catalysed oxidation of allyl alcohol by N-chlorosuccinimide in aqueous alkaline medium. The result suggests the complex formation between the catalyst and substrate. A. K. singh[117] and co-worker also reported the formation of complex between Pd(II) and substrate in the mechanism of Pd(II) catalysed oxidation of methylamine and ethylamine by Ce(IV) in perchloric acid medium. Similarly the kinetics and mechanism of palladium(II) catalysed oxidation of dimethyl sulfoxide by alkaline periodate has been reported by B. L. Koli and S. T. Nandibewoor[118]. They observed that Pd(II) form a complex with DMSO which decomposes to the product in subsequent steps. The proposed mechanism is as follows:

$$H_3IO_6^{2-} + OH^- \overset{K_1}{\rightleftharpoons} H_2IO_6^{3-} + H_2O$$

$$Pd(II) + (CH_3)_2 - S = O \overset{K_2}{\rightleftharpoons} \text{Complex (C)}$$

$$\text{Complex (C)} + H_2IO_6^{3-} \xrightarrow[\text{slow}]{k} (CH_3)_2 - \overset{+}{S} - \overset{\bullet}{O} + H_2IO_6^{4-} + Pd(II)$$



$$(CH_3)_2 - \overset{+}{S} - \overset{\bullet}{O} + H_2IO_6^{4-} + H_2O \xrightarrow{\text{fast}} H_2IO_6^{5-} + (CH_3)_2 - \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}} + 2H^+$$

After reviewing the catalytic studies of Mn(II) in the oxidation studies of various substrates with different oxidants we have investigated the kinetics of oxidation of palladium (II) by cerium (IV) in the presence of acid in order to understand the behaviour of active species of cerium (IV) and palladium (II) in acid media and to arrive at a plausible mechanism.

1.4 Amino Acids

Amino acids are simple organic compounds. Their physical and chemical properties are due to the presence of both acidic and basic group presents in the same molecule. Amino acids are less acidic than most carboxylic acids and less basic than most amines. In fact, the acidic part of the amino acid molecule is the NH_3^+ group, not a COOH group. The basic part is the COO^- group, and not free NH_2 group. Because amino acids contain both acidic and basic groups, they are amphoteric (having both acidic and basic properties). It has been shown that neutral amino acids exist as inner salts with the dipolar structure as $H_3^+NCOO^-$, these are called "Zwitter ions". This is the form that amino acids exist in even in the solid state. If we dissolve the amino acid in water, a simple solution also contains this ion. Amino acids are known to exist in the following equilibrium in aqueous solutions.

$$\mathrm{RCHNH_2COOH \rightleftharpoons RCHNH_2COO^- + H^+ \rightleftharpoons RCH(NH_3^+)COO^-}$$

The dissociation of these acids is pH dependent.

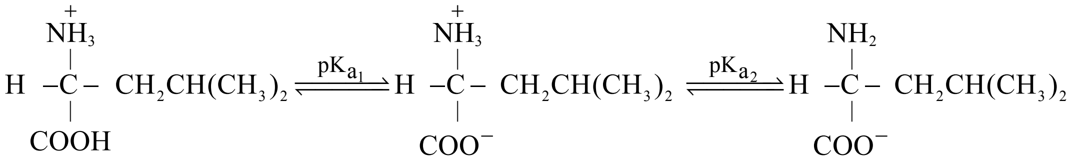
$$\mathrm{RCH(NH_3^+)COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCH(NH_3^+)COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} RCHNH_2COO^-}$$

Cation Zwitter ion Anion

The predominant form of the amino acid depends on the pH of the solution. In an acidic solution, the group is protonated to a free group, and the molecule has an overall positive charge. As the pH is raised, it loses its proton at about pH 2. This point is called pKa$_1$, the first acid-dissociation constant. As the pH is raised further, the group loses its proton at about pH 9 or 10. This point is called pKa$_2$ the second acid-dissociation constant. Above this pH, the molecule has an overall negative charge. The pH of the dilute solution of Zwitterions is determined by its basic strength and acidic strengths as:

$$\mathrm{pH} = \frac{\mathrm{pK}_{a_1} + \mathrm{pK}_{a_2}}{2}$$

Where pKa$_1$ and pKa$_2$ are the acid dissociation constant of its basic and acidic groups respectively. For leucine, pKa$_1$ and pKa$_2$ are 2.33 and 9.74 respectively, the pH of the dilute solution of leucine comes out to be 5.98. This pH 5.98 is the isoionic point of leucine where the number of negative charges on the molecule produced by protolysis equals the number of positive charges required by the gain of protons. Since the leucine molecule at this pH does not carry any net charge and is electrophoretically mobile, this point is also known as isoelectric point. Thus the ionization of leucine can be given as follows

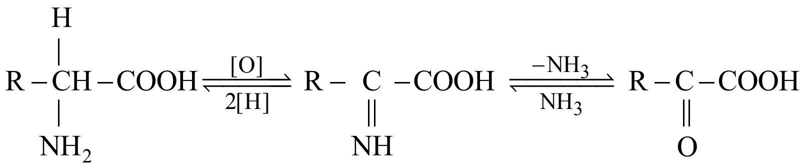


$$\mathrm{H-\overset{\overset{+}{NH_3}}{\underset{COOH}{C}}-CH_2CH(CH_3)_2 \overset{pK_{a_1}}{\rightleftharpoons} H-\overset{\overset{+}{NH_3}}{\underset{COO^-}{C}}-CH_2CH(CH_3)_2 \overset{pK_{a_2}}{\rightleftharpoons} H-\overset{NH_2}{\underset{COO^-}{C}}-CH_2CH(CH_3)_2}$$

Cation Zwitter ion Anion
Acidic ← pH → Basic
(Isoionic point)

1.5 Oxidation of Amino Acids

Oxidation reactions are of fundamental importance in nature and are key transformations in organic synthesis. Oxidation reaction of amino acid are one of the most relavent biochemical reactions because, such reactions serve as models for protein oxidation[119-121]. The kinetic and mechanistic features of a particular oxidation reaction are likely to be affected by the polar and nonpolar nature of the side chain of amino acid in solution and the active species of the oxidant[122-123]. Amino acids can undergo many kinds of reactions depending on whether a particular amino acid contains non polar or polar substituents. The amino and carboxyl functional group of amino acids is more reactive compared to the hydrocarbon moiety (RCH-) and hence only these functional group undergo chemical transformation. This property is attributed to the higher reactivity of the former compared to R. Amino acids represent organism forerunner of essential biomolecules such as proteins, hormones, enzymes; also, they may serve as energy source, losing their amino group by two pathway: transamination and oxidative deamination. The steps of oxidative deamination are resumed in the following scheme.



$$R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-COOH \underset{2[H]}{\overset{[O]}{\rightleftharpoons}} R-\underset{\underset{NH}{\|}}{C}-COOH \underset{NH_3}{\overset{-NH_3}{\rightleftharpoons}} R-\underset{\underset{O}{\|}}{C}-COOH$$

Oxidative deamination of amino acids

The study of amino acids is one of the most exiciting fields of organic chemistry. They play a significant role in a number of metabolic reactions like biosynthesis of polypeptide, protein and nucleotides. Thus, the mechanism of analogous nonenzymatic chemical processes in the oxidation of amino acids is a potential area for intensive investigation[124] in order to understand some aspects of enzyme kinetics. Amino acids are very attractive natural ligands for both toxic and essential metal ions. Besides acting simply as effective chelators, in many cases they are also reducing agents; e.g. for metal ions such as Ce(IV), V(V), Co(III) and Fe(III), depending on the acidity of the medium. There is also an indication that some amino acids may play an important role in the chemistry of chromium, especially in the environment, where Cr(V1) may present a serious hazard because of its mutagenic and carcinogenic activity[125-127]. They have been oxidized by a variety of reagents under different experimental conditions and they often undergo oxidative decarboxylation and deamination. It is well known that amino, carboxyl and side chain of amino acids undergo chemical transformations in the presence of different kinds of metal ion oxidant. The studies of the amino acids by various oxidants[128-132] both in acidic and alkaline media have been reported. Many reagents have been investigated towards oxidative decarboxylation of α-amino acids, which give nitrile[142-143] or a mixture of nitrile and aldehyde[145-148] as the products depending on the reaction conditions and reagents employed. Beside aldehyde and nitriles, α-keto-acids are also reported to be formed as oxidation product[138].

Gowda and co-workers have studied the oxidation of amino acids by various halogen oxidants viz. chloramine T[133-135], its dimer dichloramines[136] and bromamine T[137]. The oxidation product is aldehyde via hydrolysis of imine intermediate. However, Vivekanandam et al.[138] showed for the oxidation of imine by another molecule of chloramine T to nitrile. The kinetics and mechanism of some neutral and acidic α-amino acids by tetrabutylammonium tribromide in aqueous acetic acid medium was reported, the product are corresponding aldehydes[139]. Chloride ion catalysed oxidation of few amino acids by 1-chlorobenzotriozole in acidic medium has been reported[140] and oxidation of these acids to nitrile as product take place. The electron flow during the oxidation from the substrate to the oxidant is via an intermediate. The halogeno complex attacks the N of the amino group of the amino acid in the slow step, yielding mono-N-chloro derivative of amino acid, which then interact with a second molecule of the complex to form N, N-dichloro derivative. This derivative undergoes decomposition to HCl and CO_2, leading to the nitrile as a product. It is very much surprising, that such an N-chloro derivative of triazole undergoes four electron changes whereas, chloramine T being a better oxidant interacts with amino acid in a two electron transfer step.

Yathiragen et al.[141] reported the kinetic studies of the oxidation of L-isoleucine and L-ornithine hydrochloride by N-bromobenzensulphonamide in perchloric acid medium. The rate showed first order dependence on both [BAB] and amino acid and inverse first order dependence on [H^+] for [ISL] and first order depence on [H^+] for [ORH]. Isovaleronitrile and 3-(methylamino) propionitrile were identified as the products. Oxidation with 1-chlorobenzotriozole(CBT)[140] and trichloroisocynuric acid[142-143] also reported the product as nitriles. However A. K. Singh et al.[144] reported the oxidation of valine by N-bromophthalimide in presence of chloro complex of Pd(II) as homogeneous catalyst. The products were identified as a mixture of nitriles and aldehyde. Oxidation with other oxidizing agents such as sodium hypobromite[145], N-bromosuccinimide[146], tert-butyl hypochlorite[147], chloramine T[148], a mixture of aldehyde and nitrile was formed in varying ratios depending on reaction condition employed.

N. M. I. Alhaji et al.[149] studied the the kinetics of oxidation of glutamic acid with N-bromophthalimide (NBP) in perchloric acid medium. The reaction is first order each in NBP and glutamic acid and is negative fractional order in [H^+]. The main product of the reaction was succinic acid. The oxidation of glutamic and aspartic acid by N-bromobenzensulphonamide[150] in aqueous perchloric acid gives corresponding acid as product.

The study of Ag(I) catalysed oxidation of L-leucine by cerium(IV) in sulphuric acid medium has been reported[151]. The oxidation product was aldehyde rather than nitriles.

$$\mathrm{RCH\,\overset{+}{N}H_3\,COOH + Ag^1 \xrightarrow{K} RCH(H_3N^+)COOH - Ag^1}$$

$$\mathrm{RCH(H_3N^+)COOH - Ag^1 + Ce(SO_4)_2 \xrightarrow[slow]{k} RCH(H_3N^+)COOH - Ag(II)}$$
$$\mathrm{+\,Ce(III) + 2SO_4^{2-}}$$

$$\mathrm{RCH(H_3N^+)COOH - Ag(II) \longrightarrow Ag^1 + RCH(H_3N^+)CO\dot{O} + H^+}$$

$$\mathrm{RCH(H_3N^+)CO\dot{O} + Ce(SO_4)_2 + H_2O \longrightarrow RCHO + H^+ + 2SO_4^{2-}}$$
$$\mathrm{+ Ce(III) + CO_2 + \overset{+}{N}H_4}$$

Where R = $-CH_2-CH-(CH_3)_2$

Amino acid are reported to form an adduct with Ag(I) owing to availability of electron pair on oxygen atom. Therefore, an adduct between Ag(I) and leucine is initially formed that on further interaction with Ce(IV) yields another adduct of higher valent silver. The results suggests that L-leucine combines with catalyst Ag(I) to form complex, which then reacts in a slow step with one mole $Ce(SO_4)_2$ to give the product Ce(III), complex, H^+, and $2SO_4^{2-}$ with regeneration of the catalyst Ag(I). The complex reacts with another mole of $Ce(SO_4)_2$ in a further fast step to give the products, Ce(III), isopentanaldehyde, CO_2 and ammonia.

K. Vivekanandan and R. Lakshmi Narayanan[152] also reported the oxidation of essential amino acids like valine, leucine, isoleucine, threonine, phenylalanine and histidine by nicotinium dichromate (NDC) in aqueous perchloric acid medium. The main product of reaction is aldehyde and the reaction has first order dependence with [NDC]. The order of the reaction is fractional with respect to amino acids and second order with respect to perchloric acid. Mechanism was proposed involving complexation between NDC and amino acids.

$$\mathrm{NDC + H^+ \overset{K_1}{\rightleftharpoons} NDCH^+}$$

$$\mathrm{S + H^+ \overset{K_2}{\rightleftharpoons} SH^+}$$

$$\mathrm{NDCH^+ + SH^+ \xrightarrow[slow]{k_3} [Complex]}$$

$$\mathrm{[Complex] \xrightarrow[fast]{K_4} HCHO + Cr(IV)}$$

$$\frac{\mathrm{K_1K_2[NDC][S][H^+]^2}}{\mathrm{1 + K_2[S]}}$$

The above mechanism leads to the following rate law:

$$\text{rate} = k_3\,[\text{Complex}]$$

$$= \frac{K_1K_2k_3[\text{NDC}][\text{S}][\text{H}^+]^2}{1+K_2[\text{S}]}$$

B. Mohanty et al.[153] studied the oxidation of L-lysine by alkaline permanganate ion in alkaline medium catalysed by Cu(II), Ni(II) and Zn(II). The product obtained is aldehyde. H. Iloukhani and H. Bahrani[154] studied the kinetics and mechanism of the permanganic oxidation of L-glutamine in sulphuric acid in absence and presence of silver(I) and the product reported was aldehyde. The result suggests that an adduct is formed between silver(I) and L-glutamine in a fast step before it is oxidized by manganese(VII) in a slow step to yield the silver(III) substrate adduct. This silver(III) adduct might then disproportionate in subsequent fast step to give the final product. The reaction scheme taking L-glutamine could be written as the following steps:

$$\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH(NH}_2\text{)COOH} + \text{Ag}^+ \xrightleftharpoons[\text{fast}]{K_1} (\text{adduct})^+$$

$$(\text{Addcut})^+ + \text{Mn(VII)} \xrightarrow[\text{slow}]{k_c^n} (\text{Addcut})^{3+} + \text{Mn(V)}$$

$$(\text{Addcut})^{3+} \xrightarrow[\text{fast}]{\text{H}_2\text{O}} \text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH(NH}_2\text{)COO}^+ + \text{Ag}^+ + \text{H}^+$$

$$\text{H}_2\text{NCO(CH}_2)_2\text{CH(NH}_2\text{)COO}^+ \xrightarrow[\text{fast}]{\text{H}_2\text{O}} \text{H}_2\text{NCO(CH}_2)_2\text{CHO} + \text{CO}_2 + \text{NH}_3 + \text{H}^+$$

$$2\text{Mn(V)} \xrightarrow{\text{fast}} \text{Mn(VII)} + \text{Mn(III)}$$

$$2\text{Mn(III)} \xrightarrow{\text{fast}} \text{Mn(IV)} + \text{Mn(II)}$$

$$\text{Mn(V)} + \text{Mn(IV)} \xrightarrow{\text{fast}} \text{Mn(VIII)} + \text{Mn(II)}$$

A similar study of uncatalysed and Ru(III) catalysed oxidation of L-proline by heptavalent manganate in aqueous alkaline medium[155] is reported. The order in both permanganate and Ru(III) was found to be unity. The oxidation product was aldehyde. In another study by Sadhanasenapati[156] the product reported was α-keto acid in oxidation of L-histidine by permanganate in aqueous alkaline medium.

Similarly N. P. Shetti and co-workers[157] also reported the product as acid in the oxidation of L-tryptophan by diperiodatocuprate(III) catalysed by Ru(III) in aqueous alkaline media. Whereas in the study of Os(VIII)/ Ru(III) catalysed oxidation of L-lysine by diperiodatocuperate(III) in aqueous alkaline medium reported by D. C. Hiremath et al.**[158]**, the reaction product was identified as corresponding aldehyde. Another study of Ru(III) catalysed oxidation of L-lysine by diperiodatoargentate(III) in aqueous alkaline media by R. R. Hosmani and S. T. Nandibewoor**[159]** also reported the product was aldehyde.

S. B. Haveri et al.**[160]** studied the oxidation of L-leucine by chromium(VI) in perchloric acid medium. The result suggest that $HCrO_4^-$ reacts with L-leucine to form a complex, which decomposes in rate determining step to give an intermediate, chromium(V) species, a free radical derived from leucine and CO_2 is liberated. In the subsequent steps, acid chromate reacts giving aldehyde as the final product. The proposed mechanism is given as below:

$$CrO_4^{2-} + H^+ \overset{K_1}{\rightleftharpoons} HCrO_4^-$$

$$HCrO_4^- + RCH(\overset{+}{N}H_3) - COO^- \overset{K_2}{\rightleftharpoons} \text{Complex (C)}$$

$$R\overset{\bullet}{C}HNH_2 + HCrO_4^- + H_2O \xrightarrow{\text{fast}} RCHO + H_2CrO_4^- + NH_3$$

$$2RCH(\overset{+}{N}H_3) - COO^- + 2H_2CrO_4^- \xrightarrow{\text{fast}} 2R\overset{\bullet}{C}HNH_2 + 2CO_2 + 2H_3CrO_4^-$$

$$2R\overset{\bullet}{C}HNH_2 + 2H_3CrO_4^- \xrightarrow{\text{fast}} 2RCHO + 2NH_3 + 2CrO_2^- + 2H_2O$$

Where R = $-CH_2-CH-(CH_3)_2$

On the other hand the oxidation of L-cystine by chromium(VI) in perchloric acid medium was studied by K. K. Adari and co-workers**[161]**. It is observed that the order with respect to cystine is fractional, whereas chromium(VI) follows first order kinetics. Cystic acid found to be the main product. Z. Khan and K. Din**[162]** also reported the product as acid in the oxidative degradation of DL-serine by chromium(VI) in aqueous sulphuric acid medium.

Few kinetic results of the oxidation of amino acids by cerium(IV) in acid medium have been given in **Table 1.1.**

Table 1.1: Reported results of oxidation of amino acids by ce(IV) in acidic medium

S. No.	Amino Acid	Oxidant	Catalyst	Medium	Products	Activation Parameters				Ref.
						ΔE kJ mol^{-1}	ΔS JK^{-1}mol^{-1}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	
1	Alanine	Cerium(IV)	Mn(II)	H_2SO_4	Aldehyde	40.19	-82.02	37.59	80.57	91
2	Valine	Cerium(IV)	Ag(I)	$HClO_4$	Aldehyde	97	-77	44	69	167
3	L-leucine	Cerium(IV)	Ag(I)	H_2SO_4	Aldehyde	59.51	–87.08	56.82	84.92	151
4	Alanine	Cerium(IV)	Ag(I)	$HClO_4$	Aldehyde	18.9	–10.9	–	–	163
5	DL-Methionine	Cerium(IV)	–	$HClO_4$	Aldehyde	27.3	–196	24.7	85.5	164
6	Glycine Serine Glutamic Acid	Cerium(IV)	Mn(II)	H_2SO_4	Aldehyde	–	–258 −270 −261	16.6 12.7 15.2	97.4 97.5 97.0	165
7	L-Glutamic Acid	Cerium(IV)	Iodine	H_2SO_4	Carboxylic Acid	23±1	–88±2.21	21±1	47±2	36
8	Glutamic Acid Aspartic Acid	Cerium(IV)	Ag(I)	$HClO_4$	Aldehyde	67.9 68.4	−36.5 −57.1	−	79.0 86.0	166

9	L-Glycine	Cerium(IV)	Ag(I)	H_2SO_4	Aldehyde	107.42	–49.58	104.75	120.76	55
10	L-Methionine N-acetyl L-Methionine	Cerium(IV)	–	H_2SO_4	Methionine Sulphoxide N- Methyl Sulphoxide	61.08 66.85	–51.55 –31.87	63.52 64.50	76.19 73.51	174
11	Glutamic Acid Aspartic Acid	Cerium(IV)	Ag(I)	HNO_3	Aldehyde	67.9 68.4	−36.5 −57.1	–	79.0 86.0	43
12	L-Serine	Cerium(IV)	Ag(I)	H_2SO_4	Aldehyde	66.65	–64.25	64.21	188.89	168
13	L-Cystine	Cerium(IV)	–	H_2SO_4	Cysteic Acid	57.4	–122.7	–	–	169
14	L-Alanine	Cerium(IV)	Ag(I)	H_2SO_4	Aldehyde	63.85	–70.06	61.37	86.22	33
15	L-Leucine	Cerium(IV)	K(I)	H_2SO_4	Aldehyde	–	–	–	–	170
16	Hydroxylysine	Cerium(IV)	Ag(I)	$HClO_4$	Aldehyde	–	–	–	–	171
17	L-Tyrosine N-Acetyl L-Tyrosine	Cerium(IV)	Ag(I)	H_2SO_4	Aldehyde	125.08 74.60	−177.27 −185.81	122.06 72.17	81.87 126.61	172
18	Lysine	Cerium(IV)	Ag(I)	$HClO_4$	Aldehyde	–	–	–	–	173

A systematic kinetic study of the oxidation of amino acids namely leucine, serine, valine and aspartic acid by cerium(IV) in sulphuric acid medium was carried out to explain the mechanistic aspects of these oxidations and to understand the active form of cerium(IV) in aqueous acidic medium. The present study is carried out to identify the rate of oxidation, the catalytic effect of Mn (II) ion and Pd (II), product formed and to propose a suitable mechanism. The results have been discussed in the subsequent chapters.

1.6 Scope of the Work

Oxidation of amino acids is of great importance both from a chemical point of view and from its bearing on the mechanism of amino acid metabolism. Amino acids not only act as building blocks in protein synthesis but also play a significant role in the metabolism. Amino acids are the monomers of protein which find a large number of applications in different biochemical processes such as nutrition, metabolism and fortification of seeds and specially in the synthesis of the advanced nanomaterials as reducing, capping and stabilizing agents. Oxidative decarboxylation of amino acids is one of the well reported biochemical processes. The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidant to yield the different products. Ce(IV) is well known oxidant in acid media having the reduction potential of the couple Ce(IV)/Ce(III) 1.70 V. Cerium(IV) is one of the most important one equivalent oxidant in acid medium which has been used in numerous kinetic, mechanistic and analytic studies. The basic advantage of cerium(IV) over other oxidants is its reduction to a single substance cerium(III), without any intermediate reactions. It is a strong oxidant under acidic condition and is stable towards heat and light.

Thus the study of kinetics and mechanism of oxidation of amino acids using Ce(IV) as oxidant, Pd(II) and Mn(II) as a catalyst is very important from biochemical and kinetic view point points.

1.7 References

1. H. D. Jakubke and H. Jersehkeit, ***"Amino Acids, Peptides and Proteins"***, Wiley, New York, 1977; H. C. Freeman, ***Adu. Protien Chem.,*** **22,** 258, 1967.
2. A. H. Kunz, ***J. Am. Chem. Soc.,*** **53,** 98, 1931.
3. A. A. Noyes and C. S. Garner, ***J. Am. Chem. Soc.,*** **58,** 1265, 1936.
4. G. F. Smith and C. A. Getzs, ***Ind. Eng. Chem. Anal. Ed.,*** **10,** 191, 1938.
5. E. Wadsworth, F. R. Duke and C. A. Goetz, ***Anal. Chem.,*** **29,** 1824, 1957.
6. M. S. Sherrill, C. B. King and R. C. Spooner***, J. Am. Chem. Soc.,*** **65,** 170, 1943.
7. T. J. Hardwick and E. Robertson, ***Can. J. Chem.,*** **29,** 818, 1951.
8. H. G. Offner and D. A. Skoog, ***Anal. Chem.,*** **38**, 1520, 1996.
9. A. Roy and A. K. Das, ***Ind. J. Chem.,*** **41A,** 2468, 2002.
10. L. J. Heidt and M. E. Smith, ***J. Amer. Chem. Soc.,*** **70,** 2476, 1948.
11. M. Jabbari and F. Gharib, ***Monatsh. Chem.,*** 143, 997, 2012.
12. A. Paulenova, S. E. Creager, J. D. Navratil and Y. Wei***, J. Power Sources,*** **109,** 431, 2002.
13. A. Katafias, ***Trans. Met. Chem.,*** **31,** 907, 2006.
14. P. Sharma, S. Hemkar, C. L. Khandelwal and P. D. Sharma, ***J. Korean Chem. Soc.,*** **56,** 28, 2012.
15. K. K. Sengupta, ***Ind. J. Chem.,*** **2,** 267, 1963.
16. K. K. Sengupta and S. Aditya, ***J. Ind. Chem. Soc.,*** 4**0,** 823, 1963.
17. B. Singh, M. Singh and D. Kesarvani, ***Ind. J. Chem.,*** **41A,** 547, 2002.
18. M. E. Armenta and F. A. Diaz, ***Environ. Sci. Tech.,*** **39,** 5872, 2005.
19. A. G. Jadhav, V. V. Gaikwad and N. T. Patel, ***Orient. J. Chem.,*** **26,** 1183, 2010.
20. M. B. Bellakki, R. T. Mahesh and S. T. Nandibewoor, ***Biol. Reac. Mech.,*** **6,** 59, 2006.
21. Y. Zhang and R. A. Flowers, ***J. Org. Chem.,*** **68,** 4560, 2003.
22. R. A. Singh and A. Singh, ***Asian J. Chem.,*** **18,** 2868, 2006.

23. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **26,** 241, 2001.
24. Y. Zhai, H. Liu, L. Yang, G. Yang, W. Song and Y. Liu, ***Chem. Res. Chin. Univ.,*** **23,** 333, 2007.
25. P. K. Tandon, M. Purwar, S. Singh and N. Srivastava, ***J. Mol. Catal. A: Chemical,*** **284,** 120, 2008.
26. U. Kushwaha, A. K. Singh and A. Singh, ***Asian J. Chem.,*** **24***,* 2373, 2012.
27. S. B. Hanna and R. K. Hessley, ***Inorg. Nucl. Chem. Lett.,*** **7,** 83, 1971.
28. D. V. Naik, K. S. Byadagi, S. T. Nandibewoor and S. A. Chimatadar**,** ***Montash. Chem.,*** **144,** 1307, 2013.
29. K. A. Thabaj, D. S. Munavalli, S. A. Chimatadar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **32,** 902, 2007.
30. R. V. Hosahalli, A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, ***Int. J. Chem. Kinet.,*** **42,** 440, 2010.
31. P. K. Tandon, S. Z. Khanam, S. C. Yadav and R. C. Shukla, ***Trans. Met. Chem.,*** **36,** 739, 2011.
32. R. K. Patil, S. A. Chimatadar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **33,** 625, 2008.
33. T. Sumathi, P. Shanmugasundaram and G. Chandramohan, ***Arab. J. Chem.,*** **4,** 427, 2011.
34. K. K. Adari, A. Nowduri and V. Parvataneni, ***Acta. Chim. Slov.,*** **55,** 425, 2008.
35. P. K. Tandon, M. Purwar, P. B. Dwivedi and M. Srivastava, ***Trans. Met. Chem.,*** 33, 791, 2008.
36. S. A. Chimatadar, S. V. Madawale and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **32,** 634, 2007.
37. P. K. Tandon, P. B. Dwivedi, M. Purwar and S. Sing, ***The Open Catal. J.,*** **2,** 7, 2009.
38. P. K. Satapathy, D. K. Baral, A. S. Aswar and P. Mohanty, ***Ind. J. Chem. Tech.,*** **20,** 271, 2013.
39. P. K. Tandon, S. Sahgal, Gayatri, M. Purwar and M. Dhusia, ***J. Mol. Catal. A: Chemical,*** **250,** 203, 2006.

40. P. K. Tandon, S. Z. Khanam and S. B. Singh, ***The Open Catal. J.,*** **5,** 1, 2012.
41. M. Bulattin, M. Meti, S. T. Nandibewoor and S. Chimatadar, ***J. Sol. Chem.,*** **44,** 152, 2015.
42. S. Mathur, M. B. Yadav and V. Devra, ***Int. J. Res. Phys. Chem.,*** **5,** 1, 2015.
43. A. Prakash, P. Dwivedi, M. N. Srivastava and B. B. L. Saxena, ***Nat. Acad.,*** 107, 1988.
44. N. Datt, R. R. Nagori and R. N. Mehrotra, ***Canad. J. Chem.,*** **64,** 19, 1986.
45. S. M. Tuwar, S. T. Nandibewoor and J. R. Raju, ***Ind. J. Chem.,*** **29A,** 235, 1990.
46. A. Mills and S. Giddings, ***Inorg. Chim. Acta.,*** **158,** 49, 1989.
47. S. A. Chimatadar, S. T. Nandibewoor and J. R. Raju, ***Ind. J. Chem.,*** **28A,** 902, 1989.
48. L. S. A. Dikshitulu, V. Hanumantharao and S. N. Dindi, ***Ind. J. Chem.,*** **19A,** 203, 1980.
49. W. A. Waters and I. R. Wilson, ***J. Chem. Soc.*** **A,** 534, 1966.
50. W. S. Bai, Y. Q. Zhai, H. M. Liu, H. Y. Lu and W. Y. Song, ***Ind. J. Chem.*** **47A,** 1194, 2008.
51. G. C. Pant, ***"Oxidation by Metal Ions in Solution",*** Ph. D. Thesis, Kumaun University, 1993.
52. F. P. Cavasino, R. Cervellati, R. Lombardo and M. L. T. Liveri, ***J. Phys. Chem. B,*** **103,** 4285, 1999.
53. K. Karunakaran and K. P. Elango, ***React. Kinet. Catal. Lett.,*** **62,** 353, 1997.
54. R. A. Singh, ***Asian J. Chem.,*** **21,** 863, 2009.
55. T. Sumathi, P. Shanmugasundaram, G. Chandarmohan, D. Deepa and R. Renganatha, ***Int. J. Chem. Sci. Tech.,*** **2,** 44, 2012.
56. M. K. Ghosh and S. K. Rajput, ***Chem. Sci. J.,*** **77,** 1, 2012.
57. M. G. R. Reddy, B. Sethuram and T. N. Rao, ***Curr. Sci.,*** **42,** 677, 1973.
58. B. P. Sinha and H. P. Mathur, ***Z. Phys. Chem.,*** **246,** 342, 1971.
59. R. Anantaraman and M. R. Nair, ***Ind. J. Chem.,*** **14A,** 45, 1976.

60. W. Y. Song and Q. M. Jiang, ***Acta. Chim. Sin.,*** **63,** 109, 2005.

61. A. K. Singh, S. Srivastava, J. Srivastava, R. Srivastava and P. J. Singh, ***J. Mol. Catal. A: Chemical,*** **278,** 72, 2007.

62. R. V. Hosahalli, K. S. Bayadagi, S. T. Nandibewoor and S. A. Chimatadar, ***Kinet. Catal.,*** **53,** 65, 2012.

63. A. K. Singh, R. Srivastava, S. Srivastava, J. Srivastava, S. Rahamani and B. Singh, ***J. Mol. Catal. A: Chemical,*** **310,** 64, 2009.

64. A. K. Singh, R. K. Singh, R. Srivastava, S. Srivastava, J. Srivastava and S. Rahamani, ***Trans. Met. Chem.,*** **35,** 349, 2010.

65. J. M. Li, X. G. Meng, C. W. Hu, J. Du and X. C. Zeng, ***J. Mol. Catal. A: Chemical,*** **299,** 102, 2009.

66. S. O. Olusanya and E. O. Odebunmi, ***The Pac. J. Sci. Tech.,*** **12,** 328, 2011.

67. V. C. Seregar, C. V. Hiremath and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **31,** 541, 2006.

68. A. K. Singh, S. Yadav, R. Srivastava, J. Srivastava and S. Rahmani, ***J. Organomet. Chem.,*** **695,** 2213, 2010.

69. M. C. Day and J. Selbin, ***"Theoritical Inorganic Chemistry",*** Reinhold Book Corp: New York, USA, 1964.

70. H. S. Srivatava, K. Singh, M. Shukla and N. Pandey, ***Oxid. Commun.,*** **24,** 558, 2001.

71. R. D. Kaushik, R. M. Agarwal and J. Shing, ***Res. J. Pharm. Biol. Chem. Sci.,*** **5,** 1644, 2014.

72. I. F. Dolmanova, V. P. Poddubienko and V. M. Peshkova, ***Zh. Anal. Khim.,*** **25,** 2146, 1970.

73. R. D. Kaushik, A. K. Chaubey and R. P. Singh, ***Ind. J. Environ. Ecoplan.,*** **7,** 29, 2003.

74. R. D. Kaushik, Amrita and S. Devi, ***J. Curr. Sci,*** **3,** 2003.

75. S. L. Oswal, ***J. Ind. Chem. Soc.,*** **63,** 738, 1986.

76. T. J. Kemp and W. A. Water, ***J. Chem. Soc.,*** 1610, 1964.

77. Y. R. Sharma, K. C. Rajanna and P. K. Saiprakash, ***Ind. J. Chem.,*** **19A,** 872, 1980.

78. C. S. Reddy, ***Oxid. Commun.,*** **29,** 897, 2006.
79. P. K. Saiprakash and B. Sethuram, ***J. Ind. Chem. Soc.,*** **50,** 211, 1973.
80. R. D. Kaushik, R. Agarwal, R. Tyagi, P. Singh and O. Singh, ***Bullet. Chem. React. Engin. Catal.,*** **10,** 78, 2015.
81. M. Sundar, D. Easwaramoorthy, S. K. Rani and I. M. Bilal, ***Catal. Comm.,*** **9,** 2340, 2008.
82. B. Pare, M. Ayachit and S. B. Jonnalagadda, ***Ind. J. Chem.,*** **47A,** 1222, 2008.
83. Y. R. Sharma and P. K. Saiprakash, ***Ind. J. Chem.,*** **19A,** 1175, 1980.
84. P. S. Radhakrishmurti and M. K. Mohanti, ***Ind. J. chem.,*** **9,** 57, 1971.
85. A. S. Ogunja, E. O. Odebunmi and S. O. Owalude, ***The Pac. J. Sci. Tech.,*** **10,** 451, 2009.
86. C. F. Huber and G. P. Haight, ***J. Am. Chem. Soc.,*** **98,** 4128, 1976.
87. Z. Khan, M. Y. Dar, P. S. S. Babu and K. Din, ***Ind. J. Chem.,*** **42A,** 1060, 2004.
88. M. Ilyas, M. A. Malik, S. M. Z. Andrabi and Z. Khan, ***Res. Lett. Phys. Chem., Article ID 82901,*** 2007.
89. E. O. Odebunmi, A. S. Ogunlaja and S. O. Owalude, J. ***Chil. Chem. Soc.,*** **55,** 293, 2010.
90. S. K. Rani, D. Easwaramoorthy, I. M. Bilal and M. Palanichamy, ***App. Catal. A: General,*** **369,** 1, 2009.
91. S. Mathur, M. B. Yadav and V. Devra, ***Int. J. Innov. Biol. Chem. Sci.,*** **6,** 23, 2015.
92. A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, ***Trans. Met. Chem.,*** **34,** 711, 2009.
93. C. S. Reddy, ***Ind. J. Chem.,*** **46A,** 407, 2007.
94. R. H. Carbtree, ***"The Organometallic Chemistry of Transitions Metals",*** 4th ed., John Wiley and Sons, New Jersey, 1, 2005.
95. F. R. Hartley, ***"Chemistry of the Platinum Group Metals; Recent Developments",*** Elsevier, Amsterdam, New York, 11, 1991.
96. R. J. Mureinik and E. Pross, ***J. Coord. Chem.,*** **8,** 127, 1978.

97. M. G. Campbell, D. C. Powers, J. Raynaud, M. J. Graham, P. Xie, E. Lee and T. Ritter, ***Nature Chem.,*** **3,** 949, 2011; D. C. Powers and T. Ritter, ***Top. Organomet. Chem.*** **35,** 129, 2011.

98. A. Canty, ***"Handbook of Organopalladium Chemistry of Organic Synthesis",*** E. I. Negishi, Eds., John Wiley & Sons, New York, 189, 2002.

99. K. Muniz, ***Angew Chem. Int. Ed. Engl.,*** **48,** 9412, 2009.

100. E. I. Negishi, ***"Handbook of Organopalladium Chemistry of Organic Synthesis",*** E. I. Negishi, Eds. John Wiley & Sons, New York, 17, 2002.

101. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **26,** 662, 2001.

102. S. Srivastava and P. Singh, ***Bull. Catal. Soc. Ind.,*** **7,** 12, 2008.

103. S. Srivatava and P. Singh, ***J. Oxid. Commun. Book-4,*** **31,** 853, 2008.

104. L. I. Elding, ***Inorg. Chim. Acta.,*** **6,** 647, 1972.

105. C. D. Tait, D. R. Janecky and P. S. Z. Rogers, ***Geoch. Cosmoch. Acta.,*** **55,** 1253, 1991.

106. S. A. Wood, ***Geoch. Cosmach. Acta.,*** **55,** 1759, 1991.

107. R. H. Byrne and L. R. Kump, ***Geoch. Cosmoch. Acta.***, **57,** 1151, 1993.

108. P. M. Henry, ***"Palladium (II) Catalysed Oxidation of Hydrocarbon"*** D. Reidal Publishing Company: Dordecht**,** 11, 1980.

109. A. K. Singh, J. Srivastava, S. Rahmani and V. Singh, ***Carbohyd. Res.,*** 341, 397, 2006.

110. V. I. Shlenskaya and A. A. Biryukov, ***Russ. J. Inorg. Chem.,*** **11,** 28, 1966.

111. G. H. Ayres, ***Anal. Chem.,*** 24, 1622, 1953.

112. M. K. Ghosh and S. K. Rajput, ***Am. Chem. Sci. J.,*** **4,** 384, 2014.

113. K. C. Gupta, A. Sharma and V. D. Mishra, ***Tetrahydron,*** **37,** 2887, 1981.

114. A. Agarwal, G. Sharma, C. L. Khandelwal and P. D. Sharma, ***Inorg. React. Mech.,*** **4,** 233, 2002.

115. P. Singh, ***Ethiop. J. Sci.,*** **34,** 133, 2011.

116. N. N. Halligudi, S. M. Desai and S. T. Nandibewoor, ***Ind. J. Chem.,*** **38A,** 943, 1999.

117. A. K. Singh, J. Jaiswal, R. A. Singh and K. Singh, ***Asian J. Chem.,*** **21,** 858, 2009.

118. B. L. Koli and S. T. Nandibewoor, ***Ind. J. Chem.,*** **48A,** 958, 2009.

119. C. L. Hawkins, D. I. Pattison and M. J. Davies, ***Amino Acids,*** **25,** 259, 2003.

120. E. R. Stadtman, ***Ann. Review Biochem.,*** **62,** 797, 1993.

121. E. R. Stadtman and R. L. Levine, ***Amino Acids,*** **25,** 2007, 2003.

122. P. Faller, A. W. Retherford and R. J. Debus, ***Biochemistry,*** **41,** 12914, 2002.

123. C. Giulivi and K. J. A. Davies, ***J. Biol. Chem.,*** **276,** 24129, 2001.

124. I. B. Anweting, J. F. Iyun and S. O. Idris, ***Adv. Appl. Sci. Res.,*** **3,** 3401, 2012.

125. C. B. Klein and L. W. Chang, ***"Taxicology of Metals",*** CRC., Lewis, Publishers, New York, 1996.

126. S. A. Katz and H. Salem, ***"The Biological and Environmental Chemistry of Chromium",*** VCH, Publishers, New Yark, 1994.

127. J. Barnhart, ***J. Soil Contamin.,*** **6,** 561, 1997.

128. A. K. Singh, R. K. Singh, J. Srivastav, S. Rahman and S. Yadav, ***Ind. J. Chem.,*** **51A,** 681, 2012.

129. B. Jain, A. K. Singh and R. Negi, ***J. Iran. Chem. Soc.,*** **12,** 1717, 2015.

130. A. S. Onkar, P. N. Naik, S. D. Gunagi, S. T. Nandibewoor and S. A. Chimatadar, ***Ind. J. Chem.,*** **51A,** 1574, 2012.

131. D. Garg and S. Kothari, ***J. Ind. Chem. Soc.,*** **83,** 172, 2006.

132. C. Song, L. Chen and J. Shan, ***Res. Lett. Inorg. Chem.,*** **2008** (Article ID 786857), 2008.

133. B. T. Gowda and D. S. Mahadevappa, ***J. Chem. Soc. Perkin Trans.,*** **2,** 323, 1983.

134. B. T. Gowda, P. J. M. Rao and S. P. Nayak, ***Oxid. Commun.,*****23,** 459, 2000.

135. B. T. Gowda and P. Ramachandra, ***J. Ind. Chem. Soc.,*** **67,** 632, 1990.

136. B. T. Gowda and P. J. M. Rao, ***Bull. Chem. Soc. Jpn.,*** **62,** 3303, 1989.

137. B. T. Gowda and R. V. Rao, ***Ind. J. Chem.,*** **25A,** 578, 1986.

138. M. S. Ramachandran and T. S. Vivekanandam, ***Bull. Chem. Soc. Jpn.,*** **60,** 3397, 1987.

139. N. Nalwaya, A. Jain and B. L. Hiran, ***J. Ind. Chem. Soc.,*** **79,** 587, 2002.
140. R. C. Hiremath, S. M. Mayanna and N. Venkatasubramanian, ***J. Chem. Soc. Perkin Trans.,*** **2,** 1569, 1987.
141. H. S. Yathirajan, C. R. Raju, K. N. Mohana, S. Shashikant and P. Nagraja, ***Turk. J. Chem.,*** **27,** 571, 2003.
142. L. D. Luka and G. Giacomelli, ***Synlett.,*** **12,** 2180, 2004.
143. G. A. Hiegel, J. C. Lewis and J. W. Bae, ***Synth. Commun.,*** **34,** 3449, 2004.
144. A. K. Singh, B. Jain, R. Negi, Y. Katre and S. P. Singh, ***The Open Catal. J.,*** **2,** 12, 2009.
145. A. H. Friedman and S. Morgulis, ***J. Am. Chem. Soc.,*** **58,** 909, 936.
146. S. P. Mushran, J. N. Tiwari, A. K. Bose and K. Singh, ***Ind. J. Chem.,*** **16A,** 35, 1978.
147. B. T. Gowda, B. S. Moodithaya and B. H. Kumar, ***Oxid. Commun.,*** **24,** 74, 2001.
148. J. Sharma, L. Pandey, S. P. Musharan, ***Ind. J. Chem.,*** **19A,** 475, 1980.
149. N. M. I. Alhaji and S. S. L. Mary, ***E-Journal Chem.,*** **8,** 1472, 2011.
150. Puttaswamy and N. Vaz, ***Proc. Ind. Acad. Sci.,(Chem. Sci.),*** **113,** 325, 2001.
151. T. Sumathi, P. Shanmugasundaram and G. Chandramohan, ***Asian J. Chem.,*** 23, 4385, 2011.
152. K. Vivekanandan and R. L. Narayanan, ***Int. Lett. Chem. Phys. Astr.,*** **6,** 66, 2015.
153. B. Mohanty, J. Behera, S. Acharya, P. Mohanty and A. K. Patnaik, ***Chem. Sci. Trans.,*** **2,** 51, 2013.
154. H. Iloukhani and H. Bahrami, ***Int. J. Chem. Kinet.,*** **31,** 95, 1999.
155. R. S. Shettar, M. I. Hiremath and S. T. Nandibewoor, ***E-Journal Chem.,*** **2,** 91, 2005.
156. S. Senapati, A. K. Pattnaik and S. P. Das, ***Int. J. Engin. Res. Tech.,*** **1,** 1, 2012.
157. N. P. Shetti, R. R. Hosamani and S. T. Nandibewoor, ***The Open Catal. J.,*** **2,** 130, 2009.

158. D. C. Hiremath, K. T. Sirsalmath and S. T. Nandibewoor, ***Catal. Lett.*, 122,** 144, 2008.
159. R. R. Hosamani and S. T. Nandibewoor, ***J. Chem. Sci.*, 121,** 275, 2009.
160. S. B. Haveri, P. N. Naik , S. T. Nandibewoor and S. A. Chimatadar, ***J. Ind. Coun. Chem.*, 27,** 80, 2010.
161. K. K. Adari, A. Nowduri and V. Parvataneni, ***Bull. Chem. Soc. Ethiop.*, 22,** 305, 2008.
162. Z. Khan and K. Din, ***Ind. J. Chem***., **38A,** 361, 1999.
163. V. Devra, ***J. Ind. Chem. Soc.*, 82,** 290, 2005.
164. D. C. Bilehal, R. M. kulkarni and S. T. Nandibewoor, ***J. Ind. Chem. Soc.*, 80,** 91, 2003.
165. Y. R. Sharma, Y. Umadevi and P. K. Saiprakash, ***Nat. Acad. Sci. Lett.*, 3,** 9, 1980.
166. I. Sharma, V. Devra, D. Gupta, C. M. Gangwal and P. D. Sharma, ***Int. J. Chem. Kinet.*, 27,** 311, 1995.
167. M. B. Yadav, V. Devra and A. Rani, ***Ind. J. Chem.*, 49A,** 442, 2010.
168. T. Sumathi, P. Shanmugasundaram and G. Chandramohan, ***J. Saudi Chem. Soc.*, 17,** 227, 2013.
169. K. K. Adari, A. Nowduri and V. Parvataneni, ***Acta. Chim. Slov.*, 55,** 425, 2008.
170. S. M. Mursalin, S. K. Sinha and J. Mahata, ***IOSR J. Appl. Chem.*, 9,** 30, 2016.
171. S. Mathur, M. B. Yadav and V. Devra, ***J. Phys. Chem. Biophys.*, 3,** 5, 2013.
172. T. Sumathi, P. Shanmugasundaram and G. Chandramohan, ***Asian J. Chem.*, 24,** 2938, 2012.
173. M. B. Yadav, V. Devra and A. Rani. ***J. Ind. Chem. Soc.*, 86,** 600, 2009.
174. T. Sumathi, P. Shanmugasundaram and G. Chandramohan, ***Arabian J. Chem.*, 89,** 2011.

Chapter – 2

Experimental

Abstract

This chapter describes the details of various chemicals and reagents, equipments, preparation of various solutions, standardization methods and analytical procedures adopted to study the kinetics of oxidation of amino acids by cerium (IV) in acidic medium in presence of metal ion catalyst.

2.1 Chemicals

Leucine [$NH_2.CH.(COOH).(CH_3)_2CH.CH_2$]

A requisite amount of leucine (s. d-fine. Chem., AR grade) was employed. The lesser solubility of leucine in water was avoided by preparing its solutions in aqueous medium maintaining concentration of H_2SO_4 to be 0.1 mol dm^{-3}.

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.

Serine [$NH_2.CH.CH_2.OH.(COOH)$]

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

Valine [$NH_2.CH.(COOH).(CH_3)_2CH$]

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 solutions in presence of 0.1 mol dm^{-3} sulphuric acid.

Ceric (IV) Ammonium Sulphate [$(NH_4)_4Ce(SO_4)_4.2H_2O$]

The solution of ceric (IV) ammonium sulphate was prepared by dissolving ceric ammonium sulphate (E. Merck) in 1.0 mol dm^{-3} sulphuric acid and the solution was standardized by titrating an aliquot of the test solution against standard iron (II) ammonium sulphate (E. Merck) employing ferroin as an indicator[1].

The titration was always made in the presence of 1.0 mol dm^{-3} H_2SO_4 to obtain a clear and stable colour change of the indicator at the equivalence point.

The concentration of hydrogen ion present in these solutions was determined by titrating a known aliquot of the solution against pre-standardized sodium hydroxide solution using phenolphthalein as an indicator[2].

Manganese Sulphate ($MnSO_4$)

The stock solution of Mn(II) was prepared by dissolving manganese sulphate (AR) in doubly distilled water. Dilute solutions of manganese (II) were made from the stock solution as required.

Palladium (II) Chloride ($PdCl_2$)

Palladium(II) chloride (Johnson Matthey) was prepared in HCl (0.20 mol dm^{-3}) and assayed by complexometric titration with EDTA[3]. Dilute solution of palladium(II) were made from the stock solution as required.

Sodium Bisulphate ($NaHSO_4$)

Sodium bisulphate solution of required concentration was prepared by dissolving requisite amount of $NaHSO_4$ in doubly distilled water.

Cerium(III) Sulphate ($Ce_2(SO_4)_3$)

Cerium(III) solution was prepared by dissolving Cerium(III) sulphate, $Ce_2(SO_4)_3$ (BDH), in doubly distilled water.

Ferrous Ammonium Sulphate [$(NH_4)_2.Fe(SO_4)_2.6H_2O$]

The solution of ferrous ammonium sulphate (BDH, AR grade) was prepared by dissolving the requisite quantity of the salt in doubly distilled water containing dilute sulphuric acid (H_2SO_4) to check hydrolysis. These solutions were prepared afresh as and when required in kinetic study.

Sodium Bicarbonate [$NaHCO_3$]

Stock solution of sodium bicarbonate was prepared by dissolving 4 gm of sodium bicarbonate (A. R.) in 100 ml of doubly distilled water.

Sulphuric Acid [H_2SO_4]

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

Sodium Sulphate (Na_2SO_4)

Sodium sulphate solution of required concentration was prepared by dissolving requisite amount of the salt in doubly distilled water.

Sodium Chloride (NaCl)

Sodium chloride solution of required concentration was prepared by dissolving requisite amount of sodium chloride in doubly distilled water.

Oxalic Acid [$(COOH)_2$]

Oxalic acid (BDH, AR grade) is a primary standard and yields a stable solution in doubly distilled water. The solution was kept in dark at ambient temperature to check any photolytic decomposition.

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

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

Ferroin Indicator ($[Fe(\textit{o}\text{-phen})_3]SO_4$)

Ferroin, (BDH, AR grade) was used as an end point indicator for cerium(IV) and amino acid titration.

2, 4-Dinitrophenylhydrazine

The reagent is prepared by means of Brady's test for aldehyde produced from amino acid. Requisite amount of 2, 4-Dinitrophenylhydrazine was heated with 2.0 mol dm^{-3} HCl added cautiously with cooling and 10 ml of doubly distilled water was added.

Nesseler′s Reagent

100 gm of mercury (II) iodide and 70 gm of potassium iodide were dissolved in 100 ml doubly distilled water. The resulting solution was added with stirring to a solution of 16 gm of NaOH in 700 ml deionized water. This was then diluted to one litre with deionzed water. The precipitate was allowed to settle for 3 days and the supernatant liquid was decanted and kept in a brown bottle.

2.2 Equipments

pH-Meter

Systronic digital pH meter, model 335 was used for the determination of pH of the reaction mixtures with the maximum uncertainity in pH of ± 0.01 unit.

Spectrophotometer

UV-Vis spectroscopy offers a relatively straight forward and effective way for quantitatively characterizing both organic and inorganic compounds. Furthermore, as it operates on the principle of absorbance of photons that promotes the molecules to an excited states, it is an ideal technique for determining the electronic properties such as the band gap of a molecule.

Visible spectrophotometer (Systronic 166) was used for spectrophotometric measurements. Spectrophotometer can be used to determine kinetics and the rate constant of a chemical reaction. The rate constant of a particular reaction can be determined by measuring visible absorbance at specific time intervals.

The calibration curve was obtained in term of absorbance of cerium(IV). Since the rate of reaction is directly proportional to the concentration of the cerium(IV), it was necessary to find out the range of concentration of cerium(IV) in sulphuric acid in the presence of amino acid over which Beer's law was applicable. The spectrophotometeric study of the solution containing all the reagents with Ce(IV) in sulphuric acid medium showed that the reaction can be monitored spectrophotometrically by measuring the absorbance of cerium(IV) at 360 nm where cerium(IV) has considerable absorbance and other ions have no contribution towards absorbance. At this wavelength absorbance values were obtained for different concentration of cerium(IV) solution with other reagent between the concentration range 5×10^{-5} to 5×10^{-4} mol dm^{-3}. The graph between absorbance and concentration was linear which indicates the applicability of the Beer's law for the Ce(IV) under experimental conditions used in the study. The plot is given in **Figure 2.1.**

As part of this research work a double beam LAB INDIA3000^{+}, UV-Vis spectrophotometer with UV path length 1.0 cm in the spectral range 200-800 nm was used for optical characterization.

Fourier Transfer Infrared Spectrophotometer (FTIR)

FTIR offers quantitative and qualitative analysis for organic and inorganic samples. FTIR spectroscopy identifies chemical bonds in a molecule by producing an IR spectrum. The spectra produce a profile of the sample, a distinctive molecule fingerprint that can be used to screen and scan samples for many different compounds. FTIR is an effective analytical instrument for detecting graphs and characterizing covalent bonding information. FTIR spectrophotometer (Alpha-T model, Bruker, Germany) is used to record the FTIR spectra in the range of 400-4000 cm^{-1} by mixing the sample with dried KBr (in 1:20 weight ratio) with a resolution of 4 cm^{-1}.

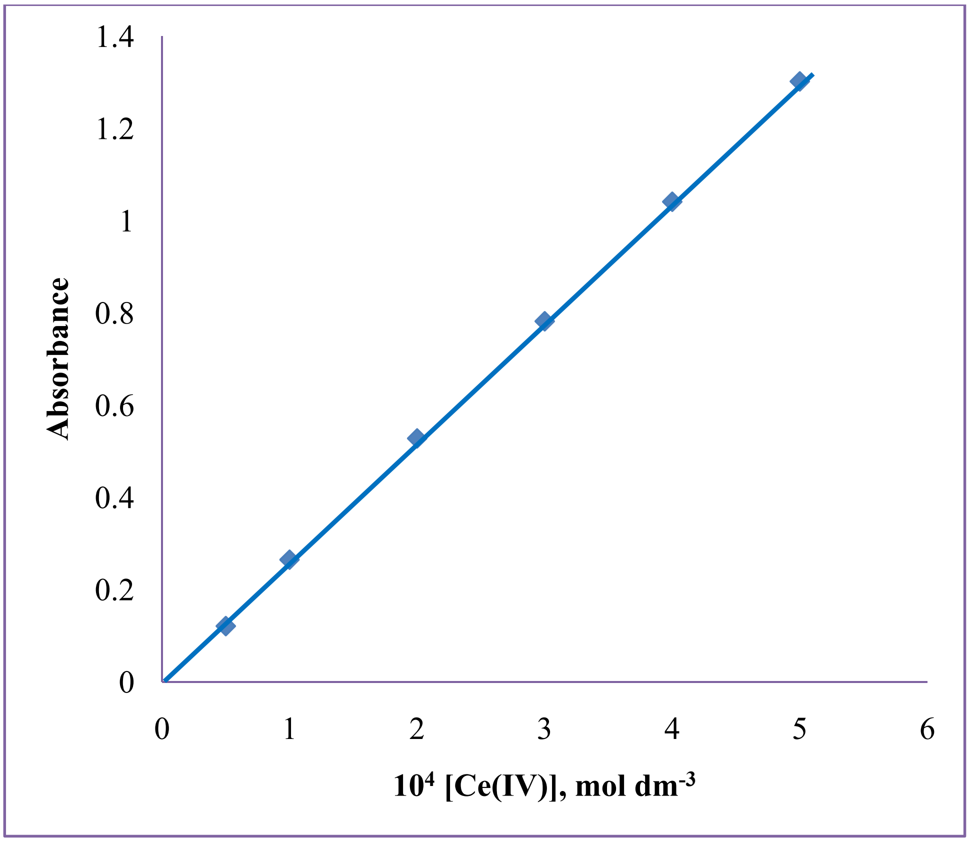


Figure 2.1: Plot between absorbance and concentration of cerium(IV)

Thermostat

Serological water bath (Macro Scientific) temperature range 30°C -110°C was used. All kinetic studies were done using thermostated at temperature varying from 40°C to 50°C.

Electronic Balance

Shimadzu electronic Balance, A × 200 was used for weighing works. The least count of balance is 0.0001 mg.

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, second distillation being from alkaline potassium permanganate solution in all glass assembly, was employed in all the preparations and kinetic studies. The glass vessels employed for storing the solutions and also for kinetic studies were either of Corning or Borosil make. The instruments as discussed earlier were frequently used as and when desired in kinetic studies. Kinetic procedure methodology[5] adopted for the monitoring of kinetics and analysis of the kinetic results is given in concerned chapters.

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 ultra pure water purification system (Millipore Elix Model), was employed in all the preparations and kinetic studies.

The glass vessels employed for storing the solutions and also for kinetic studies were either of Corning or Borosil make. The instruments as discussed earlier were frequently used as and when desired in kinetic studies. Kinetic procedure methodology[5] adopted for the monitoring of kinetics and analysis of the kinetic results is given in concerned chapters.

2.3 References

1. I. M. Kolthoff and R. Belcher ***''Volumetric Analysis''***, Vol.III, Interscience, New York, 602, 1957.
2. C. J. Bottaglia and J. O. Edwards, ***Inorg. Chem.,*** 4, 552, 1965.
3. Schwar Zenbach, G and Flaschka H., ***"Complexometric Titrations"*** (Methuen and Co., Landon), 250, 1969.
4. A. I. Vogel, ***''A Textbook of Quantitative Inorganic Analysis",*** Longmans, 3, 240, 1961.
5. M. Latshaw, ***J. Am. Chem. Soc.,*** **47,** 793, 1925.

Chapter – 3

Mechanistic and Kinetic Study of Manganese(II) Catalysed Oxidation of Serine by Cerium(IV) in Sulphuric Acid Medium

Abstract

Kinetics of manganese(II) catalysed oxidation of serine by cerium(IV) has been studied in sulphuric acid medium at 45°C. The reaction follows first order kinetics with respect to [Mn(II)] while negative effect was observed for the variation of [H^+] on the rate of reaction. The reaction exhibits first order kinetics with respect to serine at its lower concentrations and tends towards zero order at its higher concentration. The reaction is first order with respect to Ce(IV). Under the experimental condition, the kinetically active species of cerium(IV) has been found to be $Ce(SO_4)_2$. The rate constants observed at three different temperatures were utilized to determine the activation parameters. A plausible mechanism has been proposed from the results of kinetic studies, reaction stoichiometry and product analysis.

$$k' = \frac{kK[Ser]}{1 + K[H^+][Ser]}$$

Where k′ is second order rate constant.

3.1 Introduction

Oxidation reactions are of fundamental importance in nature and are key transformations in organic synthesis. We know that amino acids are molecules containing an amine group, a carboxylic acid group and a side chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen and nitrogen. The kinetics and mechanism of oxidation of amino acids have been studied previously by some researchers[1-2]. However, the mechanism is different in the different reaction systems. These oxidation reactions display diverse reaction mechanisms, oxidative deamination[3-5] and decarboxylation.

The oxidation of serine has received much attention because of strengthening the immune system by providing antibodies and synthesizes fatty acid sheath around nerves fibres[6]. Oxidation of serine by some inorganic oxidants has been studied[7-8] in both acidic and alkaline medium.

Ce(IV) solution in acidic media is stable for long time and is not influenced by light and increasing temperature for short time[9]. There are numerous mechanistic studies of oxidation of organic compounds apart from useful synthetic studies[10] in which cerium(IV) has been employed as an oxidant in acid sulphate medium. Transition metal ions have been extensively used[11] as catalyst for affecting a number of reactions. In recent times, the studies on the use of transition metal ions either alone or as binary mixtures as catalysts in many redox reactions have been gaining interest. Mn(II) has been used as a homogenous catalyst in various redox reactions[12] and its efficiency as a catalyst can be visualised from the oxidation studies of various organic substrates involving different oxidants[13-16]. The mechanism of catalysis is quite complicated due the formation of different intermediate complexes, free radicals and different oxidation states of manganese. Preliminary experimental results indicate that the reaction of serine with cerium(IV) in acid medium, without a catalyst was sluggish, but the reaction became facile in the presence of a small amount of Mn(II) catalyst. Therefore, in order to explore the mechanism of serine-cerium(IV) reactions and also to study the catalytic action of Mn(II), the manganous ion has been selected as a catalyst.

3.2 Experimental

The details regarding the preparation and standardization of reagent solution have already been given in chapter 2 (Experimental). However, all other reagents were either of Anala R or G.R. grade and used as supplied without any further treatment. Doubly distilled water was employed throughout the study.

3.2.1 Kinetic Measurements

Appropriate quantities of the solution were placed in separate glass vessels and kept for at least 15 minutes in a thermostatted water bath at 45°C. The calculated amounts of each reactant were then added together in a particular glass vessel followed by the requisite amount of double distilled water. The reaction mixture was then placed in a thermostatted water bath maintained at constant temperature of 45°C (±5%) and the reaction was initiated by adding the requisite amount of oxidant solution placed separately in the same water bath. The reaction was followed by measuring the absorption of cerium(IV) at 360 nm with time in a 1 cm cell placed in the Systronics(166) Visible spectrophotometer. All kinetic measurements were performed under pseudo first order conditions with serine concentration in excess over cerium(IV) at a constant ionic strength of 1.50 mol dm^{-3}. The applicability of Beer's law verified between 5×10^{-5} to 5×10^{-4} mol dm^{-3} at 360 nm under the reaction conditions with the molar extinction coefficient[17] $\varepsilon = 2622\ dm^3\ mol^{-1}\ cm^{-1}$. The pseudo first order rate constants (k_{obs}) were obtained from the slope of the plots of log absorbance versus time. The observed rate constants were reproducible within the experimental error ±5%. The cerium(IV) solution was thermally stable in the visible region and undergoes photochemical decomposition only in the UV region. The spectral changes during the chemical reaction for the standard condition at 45°C are given in **Figure 3.1**.

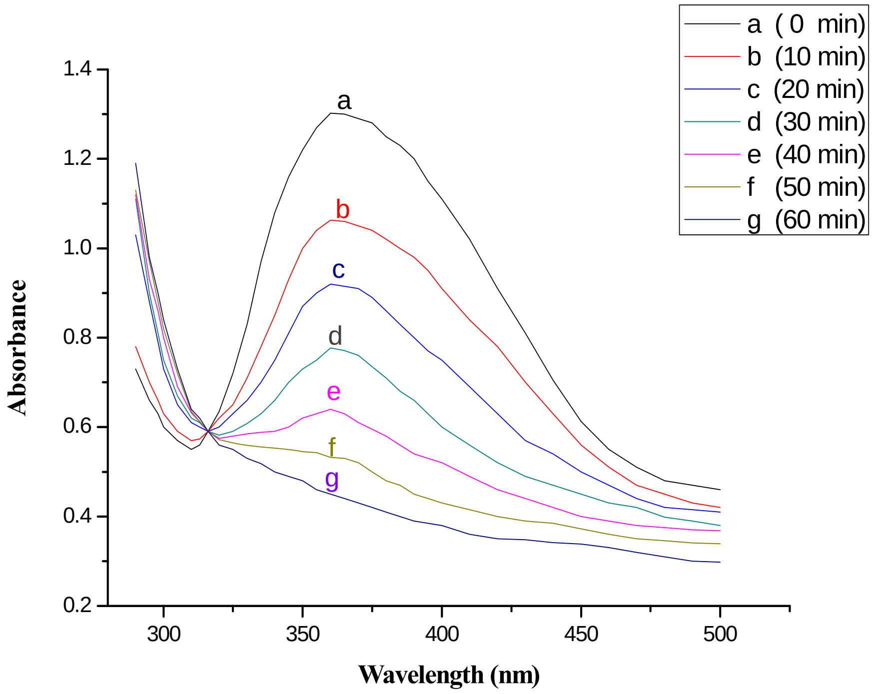
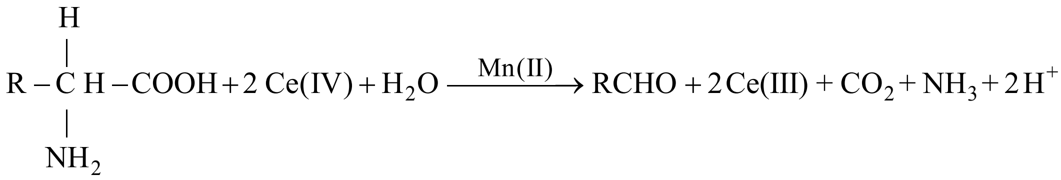


Figure: 3.1: Spectral changes during the oxidation of serine by cerium(IV) in aqueous sulphuric acid medium at 45°C (time 0-60 minutes)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Ser] = 5.0×10^{-3} mol dm^{-3};
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3};
I = 1.50 mol dm^{-3}; Temp. = 45°C

3.2.2 Stoichiometry and Product Analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [Serine] at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24 hours at 318 K. After completion of the reaction, the remaining Ce(IV) was estimated in different sets of the experiment. The results indicated that two moles of Ce(IV) were consumed by one mole of serine as given by equation (1).



$$R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-COOH+2\,Ce(IV)+H_2O \xrightarrow{Mn(II)} RCHO+2Ce(III)+CO_2+NH_3+2H^+ \quad (1)$$

Where R = $-CH_2OH$

The oxidation products were identified as Ce(III), 2-hydroxyethanal, ammonia and carbon dioxide. 2-hydroxyethanal was confirmed by the IR spectrum of the corresponding hydrazone. The reaction mixture was treated with acidified 2,4−dinitrophenyl hydrazine solution, which yielded a 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 **(Figure 3.2)**. The other product ammonia was detected by Nesseler's reagent test[18] and CO_2 was qualitatively detected by passing the liberated gas through a tube containing lime water.

3.3 Results

3.3.1 Cerium(IV) Dependence

The concentration of cerium(IV) was varied from 5.0×10^{-5} to 5.0×10^{-4} mol dm^{-3} at fixed concentration of $[H^+]$ = 1.0 mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and I =1.50 mol dm^{-3} at three different concentration of serine viz. 5.0×10^{-3}, 7.0×10^{-3} and 9.0×10^{-3} mol dm^{-3} at 45°C. The order with respect to cerium(IV) was found to be unity, since the rate constant (k_{obs}) was almost constant at different Ce(IV) concentration. Results are given in **Table 3.1, 3.2** and **3.3**. The pseudo-first order plots under these conditions were almost parallel and linear

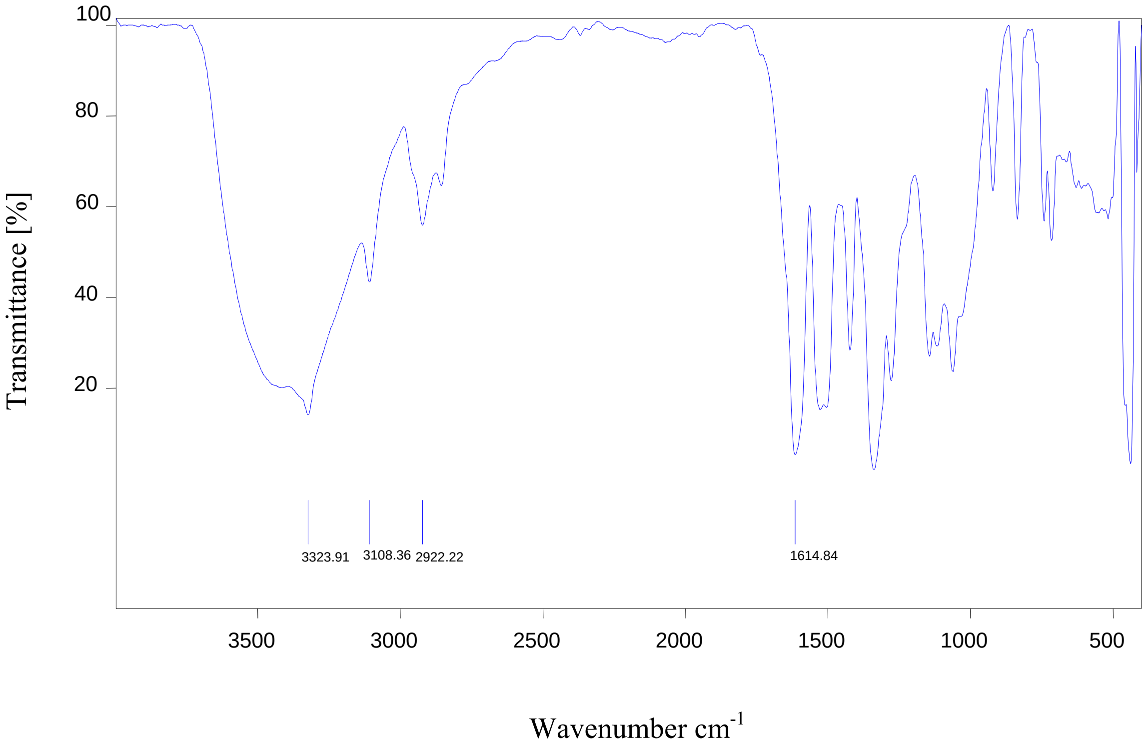


Figure 3.2: FT-IR Spectra of final product of oxidation of serine

Table 3.1: Variation of cerium(IV)

[Ser] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes	**Absorbance**					
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.103	0.219	0.435	0.669	0.856	1.068
20	0.086	0.192	0.375	0.569	0.712	0.926
30	0.071	0.159	0.321	0 .468	0.608	0.789
40	0.061	0.139	0.268	0.402	0.507	0.649
50	0.051	0.115	0.225	0.348	0.431	0.541
60	0.043	0.096	0.194	0.294	0.364	0.462
80	0.029	0.068	0.133	0.174	0.256	0.317
10^4(k_{obs}), sec^{-1}	**2.89**	**2.84**	**2.86**	**2.84**	**2.82**	**2.89**

Table 3.2: Variation of cerium(IV)

[Ser] = 7.0×10^{-3} mol dm^{-3} **Temp. = 45°C**
[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.096	0.212	0.425	0.642	0.808	1.039
20	0.076	0.159	0.329	0.522	0.651	0.809
30	0.059	0.128	0.254	0 .404	0.520	0.662
40	0.046	0.107	0.205	0.315	0.403	0.508
50	0.037	0.087	0.168	0.244	0.330	0.417
60	0.030	0.069	0.128	0.194	0.250	0.320
80	0.018	0.037	0.084	0.118	0.156	0.209
10^4(k_{obs}), sec^{-1}	**3.92**	**3.93**	**3.91**	**3.94**	**3.95**	**3.93**

Table 3.3: Variation of cerium(IV)

[Ser] = 9.0×10^{-3} mol dm^{-3} **Temp. = 45°C**
[H^{+}] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes	**Absorbance**					
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.087	0.193	0.386	0.591	0.756	0.952
20	0.065	0.142	0.284	0.446	0.579	0.723
30	0.050	0.109	0.213	0 .332	0.429	0.542
40	0.036	0.079	0.156	0.251	0.309	0.392
50	0.027	0.057	0.119	0.183	0.234	0.289
60	0.020	0.042	0.088	0.132	0.168	0.213
80	0.014	0.023	0.048	0.073	0.092	0.116
10^4(k_{obs}), sec^{-1}	**5.10**	**5.08**	**5.09**	**5.07**	**5.08**	**5.09**

over 80% completion of the reaction also indicates first order with respect to Ce(IV) **(Figure 3.3)**.

3.3.2 Serine Dependence

The serine concentration was varied in the concentration range of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} at fixed concentration of [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3}, I = 1.50 mol dm^{-3} at 40°C, 45°C and 50°C temperature respectively. Observed reaction order of serine is (0.68) obtained from the linear regression of log k_{obs} versus log concentration of serine, indicating fractional order with respect to serine. The reaction exhibits first order kinetics with respect to serine at its lower concentration that tends towards zero order at its higher concentration **(Figure 3.4)**. Results are given in **Table 3.4, 3.5 and 3.6**.

3.3.3 Manganese(II) Dependence

The effect of catalyst concentration on the reaction was studied between the concentration range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at constant concentration of [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Ser] = 5.0×10^{-3} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3} and I = 1.50 mol dm^{-3} at 45°C. Observed reaction order of [Mn(II)] can be obtained from the linear regression of log k_{obs} versus log [Mn(II)] (n = 1.0 at 318 K). This indicates that the reaction is of first order with respect to Mn(II). k_{obs} versus Mn(II) yielded good linear plots **(Figure 3.5)** passing through the origin. Results are given in **Table 3.7**

3.3.4 Hydrogen Ion Dependence

The effect of H^{+} concentration on the reaction rate was studied in the range 0.20 mol dm^{-3} to 1.0 mol dm^{-3} at constant concentration of [Ser] = 5.0×10^{-3} mol dm^{-3}, [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and ionic strength of 1.50 mol dm^{-3} at 45°C. The results are represented in **Table 3.8.** According to results it was found that the rate of reaction decreases with increase of sulphuric acid concentration in Mn(II) catalysed oxidation. The order with

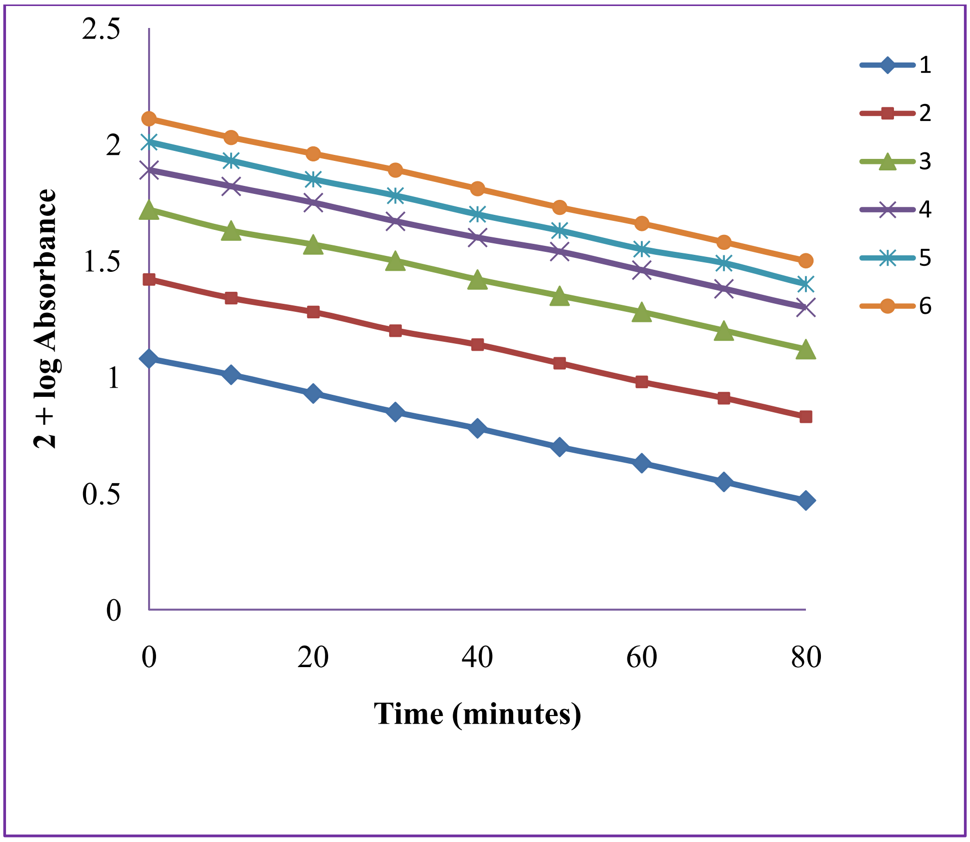


Figure 3.3: Pseudo first order plots for the variation of cerium(IV)

[Ser] = 5.0×10^{-3} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; I = 1.50 mol dm^{-3}; Temp.= 45°C;

[Ce(IV)] = (1) 0.50×10^{-4} mol dm^{-3}; (2) 1.0×10^{-4} mol dm^{-3};

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

(5) 4.0×10^{-4} mol dm^{-3}; (6) 5.0×10^{-4} mol dm^{-3}.

(Ref. Table- 3.1)

Table 3.4: Variation of serine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 40°C**

[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^3[Ser], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.172	(20) 1.102	1.148	1.136	1.123	1.078	1.101	1.055	1.051	1.051
20	(60) 0.997	(40) 0.973	1.025	1.023	0.983	0.941	0.928	0.905	0.887	0.886
30	(80) 0.902	(60) 0.836	0.921	0.905	0.855	0.799	0.769	0.735	0.734	0.734
40	(120) 0.735	(80) 0.708	0.842	0.782	0.746	0.668	0.641	0.612	0.613	0.614
50	(140) 0.662	(100) 0.624	0.729	0.701	0.659	0.568	0.543	0.511	0.492	0.492
60	(160) 0.613	(120) 0.503	0.672	0.608	0.553	0.472	0.455	0.423	0.409	0.409
80	(180) 0.543	(140) 0.472	0.552	0.484	0.420	0.349	0.312	0.288	0.276	0.276
10^4(k_{obs}), sec^{-1}	**0.75**	**1.25**	**1.72**	**2.05**	**2.35**	**2.70**	**2.95**	**3.11**	**3.21**	**3.21**

Figures in parentheses denote time in minutes

Table 3.5: Variation of serine

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 45°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^3[Ser], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.156	(20) 1.093	1.135	1.088	1.068	1.051	1.041	1.039	1.039	1.037
20	(60) 0.975	(40) 0.896	1.002	0.803	0.926	0.886	0.866	0.858	0.858	0.853
30	(80) 0.832	(60) 0.756	0.887	0.713	0.789	0.734	0.689	0.682	0.682	0.680
40	(120) 0.668	(80) 0.604	0.787	0.624	0.649	0.613	0.557	0.552	0.552	0.550
50	(140) 0.596	(100) 0.508	0.684	0.553	0.541	0.492	0.454	0.450	0.450	0.449
60	(160) 0.532	(120) 0.448	0.608	0.489	0.462	0.408	0.369	0.364	0.363	0.361
80	(180) 0.469	(140) 0.369	0.472	0.375	0.317	0.276	0.243	0.238	0.238	0.236
$10^4(k_{obs})$, sec^{-1}	**0.91**	**1.55**	**2.11**	**2.59**	**2.89**	**3.21**	**3.49**	**3.51**	**3.51**	**3.52**

Figures in parentheses denote time in minutes

Table 3.6: Variation of serine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 50°C**

[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^3[Ser], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.134	1.138	1.077	1.056	1.039	1.036	1.018	1.009	1.004	1.004
20	(60) 0.837	1.039	0.948	0.897	0.846	0.835	0.823	0.812	0.789	0.789
30	(80) 0.709	(40) 0.803	0.805	0.749	0.703	0.668	0.642	0.634	0.613	0.613
40	(120) 0.546	(60) 0.623	0.683	0.612	0.552	0.532	0.493	0.486	0.476	0.476
50	(140) 0.462	(80) 0.489	0.586	0509	0.453	0.423	0.402	0.385	0.365	0.364
60	(160) 0.403	(100) 0.384	0.483	0.426	0.369	0.346	0.312	0.298	0.283	0.282
80	(180) 0.342	(120) 0.306	0.348	0.289	0.238	0.216	0.188	0.178	0.172	0.172
10^4(k_{obs}), sec^{-1}	**1.21**	**2.01**	**2.71**	**3.10**	**3.51**	**3.75**	**4.01**	**4.10**	**4.21**	**4.21**

Figures in parentheses denote time in minutes

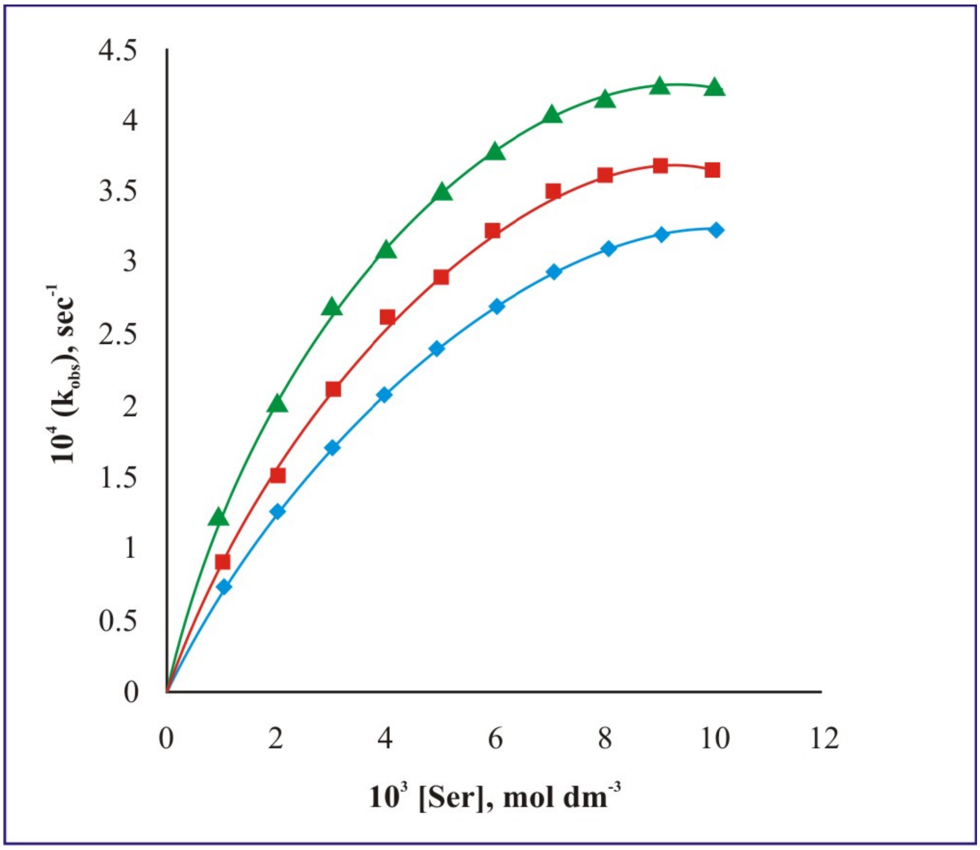


Figure 3.4: Variation of serine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Mn(II)] = 5.0×10^{-5} mol dm^{-3};

[H^+] = 1.0 mol dm^{-3}; I = 1.50 mol dm^{-3};

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table- 3.4, 3.5 and 3.6)

Table 3.7: Variation of manganese(II)

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 45°C**

[Ser] = 5.0 × 10^{-3} mol dm^{-3} **[H^+] = 1.0 mol dm^{-3}**

10^5 [Mn(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.213	(20) 1.142	1.144	1.123	1.068	1.035	1.007	0.985	0.959	0.901
20	(60) 1.052	(40) 0.967	1.036	0.993	0.926	0.856	0.807	0.769	0.703	0.659
30	(80) 0.996	(80) 0.713	0.915	0.857	0.789	0.698	0.623	0.586	0.519	0.463
40	(120) 0.856	(100) 0.613	0.816	0.750	0.649	0.569	0.487	0.443	0.376	0.319
50	(140) 0.785	(120) 0.528	0.735	0.639	0.541	0.465	0.376	0.326	0.273	0.203
60	(160) 0.735	(140) 0.456	0.649	0.554	0.462	0.368	0.294	0.249	0.201	0.162
80	(180) 0.676	(160) 0.389	0.538	0.420	0.317	0.234	0.174	0.138	0.109	0.076
$10^4(k_{obs})$, sec^{-1}	**0.58**	**1.17**	**1.82**	**2.38**	**2.89**	**3.54**	**4.12**	**4.65**	**5.12**	**5.84**
$10^2(k')$, dm^3 mol^{-1} sec^{-1}	**5.80**	**5.85**	**5.86**	**5.87**	**5.78**	**5.83**	**5.88**	**5.81**	**5.83**	**5.84**

Figures in parentheses denote time in minutes

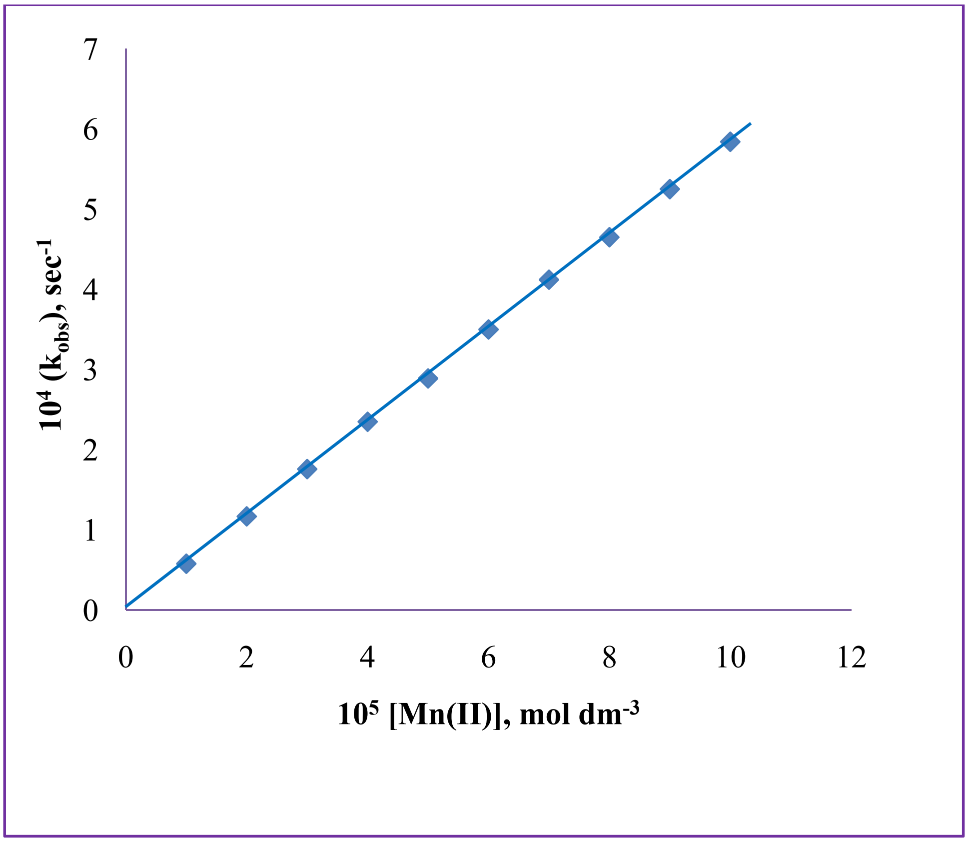


Figure 3.5: Variation of manganese(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Ser] = 5.0×10^{-3} mol dm^{-3};

[H^+] = 1.0 mol dm^{-3}; I = 1.50 mol dm^{-3}; Temp.= 45°C

(Ref. Table 3.7)

Table 3.8: Variation of hydrogen ion

[Ser] = 5.0 × 10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0 × 10^{-5} mol dm^{-3}

[H^+], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.811	0.915	0.998	1.042	1.068
20	0.559	0.685	0.718	0.869	0.926
30	0.439	0.489	0.496	0.698	0.789
40	0.221	0.349	0.461	0.569	0.649
50	0.146	0.247	0.359	0.465	0.541
60	0.093	0.181	0.273	0.375	0.462
80	0.035	0.092	0.163	0.246	0.317
10^4(k_{obs}), sec^{-1}	**7.31**	**5.52**	**4.31**	**3.46**	**2.89**

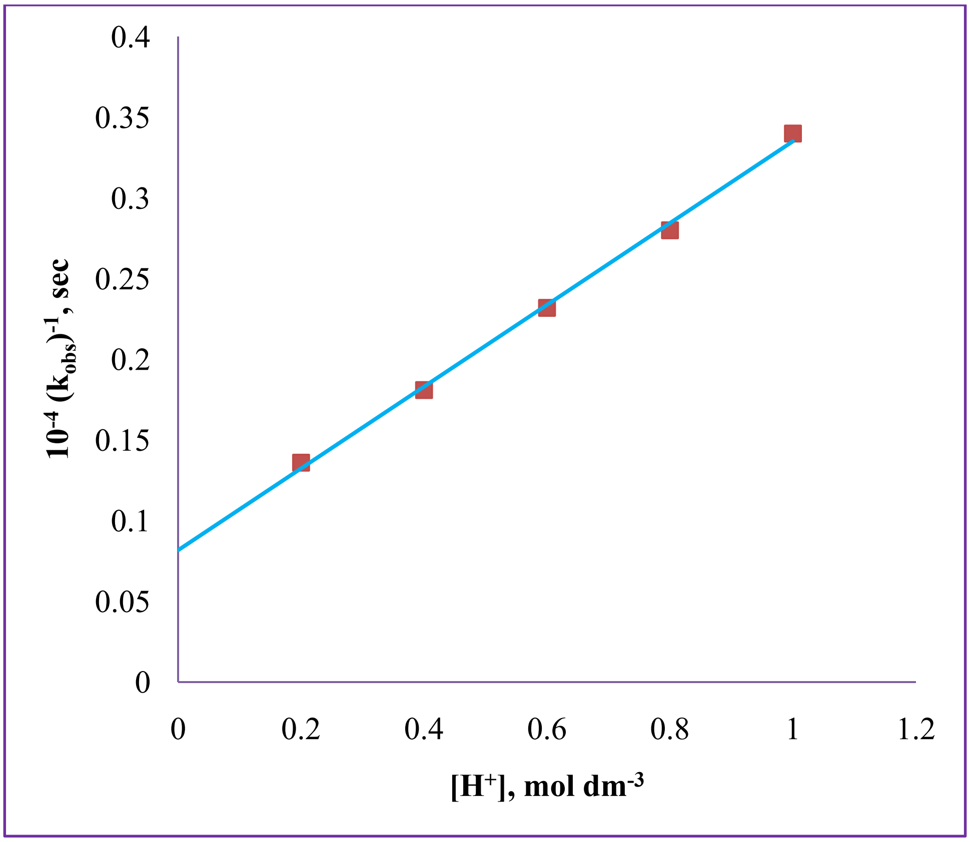


Figure 3.6: Variation of hydrogen ion

[Ce(IV)]	= 5.0×10^{-4} mol dm^{-3};	[Ser]	= 5.0×10^{-3} mol dm^{-3};
[Mn(II)]	= 5.0×10^{-5} mol dm^{-3};	[HSO_4^-]	= 1.0 mol dm^{-3};
I	= 1.50 mol dm^{-3};	Temp.	= 45°C

(Ref. Table 3.8)

respect to [H^+] was negative. A plot of 1/ k_{obs} versus [H^+] gives a straight line with positive slope and intercept **(Figure 3.6)**.

3.3.5 Effect of [HSO_4^-]

The reaction rate were measured with various [HSO_4^-] = 0.2 to 1.0 mol dm^{-3} at fixed concentration of [Ser] = 5.0×10^{-3} mol dm^{-3}, [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and ionic strength of 1.50 mol dm^{-3} at 45°C. The graphical plot of of $1/k_{obs}$ versus [HSO_4^-] is found to be linear with positive intercept and slope **(Figure 3.7)**, which indicates that the rate of the reaction is inversely proportional to the HSO_4^- ion concentration. Results are given in **Table 3.9**.

3.3.6 Effect of Ionic Strength

The effect of ionic strength on the rate was studied by employing sodium sulphate from 1.0 to 2.0 mol dm^{-3} at fixed concentration of [Ser] = 5.0×10^{-3} mol dm^{-3}, [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and [H^+] = 1.0 mol dm^{-3} at 45°C. The rate of reaction slightly increases with increasing ionic strength **(Figure 3.8)**. Results are given in **Table 3.10**.

3.3.7 Effect of Added Products

The effect of initially added product, Ce(III) was studied from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at fixed concentration of [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Ser] = 5.0×10^{-3} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and I = 1.50 mol dm^{-3} at 45°C. No significant effect on the rate of reaction was observed. Results are given in **Table 3.11**.

3.3.8 Test for Free Radical

To test for the presence of free radicals in the reaction, acetonitrile solution was added to reaction mixtures containing the substrate and the cerium(IV) solution. When the reaction mixture was diluted with the methanol a precipitate

Table 3.9: Variation of [HSO_4^-]

[Ser] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

[HSO_4^-], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.811	0.898	0.969	1.017	1.026
20	0.559	0.667	0.735	0.823	0.846
30	0.439	0.463	0.543	0.643	0.659
40	0.221	0.319	0.404	0.504	0.518
50	0.146	0.234	0.294	0.394	0.412
60	0.093	0.162	0.221	0.312	0.328
80	0.035	0.070	0.118	0.187	0.207
$10^4(k_{obs})$, sec^{-1}	**7.31**	**6.01**	**4.92**	**4.02**	**3.85**

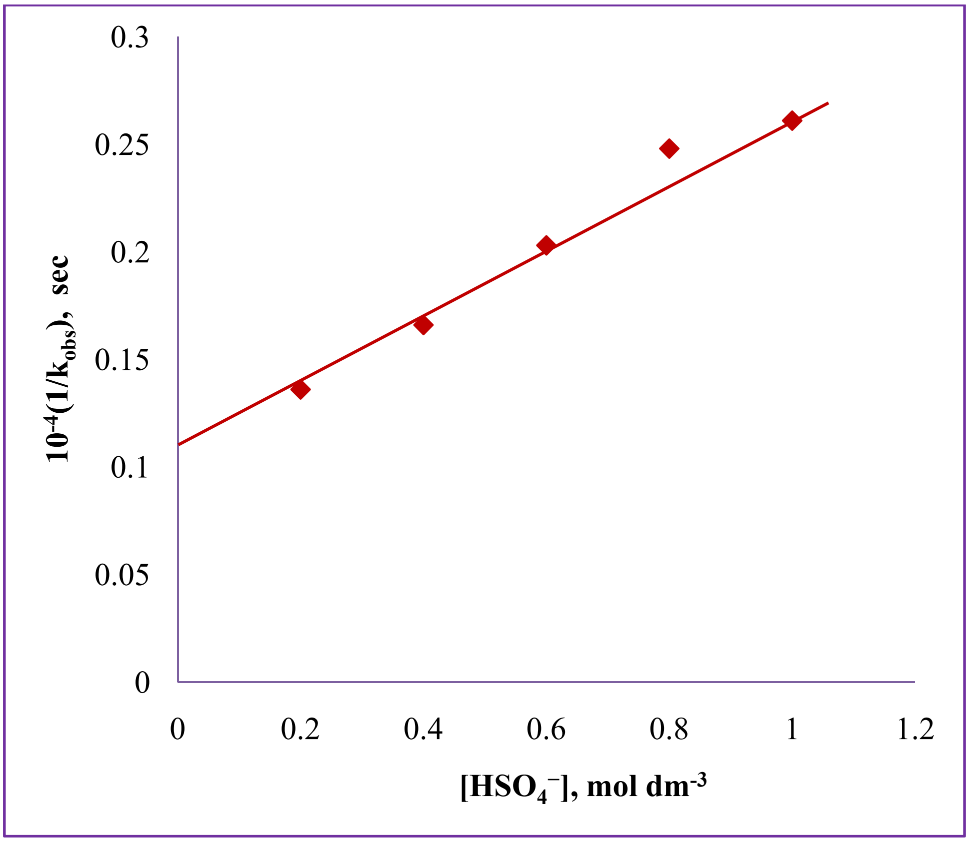


Figure 3.7: Linear plot of $1/k_{obs}$ versus $[HSO_4^-]$

$[Ce(IV)] = 5.0\times10^{-4}$ mol dm^{-3}; $[Ser] = 5.0 \times 10^{-3}$ mol dm^{-3};

$[Mn(II)] = 5.0\times10^{-5}$ mol dm^{-3}; $[H^+] = 0.20$ mol dm^{-3};

I = 1.50 mol dm^{-3}; Temp.= 45°C

(Ref. Table 3.9)

Table 3.10: Variation of ionic strength

[Ser] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **[H^+] = 1.0 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

I, mol dm^{-3}	**1.0**	**1.25**	**1.50**	**1.75**	**2.0**
Time in minutes	**Absorbance**				
0	1.302	1.302	1.302	1.302	1.302
10	1.068	1.066	1.065	1.064	1.063
20	0.926	0.923	0.919	0.912	0.899
30	0.789	0.782	0.778	0.771	0.761
40	0.649	0.644	0.639	0.631	0.623
50	0.541	0.537	0.531	0.524	0.517
60	0.462	0.457	0.451	0.443	0.435
80	0.317	0.314	0.313	0.312	0.311
$10^4(k_{obs})$, sec^{-1}	**2.89**	**2.92**	**2.94**	**2.96**	**2.99**

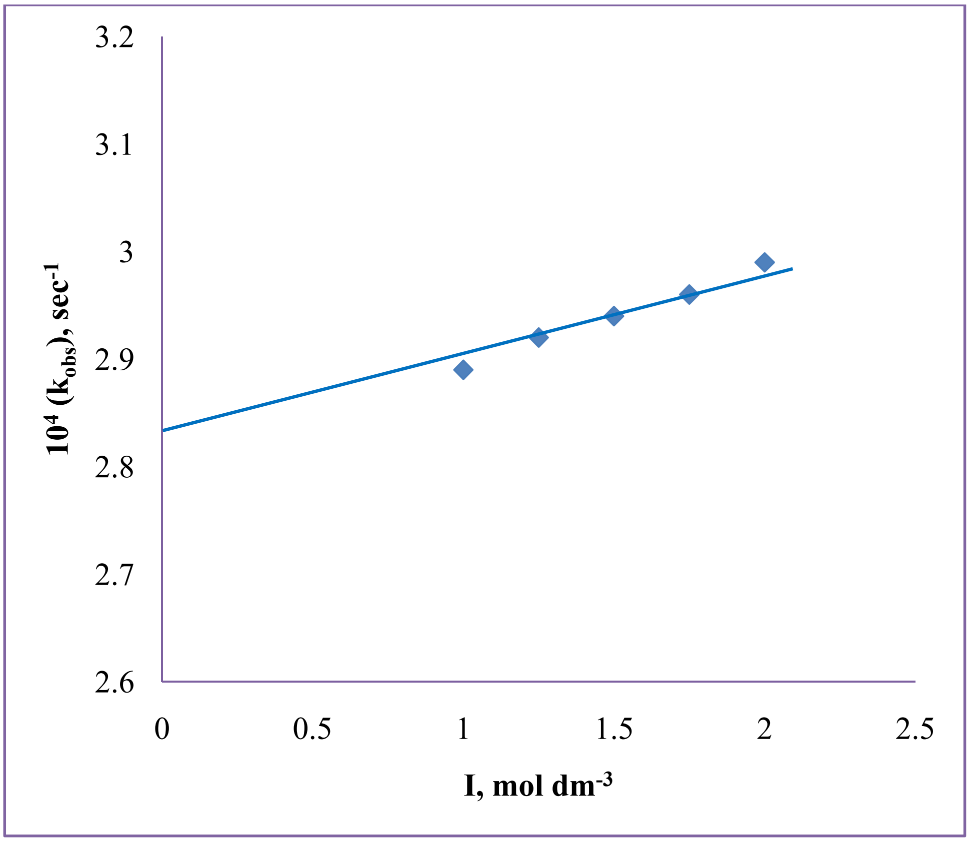


Figure 3.8: Variation of ionic strength

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Ser] = 5.0×10^{-3} mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; [H^+] = 1.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 3.10)

Table 3.11: Effect of cerium(III)

[Ser] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3} **$[H^+]$ = 1.0 mol dm^{-3}**

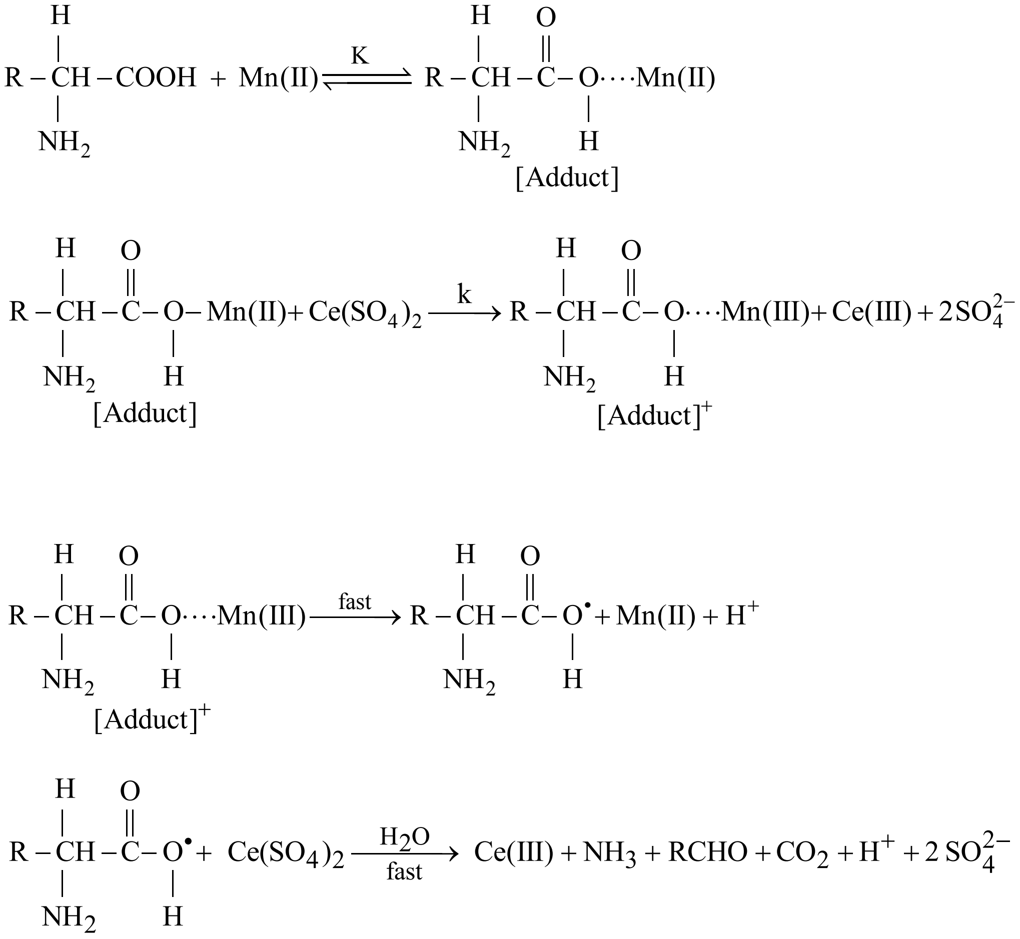
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}

[Ce(III)], mol dm^{-3}	**1.0**	**2.5**	**5.0**	**7.5**	**10.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	1.067	1.066	1.065	1.068	1.063
20	0.924	0.923	0.919	0.925	0.920
30	0.787	0.782	0.778	0.788	0.781
40	0.647	0.644	0.639	0.648	0.643
50	0.540	0.537	0.531	0.541	0.536
60	0.460	0.457	0.451	0.461	0.456
80	0.316	0.314	0.313	0.318	0.314
$10^4(k_{obs})$, sec^{-1}	**2.91**	**2.92**	**2.94**	**2.90**	**2.93**

was formed in the reaction mixture. This confirms the formation of free radicals in the redox reactions under investigation.

3.4 Discussion

The uncatalysed cerium(IV) oxidation of serine is very slow in sulphuric acid under the present experimental conditions. However, the reaction is appreciably faster in the presence of a minute quantity (10^{-5} mol dm^{-3}) of manganese(II) in sulphuric acid . In the presence of perchloric acid, manganese(II) catalysis is much less efficient, possibly due to presence of active cerium(IV) species, $Ce(OH)^{3+}$ in such media. Hence, the present study was undertaken in sulphuric acid medium. The reaction is first order with respect to cerium(IV) and manganese(II) concentrations, and the order with respect to serine varies from first to zero order. The effect of hydrogen ions on the rate was studied by adding sulphuric acid and it was found that as the sulphuric acid concentration increased in the reaction mixture, the rate of reaction decreased. This is due to formation[19] of an active inhibitor $H_2Ce(SO_4)_2^{2-}$. The order with H^+ ion concentration was less than unity and negative. As the sulphuric acid concentration increases, the H^+ concentration increases, but there is also a corresponding increase in HSO_4^- ion concentration. Since the rate is inversely dependent on the HSO_4^- concentration, the overall effect of adding sulphuric acid would be to lower the rate. Similar behaviour has been reported in the oxidation of antimony(III)[20], mandelic acid[21], malic acid[22], fructose[23] and L-glutamic acid[24] by cerium(IV). The amino acid dependence from first to zero order can be ascribed to complexation with cerium (IV) or manganese (II). The adduct formation between Ce^{4+} and serine was ruled out on the premise that the absorbance of Ce^{4+} did not change at the addition of excess serine. Therefore it appears that an adduct between manganese(II) and serine is initially formed that on further interaction with cerium(IV) yields another adduct of higher valent manganese. The formation of the complex was implicated by non zero intercept of the plot of 1/ k' versus 1/ serine **(Figure 3.9)**. Complex formation between amino acid and manganese(II) has also been reported in literature[25-26]. The results suggests that serine combines with catalyst Mn(II) to form a adduct, which then reacts in a slow step with one mole of $Ce(SO_4)_2$ to give the product cerium(III), complex-serine and SO_4^{2-}. The $[\mathrm{Adduct}]^+$ is converted in a free radical derived from serine and Mn(II) catalyst is regenerated. The free radical then reacts with another mole of $Ce(SO_4)_2$ in a further fast step to give cerium(III), 2-hydroxyethanal, ammonia and carbon dioxide. The results are accommodated in **scheme- 3.1**.



$$\mathrm{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-COOH + Mn(II) \underset{}{\overset{K}{\rightleftharpoons}} \underset{[Adduct]}{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O\cdots Mn(II)}} \qquad (2)$$

$$\mathrm{\underset{[Adduct]}{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O-Mn(II)}+Ce(SO_4)_2 \xrightarrow{k} \underset{[Adduct]^+}{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O\cdots Mn(III)}+Ce(III)+2SO_4^{2-}} \qquad (3)$$

$$\mathrm{\underset{[Adduct]^+}{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O\cdots Mn(III)} \xrightarrow{fast} R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O^{\bullet}+Mn(II)+H^+} \qquad (4)$$

$$\mathrm{R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-O^{\bullet}+ Ce(SO_4)_2 \xrightarrow[fast]{H_2O} Ce(III)+NH_3+RCHO+CO_2+H^+ +2\,SO_4^{2-}} \qquad (5)$$

Where R= $-CH_2OH$

Scheme -3.1

The proposed mechanism leads to the rate law (6)

$$\frac{-d[\mathrm{Ce(IV)}]}{dt}=\frac{kK[\mathrm{Ce(IV)}][\mathrm{Ser}][\mathrm{Mn(II)}]}{1+K[\mathrm{H}^+][\mathrm{Ser}]} \qquad (6)$$

$$\frac{-d[\mathrm{Ce(IV)}]/dt}{[\mathrm{Ce(IV)}]}=k_{obs}=\frac{kK[\mathrm{Ser}][\mathrm{Mn(II)}]}{1+K[\mathrm{H}^+][\mathrm{Ser}]} \qquad (7)$$

Where k_{obs} is pseudo first order rate constant. Since the order with respect to manganese(II) is one **(Table-3.7)**, the rate law further change to (8)

$$k' = \frac{kK[Ser]}{1 + K[H^+][Ser]} \tag{8}$$

Where k' = second order rate constant

After rearranging equation (8)

$$\frac{1}{k'} = \frac{1}{kK[Ser]} + \frac{[H^+]}{k} \tag{9}$$

A plot of $1/k'$ versus 1/[Ser] was made from equation (9) at constant hydrogen ion concentration that yielded straight line with nonzero intercept **(Figure 3.9)**. The value of rate constant (k) of the slow step of **scheme-3.1** was obtained from the intercept. The ratio of intercept and slope of the line yielded the value of formation constant (K) to be 219 dm^3 mol^{-1}. The value of K obtained in the title reaction in comparision to K= 204 dm^3 mol^{-1} for cerium(IV) glutamic acid in 1.0 M H_2SO_4 at 35°C, indicates strong complexation in H_2SO_4 medium[**24**].

Cerium(IV) is known to form strong cerium(IV)-sulphato complexes in sulphuric acid medium, the important cerium(IV)-sulphato complexes are $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ and relevant equilibrium are[**27**]:

$$Ce^{4+} + HSO_4^- \rightleftharpoons Ce(SO_4)^{2+} + H^+ \qquad Q_1 = 3500 \tag{10}$$

$$Ce(SO_4)^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ \quad Q_2 = 200 \tag{11}$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \qquad Q_3 = 3.4 \tag{12}$$

Among the different sulphato species, the kinetically active species should be inferred on the basis of kinetic data, not according to the magnitude of concentration[**28**]. Considering the range of concentration of acid in which the present study was performed and the steep fall in rate of the reaction with increasing concentration of sulphuric acid indicates that the other species would be present in insignificantly small concentration and may be considered

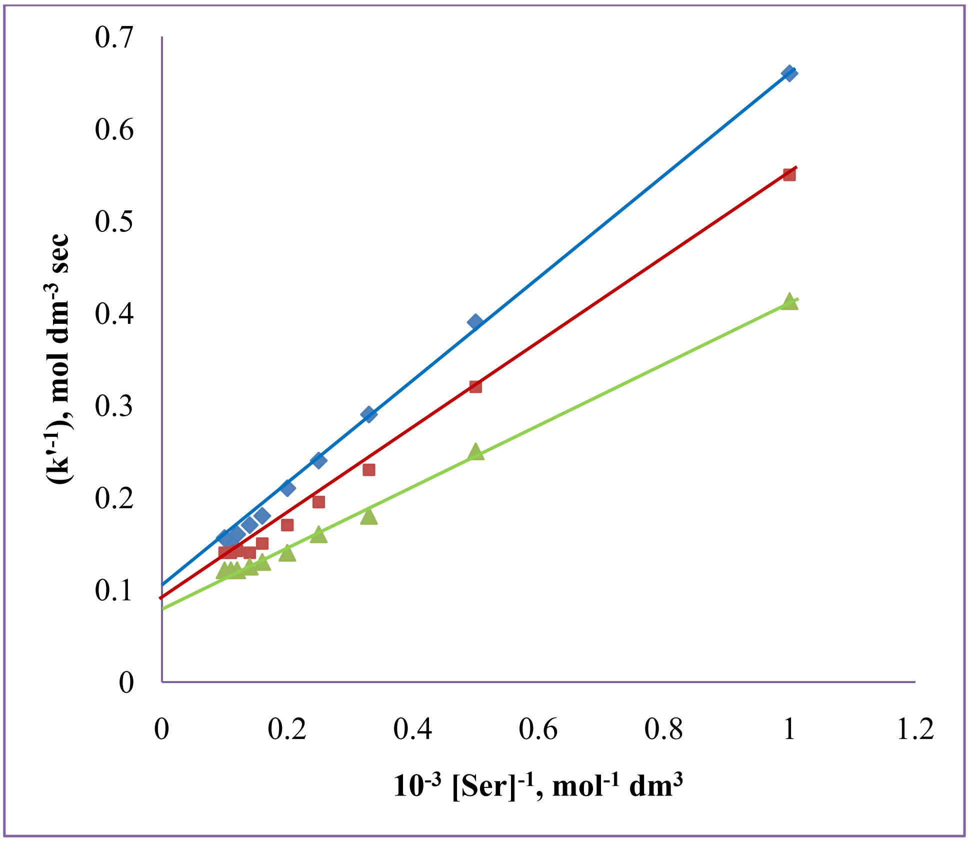


Figure 3.9: A plot of 1/k′ versus 1/[Ser]

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Mn(II)] = 5.0×10^{-5} mol dm^{-3};
[H$^+$] = 1.0 mol dm^{-3}; I = 1.50 mol dm^{-3};
Temp. = (◆) 40°C; (■) 45°C; (▲) 50°C

negligible[29]. Thus, $Ce(SO_4)_2$ has been taken as the reactive species of cerium(IV) in aqueous sulphuric acid medium. In light of equilibrium step (10-12) inverse bisulphate dependence **(Figure 3.7)** can be explained by assuming $Ce(SO_4)_2$ as the reactive species. A small influence of ionic strength on the value of experimental rate constant is in agreement with the idea that a non charged particle $Ce(SO_4)_2$ enters in to reaction in the rate determining step, which further confirms $Ce(SO_4)_2$ as the kinetically active species in the present study. In the oxidation of alanine[30] and L-leucine[31] by cerium(IV) in sulphuric acid-sulphate media, $Ce(SO_4)_2$ had been identified as the active species, which support the present work. The concentration of $Ce(SO_4)_2$ can be approximately obtained, according to the mass balance, equation (13) is obtained:

$$[Ce(IV)]_T = [Ce^{4+}] + [Ce(SO_4)^{2+}] + [Ce(SO_4)_2] + [HCe(SO_4)_3^-] \tag{13}$$

From equations (10)-(12), the following equations can be derived:

$$[Ce^{4+}] = \frac{[Ce(SO_4)_2][H^+]^2}{Q_1Q_2[HSO_4^-]^2}$$

$$[Ce(SO_4)^{2+}] = \frac{[Ce(SO_4)_2][H^+]}{Q_2[HSO_4^-]}$$

$$HCe(SO_4)_3^- = Q_3[HSO_4^-][Ce(SO_4)_2]$$

Substituting the above equations in to equation (13), we get

$$\begin{aligned}[Ce(IV)]_T = {} & \frac{[Ce(SO_4)_2][H^+]^2}{Q_1Q_2[HSO_4^-]^2} + \frac{[H^+][Ce(SO_4)_2]}{Q_2[HSO_4^-]} \\ & + [Ce(SO_4)_2] + Q_3[Ce(SO_4)_2][HSO_4^-]\end{aligned} \tag{14}$$

By considering the relative magnitude of the successive formation equilibrium constants which are in the order: $Q_1 >> Q_2 >> Q_3$, the value of $\frac{[Ce(SO_4)_2][H^+]^2}{Q_1Q_2[HSO_4^-]^2}$ and $\frac{[Ce(SO_4)_2][H^+]}{Q_2[HSO_4^-]}$ are much less than the latter two terms. Therefore, we get equation (15) from equation (14)

$$\begin{aligned}[Ce(IV)]_T & \approx [Ce(SO_4)_2] + Q_3Ce(SO_4)_2[HSO_4^-] \\ & = [Ce(SO_4)_2](1 + Q_3[HSO_4^-])\end{aligned} \tag{15}$$

So,

$$[\mathrm{Ce(SO_4)_2}] = \frac{[\mathrm{Ce(IV]_T}}{1+Q_3[\mathrm{HSO_4^-}]} = f[\mathrm{Ce(IV)}]_T$$

$$f = \frac{1}{1+Q_3[\mathrm{HSO_4^-}]} \tag{16}$$

Thus equation (7) can be written as:

$$k_{obs} = \frac{kK[\mathrm{Ser}][\mathrm{Mn(II)}]}{1+K[\mathrm{H^+}][\mathrm{Ser}][1+Q_3[\mathrm{HSO_4^-}]} \tag{17}$$

Assuming

$$A = \frac{kK[\mathrm{Ser}][\mathrm{Mn(II)}]}{1+K[\mathrm{H^+}][\mathrm{Ser}]} \tag{18}$$

So equation (17) becomes

$$k_{obs} = \frac{A}{1+Q_3[\mathrm{HSO_4^-}]} \tag{19}$$

$$\frac{1}{k_{obs}} = \frac{1}{A} + \frac{Q_3[\mathrm{HSO_4^-}]}{A} \tag{20}$$

Equation(20) suggest that 1/ k_{obs} versus [$\mathrm{HSO_4^-}$] should be linear and agrees with observed experiment data. From the slope Q_3/A and intercept 1/A, the ratio of slope to intercept was calculated to be 1.62 i. e. Q_3, which is good agreement with the previously reported value[32].

The activation parameters of the rate determining step have been evaluated from the linear plot of log k versus 1/T **(Figure 3.10)**. The results of **Table 3.12** show that K increases with increase of temperature, indicating the reaction is endothermic, which is consistent with $\Delta H^{\#} > 0$. The moderate value of $\Delta H^{\#}$ and $\Delta S^{\#}$ were favourable for electron transfer processes. The value of $\Delta S^{\#}$ within range of radical reaction has been ascribed[33] to the nature of electron pairing and electron unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state. A negative value of $\Delta S^{\#}$ suggests that the complex is more ordered than reactants[34].

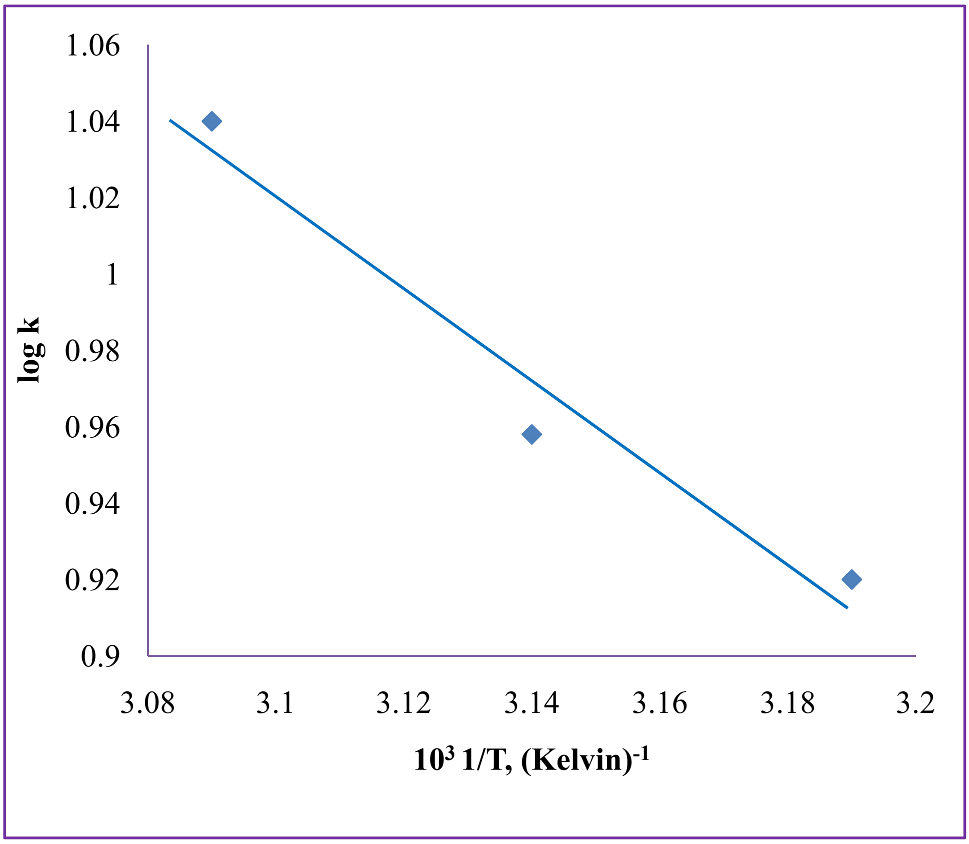


Figure 3.10: A plot of log k versus 1/T

Table 3.12: Effect of temperature on the reaction between cerium(IV) and serine catalysed by mangenese(II) in presence of sulphuric acid medium

Temperature (K)	K ($dm^3\ mol^{-1}\ s^{-1}$)	Activation parameters	K ($dm^3\ mol^{-1}$)	Thermodynamic Quantities
313	9.09	ΔE_a (kJ mol^{-1}) = 25.84	198	$\Delta H^{\#}$ (kJ mol^{-1}) = 21.06
318	10.0	$\Delta S^{\#}$ (J Kmol^{-1}) = −145.00	219	$\Delta S^{\#}$ (J K mol^{-1}) = −134.87
323	12.50	$\Delta G^{\neq}$ (kJ mol^{-1}) = 67.17	257	$\Delta G^{\#}$ (kJ mol^{-1}) = 63.94

3.5 Conclusion

The oxidation of serine by cerium(IV) experienced a slow reaction rate in sulphuric acidic media, but increased in rate in the presence of the Mn(II) catalyst. The reactive species for the oxidation of cerium(IV) in a sulphuric acidic medium was $Ce(SO_4)_2$. The rate constant of a slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to the slow step of the reaction were estimated. The observed results were explained by plausible mechanisms and the related rate laws were deduced. It can be stated that Mn(II) acts as an efficient catalyst for the oxidation of serine by cerium(IV) in sulphuric acid medium.

3.6 References

1. S. Mathur, M. B. Yadav and V. Devra, ***Int. J. Chem. Sci.,*** **13,** 641, 2015.
2. R. V. Nadh and M. Sireesha, ***Bul. Chem. Commun.,*** **47,** 13, 2015.
3. S. Huo, C. Song, J. Shan, S. Shen and H. Sun, ***J. Iran. Chem. Soc.,*** **6,** 243, 2009.
4. D. Bilehal, R. Kulkarni and S. T. Nandibewoor, ***J. Mol. Catal. A: Chemical,*** **232,** 21, 2005.
5. Y. R. Katre, A. K. Singh, G. K. Joshi and S. Patil, ***Oxid. Commun.,*** **29,** 137, 2006.
6. A. Shanmuga ***"Fundamentals of Biochemistry for Medical Students",*** 1996.
7. B. T. Gowda and D. S. Mahadevappa, ***J. Chem. Soc., Perkin Trans.,*** **2,** 323, 1983.
8. Y. R. Katre, A. K. Singh, S. Patil and G. K. Joshi, ***Oxid. Commun.,*** **29,** 129, 2006.
9. G. Nagy, E. Koros, N. Oftedal, K. Tjelflaat and P. Ruoff, ***Chem. Phys. Lett.,*** **250,** 255, 1996.
10. P. Sharma, S. Hemkar, C. L. Khandelwal and P. D. Sharma, ***J. Korean Chem. Soc.,*** **56,** 28, 2012.
11. K. R. Bhat, K. Jyothi and B. T. Gowda, ***Oxid. Commun.,*** **25,** 117, 2002.
12. R. D. Kaushik, R. M. R. Agarwal and J. Singh, ***Res. J. Pharm. Biol. Chem. Sci.,*** **5,** 1644, 2014.
13. I. M. Kolthoff, M. Kimura and E. J. Meehan, ***J. Phys. Chem.,*** **75,** 3343, 1971.
14. E. O. Odebunmi, A. S. Ogunlaja and S. O. Owalude, ***J. Chil. Chem. Soc.,*** **55,** 293, 2010.
15. J. Singh, R. Malik, O. Singh, Sushma and R. D. Kaushik, ***Int. J. Chem. Sci.,*** **12,** 445, 2014.
16. C. S. Reddy and P. S. Manjari, ***Ind. J. Chem.,*** **50A,** 979, 2011.
17. A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, ***Trans. Met. Chem.,*** **34,** 711, 2009.

18. G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denny, ***"Vogel's Text Book of Quantitative Chemical Analysis",*** 5th edn., ELBS, Longman, Essex, England,(a) p. 381, (b) p.195, 1996.
19. B. Krishna and K. C. Tewari, ***J. Chem. Soc.,*** 3097, 1961.
20. R. K. Patil, S. A. Chimatadar and S. T. Nandibewoor, ***Transit. Met. Chem.,*** **33,** 625, 2008.
21. A. McAuley and C. H. Brubaker, ***J. Chem. Soc. A,*** 960, 1966.
22. K. K. Sengupta, ***J. Ind. Chem. Soc.,*** **42,** 725, 1965.
23. R. N. Mehrotra and S. Ghosh, ***Z. Phys. Chem.,*** **231,** 91, 1966.
24. S. A. Chimatadar, S. V. Madawale and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **32,** 634. 2007.
25. B. S. Berlett, P. B. Chock, M. B. Yim and E. R. Stadtman, ***Proc. Natl. Acad. Sci. USA,*** **87,** 389, 1990.
26. S. K. Rani, D. Eswaramoorthy, I. B. Mohammed and M. Palanichamy, ***App. Catal. A: General,*** **369,** 1, 2009.
27. S. K. Mishra and Y. K. Gupta, ***J. Chem. Soc. A,*** 2918, 1970.
28. W. Y. Song, Z. H. Li and A. Z. Wang, ***Chem. J. Chin, Univ., 18***, 1842, 1997.
29. P. K. Tandon, S. Z. Khanam and S. B. Singh, ***The open Catal. J.,*** **5,** 1, 2012.
30. S. Mathur, M. B. Yadav and V. Devra***, Int. J. Innov. Bio. Chem. Sci.*** **6,** 23, 2015.
31. T. Sumathi, P. Shanmugasundram and G. Chandramohan, ***Asian J. Chem.,*** **23,** 4385, 2011.
32. S. K. Mondal, D. Kar, M. Das and A. K. Das, ***Ind. J. Chem.,*** **37A,**765, 1998.
33. C. Walling ***"Free Radicals in Solutions",*** Academic Press, New York, p 38, 1957.
34. D. C. Bilehal, R. M. Kulkarni and S. T. Nandibewoor, ***J. Ind. Chem. Soc.,*** **80,** 91, 2003.

Chapter – 4

Mechanistic and Kinetic Study of Oxidation of Valine by Cerium(IV) in Presence of Palladium(II) in Sulphuric Acid Medium

Abstract

The reaction of valine (Val) with ceric ion has been kinetically studied in aqueous sulphuric acid medium in the presence of palladium(II) as catalyst using a spectrophotometric method at 45°C temperature. The reaction was studied under pseudo first order conditions with respect to cerium(IV). The results exhibits first order each in cerium(IV) and palladium(II) and a positive fractional order with respect to [Val]. The rate decreases with the increase of [HSO_4^-] and increases with increase of [H^+]. The stoichiometry of the reaction was found to be 1:2. 2-methylpropanal and Ce(III) were identified as the reaction product. Added products do not have any significant effect on the reaction rate. A suitable mechanism was proposed to account for the kinetic data, so that the rate equations derived for this mechanism could explain all observed results.

$$k_{obs} = \frac{2kK[Pd(II][Val][H^+]}{K[Val][H^+]+1}$$

4.1 Introduction

Cerium(IV), an unusually strong one electron oxidant has been frequently used from the synthetic point of view[1]. Generally in the synthetic studies, use of transition metal ion as catalyst under homogenous conditions has not been attended properly. The use of ceric ion as an oxidant which reacts via a one electron step is of substantial importance and of interest in many fields in chemistry[2-5]. The oxidation of variety of organic and inorganic compounds by cerium(IV) in acidic media has been the subject of several studies[2-4]. In all cases, evidence of a free radical was observed and reduction of Ce(IV) to Ce(III) by one electron transfer was postulated. In these studies, it has been pointed out that oxidation by cerium(IV) is complicated by complexation steps and reaction intermediates and postulation of a detailed mechanism has seldom been possible. In perchloric acid media, hydrolytic equilibria lead to at least three cerium(IV) species, where as in sulphuric acid medium, several sulphate complex species of the metal ion could also be produced[6-7].

L-Valine is an essential, non-polar, aliphatic amino acid used to hold protiens together. It is needed for muscle metabolism and coordination, tissue repair and for the maintenance of proper nitrogen balance in the body.

It has been noted that transition metal ions in the higher oxidation state can usually be stabilized by chelation with suitable complex agents, so that metal complexes formed would be good oxidants in acidic or alkaline media under appropriate conditions. However, the previous studies indicate that oxidation of amino acids by cerium(IV) in aqueous sulphuric acid is kinetically sluggish, and process can be efficiently catalysed by a variety of metal ions. Palladium(II) is known as catalyst for many reactions[8-12], but the nature of its active form in reactions remain obscure. An extensive literature survey reveals that no report is available on the oxidation kinetics of valine in the presence of Pd(II). Hence we felt it would be worthwhile to investigate the oxidative behaviour of Ce(IV) with valine to explore the kinetics and mechanistic aspects of Pd(II) chloride catalysed reaction. This study will enable to understand the complicated biological reaction in living systems and will also help to understand the catalytic activity of Pd(II) along with oxidative capacity of Ce(IV) in acid medium.

4.2 Experimental

In the present work, double distilled water was used throughout the study. A stock solution of L-Valine (E. Merck) was prepared by dissolving it in water. The cerium(IV) stock solution was obtained by dissolving cerium(IV) ammonium sulphate (E. Merck) in 1.0 mol dm^{-3} sulphuric acid and standardized with iron(II) ammonium sulphate solution. The stock solution of Palladium(II) chloride was prepared by dissolving the sample in HCl (0.20 mol dm^{-3}) and assayed by complexometric titration[13]. The stock solution of palladium(II) chloride was stored in black coated bottle to prevent photochemical decomposition and their strength was checked spectrophotometrically[14] time to time. Other chemicals and reagents such as sodium sulphate, sulphuric acid, acetonitrile used were of analytical grade.

4.2.1 Kinetic Measurements

The kinetics were followed at $45^{\circ} \pm 1^{\circ}C$ unless otherwise stated and at $I = 1.50$ mol dm^{-3}. The reaction was initiated by mixing reactant solutions thermally equilibrated at the desired temperature. Kinetic studies were carried out in sulphuric acid medium under pseudo first order conditions with a large excess of valine over cerium(IV). The reaction was followed by measuring the absorbance of unreacted Ce(IV) at 360 nm using Systronics(166) UV-Visible spectrophotometer. The spectral changes during the chemical reaction for the standard condition at $45^{\circ}C$ are given in **(Figure 4.1)**. At this wave length all other materials concerned have negligible absorption. Beer's law had been verified between 5×10^{-5} to 5×10^{-4} mol dm^{-3} of cerium(IV) at 360 nm under the reaction conditions. The molar absorption coefficient was found to be $\varepsilon = 2622$ dm^3 mol^{-1} cm^{-1}. The rate condtants (k_{obs}) were obtained from the plot of log absorbance versus time.

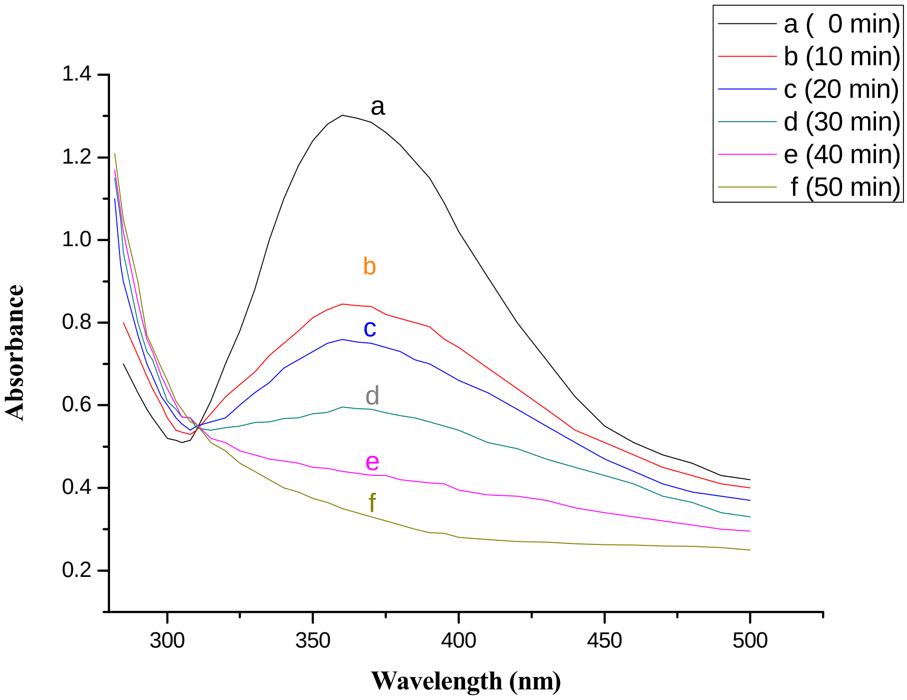


Figure 4.1: Sequential scans of absorption spectra during the course of the reaction of valine with cerium(IV) in sulphuric acid media at different time

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Val] = 5.0×10^{-3} mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3};

I = 1.50 mol dm^{-3}; Temp.= 45°C

4.2.2 Stoichiometry and Product Analysis

Different reaction mixture with different sets of concentrations of reactants where [Ce(IV)] was in excess over [Valine] at constant conditions of ionic strength, acidity and catalyst were kept at 24h at 45°C. The mixture was treated with 2,4-dinitrophenylhydrazine and the formation of hydrazones indicated the presence of aldehydes as the oxidation products of amino acids under the kinetic condition. The main products are Ce(III), 2- methylpropanal, ammonia and CO_2. 2-methylpropanal was confirmed by the IR spectrum of this hydrazone superimposed on the spectrum of corresponding hydrazone of standard sample of 2-methylpropanal. The IR peaks at 3290.69 cm^{-1}, 2967.85 cm^{-1} and 1622.82 cm^{-1} are attributed to –NH, –CH and –C=N stretching respectively **(Figure 4.2)**. Further, aldehyde group was confirmed with qualitative test such as Tollen′s reagent[15] and Schiff's reagent. Nitrile test was negative, the product generally reported in the oxidation of amino acids. Ammonia was confirmed with Nesseler's test. Therefore the stoichiometry of the reaction positive with test of aldehyde can be represented by following equation:

$$(CH_3)_2CHCH(NH_2)COOH + 2Ce(IV) + H_2O \xrightarrow{Pd(II)} (CH_3)_2CHCHO + NH_3 + CO_2 + 2Ce(III) + 2H^+$$

4. 3 Results

4.3.1 Cerium(IV) Dependence

The reaction rate was measured with various [Ce(IV)] = 5×10^{-5} to 5×10^{-4} mol dm^{-3} at three concentration of [Val] = 2.5×10^{-3} mol dm^{-3}, 5×10^{-3} mol dm^{-3} and 7.5×10^{-3} mol dm^{-3} respectively, $[H^+]$ = 1.0 mol dm^{-3}, I = 1.50 mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3} and temperature = 45°C. The plot of log absorbance versus time was linear **(Figure 4.3)**, indicating that the reaction is first order with respect to [Ce(IV)]. The pseudo first order rate constants (k_{obs}) are independent of the [Ce(IV)]. Results are given in **Table 4.1, 4.2** and **4.3**.

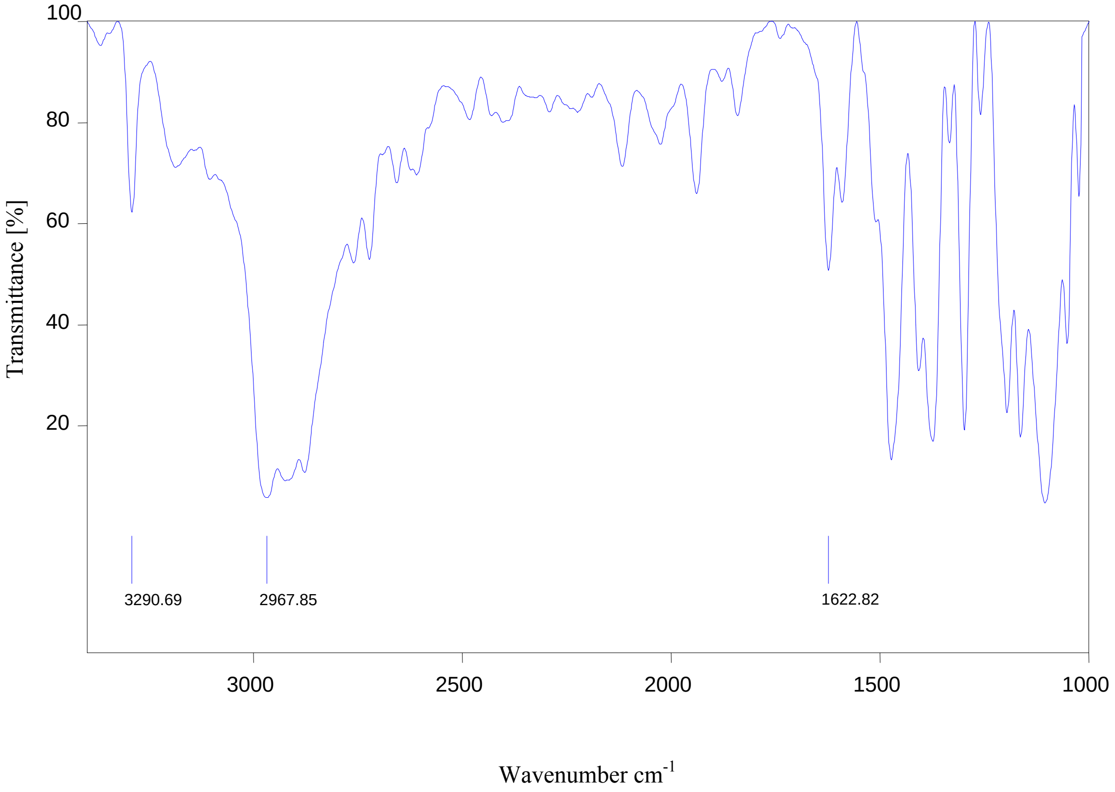


Figure 4.2: FT-IR Spectra of oxidation product of valine

Table 4.1: Variation of cerium(IV)

[Val] = 2.5×10^{-3} mol dm^{-3}
Temp. = 45°C
[H^{+}] = 1.0 mol dm^{-3}
I = 1.50 mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

10^4 [Ce (IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes	**Absorbance**					
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.112	0.235	0.456	0.706	0.896	1.149
20	0.092	0.205	0.406	0.619	0.786	1.009
30	0.080	0.175	0.356	0.554	0.694	0.889
40	0.072	0.154	0.321	0.479	0.593	0.772
50	0.062	0.138	0.279	0.419	0.532	0.706
60	0.054	0.121	0.242	0.369	0.459	0.586
80	0.041	0.093	0.191	0.289	0.348	0.442
10^4 (k_{obs}), sec^{-1}	**2.21**	**2.21**	**2.22**	**2.20**	**2.19**	**2.21**

Table 4.2: Variation of cerium(IV)

[Val] = 5.0 × 10^{-3} mol dm^{-3} **Temp. = 45°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^4 [Ce (IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.094	0.201	0.403	0.612	0.801	0.994
20	0.071	0.155	0.320	0.465	0.612	0.761
30	0.055	0.118	0.241	0.368	0.476	0.581
40	0.041	0.092	0.184	0.278	0.361	0.452
50	0.033	0.070	0.141	0.217	0.272	0.342
60	0.025	0.054	0.106	0.167	0.211	0.261
80	0.015	0.032	0.064	0.096	0.121	0.159
10^4 (k_{obs}), sec^{-1}	**4.43**	**4.41**	**4.41**	**4.45**	**4.41**	**4.41**

Table 4.3: Variation of cerium(IV)

[Val] = 7.5× 10^{-3} mol dm^{-3} **Temp. = 45°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^4 [Ce (IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	(0) 0.121	(0) 0.265	0.528	0.782	1.041	1.302
10	(5) 0.098	(5) 0.216	0.354	0.536	0.703	0.889
20	(10) 0.081	(10) 0.179	0.242	0.367	0.442	0.609
30	(15) 0.068	(15) 0.146	0.165	0.253	0.323	0.403
40	(20) 0.055	(20) 0.123	0.112	0.167	0.216	0.274
50	(30) 0.038	(30) 0.082	0.076	0.116	0.146	0.186
60	(40) 0.025	(40) 0.055	0.051	0.079	0.123	0.127
80	(50) 0.017	(60) 0.025	0.024	0.036	0.043	0.057
10^4 (k_{obs}), sec^{-1}	**6.54**	**6.52**	**6.53**	**6.51**	**6.52**	**6.50**

Figures in parentheses denote time in minutes

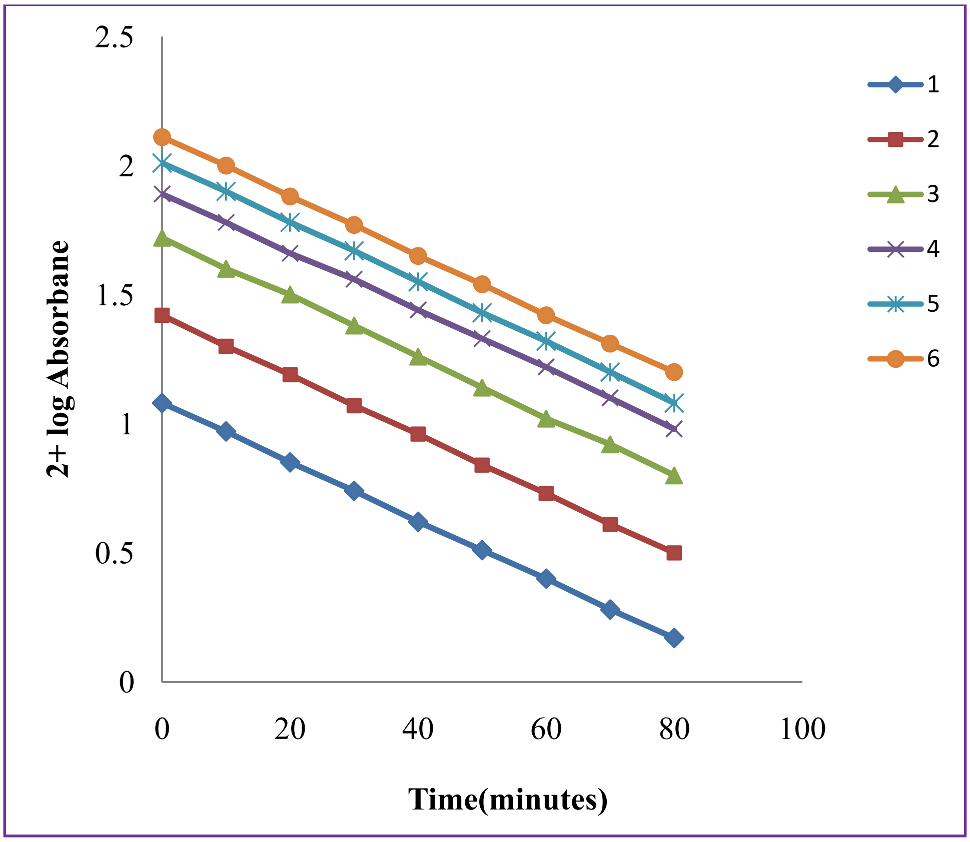


Figure 4.3: Psuedo first order plots for the variation of cerium(IV)

[Val] = 5.0×10^{-3} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; I = 1.50 mol dm^{-3}; Temp. = 45°C;

[Ce(IV)] = (1) 0.50×10^{-4} mol dm^{-3}; (2) 1.0×10^{-4} mol dm^{-3};

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

(5) 4.0×10^{-4} mol dm^{-3}; (6) 5.0×10^{-4} mol dm^{-3}.

(Ref. Table 4.2)

4.3.2 Valine Dependence

The kinetic runs were carried out with various concentrations (1×10^{-3} to 1×10^{-2} mol dm^{-3}) of valine at fixed [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3}, I = 1.50 mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3} and temperature = 40°C, 45°C and 50°C respectively, the rate constants (k_{obs}) increases with the increase of [Val] **(Figure 4.4)**. Results are given in **Table 4.4, 4.5 and 4.6**. Observed reaction order of valine is 0.65 obtained from the linear regression of log k_{obs} versus log [Val], indicating fractional order with respect to valine. The plot of 1/ k_{obs} versus 1/ [Val] exhibits excellence linearity with positive intercept and slope.

4.3.3 Palladium(II) Dependence

At fixed [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [Val] = 5×10^{-3} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3} and I =1.50 mol dm^{-3}, Pd(II) was varied from 1×10^{-5} to 1×10^{-4} mol dm^{-3} at three temperatures 40°C, 45°C, 50°C respectively. The rate constants (k_{obs}) increases with the increase of [Pd(II)] **(Figure 4.5)**. Results are given in **Table 4.7, 4.8 and 4.9**. Observed reaction order of palladium(II) obtained from the plot of log k_{obs} versus log [Pd(II)] is 1.0, which indicates that the reaction is of first order with respect to [Pd(II)]. 1/ k_{obs} versus 1/ [Pd(II)] yielded good linear plots passing through the origin.

4.3.4 Hydrogen Ion Dependence

The reaction rate were measured with various [H^{+}] = 0.20 to 1.0 mol dm^{-3} at fixed [HSO_4^{-}], ([HSO_4^{-}] =1.0 mol dm^{-3} from H_2SO_4 and $NaHSO_4$), [Val] = 5×10^{-3} mol dm^{-3}, [Ce(IV)] = 5×10^{-4} mol dm^{-3}, I = 1.50 mol dm^{-3}, [Pd(II)] =5×10^{-5} mol dm^{-3}. The rate of reaction increases with increase of [H^{+}] **(Figure 4.6)**, observed reaction order of [H^{+}] is 0.60 obtained from plot of log k_{obs} versus log [H^{+}] indicating that reaction is of positive fractional order with respect to [H^{+}]. Results are given in **Table 4.10.**

Table 4.4: Variation of valine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 40°C**
[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

10^3 [Val], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.102	1.138	1.098	1.069	1.048	1.031	1.026	1.015	1.003	0.998
20	(60) 0.845	1.024	0.961	0.925	0.864	0.839	0.804	0.763	0.751	0.732
30	(80) 0.715	(40) 0.768	0.802	0.768	0.704	0.664	0.634	0.609	0.584	0.558
40	(120) 0.527	(60) 0.613	0.701	0.634	0.578	0.557	0.512	0.482	0.465	0.446
50	(140) 0.465	(80) 0.489	0.611	0.542	0.461	0.438	0.409	0.384	0.349	0.339
60	(160) 0.403	(100) 0.368	0.529	0.452	0.388	0.361	0.328	0.298	0.274	0.266
80	(180) 0.352	(120) 0.267	0.384	0.319	0.261	0.217	0.208	0.182	0.169	0.163
10^4 (k_{obs}), sec^{-1}	**1.15**	**2.01**	**2.49**	**2.87**	**3.26**	**3.64**	**3.83**	**4.03**	**4.22**	**4.31**

Figures in parentheses denote time in minutes

Table 4.5: Variation of valine

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 45°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^3 [Val], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.148	1.074	1.042	1.015	0.994	0.979	0.961	0.952	0.929	0.919
20	(40) 1.025	0.932	0.837	0.804	0.768	0.718	0.684	0.674	0.652	0.642
30	(60) 0.921	0.774	0.684	0.621	0.589	0.531	0.511	0.483	0.473	0.443
40	(80) 0.842	0.651	0.557	0.485	0.448	0.402	0.384	0.367	0.351	0.341
50	(100) 0.729	0.561	0.456	0.378	0.352	0.308	0.294	0.261	0.254	0.242
60	(120) 0.672	0.476	0.367	0.291	0.268	0.231	0.211	0.194	0.185	0.176
80	(140) 0.552	0.339	0.246	0.182	0.159	0.128	0.115	0.105	0.096	0.092
$10^4(k_{obs})$, sec^{-1}	**1.72**	**2.78**	**3.45**	**4.03**	**4.41**	**4.79**	**4.98**	**5.18**	**5.37**	**5.46**

Figures in parentheses denote time in minutes

Table 4.6: Variation of valine

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 50°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^3 [Val], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	1.074	1.015	0.979	0.929	0.904	0.881	0.860	0.841	0.829	0.819
20	0.932	0.804	0.718	0.652	0.642	0.601	0.584	0.558	0.542	0.532
30	0.774	0.621	0.531	0.473	0.443	0.412	0.394	0.374	0.349	0.339
40	0.651	0.485	0.402	0.351	0.321	0.278	0.267	0.248	0.237	0.231
50	0.561	0.378	0.308	0.254	0.223	0.198	0.179	0.164	0.153	0.146
60	0.476	0.291	0.231	0.185	0.161	0.133	0.121	0.112	0.102	0.096
80	0.339	0.182	0.128	0.096	0.077	0.060	0.056	0.048	0.043	0.040
10^4 (k_{obs}), sec^{-1}	**2.78**	**4.03**	**4.79**	**5.37**	**5.75**	**6.33**	**6.52**	**6.81**	**7.00**	**7.10**

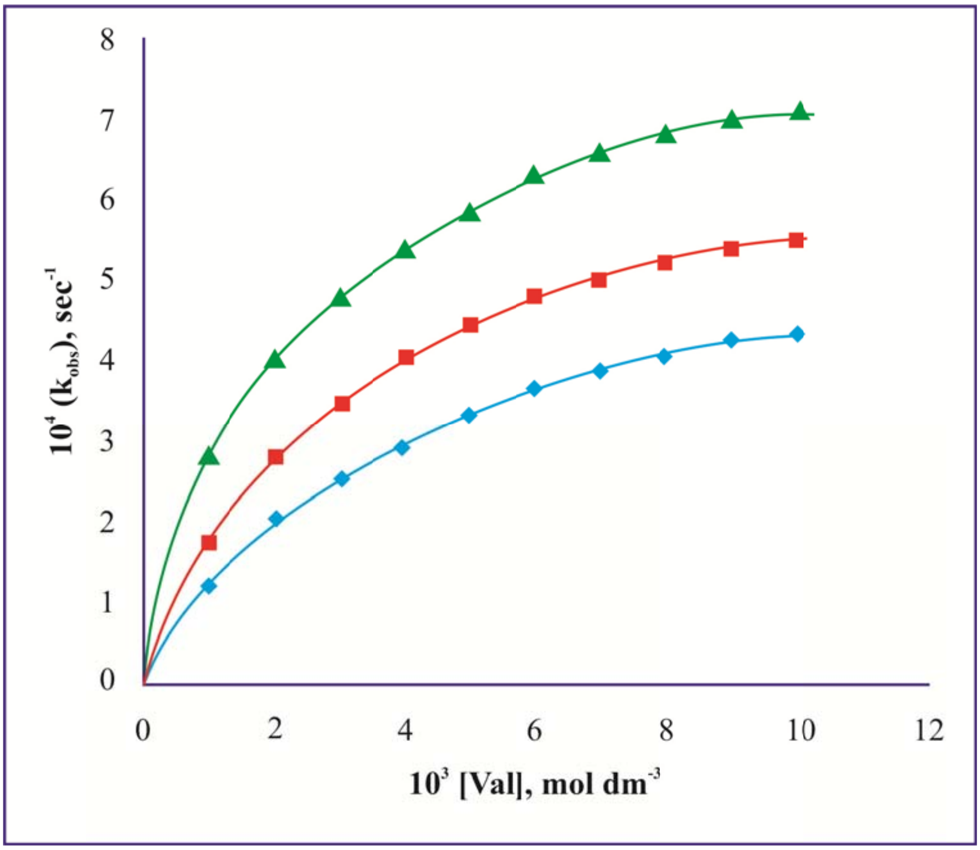


Fig 4.4: Variation of valine

$[Ce(IV)] = 5.0\times10^{-4}$ mol dm^{-3}; $[H^+] = 1.0$ mol dm^{-3};

$[Pd(II)] = 5.0\times10^{-5}$ mol dm^{-3}; I = 1.50 mol dm^{-3};

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table 4.4, 4.5 and 4.6)

Table 4.7: Variation of palladium(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 40°C**

[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Val] = 5.0×10^{-3} mol dm^{-3}

10^5 [Pd(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.204	(20) 1.076	1.140	1.098	1.058	1.031	1.003	0.979	0.912	0.889
20	(60) 1.052	(40) 0.947	1.009	0.961	0.886	0.821	0.771	0.702	0.642	0.612
30	(80) 0.956	(80) 0.709	0.904	0.802	0.729	0.652	0.598	0.534	0.462	0.424
40	(120) 0.776	(100) 0.603	0.801	0.701	0.612	0.531	0.462	0.405	0.329	0.287
50	(140) 0.703	(120) 0.485	0.721	0.611	0.497	0.423	0.349	0.291	0.231	0.192
60	(160) 0.632	(140) 0.392	0.623	0.529	0.412	0.335	0.274	0.215	0.164	0.127
80	(180) 0.556	(160) 0.343	0.502	0.384	0.294	0.217	0.169	0.128	0.083	0.060
10^4(k_{obs}), sec^{-1}	**0.67**	**1.24**	**1.91**	**2.49**	**3.07**	**3.64**	**4.22**	**4.79**	**5.66**	**6.23**

Figures in parentheses denote time in minutes

Table 4.8: Variation of palladium(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 45°C**
[H$^+$] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**
[Val] = 5.0×10^{-3} mol dm^{-3}

10^5 [Pd(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.125	(20) 1.056	1.079	1.042	0.994	0.929	0.896	0.829	0.802	0.756
20	(60) 0.923	(40) 0.862	0.921	0.834	0.768	0.663	0.621	0.556	0.506	0.439
30	(80) 0.836	(60) 0.698	0.779	0.696	0.589	0.482	0.432	0.369	0.304	0.253
40	(120) 0.679	(80) 0.568	0.664	0.554	0.448	0.349	0.298	0.236	0.192	0.152
50	(140) 0.605	(100) 0.473	0.565	0.443	0.352	0.247	0.206	0.156	0.116	0.092
60	(160) 0.543	(120) 0.389	0.484	0.367	0.268	0.181	0.146	0.102	0.073	0.053
80	(180) 0.496	(140) 0.308	0.351	0.246	0.159	0.096	0.070	0.043	0.027	0.021
10^4 (k_{obs}), sec^{-1}	**0.86**	**1.63**	**2.68**	**3.45**	**4.41**	**5.37**	**6.04**	**7.00**	**7.86**	**8.82**

Figures in parentheses denote time in minutes

Table 4.9: Variation of palladium(II)

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 50°C**

[H^+] = 1.0 mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Val] = 5.0 × 10^{-3} mol dm^{-3}

10^5 [Pd(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.076	1.120	1.042	0.994	0.912	0.841	0.802	0.732	0.702	0.667
20	(40) 0.947	0.941	0.835	0.763	0.642	0.567	0.506	0.423	0.386	0.335
30	(80) 0.709	0.826	0.682	0.587	0.462	0.378	0.304	0.243	0.211	0.172
40	(100) 0.638	0.712	0.558	0.443	0.329	0.248	0.192	0.146	0.112	0.088
50	(120) 0.546	0.609	0.451	0.335	0.231	0.161	0.116	0.084	0.061	0.044
60	(140) 0.451	0.534	0.362	0.254	0.164	0.106	0.073	0.048	0.033	0.023
80	(160) 0.391	0.414	0.246	0.159	0.083	0.048	0.027	0.018	0.016	0.015
10^4 (k_{obs}), sec^{-1}	**1.24**	**2.39**	**3.45**	**4.41**	**5.66**	**6.81**	**7.86**	**9.02**	**10.17**	**11.13**

Figures in parentheses denote time in minutes

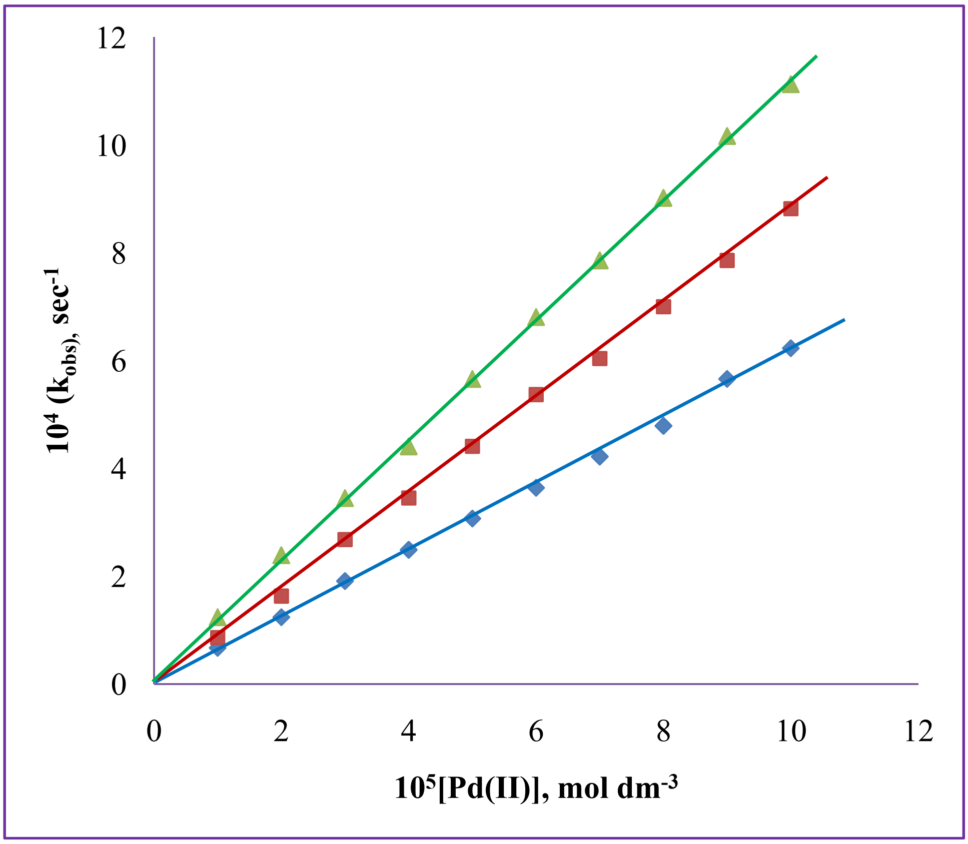


Figure 4.5: Variation of palladium(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3};

[Val] = 5.0×10^{-3} mol dm^{-3}; I = 1.50 mol dm^{-3};

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table- 4.7, 4.8 and 4.9)

Table 4.10: Variation of hydrogen ion

[Val] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **I = 1.50 mol dm^{-3}**

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

[H$^+$], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	(20) 1.036	1.074	1.048	1.027	0.994
20	(40) 0.916	0.932	0.876	0.802	0.768
30	(60) 0.649	0.774	0.718	0.643	0.589
40	(80) 0.538	0.651	0.579	0.509	0.448
50	(100) 0.432	0.561	0.469	0.406	0.352
60	(120) 0.343	0.476	0.395	0.319	0.268
80	(140) 0.273	0.339	0.261	0.210	0.159
10^4 (k_{obs}), sec^{-1}	**1.82**	**2.78**	**3.26**	**3.83**	**4.41**

Figures in parentheses denote time in minutes

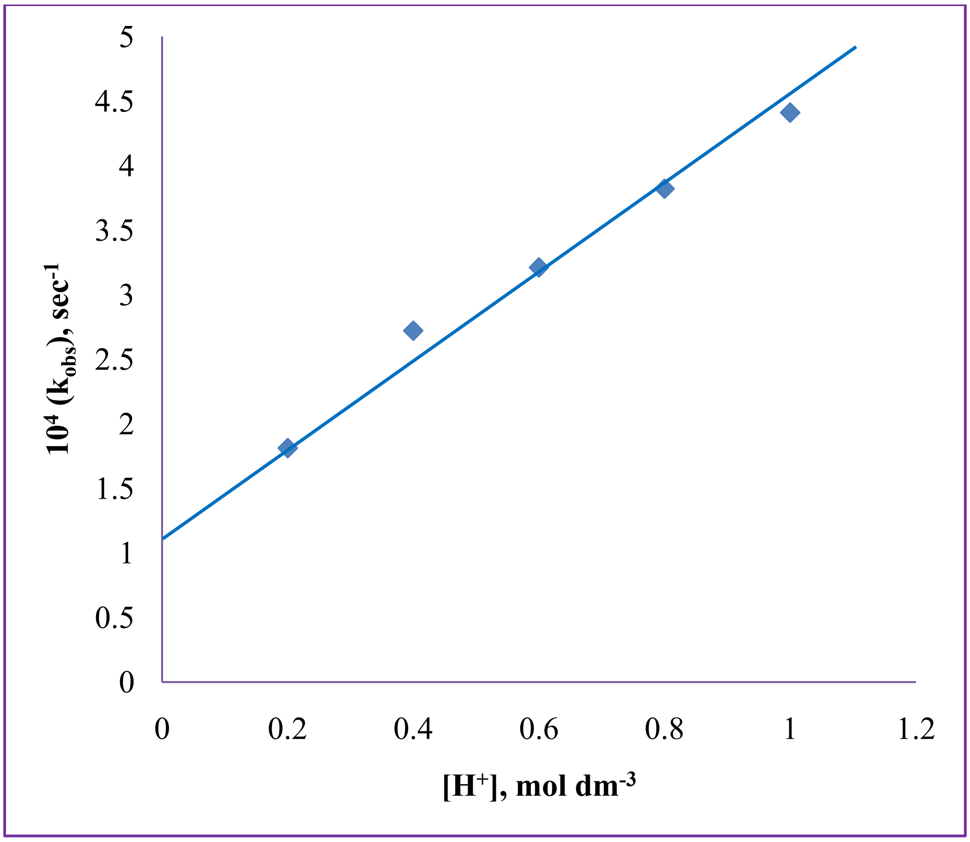


Figure 4.6: Variation of hydrogen ion

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Val] = 5.0×10^{-3} mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; [HSO_4^-] = 1.0 mol dm^{-3};

I = 1.50 mol dm^{-3}; Temp. = 45°C

(Ref. Table 4.10)

4.3.5 Effect of [HSO_4^-]

[HSO_4^-] was varied in the range of 0.20 to 1.0 mol dm^{-3} at fixed [H^+] = 0.20 mol dm^{-3}, [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [Val] = 5×10^{-3} mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3}, I = 1.50 mol dm^{-3} and temperature 45°C. Here HSO_4^- ≈ [$NaHSO_4$] + [H_2SO_4], ignoring the dissociation of [HSO_4^-] in strongly acidic medium. The rate constants (k_{obs}) decrease with increase of [HSO_4^-]. Therefore HSO_4^- shows a rate retarding effect **(Figure 4.7)**. Results are given in **Table 4.11**.

4.3.6 Effect of Ionic Strength

At fixed concentration of [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [Val] = 5×10^{-3} mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and temperature 45°C, the ionic strength was varied from 1.20 to 2.0 mol dm^{-3} by the different concentration of Na_2SO_4 it is found that ionic strength has slightly affected the rate of reaction **(Figure 4.8)**. Results are given in **Table 4.12.**

4.3.7 Effect of Chloride Ion

At fixed concentrations of [Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3}, [Val] = 5.0 × 10^{-3} mol dm^{-3}, [Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}, [H^+] = 1.0 mol dm^{-3} and temperature at 45°C , the concentration of Cl^- was varied from 1×10^{-4} to 5×10^{-4} mol dm^{-3}. The rate was uneffected by the addition of Cl^- ions **(Figure 4.9)**. Results are given in **Table 4.13**.

4.4 Discussion

Before formulating the reaction mechanism for the reaction under investigation, it is necessary to ascertain the reactive species of palladium(II) chloride in acidic medium. Palladium(II) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. Under the experimental pH range in the present investigation ($PdCl_2$) has been proposed and confirmed[16] as the reactive species dominant in the pH range 1.00 to 3.00.

Table 4.11: Variation of [HSO_4^-]

[Val] = 5.0×10^{-3} mol dm^{-3}
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

Temp. = 45°C
I = 1.50 mol dm^{-3}

[HSO_4^-], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.732	0.834	0.924	0.952	0.994
20	0.423	0.554	0.642	0.674	0.768
30	0.243	0.368	0.462	0.483	0.589
40	0.146	0.241	0.329	0.367	0.448
50	0.084	0.159	0.231	0.261	0.352
60	0.048	0.104	0.164	0.194	0.268
80	0.018	0.045	0.083	0.105	0.159
10^4 (k_{obs}), sec^{-1}	**9.02**	**6.90**	**5.66**	**5.18**	**4.41**

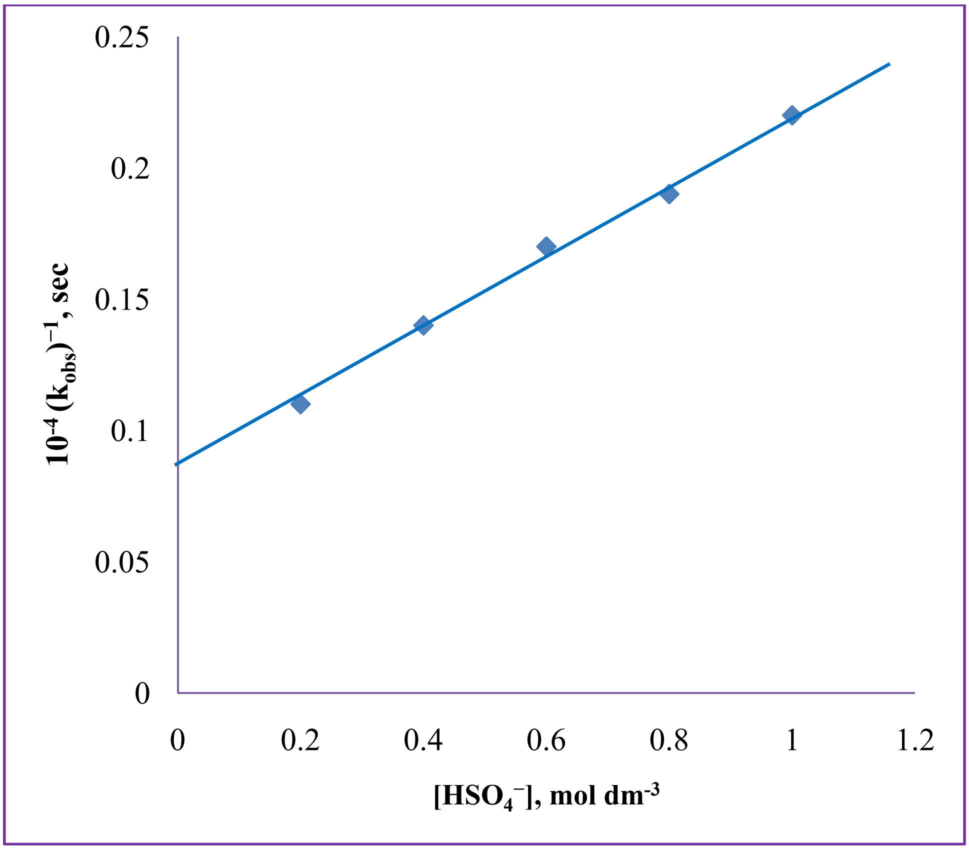


Figure 4.7: Linear plot of $1/k_{obs}$ versus $[HSO_4^-]$

$[Ce(IV)] = 5.0\times10^{-4}$ mol dm^{-3}; $[Val] = 5.0 \times 10^{-3}$ mol dm^{-3};

$[Pd(II)] = 5.0\times10^{-5}$ mol dm^{-3}; $[H^+] = 0.20$ mol dm^{-3};

I = 1.50 mol dm^{-3}; Temp. = 45°C

(Ref. Table 4.11)

Table 4.12: Variation of ionic strength

[Val] = 5.0×10^{-3} mol dm^{-3}
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

Temp. = 45°C
[H^{+}] = 1.0 mol dm^{-3}

I, mol dm^{-3}	**1.20**	**1.40**	**1.50**	**1.80**	**2.00**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.997	0.995	0.994	0.991	0.990
20	0.782	0.773	0.768	0.765	0.762
30	0.599	0.593	0.589	0.585	0.584
40	0.455	0.449	0.448	0.447	0.443
50	0.359	0.354	0.352	0.351	0.326
60	0.275	0.270	0.268	0.265	0.248
80	0.162	0.161	0.159	0.154	0 .143
10^{4} (k_{obs}), sec^{-1}	**4.32**	**4.38**	**4.41**	**4.46**	**4.65**

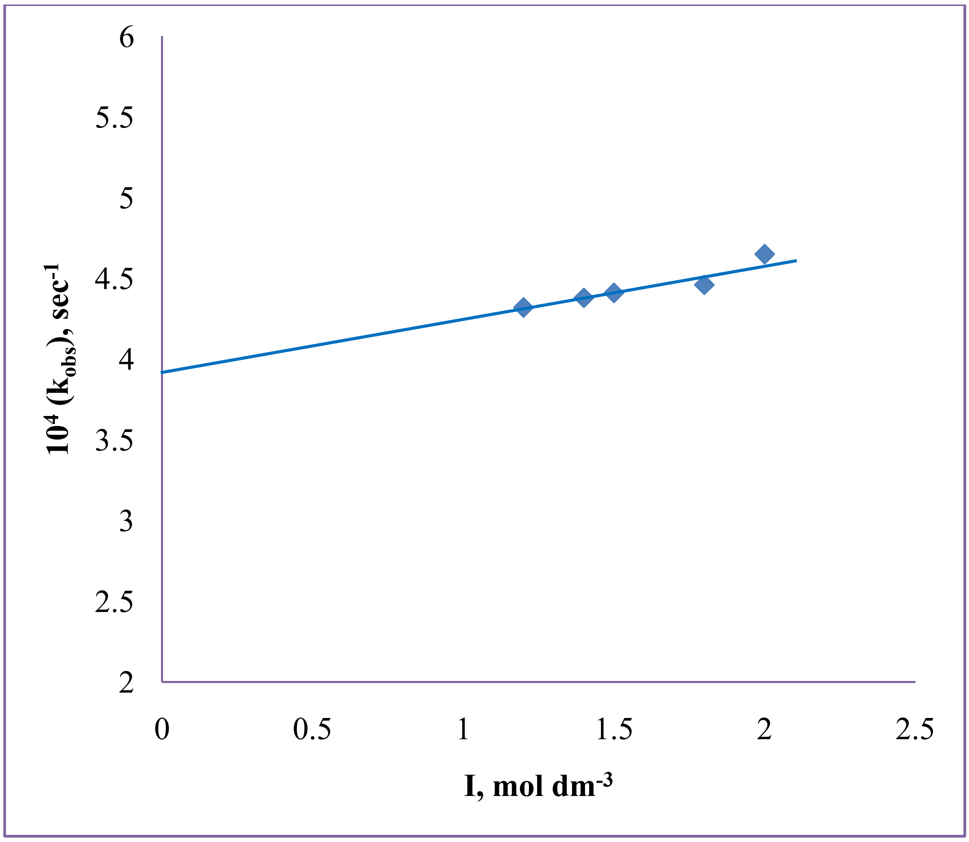


Figure 4.8: Variation of ionic strength

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Val] = 5.0×10^{-3} mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; [H^+] = 1.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 4.12)

Table: 4.13 Variation of chloride ion

[Val] = 5.0×10^{-3} mol dm^{-3}
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

Temp. = 45°C
[H^+] = 1.0 mol dm^{-3}
I = 1.50 mol dm^{-3}

[Cl^-], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.994	0.993	0.994	0.992	0.991
20	0.768	0.768	0.768	0.767	0.766
30	0.589	0.587	0.589	0.588	0.587
40	0.448	0.447	0.448	0.446	0.445
50	0.352	0.351	0.352	0.351	0.350
60	0.268	0.267	0.268	0.267	0.266
80	0.159	0.156	0.159	0.156	0.154
10^4 (k_{obs}), sec^{-1}	**4.41**	**4.42**	**4.41**	**4.42**	**4.43**

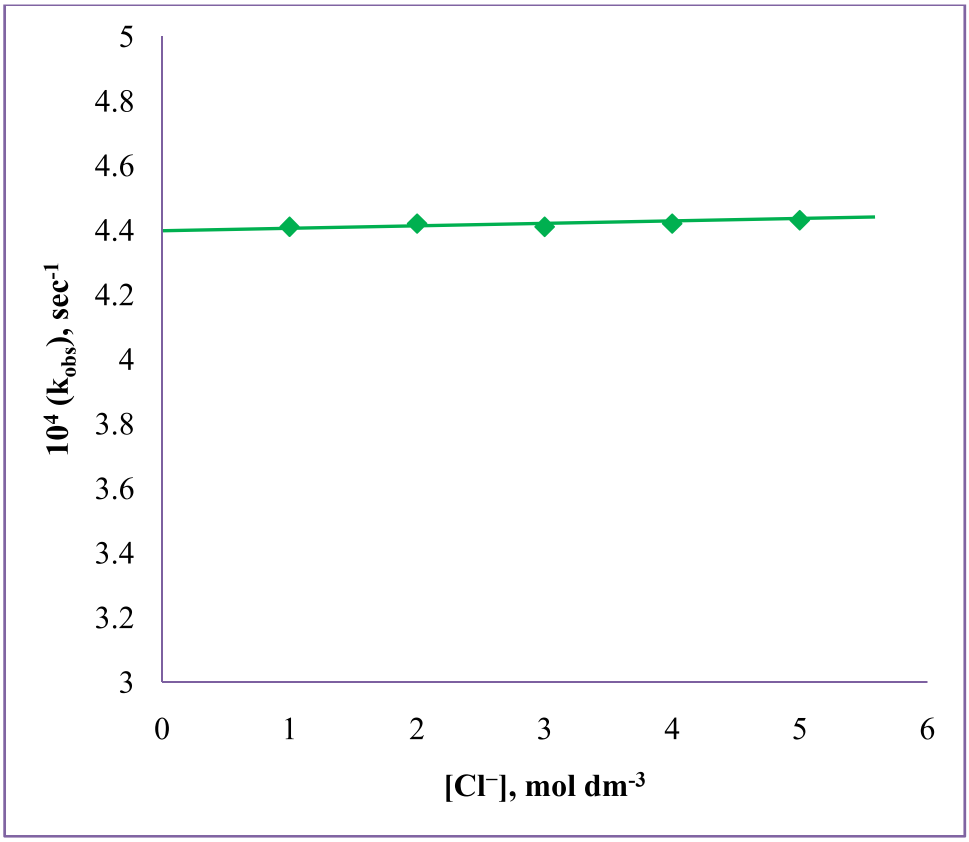


Figure 4.9: Variation of chloride ion

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Val] = 5.0×10^{-3} mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; [H^+] = 1.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 4.13)

Palladium(II) chloride is rather insoluble in aqueous solution but is soluble in hydrochloric acid and exists**[17-18]** as $[PdL_4]^{2-}$, according to the equilibrium**[19]**.

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

The existence of $PdCl_2$ exclusively in the form of $[PdCl_4]^{2-}$ is also supported by Ayres**[20]**, who has observed that when a reaction ratio of 2:1 for sodium chloride (Cl^- ions) to palladium(II) chloride is maintained, then this will result in the formation of well known tetrachloropalladate(II), $[PdCl_4]^{2-}$. Since throughout the experiments, ratio of Cl^- ion to palladium(II) chloride concentration i.e. $Cl^-/[PdCl_4]^{2-}$ was maintained more than 2, it is reasonable to assume that the species $[PdCl_4]^{2-}$ is the sole palladium(II) species in HCl**[21-22]**.

The observed fractional order with respect to valine indicates that there is possibility of complex formation between $[PdCl_4]^{2-}$ and valine in the first pre-equilibrium step. Valine is easily protonized in acid media, indicating the involvement of H^+ in the reaction in the pre-equilibrium step. $Ce(SO_4)_2$ has been found kinetically active in this study with generation of free radicals in the reaction. Platinum group metals have the ability to form complexes with organic substrates highly enhanced rates substantiate the formation of (Pd(II)-AA) complex, which slowly reacts with Ce(IV) species in the rate determining step to give products. It is also noteworthy that the reaction is note influenced by chloride ions, to be expected in Pd(II) catalysed reaction**[23-24]**. On the basis of above kinetic results, a probable reaction mechanism has been proposed **(Scheme-4.1)**.

$$H^+ + (CH_3)_2CHCH(NH_2)COOH \overset{K_1}{\rightleftharpoons} H_3N^+(CH_3)_2CHCHCOOH \quad (1)$$

$$H_3N^+(CH_3)_2CHCHCOOH + Pd(II) \overset{K_2}{\rightleftharpoons} \underset{\text{(Adduct)}}{Pd(II)\cdot H_3N^+(CH_3)_2CHCHCOOH} \quad (2)$$

$$\begin{aligned}\text{Addcut} + Ce(SO_4)_2 \xrightarrow[\text{slow}]{k} &\ Pd(III).H_3N^+(CH_3)_2CHCHCOOH\ (\text{Adduct})^+ \\ &+ Ce(III) + 2SO_4^{2-} \quad (3)\end{aligned}$$

$$(\text{Adduct})^+ \xrightarrow{\text{fast}} Pd(II) + H_2N\cdot(CH_3)_2CHCHCOO^{\bullet} + 2H^+ \quad (4)$$

$$H_2N\cdot(CH_3)_2CHCHCOO^{\bullet} + Ce(SO_4)_2 \xrightarrow[H_2O]{fast} (CH_3)_2CHCHO + Ce(III)$$
$$+ 2SO_4^{2-} + H^+ + NH_3 + CO_2 \quad (5)$$

Scheme-4.1

According to the present mechanism applying the steady state condition to the free radicals,

$$\frac{-d[Ce(IV)]}{dt} = \frac{2kK[Pd(II)][Ce(IV)][Val][H^+]}{K[Val][H^+]+1} \quad (6)$$

Where $K = K_1\ K_2$

$$\frac{-d[Ce(IV)]/dt}{[Ce(IV)]} = k_{obs} = \frac{2kK[Pd(II)][Val][H^+]}{K[Val][H^+]+1} \quad (7)$$

Rearrangement of equation (7)

$$\frac{1}{k_{obs}} = \frac{K[Val][H^+]+1}{2kK[Pd(II)][Val][H^+]}$$

$$= \frac{1}{2k[Pd(II)]} + \frac{1}{2kK[Val][H^+]}\cdot\frac{1}{[Pd(II)]} \quad (8)$$

$$= \frac{1}{2k[Pd(II)]} + \frac{1}{2kK[Pd(II)][H^+]}\cdot\frac{1}{[Val]} \quad (9)$$

$$= \frac{1}{2k[Pd(II)]} + \frac{1}{2kK[Pd(II)][Val]}\cdot\frac{1}{[H^+]} \quad (10)$$

Equation (7) suggest that order with respect to palladium(II) is 1.0, less than one in valine and less than one in [H^+], which is consistent with the result of our experiments. Equation (8) suggest that 1/ k_{obs} versus 1/ Pd(II) at constant [Val], [H^+] should yield good linear plots through the origin **(Figure 4.10)**. Equation (9) suggests that 1/ k_{obs} versus 1/ [Val] at fixed [Pd(II)] and [H^+] should be linear plots with positive intercept **(Figure 4.11)**. Equation (10) suggests that the plot of 1/k_{obs} versus 1/ [H^+] at constant [Pd(II)] and [Val] should also be linear with positive intercept.

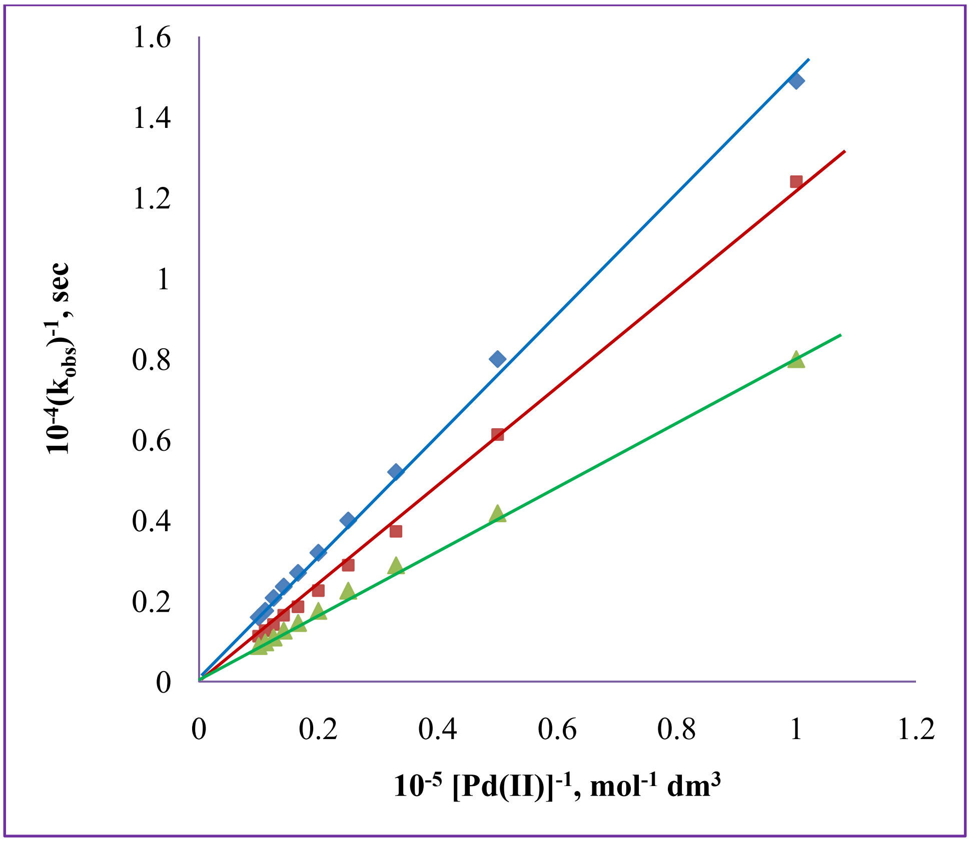


Figure 4.10: A plot of 1/k_{obs} versus 1/[Pd(II)]$^{-1}$

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [H^{+}] = 1.0 mol dm^{-3};

[Val] = 5.0×10^{-3} mol dm^{-3}; I = 1.50 mol dm^{-3};

Temp. = (◆) 40°C; (■) 45°C; (▲) 50°C

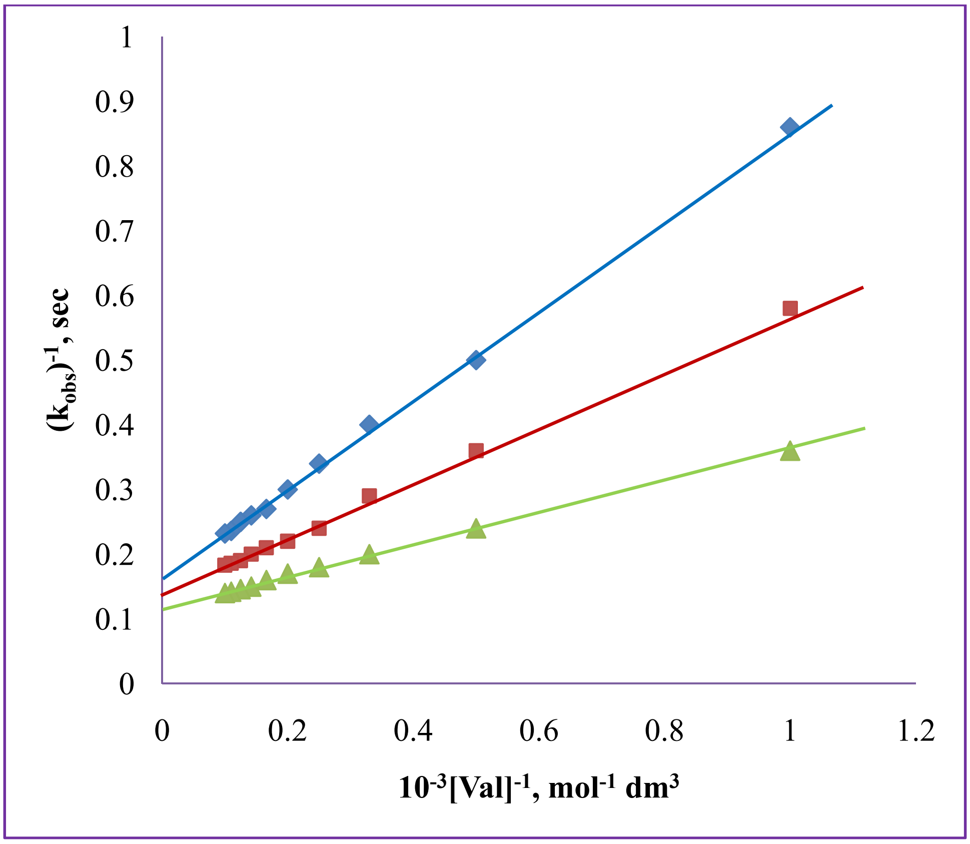


Figure 4.11: A plot of $1/k_{obs}$ versus 1/[Val]

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [H^+] = 1.0 mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; I = 1.50 mol dm^{-3};

Temp. = (◆) 40°C; (■) 45°C; (▲) 50°C

Under the experimental conditions in aqueous sulphuric acid medium, the important Ce(IV) sulphato complexs are $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ and relevant equilibria are[25]:

$$Ce^{4+} + HSO_4^- \overset{Q_1}{\rightleftharpoons} Ce(SO_4)^{2+} + H^+ \tag{11}$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{Q_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \tag{12}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{Q_3}{\rightleftharpoons} HCe(SO_4)_3^- \tag{13}$$

The value of equilibrium constants are $Q_1 = 3.5 \times 10^3$ (25°C), $Q_2 = 2 \times 10^2$ (25°C) and $Q_3 = 0.6$ (at 20°C). Insignificant amount of unhydrolyzed species of cerium(IV) would also exist along with these sulphato complexes. In the light of equilibrium (11-13), inverse bisulphate dependence **(Figure 4.7)** can be explained by assuming $Ce(SO_4)_2$ as the reactive species. The concentration of this active species is given by equation (14)

$$Ce(SO_4)_2 = \frac{[Ce(IV)]_T}{1 + Q_3[HSO_4^-]} \tag{14}$$

$$= f\,[Ce(IV)]_T$$

Thus equation (7) can be written as

$$k_{obs} = \frac{2kK[Pd(II)][Val][H^+]}{\left[K[Val][H^+]+1\right]\left[1+Q_3[HSO_4^-]\right]} \tag{15}$$

Assuming $C = \dfrac{2kK[Pd(II)][Val][H^+]}{K[Val][H^+]+1}$

Equation (15) may be written as

$$k_{obs} = \frac{C}{1+Q_3[HSO_4^-]} \tag{16}$$

$$\frac{1}{k_{obs}} = \frac{1}{C} + \frac{Q_3[HSO_4^-]}{C} \tag{17}$$

Equation (17) suggest that 1/ k_{obs} versus $[HSO_4^-]$ should be linear and agrees with observed experimental data. From the slope (Q_3/C) and intercept ($1/C$) obtained by the linear plot of 1/ k_{obs} versus $[HSO_4^-]$ **(Figure 4.7)**, the ratio of slope to intercept was calculated to be 1.71 i. e. Q_3 was estimated to be 1.71 according to equation (17), which is good agreement with the previously reported value[25-26]. All the above results show that $Ce(SO_4)_2$ is the kinetically active species. Furthermore the rate of reaction slightly affected by ionic strength, indicate that there must be a neutral molecule in the rate determining step, which confirms $Ce(SO_4)_2$ as the kinetically active species in present study.

From equation (9), it can be seen that the intercept of the linear plot of 1/ k_{obs} versus 1/ [Val] is 1/ 2k[Pd(II)] and the slope is 1/ 2kK[Pd(II)][H^+]. From the intercept and slope in **Figure 4.11**, rate constants (k) and formation constants (K) at different temperature have been evaluated. Data in **Table 4.14** shows that formation constants (K) increases with increase of temperature, indicating that the reaction is an endothermic reaction, which is consistent with $\Delta H^{\#} > 0$. This supports the proposed mechanism. Activation parameters of rate determining step have been evaluated as $E_a = 45.95$ kJ mol^{-1}, $\Delta H^{\#} = 42.12$ kJ mol^{-1}, $\Delta S^{\#} = -84.55$ JK mol^{-1} and $\Delta G^{\#} = 72.83$ kJ mol^{-1}, log A = 8.45 from the linear plot of log k versus 1/ T **(Figure 4.12)**. Thermodynamic quantities were evaluated from the plot of log K versus 1/T **(Figure 4.13)**. The sizable negative entropy of activation is in agreement with the formation of activated complex involved in the reaction and the complex is more ordered than the reactants[27]. The catalyst, Pd(II) alters the path of the reaction by lowering the energy barrier, that is, it provides an alternative pathway which lowers activation parameters for the reaction[28].

4.5 Conclusion

The reaction between valine and cerium(IV) is very slow at room temperature. The reaction occurs in measurable quantities at 45°C and 1M H_2SO_4 concentration in the presence of palladium(II) catalyst. The order with respect to oxidant and catalyst are found to be unity and less than unity with respect to reductant. The main active species of cerium(IV) is considered as $Ce(SO_4)_2$, although other species might be active to a much lesser extent. The overall mechanistic sequence described here is consistent with product, kinetic and mechanistic study.

Table 4.14: Effect of temperature on the reaction between cerium(IV) and valine catalysed by palladium(II) in sulphuric acid medium

Temperature (K)	k (dm^3 mol^{-1} s^{-1})	Activation parameters	K (dm^3 mol^{-1})	Thermodynamic Quantities
313	5.88	E_a (kJ mol^{-1}) = 45.95	193	ΔH (kJ mol^{-1}) = 42.12
318	7.14	$\Delta S^{\#}$ ($JK^{-1}mol^{-1}$) = −84.55	215	ΔS (J K^{-1} mol^{-1}) = −65.03
323	10.0	$\Delta G^{\#}$ (kJ mol^{-1}) = 72.83	243	ΔG (kJ mol^{-1}) = 62.79
		log A = 8.45		

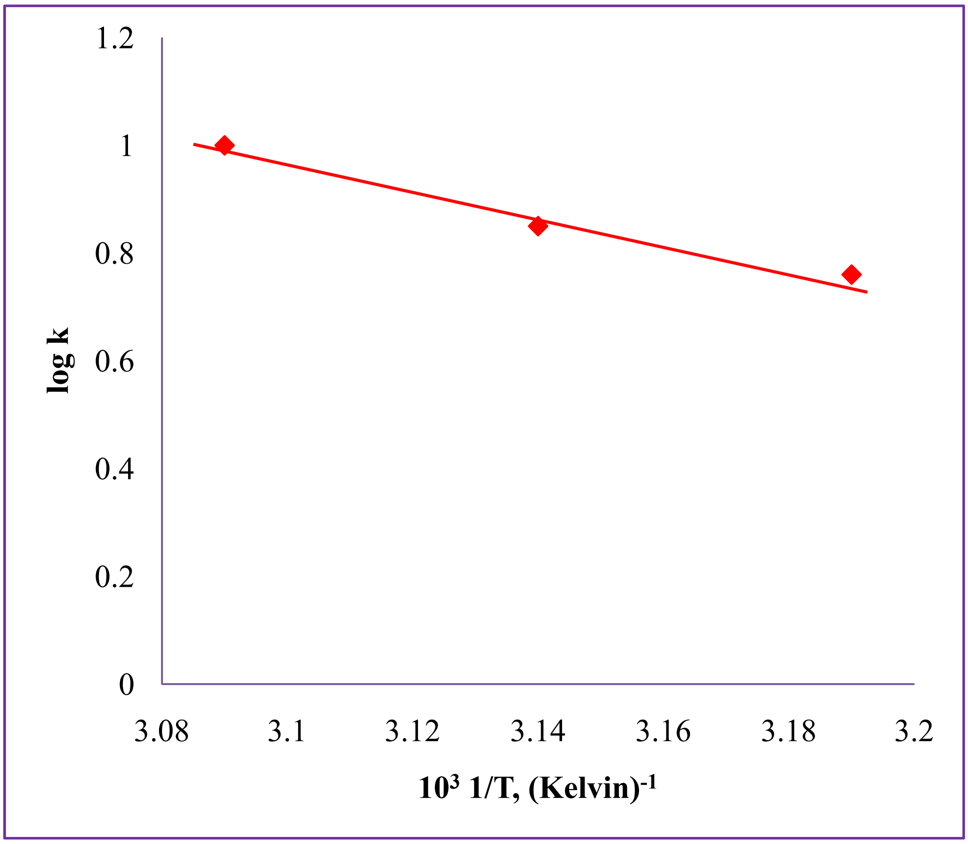


Figure 4.12: A plot of log k versus 1/T

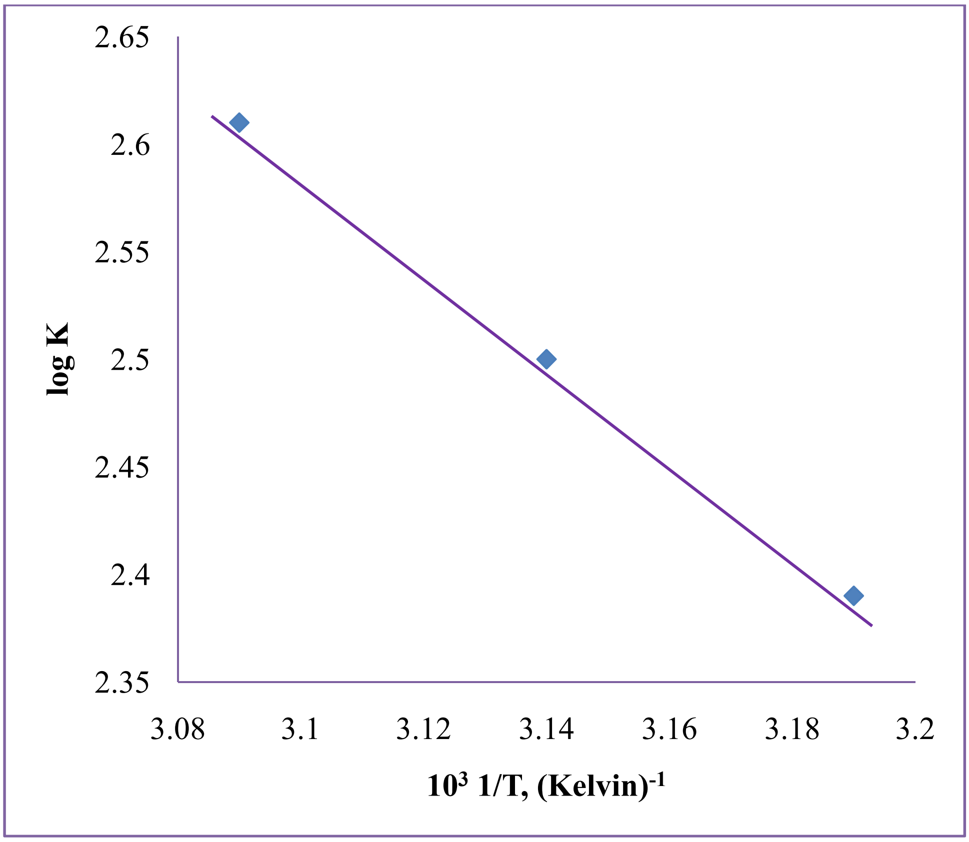


Figure 4.13: A plot of log K versus 1/T

4.6 References

1. T.L. Ho, ***"Organic Syntheses by Oxidation with Metal Compounds"*** de Jonge, C.R.H. Eds. Plenum New York, 569, 1986.
2. S. A. Chimatadar, S. V. Madawale and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **32,** 634, 2007.
3. K. K. Adari, A. Nowduri and V. Parvataneni, ***Acta. Chim. Slov.*****, 55,** 425, 2008.
4. P. K. Tandon, M. Purwar, P. B. Dwivedi and M. Srivastava, ***Trans. Met. Chem.,*** **33,** 791, 2008.
5. M. B. Yadav, V. Devra and A. Rani, ***Ind. J. Chem.,*** **49A,** 442, 2010.
6. R. K. Patil, S. A. Chimatdar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **33,** 625, 2008.
7. K. Din, M. S. Ali and Z. Khan, ***Colloid. Polym. Sci. (USA),*** **10,** 284, 2005.
8. I. S. Ahmed and C. Mohammad, ***J. Chem. Kinet.,*** **11,** 813, 1985.
9. M. K. Ghosh and S. K Rajput, ***Am. Chem. Sci. J.,*** **4,** 384, 2014.
10. A. K. Singh, D. Chopra, S. Rahmani and B. Singh, ***Carbohy. Res.,*** **314,** 157, 1998,
11. A. Shukla, S. Gupta and S. K. Upadhyay, ***Int. J. Chem. Kinet.,*** **23,** 279, 1991.
12. A. C. Singh, A. K. Singh and B. Singh, ***Ind. J. Chem.,*** **44,** 476, 2005.
13. G. Schwarzenbach and H. Flaschka, ***"Complexometric titration"*** (Methuen and Co. London), 250, 1969.
14. H. S. Gowda and B. Keshayan, ***J. Ind. Chem. Soc.,*** **53,** 688, 1976.
15. F. Feigl, "***Spot Test in Organic Analysis",*** Elsevier, Amsterdam, 195, 1966.
16. M. H. Kondarasaiah, S. Ananda, Puttaswamy and N. M. M. Gowda, ***Synth. React. Inorg. Met.-Org. Chem.,*** **33,** 1145, 2003.
17. F. A. Cotton and G. Wilkinson, ***"Advanced Inorganic Chemistry",*** 5th Edn (Wiley), 1026, 1988.
18. G. P. Tikhonova and S. N. Bovkovets, ***Russ. J. Inorg. Chem.,*** **23,** 813, 1973.

19. V. I. Schlenskaya and A. A. Biryukov, ***Russ. J. Inorg. Chem.,*** **11,** 28, 1966.
20. G. H. Ayres, ***Anal. Chem.*****, 24,** 1622, 1953.
21. R. Saxena, A. Shukla and S. K. Upadhyay, ***Trans. Met. Chem.,*** **19,** 91, 1994.
22. A. K. Singh, S. Rashmi, V. K. Singh, D. Kesarwani and B. Singh, ***Ind. J. Chem.,*** **40A,** 519, 2001.
23. G. P. Tikkonova and S. Bovkovets, ***Russ. J. Inorg. Chem.,*** **23,** 1687, 1978.
24. S. M. Tuwar, S. T. Nandibewoor and J. R. Raju, ***Ind. J. Chem.,*** **29A,** 235, 1990.
25. S. K. Mishra and Y. K. Gupta, ***J. Chem. Soc. A,*** 2918, 1970.
26. S. K. Mondal, D. Kar, M. Das and A. K. Das, ***Ind. J. Chem.,*** **37A,** 765, 1998.
27. A. Weissberger, ***"Investigations of Rates and Mechanisms*****",** Technique of Chemistry, Vol. 6, edited by E. S. Lewis (Wiley Interscience, New York), 1978.
28. S. V. Rao and V. Jagannadham, ***React. Kinet. Catal. Lett.,*** **27,** 239, 1985; S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **26,** 241, 2001.

Chapter – 5

Mechanistic and Kinetic Study of Manganese(II) Catalysed Oxidation of Leucine by Cerium(IV) in Sulphuric Acid Medium

Abstract

The kinetics and mechanism of manganese(II) catalysed oxidation of leucine by cerium(IV) in sulphuric acid media has been investigated at 45°C. The reaction was first order with cerium(IV) and manganese(II). The order with respect to leucine varies from first to zero order as the concentration increases. Increase in [H^+] and [HSO_4^-] decreased the rate of reaction. Under the experimental conditions, the kinetically active species of cerium(IV) has been found to be $Ce(SO_4)_2$. On the basis of experimental results, a suitable mechanism has been proposed.

$$k_{obs} = \frac{kK[Leu][Mn(II)]}{1 + K[H^+][Leu]}$$

Where k_{obs} is pseudo first order rate constant. The rate constants of the rate determining step together with the activation parameters were evaluated.

5.1 Introduction

Oxidative decarboxylation of amino acids has its obvious importance in photochemical and biochemical fields. The reaction and mechanism of amino acids oxidation are relevant in understanding the biosynthesis of polypeptides, nucleotides and proteins. Amino acids can undergo many kinds of reactions depending on whether particular amino acids contain non polar or polar substituents. Generally the amino and carboxyl functional groups in $RCH(NH_2)COOH$ undergo chemical transformation while the hydrocarbon moiety (RCH-) remain intact. This property is attributed to the higher reactivity of the former compared to hydrocarbon. The oxidation of amino acids is of interest as the oxidation products differ for different oxidant[1-2]. Thus the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant. L-leucine is an essential amino acid. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So oxidation of L-leucine may help in understanding some aspects of enzyme kinetics.

Cerium(IV) is a well known oxidant[3-6] having the Ce(IV)/Ce(III) couple[7] at 1.70V but stable only in high acid concentration. The oxidation of organic compounds by cerium(IV) usually proceeds via an intermediate complex[8-10]. In sulphate media several sulphate complexes[11-14] of cerium(IV) forms, but these have not been studied in depth so far. The oxidation of leucine by cerium(IV) was studied earlier[15] but to the best of our knowledge there are no reports on the manganese(II) catalysed oxidation of leucine by cerium(IV). The slow reaction of cerium(IV) oxidation of L-leucine is catalysed by a minute amount (10^{-5}mol dm^{-3}) of manganese(II) in aqueous sulphuric acid. In this study, we have investigated the manganese(II) catalysed oxidation of L-leucine by cerium(IV) in order to understand the behaviour of the active species of oxidant and catalyst in sulphuric acid media.

5.2 Experimental

Chemicals of pure quality were used without further purification. Stock solution of manganese(II) was prepared in double distilled water. Ce(IV) stock solution was prepared by dissolving ceric ammonium sulphate in 1.0 M sulphuric acid and standardized with iron(II) ammonium sulphate solution using ferroin as an indicator. Since the solubility of leucine in water is slow, the solution was therefore prepared in the presence of 0.1 mol dm^{-3} sulphuric acid for the higher amino acid concentration. Other chemicals and reagents such as sodium sulphate, sulphuric acid and acetonitrile were used of analytical grade with 99.9% purity. The stock solutions were diluted as required and standardized before use in kinetic reaction.

5.2.1 Kinetic Measurements

Kinetic studies were carried out in sulphuric acid medium at 45°C under pseudo first order conditions with a large excess of leucine over cerium(IV). The progress of reaction was followed by measuring the absorbance of cerium(IV) at 360 nm using Systronics(166) Visible spectrophotometer at different time intervals. Application of Beer's law under reaction condition was verified between 5×10^{-5} to 5×10^{-4} mol dm^{-3} of Ce(IV) and molar extinction coefficient**[16]** was found to be $\mathcal{E} = 2622$ dm^3 mol^{-1} cm^{-1}. The kinetic of reactions were allowed for more than 80% completion of reaction and first order kinetic was observed. The spectral changes during the chemical reaction for the standard condition at 45°C are given in **Figure 5.1**. The pseudo first order rate constants (k_{obs}) were obtained from the slope of the plots of log absorbance versus time. The observed rate constants were reproducible within the experimental error ±5%.

5.2.2 Stoichiometry and Product Analysis

Several reaction mixtures with [Leucine] >> [Ce(IV)] were prepared keeping Mn(II), H^+ and ionic strength fixed. After the complete reaction, the reaction mixtures were treated with 2,4-dinitrophenyl hydrazine. The formation of

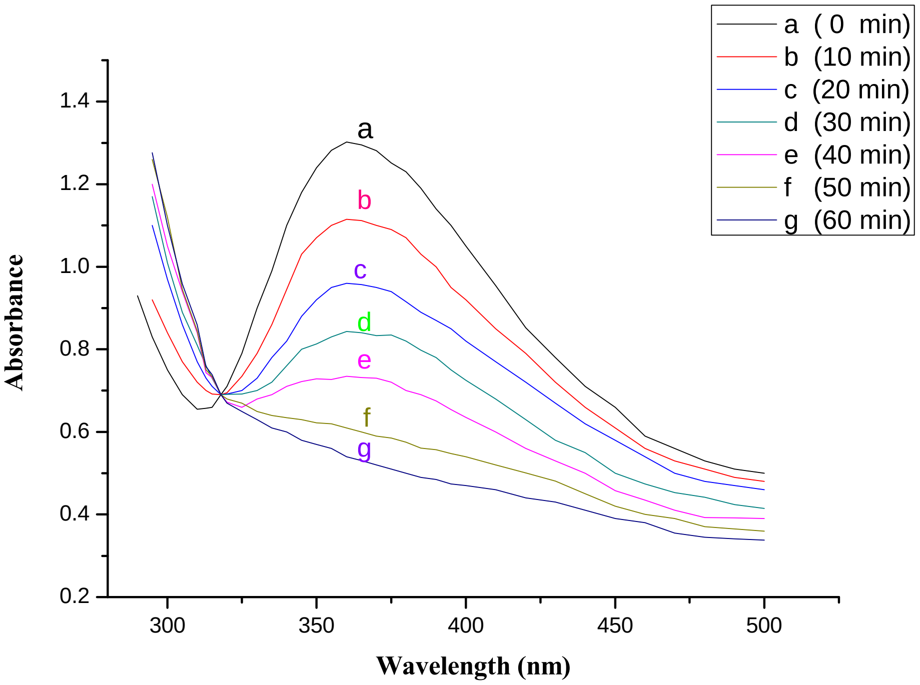


Figure 5.1: Sequential scans of absorption spectra during the course of the reaction of leucine with cerium(IV) in sulphuric acid media at different time

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm^{-3}; $[Leu] = 5.0 \times 10^{-3}$ mol dm^{-3};
$[H^+] = 1.0$ mol dm^{-3}; $I = 2.0$ mol dm^{-3};
$[Mn(II)] = 5.0 \times 10^{-5}$ mol dm^{-3}; Temp. = 45°C

hydrazones indicated the presence of aldehyde as the oxidation products of amino acids under the kinetic condition. The presence of aldehyde was confirmed by converting it into 2,4-dinitrophenyl hydrazone and comparing it with an authentic sample(m.p.). The main reaction products were identified as cerium(III), 3-methylbutanal, ammonia and CO_2. The nature of 3-methylbutanal was further confirmed by its IR spectrum. The IR peacks at 3421.68 cm^{-1}, 2905.18 cm^{-1} and 1624.65 cm^{-1} are attributed to –NH, −CH and −C=N stretching respectively **(Figure 5.2)**. Ammonia was confirmed with Nesseler's[17] test and CO_2 was qualitatively detected by passing the liberated gas through a tube containing lime water. Therefore the stoichiometry of the reaction with positive test of an aldehyde can be represented by equation (1).

$$\mathrm{RCH(NH_2)COOH + 2Ce(IV) + H_2O \longrightarrow RCHO + 2Ce(III) + NH_3 + CO_2 + 2H^+} \quad (1)$$

$$\mathrm{R = (CH_3)_2\,CH\text{-}CH_2-}$$

5.3 Results

5.3.1 Cerium(IV) Dependence

The cerium(IV) concentration was varied from 5×10^{-5} to 5×10^{-4} mol dm^{-3} at different concentration of leucine viz. 5×10^{-3} mol dm^{-3}, 7.5×10^{-3} mol dm^{-3} and 10×10^{-3} mol dm^{-3} respectively at fixed concentration of $[H^+]$ =1.0 mol dm^{-3}, [Mn(II)] = 5×10^{-5} mol dm^{-3} and I = 2.0 mol dm^{-3} at temperature 45°C. Pseudo first order plots were made, the pseudo first order plots were linear over three half lives **(Figure 5.3)**. The pseudo first order rate constants (k_{obs}) were found to be independent of the initial Ce(IV) concentration, commensurate with a first order process with respect to oxidant. Results are given in **Table 5.1**, **5.2** and **5.3**.

5.3.2 Leucine Dependence

The concentration of leucine was varied from 1×10^{-3} to 1×10^{-2} mol dm^{-3} at fixed concentration of cerium(IV) = 5×10^{-4} mol dm^{-3}, $[H^+]$ = 1.0 mol dm^{-3}, [Mn(II)] = 5×10^{-5} mol dm^{-3} and I = 2.0 mol dm^{-3} at three temperature viz. 40°C, 45°C and 50°C respectively. Results are given in table **5.4, 5.5 and 5.6.** The rate of

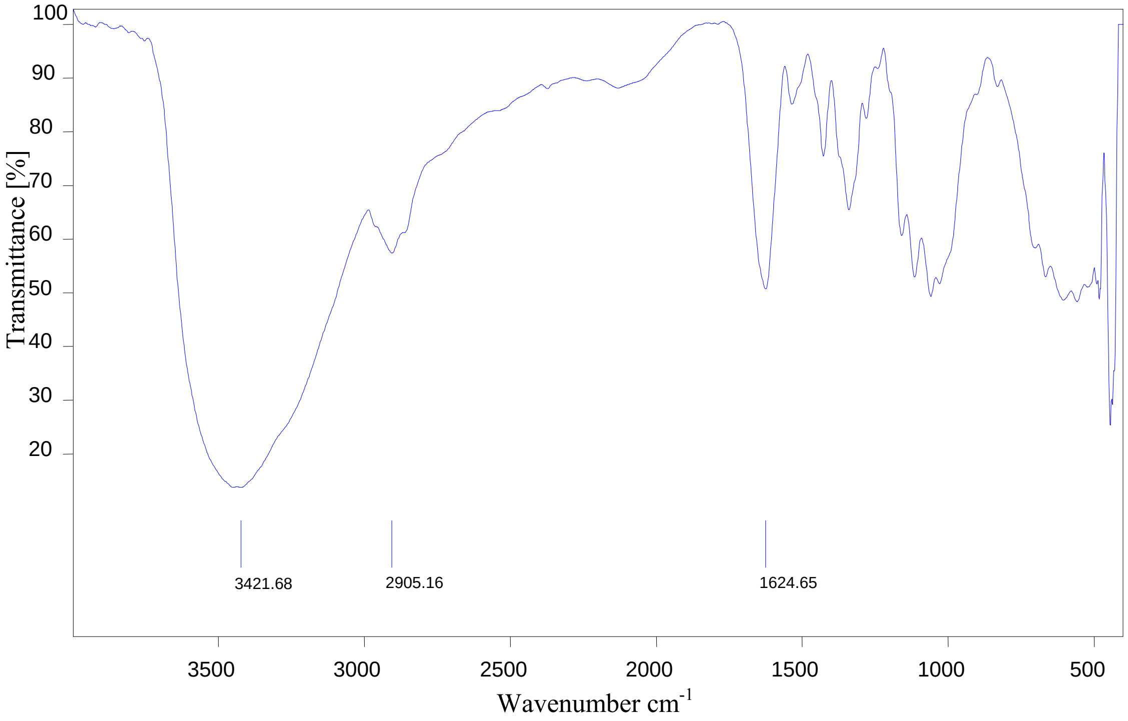


Figure 5.2: FT-IR Spectrum of oxidation product of leucine

Table 5.1: Variation of cerium(IV)

[Leu] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**
[H^{+}] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.106	0.231	0.445	0.695	0.878	1.141
20	0.894	0.201	0.385	0.605	0.758	0.971
30	0.773	0.168	0.334	0 .532	0.661	0.846
40	0.067	0.146	0.291	0.445	0.569	0.725
50	0.057	0.126	0.256	0.385	0.498	0.624
60	0.050	0.112	0.210	0.335	0.420	0.548
80	0.037	0.082	0.161	0.242	0.318	0.406
10^4 (k_{obs}), sec^{-1}	**2.47**	**2.47**	**2.45**	**2.49**	**2.41**	**2.42**

Table 5.2: Variation of cerium(IV)

[Leu] = 7.5×10^{-3} mol dm^{-3} **Temp. = 45°C**
[H$^+$] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.096	0.216	0.431	0.645	0.826	1.056
20	0.076	0.169	0.349	0.526	0.657	0.846
30	0.061	0.134	0.276	0 .409	0.526	0.672
40	0.049	0.109	0.231	0.322	0.416	0.529
50	0.039	0.089	0.183	0.259	0.332	0.423
60	0.031	0.071	0.152	0.213	0.265	0.349
80	0.019	0.044	0.085	0.132	0.168	0.223
10^4 (k_{obs}), sec^{-1}	**3.75**	**3.75**	**3.76**	**3.74**	**3.72**	**3.74**

Table 5.3: Variation of cerium(IV)

[Leu] = 10.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[H^{+}] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^4[Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes	**Absorbance**					
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.090	0.195	0.392	0.596	0.765	0.965
20	0.067	0.146	0.306	0.449	0.586	0.735
30	0.051	0.111	0.234	0 .336	0.432	0.556
40	0.037	0.082	0.172	0.256	0.323	0.402
50	0.028	0.061	0.127	0.189	0.243	0.306
60	0.021	0.046	0.095	0.141	0.179	0.223
80	0.012	0.026	0.052	0.076	0.103	0.128
10^4 (k_{obs}), sec^{-1}	**4.91**	**4.89**	**4.88**	**4.91**	**4.89**	**4.89**

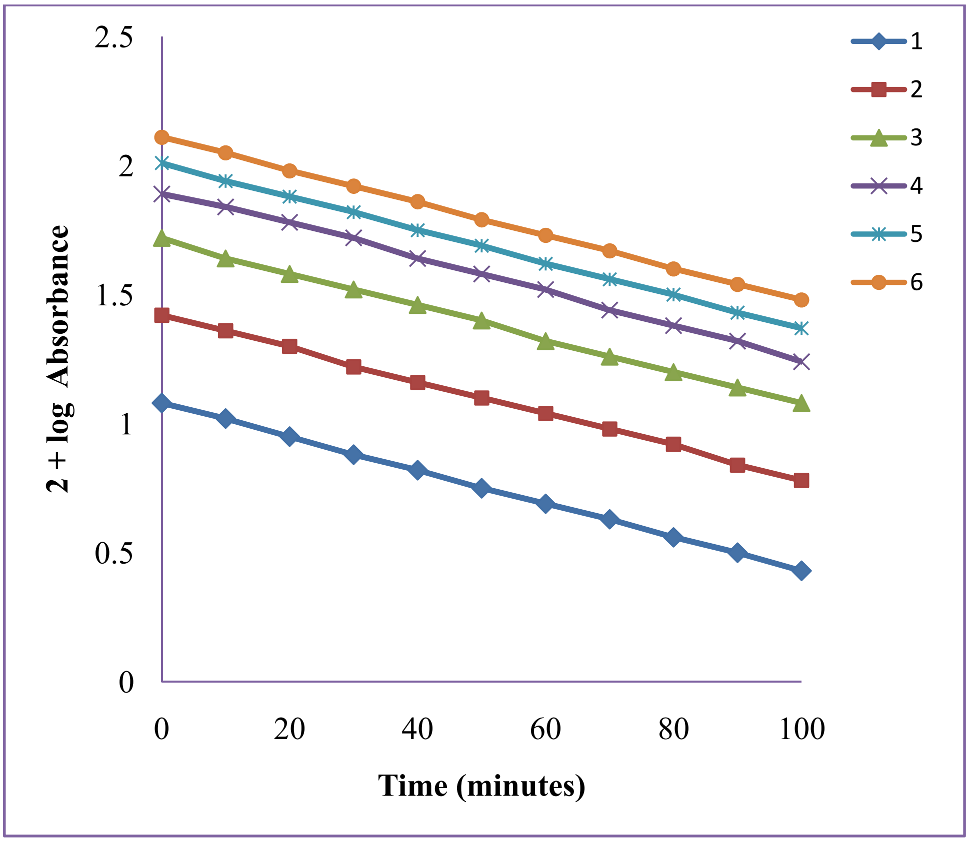


Figure 5.3: Pseudo first order plots for the variation of cerium(IV)

[Leu] = 5.0×10^{-3} mol dm^{-3}; [H^{+}] = 1.0 mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; I = 2.0 mol dm^{-3}, Temp.= 45°C;

[Ce(IV)] = (1) 0.50×10^{-4} mol dm^{-3}; (2) 1.0×10^{-4} mol dm^{-3};

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

(5) 4.0×10^{-4} mol dm^{-3}; (6) 5.0×10^{-4} mol dm^{-3}.

(Ref. Table 5.1)

Table 5.4: Variation of leucine

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **Temp. = 40°C**

[H$^+$] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**

[Mn(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^3 [Leu], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes					**Absorbance**					
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.204	(20) 1.141	1.162	1.141	1.135	1.115	1.087	1.086	1.082	1.082
20	(60) 1.052	(40) 0.978	1.091	1.042	1.002	0.991	0.945	0.938	0.927	0.926
30	(80) 0.956	(60) 0.867	1.001	0.941	0.887	0.846	0.823	0.804	0.795	0.796
40	(120) 0.836	(80) 0.758	0.928	0.843	0.787	0.734	0.705	0.685	0.674	0.674
50	(140) 0.769	(100) 0.669	(80) 0.658	0.752	0.684	0.643	0.599	0.578	0.574	0.574
60	(160) 0.703	(120) 0.569	(100) 0.556	0.672	0.608	0.543	0.521	0.495	0.485	0.483
80	(180) 0.623	(140) 0.496	(120) 0.463	0.536	0.472	0.405	0.374	0.373	0.362	0.362
10^4 (k_{obs}), sec^{-1}	**0.67**	**1.10**	**1.40**	**1.83**	**2.11**	**2.41**	**2.60**	**2.62**	**2.64**	**2.64**

Figures in parentheses denote time in minutes

Table 5.5: Variation of leucine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 45°C**
[H$^+$] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^3 [Leu], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.182	(20) 1.112	1.146	1.130	1.114	1.076	1.073	1.061	1.061	1.060
20	(60) 0.965	(40) 0.942	1.063	1.016	0.961	0.937	0.919	0.916	0.916	0.913
30	(80) 0.886	(60) 0.801	0.942	0.874	0.845	0.807	0.779	0.761	0.761	0.764
40	(120) 0.713	(80) 0.701	0.864	0.765	0.732	0.678	0.654	0.642	0.642	0.640
50	(140) 0.636	(100) 0.579	0.765	0.669	0.619	0.579	0.558	0.536	0.536	0.534
60	(160) 0.568	(120) 0.504	0.694	0.576	0.545	0.487	0.459	0.444	0.443	0.442
80	(180) 0.505	(140) 0.435	0.551	0.444	0.402	0.352	0.336	0.298	0.298	0.297
10^4 (k_{obs}), sec^{-1}	**0.81**	**1.32**	**1.74**	**2.21**	**2.42**	**2.72**	**2.81**	**3.01**	**3.01**	**3.02**

Figures in parentheses denote time in minutes

Table 5.6: Variation of leucine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **Temp. = 50°C**

[H^{+}] = 1.0 mol dm^{-3} **I = 2.0 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

10^3 [Leu], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.125	1.061	1.135	1.094	1.070	1.055	1.043	1.036	1.040	1.036
20	(60) 0.875	1.061	1.001	0.968	0.923	0.905	0.879	0.864	0.862	0.864
30	(80) 0.785	(40) 0.865	0.875	0.821	0.789	0.735	0.714	0.698	0.696	0.697
40	(100) 0.685	(60) 0.694	0.781	0.712	0.675	0.612	0.578	0.556	0.554	0.556
50	(120) 0.586	(80) 0.564	0.684	0.612	0.554	0.511	0.485	0.456	0.454	0.456
60	(140) 0.527	(100) 0.461	0.610	0.532	0.475	0.487	0.389	0.369	0.370	0.369
80	(160) 0.456	(120) 0.334	0.472	0.382	0.321	0.288	0.252	0.235	0.241	0.235
10^4 (k_{obs}), sec^{-1}	**1.03**	**1.70**	**2.11**	**2.52**	**2.81**	**3.11**	**3.41**	**3.53**	**3.50**	**3.53**

Figures in parentheses denote time in minute reaction initially increases and then tends towards a limiting value with further increasing concentration of leucine **(Figure 5.4)**.

5.3.3 Manganese(II) Dependence

At fixed concentration of oxidant, substrate, acid at 5×10^{-4}, 5×10^{-3} and 1.0 mol dm^{-3} respectively and at I = 2.0 mol dm^{-3}, the manganese(II) concentration was varied between 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3}. As the concentration increases, the rate of reaction also increases **(Figure 5.5)**. Results are given in **Table 5.7.** The order with respect to manganese(II) was found to be unity.

5.3.4 Hydrogen Ion Dependence

At fixed concentration of [Leu] = 5×10^{-3} mol dm^{-3}, [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [Mn(II)] = 5×10^{-5} mol dm^{-3} and I = 2.0 mol dm^{-3} at 45°C, [H$^+$] was varied from 0.20 to 1.0 mol dm^{-3}. The rate was found to decrease with increasing sulphuric acid concentration **(Figure 5.6)**. The order with respect to [H$^+$] was negative as found from a plot of log k_{obs} versus log [H$^+$]. Results are given in **Table 5.8**.

5.3.5 Effect of [HSO_4^-]

The reaction rate were measured with various [HSO_4^-] = 0.20 to 1.0 mol dm^{-3} at fixed concentration of [Leu] = 5.0×10^{-3} mol dm^{-3}, [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and ionic strength of 2.0 mol dm^{-3} at 45°C. The rate of reaction decreased with increase in [HSO_4^-] which indicates that the order with respect to [HSO_4^-] was negative. Results are given in **Table 5.9**. The plot of 1/ k_{obs} versus [HSO_4^-] was found to be linear with positive intercept and slope **(Figure 5.7)**.

5.3.6 Effect of Ionic Strength

The ionic strength was varied from 1.50 to 2.50 mol dm^{-3} at fixed concentration of [Leu] = 5.0×10^{-3} mol dm^{-3}, [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Mn(II)] = 5.0×10^{-5} mol dm^{-3} and [H$^+$] = 1.0 mol dm^{-3} at 45°C. The rate of reaction

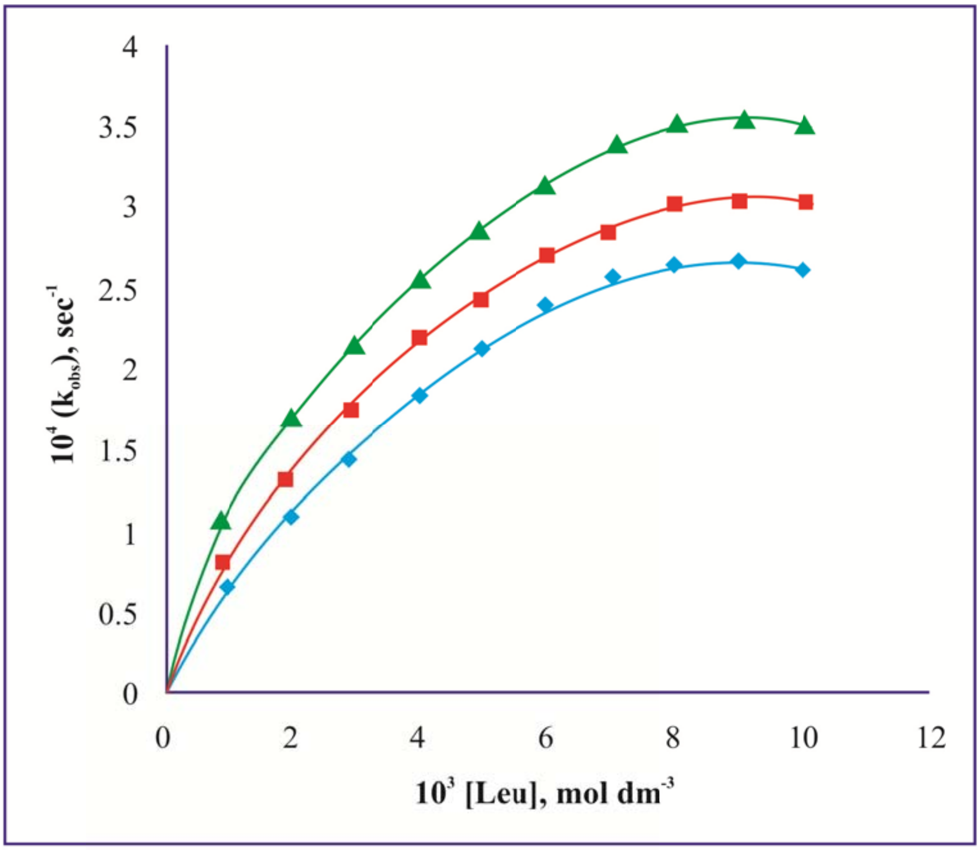


Figure 5.4: Variation of leucine

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3};

[Mn(II)] = 5.0 × 10^{-5} mol dm^{-3} ; I = 2.0 mol dm^{-3};

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table- 5.4, 5.5 and 5.6)

Table 5.7: Variation of manganese(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **[H^{+}] = 1.0 mol dm^{-3}**

[Leu] = 5.0×10^{-3} mol dm^{-3} **I = 2.0 mol dm^{-3}, Temp. = 45° C**

10^5 [Mn(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302	1.302
10	(20) 1.214	(20) 1.156	1.159	1.139	1.114	1.067	1.043	1.025	0.994	0.973
20	(60) 1.105	(60) 0.901	1.097	1.029	0.961	0.921	0.854	0.804	0.761	0.738
30	(80) 1.025	(80) 0.806	1.007	0.921	0.845	0.767	0.701	0.634	0.581	0.556
40	(120) 0.921	(120) 0.635	0.924	0.824	0.732	0.631	0.574	0.505	0.452	0.412
50	(140) 0.858	(140) 0.554	0.837	0.731	0.619	0.541	0.465	0.402	0.342	0.312
60	(160) 0.804	(160) 0.508	0.760	0.634	0.545	0.401	0.381	0.320	0.261	0.213
80	(180) 0.768	(180) 0.456	0.641	0.498	0.402	0.316	0.252	0.206	0.159	0.124
10^4 (k_{obs}), sec^{-1}	**0.48**	**0.97**	**1.45**	**1.95**	**2.42**	**2.90**	**3.41**	**3.88**	**4.41**	**4.83**
10^2 (k'), dm^3 mol^{-1} sec^{-1}	**4.80**	**4.85**	**4.83**	**4.87**	**4.84**	**4.83**	**4.87**	**4.83**	**4.87**	**4.82**

Figures in parentheses denote time in minutes

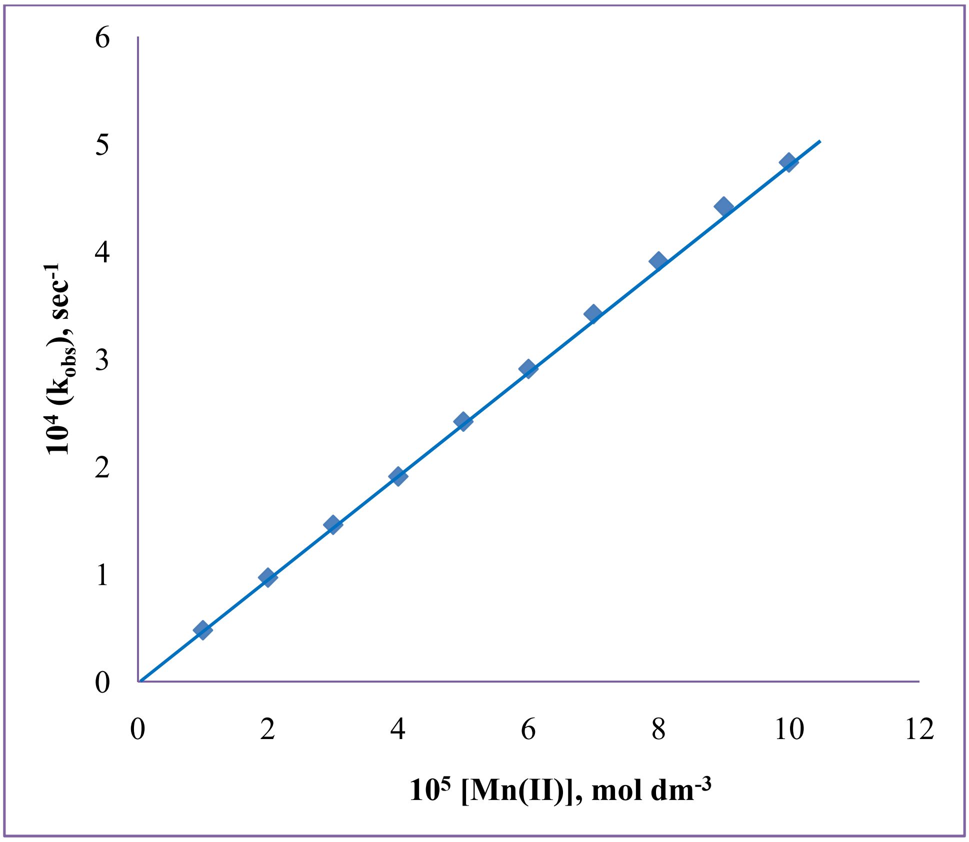


Figure 5.5: Variation of manganese(II)

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [H^+] = 1.0 mol dm^{-3};

[Leu] = 5.0×10^{-3} mol dm^{-3}; I = 2.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 5.7)

Table 5.8: Variation of hydrogen ion

[Leu] = 5.0 × 10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3} **I = 2.0 mol dm^{-3}**

[Mn(II)] = 5.0 × 10^{-5} mol dm^{-3}

[H^+], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.840	0.993	1.043	1.075	1.114
20	0.579	0.761	0.853	0.951	0.961
30	0.382	0.586	0.703	0.798	0.845
40	0.253	0.451	0.587	0.674	0.732
50	0.169	0.343	0.469	0.568	0.619
60	0.112	0.268	0.381	0.485	0.545
80	0.048	0.156	0.252	0.341	0.402
10^4 (k_{obs}), sec^{-1}	**6.82**	**4.43**	**3.41**	**2.77**	**2.42**

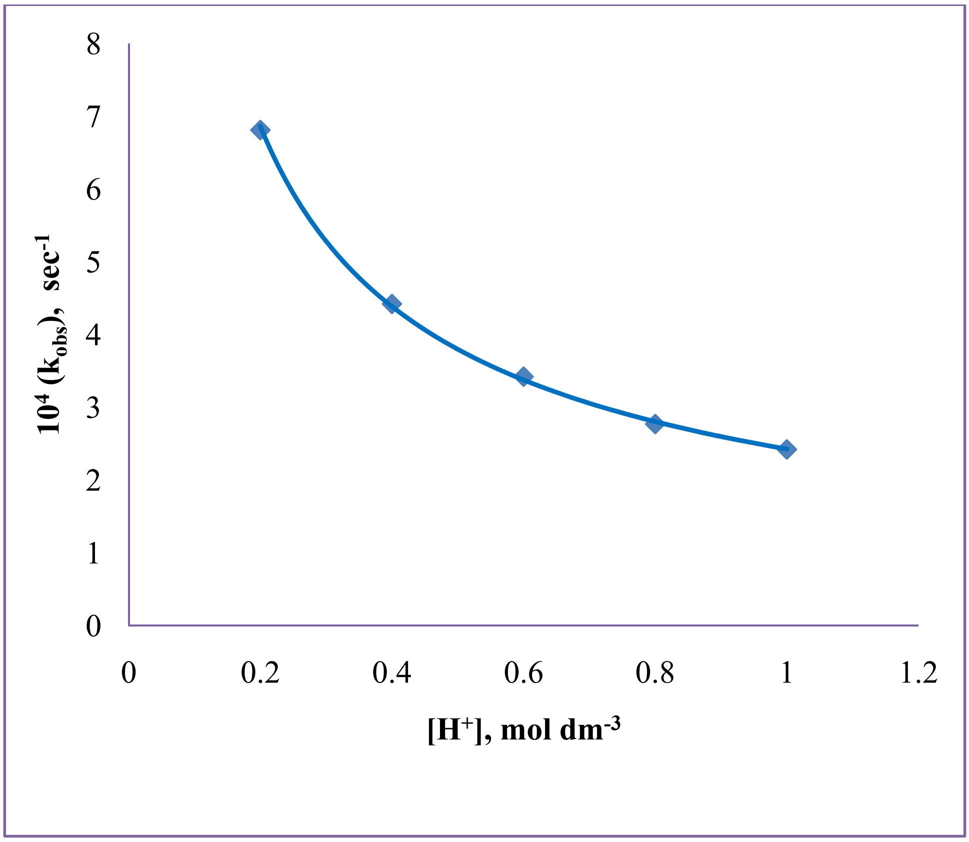


Figure 5.6: Variation of hydrogen ion

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Leu] = 5.0×10^{-3} mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; [HSO_4^-] = 1.0 mol dm^{-3};

I = 2.0 mol dm^{-3}; Temp. = 45°C

(Ref. Table 5.8)

Table 5.9: Variation of [HSO_4^-]

[Leu] = 5.0×10^{-3} mol dm^{-3} **Temp. = 45°C**

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3} **I = 2.0 mol dm^{-3}**

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}

[HSO_4^-], mol dm^{-3}	**0.20**	**0.40**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	0.840	0.931	0.986	1.018	1.041
20	0.579	0.705	0.738	0.812	0.864
30	0.382	0.509	0.569	0.644	0.702
40	0.253	0.368	0.421	0.507	0.567
50	0.169	0.265	0.318	0.394	0.462
60	0.112	0.192	0.243	0.314	0.375
80	0.048	0.097	0.139	0.188	0.241
10^4 (k_{obs}), sec^{-1}	**6.82**	**5.33**	**4.64**	**4.01**	**3.50**

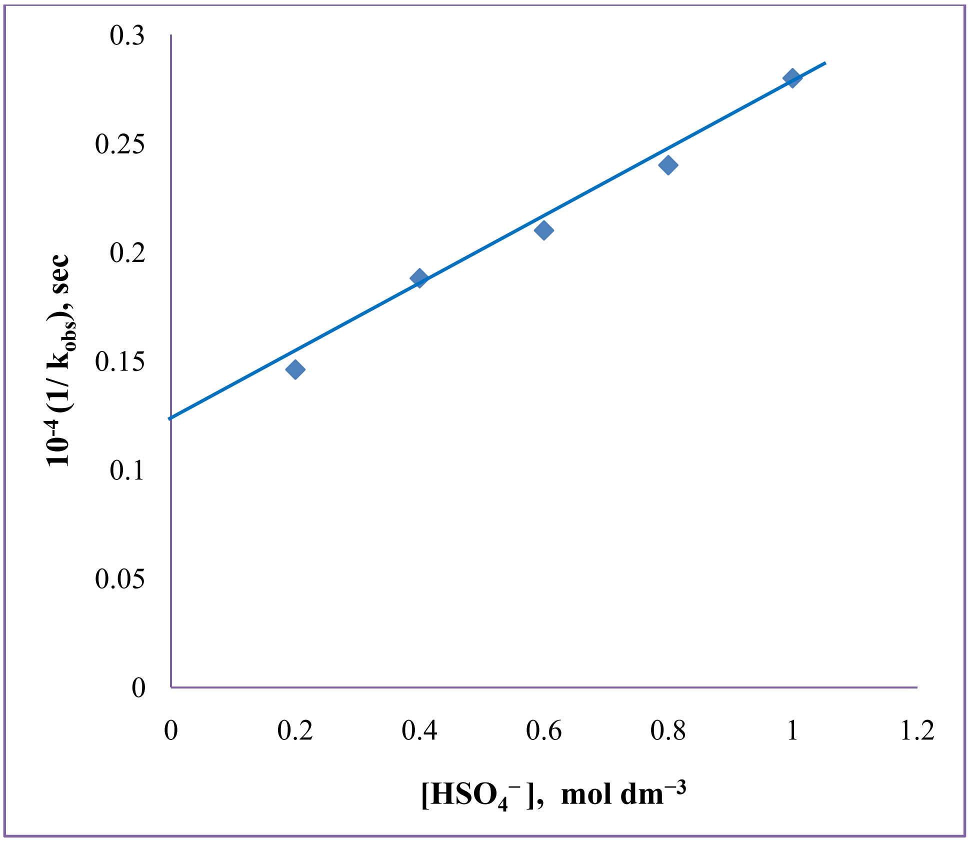


Figure 5.7: Linear plot of 1/k_{obs} versus [HSO_4^-]

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Leu] = 5.0×10^{-3} mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; [H^+] = 0.20 mol dm^{-3};

I = 2.0 mol dm^{-3}; Temp .= 45˚C

(Ref. Table 5.9)

slightly increases with increasing ionic strength **(Figure 5.8)**. Results are given in**Table 5.10.**

5.3.7 Effect of Added Product

The effect of initially added product, Ce(III) was studied from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at fixed concentration of [Ce(IV)] = 5.0×10^{-4} mol dm^{-3}, [Leu] = 5.0×10^{-3} mol dm^{-3}, [H^{+}] = 1.0 mol dm^{-3} and I = 2.0 mol dm^{-3} at 45°C. No significant effect on the rate of reaction was observed. Results are given in **Table 5.11.**

5.3.8 Test for Free Radical

The intervention of free radicals was examined by adding known quantity of acetonitrile in the reaction mixture and then kept for 24 hours. Diluting the reaction mixture with methanol, a precipitate was obtained, suggesting the generation of free radicals.

5.3.9 Effect of Temperature

The effect of temperature was studied by varying concentration of [Leu] = 1×10^{-3} to 1×10^{-2} mol dm^{-3} at fixed concentration of [H^{+}] = 1.0 mol dm^{-3}, [Ce(IV)] = 5×10^{-4} mol dm^{-3}, [Mn(II)] = 5×10^{-5} mol dm^{-3} and I = 2.0 mol dm^{-3} at three temperature 40°C, 45°C and 50°C respectively. The rate of reaction initially increases and then tends towards a limiting value with further increasing concentration of leucine **(Figure 5.4)**. The rate constant k of the slow step of **scheme-5.1** was obtained from the intercept of plot of 1/ k' versus 1/ [Leu] **(Figure 5.9)**. The energy of activation was obtained by the plot of log k versus 1/T **(Figure 5.10)**. The formation constant K of the first step of **scheme-5.1** were calculated from the plot of 1/ k' versus 1/ [Leu] (the ratio of intercept and slope) at three temperatures. From the different value of K at three temperatures, thermodynamic quantities were calculated from the plot of log K vesus 1/T **(Figure 5.11)**. Results are given in **Table 5.12**.

Table 5.10: Variation of ionic strength

[Leu] = 5.0×10^{-3} mol dm^{-3}
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}

Temp. = 45°C
[H$^+$] = 1.0 mol dm^{-3}

I, mol dm^{-3}	**1.50**	**1.75**	**2.0**	**2.25**	**2.50**
Time in minutes			**Absorbance**		
0	1.302	1.302	1.302	1.302	1.302
10	1.122	1.115	1.114	1.110	1.096
20	0.982	0.991	0.961	0.958	0.953
30	0.854	0.846	0.845	0.839	0.824
40	0.745	0.734	0.732	0.726	0.719
50	0.658	0.643	0.619	0.614	0.618
60	0.552	0.543	0.545	0.539	0.536
80	0.419	0.405	0.402	0.394	0.383
10^4 (k_{obs}), sec^{-1}	**2.37**	**2.41**	**2.42**	**2.47**	**2.51**

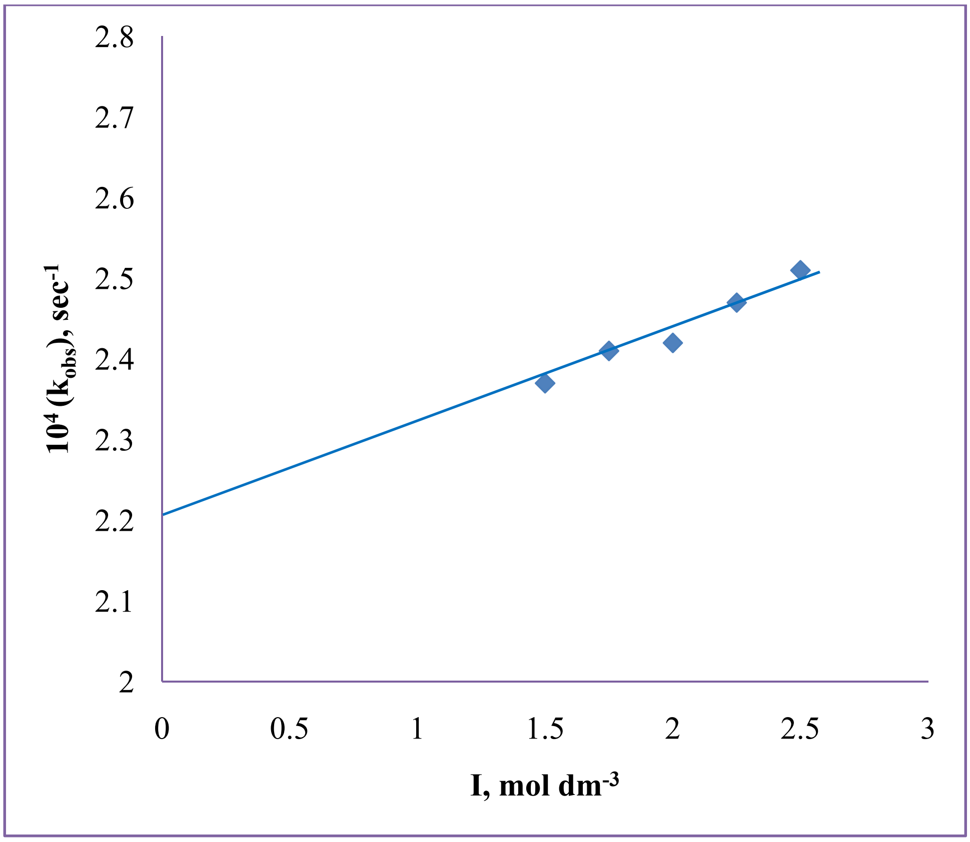


Figure 5.8: Variation of ionic strength

[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}; [Leu] = 5.0×10^{-3} mol dm^{-3};

[Mn(II)] = 5.0×10^{-5} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 5.10)

Table 5.11: Effect of cerium(III)

[Leu] = 5.0×10^{-3} mol dm^{-3}
[Mn(II)] = 5.0×10^{-5} mol dm^{-3}
[Ce(IV)] = 5.0×10^{-4} mol dm^{-3}

Temp. = 45°C
[H^{+}] = 1.0 mol dm^{-3}

10^{4}[Ce(III)], mol dm^{-3}	**1.0**	**2.5**	**5.0**	**7.5**	**10.0**
Time in minutes	**Absorbance**				
0	1.302	1.302	1.302	1.302	1.302
10	1.114	1.112	1.113	1.111	1.110
20	0.962	0.960	0.961	0.959	0.958
30	0.843	0.841	0.842	0.840	0.839
40	0.730	0.728	0.729	0.727	0.726
50	0.618	0.616	0.617	0.615	0.614
60	0.544	0.541	0.542	0.540	0.539
80	0.401	0.397	0.399	0.395	0.394
10^{4} (k_{obs}), sec^{-1}	**2.43**	**2.45**	**2.44**	**2.46**	**2.47**

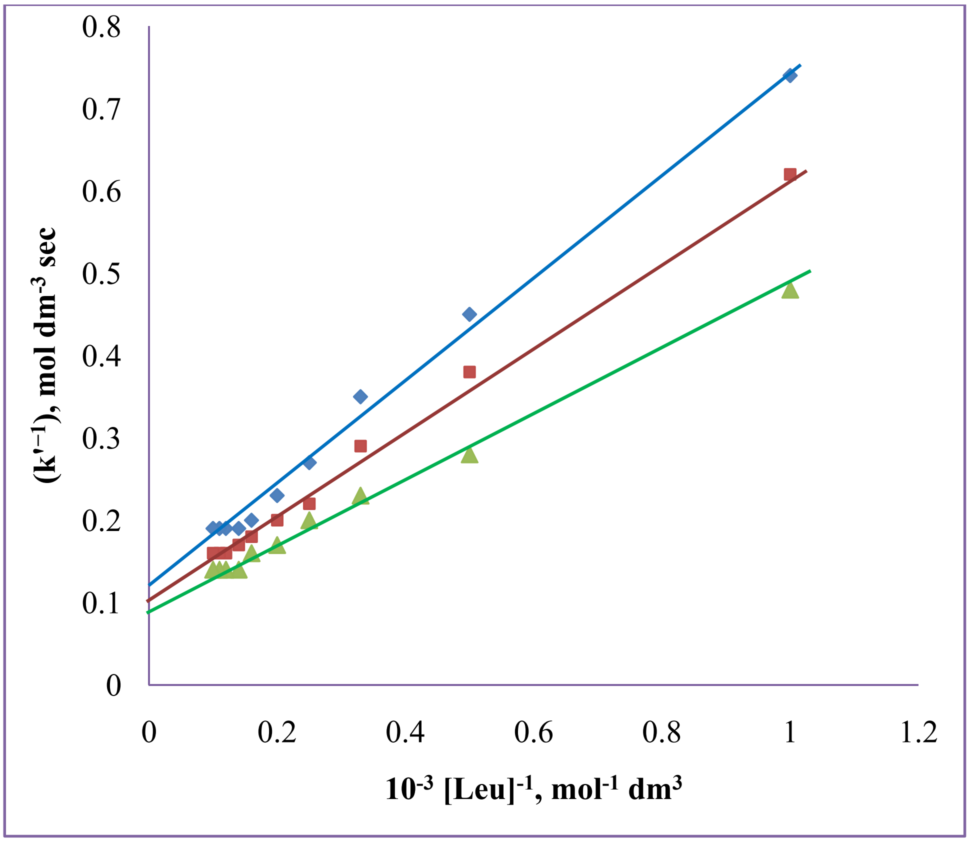


Figure 5.9: A plot of 1/k′ versus 1/[Leu]

[Ce(IV)] = 5.0 × 10^{-4} mol dm^{-3}; [Leu] = 5.0 × 10^{-3} mol dm^{-3};

[Mn(II)] = 5.0× 10^{-5} mol dm^{-3}; $[H^+]$ = 1.0 mol dm^{-3}; I = 2.0 mol dm^{-3};

Temp. = (◆) 40°C; (■) 45°C; (▲) 50°C

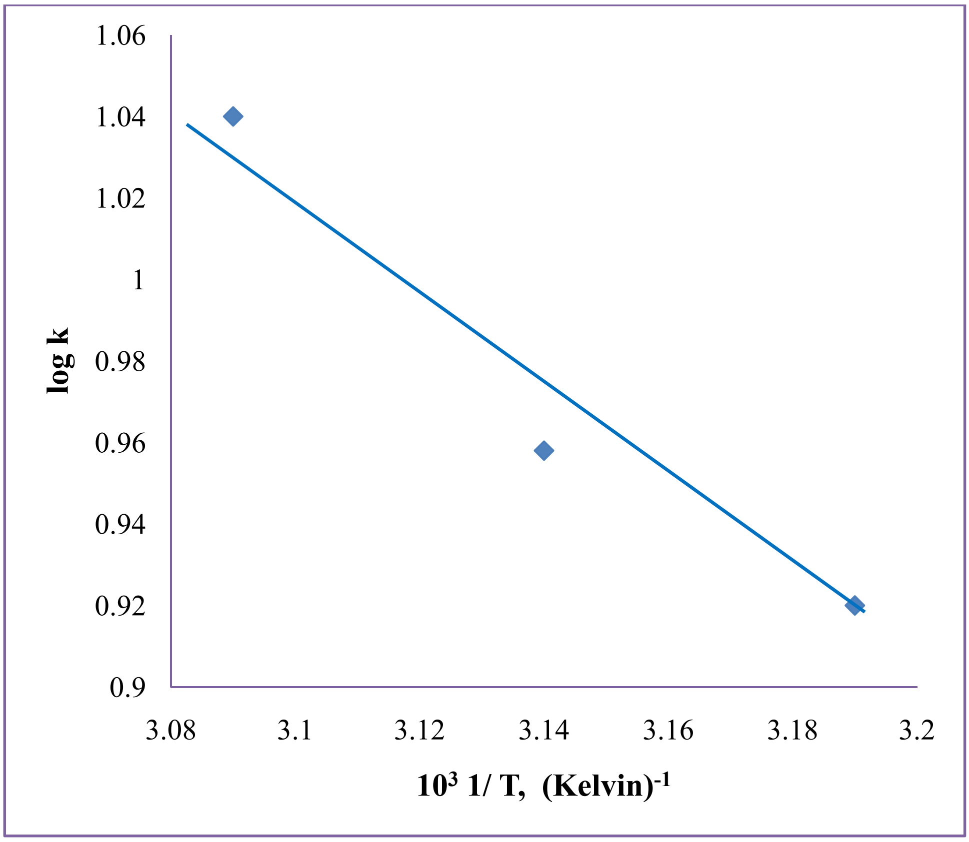


Figure 5.10: A plot of log k versus 1/T

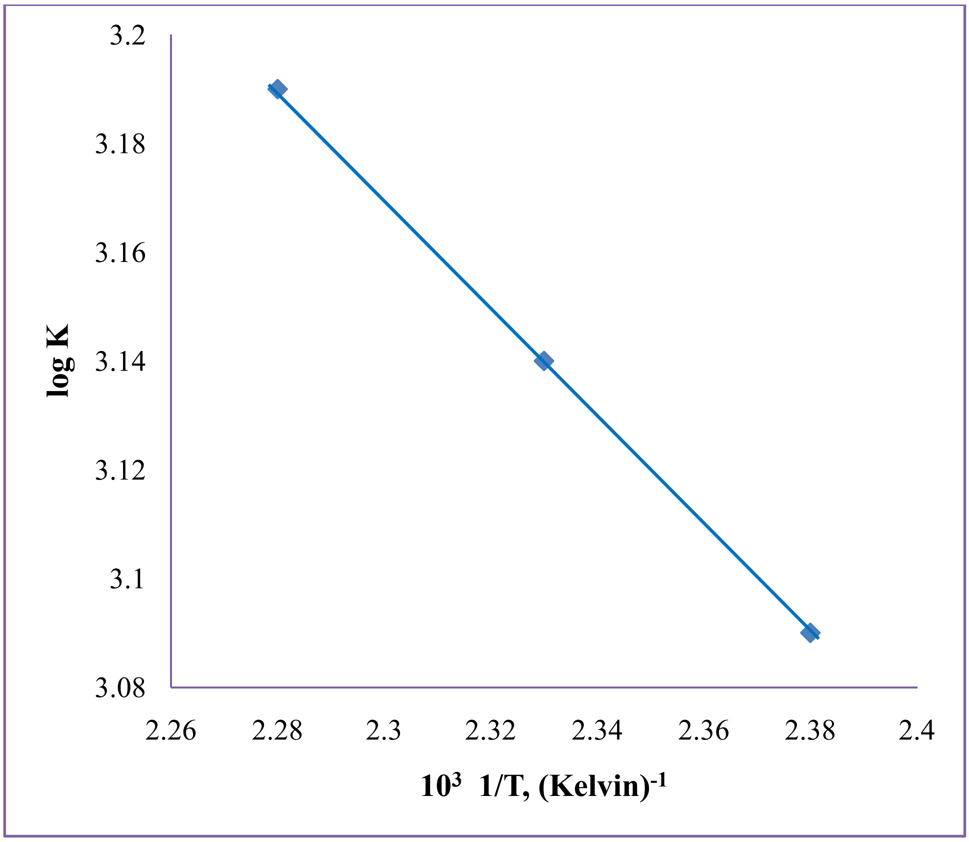


Figure 5.11: A plot of log K versus 1/T

5.4 Discussion

The cerium(IV) oxidation of leucine is slow in aqueous sulphuric acid media under the present experimental conditions. However, the rate of reaction is appreciably faster in the presence of manganese(II) in sulphuric acid. The order with respect to leucine changes from unity to zero. Such an amino acid dependence can be ascribed to complexation with cerium(IV) or manganese(II). The adduct formation between Ce^{4+} and leucine was ruled out on the premise that the absorbance of Ce^{4+} did not change at the addition of excess leucine. Therefore it appears that an adduct between manganese(II) and leucine is initially formed that on further interaction with cerium(IV) yields another adduct of higher valent manganese which collapses in a fast step to produce catalyst and free radical. The reactive species of cerium(IV) is $Ce(SO_4)_2$ in the present experimental condition and the order with respect to H^+ was negative. As the sulphuric acid concentration increases, the H^+ concentration increases, but corresponding HSO_4^- concentration also increases. Since the rate is inversely dependent on the HSO_4^- concentration the overall effect of adding sulphuric acid would be lowering the rate. Considering all these facts along with experimental results, a reaction mechanism consisting of step (2) to (5) can be proposed.

$$\mathrm{NH_2(CH_3)_2CHCH_2CH\,COOH + Mn(II) \overset{K}{\rightleftharpoons} \underset{[Adduct]}{H_2N(CH_3)_2CHCH_2CH\,COOH{\cdot}Mn(II)}} \quad (2)$$

$$\mathrm{Adduct + Ce(SO_4)_2 \xrightarrow{k} [Adduct]^+ + Ce^{3+} + 2SO_4^{2-}} \quad (3)$$

$$\mathrm{[Adduct]^+ \xrightarrow{fast} H_2N(CH_3)CHCH_2CH\,COO^{\bullet} + Mn(II) + H^+} \quad (4)$$

$$\begin{aligned}\mathrm{Ce(SO_4)_2 + H_2N(CH_3)_2CHCH_2CH\,COO^{\bullet}} &\mathrm{\xrightarrow[fast]{H_2O} (CH_3)_2CHCH_2CHO + H^+} \\ &\mathrm{+ Ce^{3+} + NH_3 + 2SO_4^{2-}}\end{aligned} \quad (5)$$

Scheme-5.1

The proposed mechanism leads to the rate law (6) to (9)

$$\frac{-d[Ce(IV)]}{dt} = \frac{kK[Ce(IV)][Leu][Mn(II)]}{1+K[H^+][Leu]} \quad (6)$$

$$\frac{-d[Ce(IV)]/dt}{[Ce(IV)]} = k_{obs} = \frac{kK[Leu][Mn(II)]}{1+K[H^+][Leu]} \quad (7)$$

Where k_{obs} is pseudo first order rate constant. Since the order with respect to manganese(II) is one **(Table 5.7)**, the rate law further change to (8)

$$k' = \frac{kK[Leu]}{1+K[H^+][Leu]} \quad (8)$$

Where k' = second order rate constant
After rearranging equation (8)

$$\frac{1}{k'} = \frac{1}{kK[Leu]} + \frac{[H^+]}{k} \quad (9)$$

A plot of $1/k'$ versus 1/ [Leu] was made from equation (9) at constant hydrogen ion concentration at three different temperatures 40°C, 45°C and 50°C yielded straight line with nonzero intercept **(Figure 5.9)**. The ratio of intercept and slope of the line yielded the value of K to be 215 $dm^3\,mol^{-1}$. The value of K obtained in the title reaction in comparision to K= 230 $dm^3\,mol^{-1}$ for cerium(IV) glutamic acid in 1.0 M H_2SO_4 at 30°C and K = 180 $dm^3\,mol^{-1}$ for cerium(IV) glycerol reaction in 0.5 M H_2SO_4 at 25°C indicates strong complexation in H_2SO_4 medium. The activation parameters of the rate determining step have been evaluated from the linear plot of log k versus 1/T. The results of **Table 5.12** show that K increases with increase of temperature, indicating the reaction is endothermic, which is consistent with $\Delta H^{\#} > 0$. The large negative value of entropy of activation ($\Delta S^{\#}$) obtained is attributed to the severe restriction of solvent molecules (Electrostriction) around the transition state**[18]** and indicates that complex is more ordered than reactants**[19]**.

Under the experimental conditions in aqueous sulphuric acid medium the important cerium(IV)-sulphato complexes are $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$ and $HCe(SO_4)_3^-$ and relevant equilibrium are-

Table 5.12: Activation parameters and thermodynamics quantities evaluated from the rate constants

Temperature (K)	k (dm^3 mol^{-1} s^{-1})	Activation parameters	K (dm^3 mol^{-1})	Thermodynamic Quantities
313	8.33	E_a (kJ mol^{-1}) = 22.97	193	$\Delta H^{\#}$ (kJ mol^{-1}) = 19.14
318	9.09	$\Delta S^{\#}$ (JK^{-1}mol^{-1}) = -154.82	215	$\Delta S^{\#}$ (JK^{-1} mol^{-1}) =140.56
323	11.11	$\Delta G^{\#}$ (kJ mol^{-1}) = 72.20	243	$\Delta G^{\#}$ (kJ mol^{-1}) = 63.83

$$Ce^{4+} + HSO_4^- \underset{}{\overset{Q_1}{\rightleftharpoons}} Ce(SO_4)^{2+} + H^+ \tag{10}$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{Q_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \tag{11}$$

$$Ce(SO_4)_2 + HSO_4^- \overset{Q_3}{\rightleftharpoons} HCe(SO_4)_3^- \tag{12}$$

The value of equilibrium constants[20] at 25°C are $Q_1 = 3.5 \times 10^3$, $Q_2 = 2 \times 10^2$, $Q_3 = 3.4$. Insignificant amount of unhydrolyzed species of cerium(IV) would also exist along with these sulphato complexes. In light of equilibrium steps (10-12) inverse bisulphate dependence **(Figure 5.7)** can be explained by assuming $Ce(SO_4)_2$ as the reactive species. The concentration of this active species is given by equation (13)

$$[Ce(SO_4)_2] = \frac{[Ce(IV)]_T}{1 + Q_3[HSO_4^-]} = f[Ce(IV)]_T \tag{13}$$

Thus equation (7) can be written as

$$k_{obs} = \frac{kK[Leu][Mn(II)]}{1 + K[H^+][Leu][1 + Q_3[HSO_4^-]} \tag{14}$$

$$\text{If } A = \frac{kK[Leu][Mn(II)]}{1 + K[H^+][Leu]}$$

So eq^n (14) becomes $k_{obs} = \frac{A}{1 + Q_3[HSO_4^-]}$ (15)

$$\frac{1}{k_{obs}} = \frac{1}{A} + \frac{Q_3[HSO_4^-]}{A} \tag{16}$$

Equation (16) suggests that a plot of 1/ k_{obs} versus $[HSO_4^-]$ should be linear and agrees with observed experimental data. From the slope Q_3/A and intercept 1/A, the ratio of slope to intercept was calculated to be 1.54 i. e. Q_3, which is in good agreement with the previously reported value[21]. All the above results show $Ce(SO_4)_2$ as the kinetically active species. Furthermore the rate constants decrease with increasing $[H^+]$. This is due to formation[22] of an active inhibitor $H_2Ce(SO_4)_2^{2-}$.

It is observed that SO_4^{2-} ions retards the rate of oxidation coupled with the observation that increase in $[H^+]$ decrease the rate, pointing to the fact that the neutral covalently bound $Ce(SO_4)_2$ is the active species of oxidant**[23]**. The slight effect of ionic strength indicate that a neutral molecule is involved in rate determining step, which further confirms the $Ce(SO_4)_2$ as the kinetically active species in the present study.

5.5 Conclusion

The reaction between leucine and cerium(IV) is very slow at room temperature. The reaction occurs in measurable quantities at 45°C and 1M H_2SO_4 concentration in the presence of manganese(II) catalyst. The order with respect to oxidant and catalyst are found to be unity and less than unity with respect to reductant. The main active species of cerium(IV) is considered as $Ce(SO_4)_2$, although other species might be active to a much lesser extent. The overall mechanistic sequence described here is consistent with product, kinetic and mechanistic study.

5.6 References

1. S. M. Deepak, S. A. Chimatadar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **33,** 535, 2008.

2. D. Laloo and M. K. Mahanti, ***J. Chem. Soc. Dalton Trans.,*** **1,** 311, 1990.

3. K. A. Thabaj, S. A. Chimatadar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **31,** 186, 2006.

4. S. A. Chimatadar, T. Basavaraj and S. T. Nandibewoor, ***Inorg. React. Mech.,*** **4,** 209, 2002.

5. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **26,** 241, 2001.

6. S. A. Chimatadar, S. T. Nandibewoor, M. I. Sambrani and J. R. Raju, ***J. Chem. Soc. Dalton Trans.,*** **3,** 573, 1987.

7. M. C. Day and J. Selbin, "***Theoretical* I*norganic Chemistry",*** Reinhold, New York, 226, 1964.

8. T. Sumathi, P. S. Sundaram, G. Chandramohan, D. Deepa and R. Renganathan, ***Int. J. Chem. Sci. Tech.,*** **2,** 44, 2012.

9. G. G. Guilbault and W.H. McCurdy Jr., ***J. Phys. Chem.,*** **67,** 283, 1963.

10. M. Ardon, ***J. Chem. Soc.,*** 1811, 1957.

11. S. A. Chimatadar, S. T. Nandibewoor and J. R. Raju, ***Ind. J. Chem.,*** **28A,** 902, 1989.

12. R. K. Patil, S. A. Chimatadar and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **33,** 625, 2008.

13. A. Katafias, ***Trans. Met. Chem.,*** **31,** 907, 2006.

14. A. Roy and A. K. Das, ***Ind. J. Chem.,*** **41A,** 2468, 2002.

15. M. B. Yadav, V. Devra and A. Rani, ***Phys. Chem. An Ind. J.,*** **4,** 21, 2009.

16. A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, ***Trans. Met. Chem.,*** **34,** 711, 2009.

17. G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denny, ***"Vogel's Text Book of Quantitative Chemical Analysis",*** 5th edn., ELBS, Longman, Essex, England,(a) p. 381, (b) p.195, 1996.

18. T. Sumati, P. S. Sundaram and G. Chandramohan, ***Arabian J. Chem.,*** **4,** 426, 2011.

19. D. C. Hiremath, T. S. Kiran and S. T. Nandibewoor, ***Int. J. Chem. Kinet.,*** **39,** 236, 2007.

20. S. K. Mishra, Y. K. Gupta, ***J. Chem. Soc. A,*** 2918, 1970.

21. S. K. Mondal, D. Kar, M. Das and A. K. Das, ***Ind. J. Chem.,*** **37A,** 765, 1998.

22. S. A. Chimatadar, S. V. Mandawale and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **32,** 634, 2007.

23. T. Sumathi, P. Shanmugasundaram, G. Chandramohan, ***Asian J. Chem.,*** **23,** 4385, 2011.

Chapter – 6

Mechanistic and Kinetic Study of Oxidation of Aspartic Acid by Cerium(IV) in Presence of Palladium(II) in Sulphuric Acid Medium

Abstract

Kinetics of palladium(II) catalysed oxidation of aspartic acid by Ce(IV) has been studied in acidic medium at 45°C. The reaction show first order kinetics with respect to Ce(IV) and Pd(II) in the oxidation of aspartic acid. The first order kinetics with respect to aspartic acid obtained at its lower concentration changes to zero order at its higher concentration. It is found that rate of reaction, decreases with increase of [HSO_4^-] and [H^+]. Effect of added product Ce(III) retards the rate of reaction. The active species of oxidant is $Ce(SO_4)_2$. A plausible mechanism has been proposed from the results of kinetic studies, reaction stoichiometry and product analysis.

6.1 Introduction

Cerium(IV) metal ion, being a strong oxidant, is widely used in the oxidation of organic substances[1-6], as well as of several inorganic substances[7-10]. The basic advantage over other oxidants is its reduction to a single substance, cerium(III), without any intermediate reactions. It is stable towards heat and light and simply undergoes one electron change. The oxidation of organic compounds by cerium(IV) in general seems to proceed via the formation of an intermediate complex[11-13]. Among the inorganic substrates which serve as ligands for cerium(IV) are chloride, bromide and hypophosphite[14]. So far the kinetics of cerium(IV) reactions is concerned, an intermediate complex between oxidant and substrate is generally considered to be the preferred mode of electron transfer.

Amino acids act as the building blocks in the synthesis of proteins and play a vital role in the metabolism. In the metabolism, amino acids are subjected to various reactions and supply precursors for many endogenous substances, e.g. haemoglobin in blood. They undergo different reactions, depending on whether a particular amino acid contains non-polar groups or polar substituents. Aspartic acid is a non-essential amino acid which is found abundantly in plant proteins especially in sprouting seeds. This can be manufactured in the body from oxalo acetic acid[15]. It is important as a general acid in enzyme centres as well as in maintaining the solubility and ionic characters of proteins. Physiologically, aspartic acid aids in the removal of ammonia, which is highly toxic to the central nervous system. Recent studies have shown that aspartic acid may increase resistance to fatigue and increase endurance[16]. Many kinetic studies have been carried out on the oxidation of aspartic acids using different oxidants[17-21] in acidic and alkaline media.

Kinetic investigations on the oxidation of amino acids catalyzed by different metal ions[22-26] are considered as a significant field of chemistry because of the role of metals in biological systems. Palladium is a rare and lustrous silvery-white metal referred to as the platinum group metals. Palladium catalysed reactions have found widespread use in many areas of organic chemistry[27], medicinal chemistry[28] and in the preparation of fine chemicals[29]. It is a versatile metal applied in homogeneous catalysis. The utility of palladium(II) chloride as a non-toxic and homogenous catalyst has been reported by several workers[30-32]. The catalysed mechanism can be quite complicated due to formation of different intermediate complexes and different oxidation states of Pd(II).

In the present investigation, we have obtained the evidence for the reactive species for the cerium(IV) in acidic medium. A perusal literature showed that there seems to be no report on the kinetics and mechanism of the oxidation of aspartic acid by cerium(IV), catalysed by palladium(II) in sulphuric acid medium. Therefore we have undertaken a careful study of oxidation of aspartic acid by cerium(IV) in presence of Pd(II) catalyst in sulphuric acid medium.

6.2 Experimental

In the present work, double distilled water was used for preparing the solutions. A stock solution of aspartic acid (E. Merck) was prepared by dissolving it in water. The Ce(IV) stock solution was obtained by dissolving cerium(IV) ammonium sulphate (E. Merck) in 1.0 mol dm^{-3} sulphuric acid and standardized with iron(II) ammonium sulphate solution (E Merck). Palladium(II) chloride (Johnson Matthey) was prepared in HCl (0.20 mol dm^{-3}) and assayed by complexometric titration with EDTA[33]. Dilute solution of palladium(II) were made from the stock solution as required. Other chemical and reagents such as Ce(III) sulphate, sodium chloride, sodium sulphate, sulphuric acid, acetonitrile used were of analytical grade.

6.2.1 Kinetic Measurements

Kinetics of oxidation of aspartic acid by cerium(IV) in presence of Pd(II) as catalyst have been investigated at 45°C in acidic medium. A solution with known concentration of Cerium(IV) and other reactants were allowed to equilibrate in a water bath at the required temperature for 20 minutes, then thoroughly mixed and quickly transferred to the absorbance cell. The reaction was followed by measuring the absorbance of unreacted Ce(IV) at 360 nm using systronics(166) UV spectrophotometer, all other species did not absorb significantly at this wave length. The applicability of Beer's law was verified between 5×10^{-5} to 5×10^{-4} mol dm^{-3} of cerium(IV) at 360 nm under the reaction conditions. The molar absorption coefficient was found to be $\varepsilon = 2622$ dm^3 mol^{-1} cm^{-1} [34]. The initial rates were obtained from [cerium(IV)] versus time plots by plane mirror method[35-36]. The initial rates were reproducible within the experimental error ±5%.

6.2.2 Stoichiometry and Product Analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [aspartic acid] at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24 hours at 45°C. The unreacted Ce(IV) was measured through absorbance at 360 nm. The main reaction products are Cerium(III), malonic acid, ammonia and CO_2. Malonic acid was identified by FTIR spectrum. The IR Spectra shows the band at 1632.07 cm^{-1} due to C=O stretching frequency of the carboxylic group and the band at 3449.28 cm^{-1} due to –OH stretching frequency of the carboxylic OH group **(Figure 6.1).** Ammonia was confirmed with Nesseler's reagent test[37] and CO_2 was qualitatively detected by lime water test. The results indicated that one mole of aspartic acid consumed four moles of cerium(IV) according to equation (1).

$$\mathrm{HOOCCH_2CH(NH_2)COOH + 4Ce(IV) + 2H_2O \xrightarrow{Pd(II)} HOOCCH_2COOH + 4H^+ + 4Ce(III) + NH_3 + CO_2} \quad (1)$$

6. 3 Results

6.3.1 Cerium(IV) Dependence

In the first set of kinetic experiment, [Ce(IV)] was varied from 5×10^{-5} to 5×10^{-4} mol dm^{-3} at fixed concentration of [Asp] = 6×10^{-3} mol dm^{-3},[H$^+$] = 0.50 mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3}, I = 1.0 mol dm^{-3} and temperature = 45°C, the order was found to be unity. Results are given in **Table 6.1.** The plot of initial rate versus [Ce(IV)] was a straight line passing through the origin **(Figure 6.2)**.

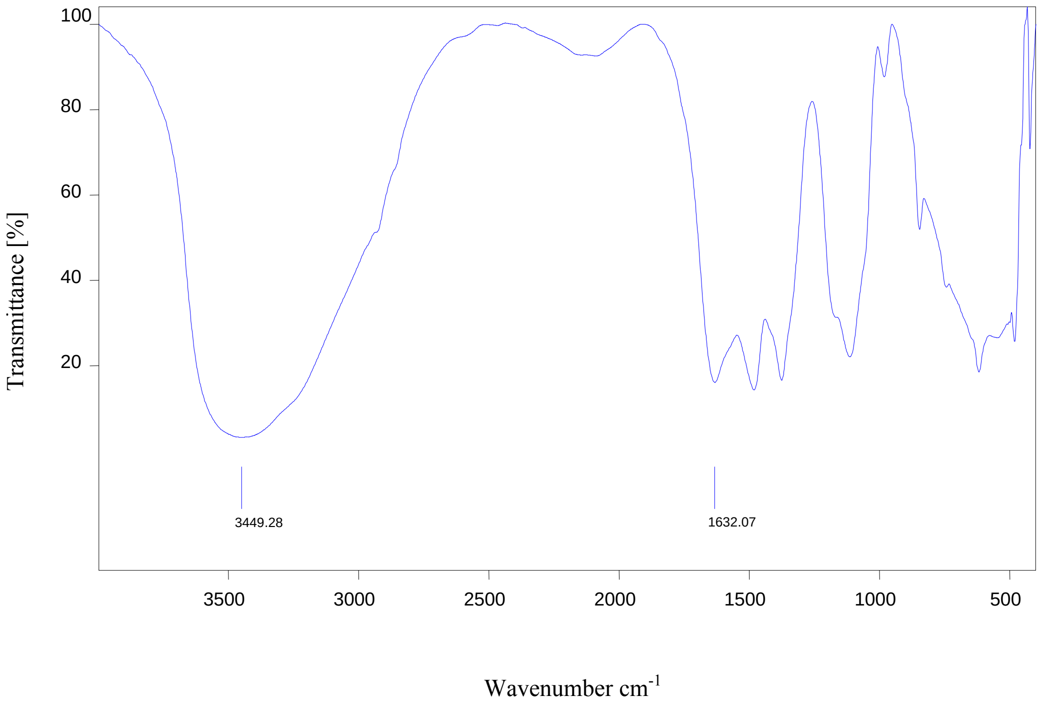


Figure 6.1: FT-IR spectra of final prodcuct of oxidation of aspartic acid

Table 6.1: Variation of cerium(IV)

[Asp] = 6.0 × 10^{-3} mol dm^{-3} **Temp. = 45°C**

[H^+] = 0.50 mol dm^{-3} **I = 1.0 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^4 [Ce(IV)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.121	0.265	0.528	0.782	1.041	1.302
10	0.092	0.194	0.414	0.620	0.818	1.017
20	0.072	0.157	0.325	0.601	0.802	0.798
30	0.053	0.121	0.252	0.399	0.640	0.655
40	0.040	0.099	0.205	0.314	0.504	0.498
50	0.031	0.078	0.168	0.236	0.325	0.414
60	0.023	0.060	0.127	0.188	0.242	0.314
80	0.013	0.036	0.084	0.110	0.147	0.189
10^7 (rate), mol dm^{-3} sec^{-1}	**0.28**	**0.68**	**1.28**	**1.95**	**2.64**	**3.25**

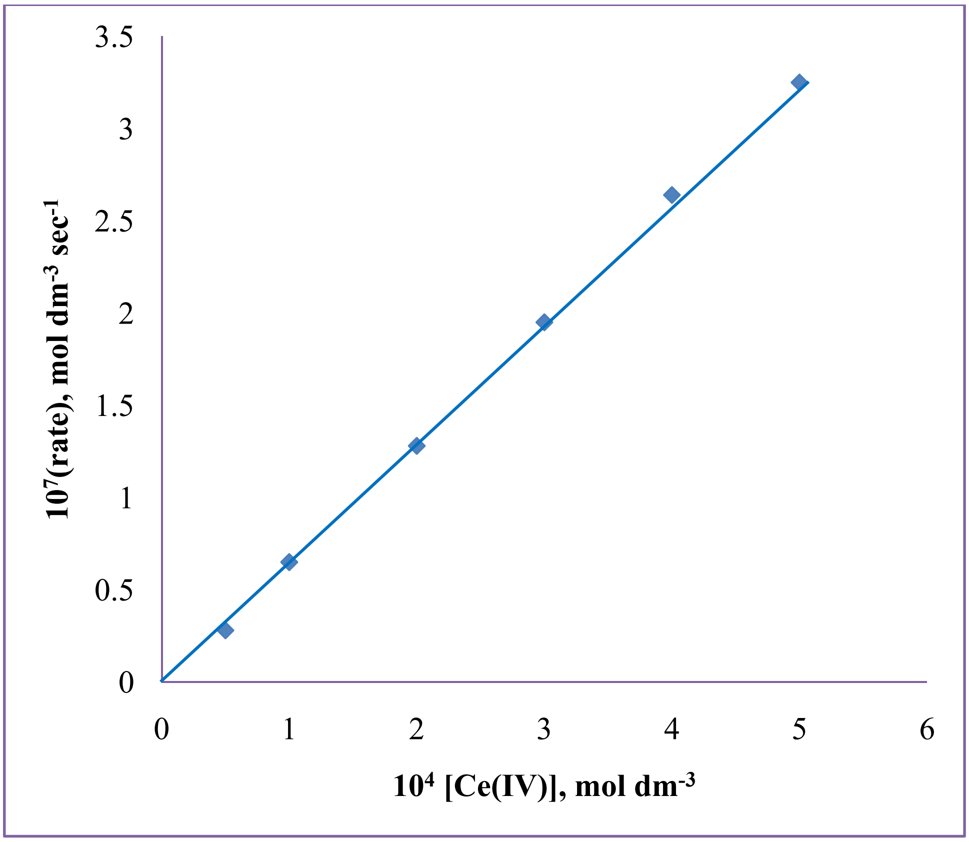


Figure 6.2: Plot of cerium(IV) versus rate

[Asp] = 6.0×10^{-3} mol dm^{-3}; [H$^+$] = 0.5 mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; I = 1.0 mol dm^{-3}; Temp.= 45°C

(Ref. Table 6.1)

6.3.2 Aspartic Acid Dependence

At a fixed [Ce(IV)] = 2×10^{-4} mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3}, [H_2SO_4] = 0.50 mol dm^{-3} and I = 1.0 mol dm^{-3}, the effect of [Asp] on the rate of reaction was studied in the concentration range 1×10^{-3} to 1×10^{-2} mol dm^{-3} at three temperature viz. 40°C, 45°C and 50°C respectively. The rate of the reaction initially increases and tends towards a limiting value with further increasing concentration of aspartic acid **(Figure 6.3)**. Results are given in **Table 6.2, 6.3 and 6.4**.

6.3.3 Palladium(II) Dependence

At fixed [Ce(IV)] = 2×10^{-4} mol dm^{-3}, [Asp] = 6×10^{-3} mol dm^{-3}, [H_2SO_4] = 0.50 mol dm^{-3} and I = 1.0 mol dm^{-3}, Pd(II) was varied from 1×10^{-5} to 1×10^{-4} mol dm^{-3} at 45°C. The rate of reaction increases with increase of Pd(II) concentration. Results are given in **Table 6.5**. The order with respect to Pd(II) was found to be one **(Figure 6.4).** Under these conditions the rate of uncatalyzed reaction is negligible in comparision to the catalyzed reaction.

6.3.4 Hydrogen Ion Dependence

At fixed concentration of [Ce(IV)] = 2×10^{-4} mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3}, [Asp] = 6×10^{-3} mol dm^{-3} and I = 1.0 mol dm^{-3}, the sulphuric acid concentration was varied between 0.20 and 1.0 mol dm^{-3} at 40°C, 45°C and 50°C respectively, the initial rate was found to decrease with increasing sulphuric acid concentration **(Table 6.6, 6.7 and 6.8)**. The [H^+] ion concentration was calculated using known ionization constants of sulphate as in the earlier studies**[38-40]**. Cerium(IV) is known to form several complexes in sulphate media**[38-39, 41]**.

$$Ce^{4+} + H_2O \xrightleftharpoons{K_{OH}} Ce(OH)^{3+} + H^+ \tag{2}$$

$$Ce^{4+} + SO_4^{2-} \xrightleftharpoons{K_1} Ce(SO_4)^{2+} \tag{3}$$

$$Ce(SO_4)^{2+} + SO_4^{2-} \xrightleftharpoons{K_2} Ce(SO_4)_2 \tag{4}$$

Table 6.2: Variation of aspartic acid

[Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3} **Temp. = 40°C**

$[H^+]$ = 0.50 mol dm^{-3} **I = 1.0 mol dm^{-3}**

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}

10^3[Asp], mol dm^{-3}	**1.0**	**2.0**	**4.0**	**6.0**	**8.0**	**1.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.485	0.460	0.425	0.427	0.414	0.403
20	0.443	0.393	0.348	0.341	0.326	0.320
30	0.406	0.337	0.284	0.275	0.253	0.251
40	0.367	0.291	0.236	0.223	0.206	0.201
50	0.334	0.247	0.178	0.180	0.170	0.164
60	0.298	0.207	0.152	0.151	0.128	0.115
80	0.240	0.147	0.099	0.095	0.085	0.081
10^7 (rate), mol dm^{-3} sec^{-1}	**0.31**	**0.56**	**0.88**	**1.10**	**1.26**	**1.36**

Table 6.3: Variation of aspartic acid

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3} **Temp. = 45°C**

[H^{+}] = 0.50 mol dm^{-3} **I = 1.0 mol dm^{-3}**

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

10^3[Asp], mol dm^{-3}	**1.0**	**2.0**	**4.0**	**6.0**	**8.0**	**1.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.473	0.452	0.430	0.414	0.396	0.388
20	0.420	0.378	0.347	0.325	0.318	0.311
30	0.370	0.316	0.273	0.252	0.246	0.242
40	0.318	0.270	0.226	0.205	0.199	0.195
50	0.283	0.216	0.184	0.168	0.160	0.169
60	0.248	0.173	0.153	0.127	0.113	0.110
80	0.190	0.116	0.101	0.083	0.078	0.072
10^7 (rate), mol dm^{-3} sec^{-1}	**0.38**	**0.65**	**1.00**	**1.28**	**1.46**	**1.58**

Table 6.4: Variation of aspartic acid

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3} **Temp. = 50°C**
[H$^+$] = 0.50 mol dm^{-3} **I = 1.0 mol dm^{-3}**
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

10^3[Asp], mol dm^{-3}	**1.0**	**2.0**	**4.0**	**6.0**	**8.0**	**1.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.474	0.440	0.418	0.392	0.387	0.384
20	0.419	0.386	0.332	0.803	0.310	0.308
30	0.373	0.306	0.256	0.634	0.240	0.237
40	0.330	0.259	0.209	0.521	0.192	0.190
50	0.290	0.210	0.172	0.403	0.158	0.157
60	0.253	0.175	0.129	0.331	0.109	0.109
80	0.194	0.118	0.087	0.076	0.069	0.066
10^7 (rate), mol dm^{-3} sec^{-1}	**0.42**	**0.74**	**1.20**	**1.50**	**1.71**	**1.82**

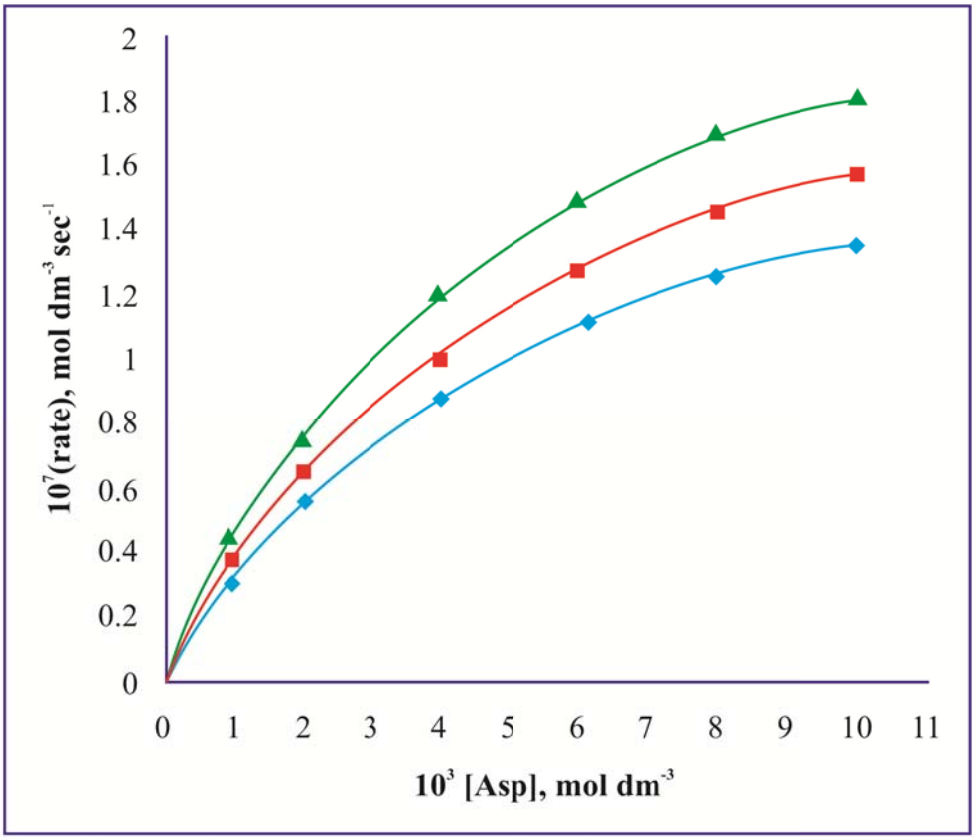


Figure 6.3: Variation of aspartic acid

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}; [Pd(II)] = 5.0×10^{-5} mol dm^{-3};

[H$^+$] = 0.50 mol dm^{-3}; I = 1.0 mol dm^{-3};

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table 6.2, 6.3 and 6.4)

Table 6.5: Variation of palladium(II)

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3} **Temp. = 45°C**

[H_2SO_4] = 0.50 mol dm^{-3} **I = 1.0 mol dm^{-3}**

[Asp] = 6.0×10^{-3} mol dm^{-3}

10^5 [Pd(II)], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**	**9.0**	**10.0**
Time in minutes	**Absorbance**									
0	0.528	0.528	0.528	0.528	0.528	0.528	0.528	0.528	0.528	0.528
10	0.492	0.464	0.437	0.429	0.414	0.388	0.383	0.378	0.376	0.373
20	0.452	0.399	0.364	0.346	0.325	0.311	0.307	0.303	0.297	0.262
30	0.415	0.343	0.302	0.275	0.252	0.242	0.236	0.234	0.228	0.223
40	0.372	0.294	0.254	0.225	0.205	0.195	0.189	0.186	0.181	0.176
50	0.341	0.250	0.206	0.181	0.168	0.159	0.156	0.153	0.149	0.144
60	0.304	0.210	0.170	0.152	0.127	0.111	0.108	0.101	0.097	0.093
80	0.244	0.152	0.112	0.098	0.083	0.073	0.066	0.065	0.060	0.055
10^7 (rate), mol dm^{-3} sec^{-1}	**0.25**	**0.51**	**0.77**	**1.05**	**1.28**	**1.58**	**1.86**	**2.13**	**2.41**	**2.66**

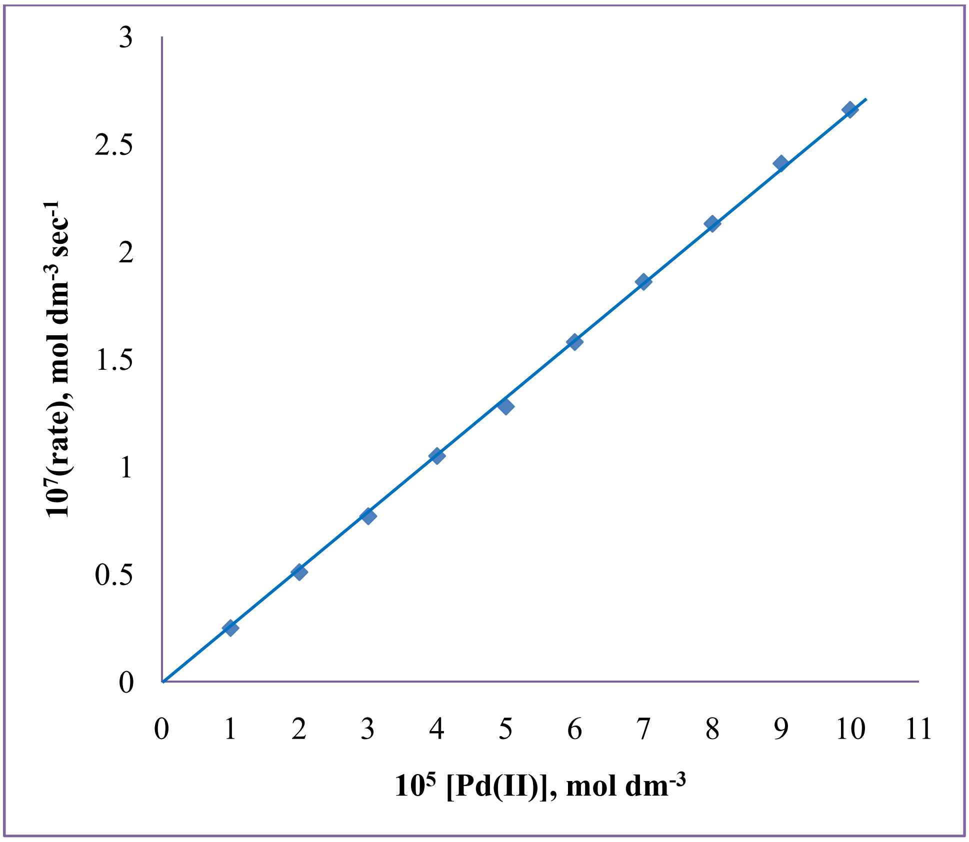


Figure 6.4: Variation of palladium(II)

$[Ce(IV)] = 2.0\times10^{-4}$ mol dm^{-3}; $[Asp] = 6.0 \times 10^{-3}$ mol dm^{-3};

$[H^+]$ = 0.50 mol dm^{-3}; I = 1.0 mol dm^{-3}; Temp. = 45° C

(Ref. Table 6.5)

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

$[Ce(IV)] = 2.0 \times 10^{-4}$ mol dm^{-3}
$[Asp] = 6.0 \times 10^{-3}$ mol dm^{-3}
$[Pd(II)] = 5.0 \times 10^{-5}$ mol dm^{-3}

Temp. = 40°C
I = 1.0 mol dm^{-3}

$[H^+]$, mol dm^{-3}	**0.20**	**0.40**	**0.50**	**0.60**	**0.80**	**1.0**
Time in minutes	**Absorbance**					
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.410	0.420	0.425	0.438	0.441	0.455
20	0.327	0.334	0.339	0.353	0.350	0.379
30	0.256	0.258	0.274	0.283	0.286	0.317
40	0.209	0.210	0.221	0.230	0.239	0.272
50	0.165	0.174	0.178	0.187	0.1186	0.218
60	0.19	0.132	0.149	0.155	0.154	0.174
80	0.082	0.088	0.094	0.102	0.104	0.118
10^7 (rate), mol dm^{-3} sec^{-1}	**1.35**	**1.21**	**1.11**	**0.99**	**0.80**	**0.64**

Table 6.7: Variation of $[H^+]$ concentration

$[Ce(IV)] = 2.0 \times 10^{-4}$ mol dm^{-3} **Temp. = 45°C**

$[Asp] = 6.0 \times 10^{-3}$ mol dm^{-3} **$I = 1.0$ mol dm^{-3}**

$[Pd(II)] = 5.0 \times 10^{-5}$ mol dm^{-3}

$[H^+]$, mol dm^{-3}	**0.20**	**0.40**	**0.50**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.386	0.408	0.420	0.425	0.430	0.449
20	0.313	0.324	0.330	0.339	0.347	0.371
30	0.241	0.252	0.256	0.267	0.283	0.309
40	0.193	0.204	0.208	0.212	0.235	0.262
50	0.157	0.167	0.171	0.174	0.178	0.213
60	0.109	0.121	0.129	0.135	0.151	0.178
80	0.072	0.080	0.085	0.098	0.099	0.121
10^7 (rate), mol dm^{-3} sec^{-1}	**1.63**	**1.40**	**1.28**	**1.13**	**0.89**	**0.72**

Table 6.8: Variation of $[H^+]$ concentration

$[Ce(IV)] = 2.0 \times 10^{-4}$ mol dm^{-3} **Temp. = 50°C**

$[Asp] = 6.0 \times 10^{-3}$ mol dm^{-3} **$I = 1.0$ mol dm^{-3}**

$[Pd(II)] = 5.0 \times 10^{-5}$ mol dm^{-3}

$[H^+]$, mol dm^{-3}	**0.20**	**0.40**	**0.50**	**0.60**	**0.80**	**1.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.380	0.390	0.394	0.416	0.430	0.439
20	0.305	0.313	0.315	0.330	0.346	0.348
30	0.283	0.243	0.240	0.259	0.277	0.285
40	0.187	0.196	0.194	0.212	0.225	0.234
50	0.154	0.162	0.160	0.167	0.182	0.182
60	0.104	0.112	0.109	0.121	0.152	0.150
80	0.066	0.070	0.071	0.086	0.099	0.102
10^7 (rate), mol dm^{-3} sec^{-1}	**2.01**	**1.69**	**1.53**	**1.33**	**1.04**	**0.82**

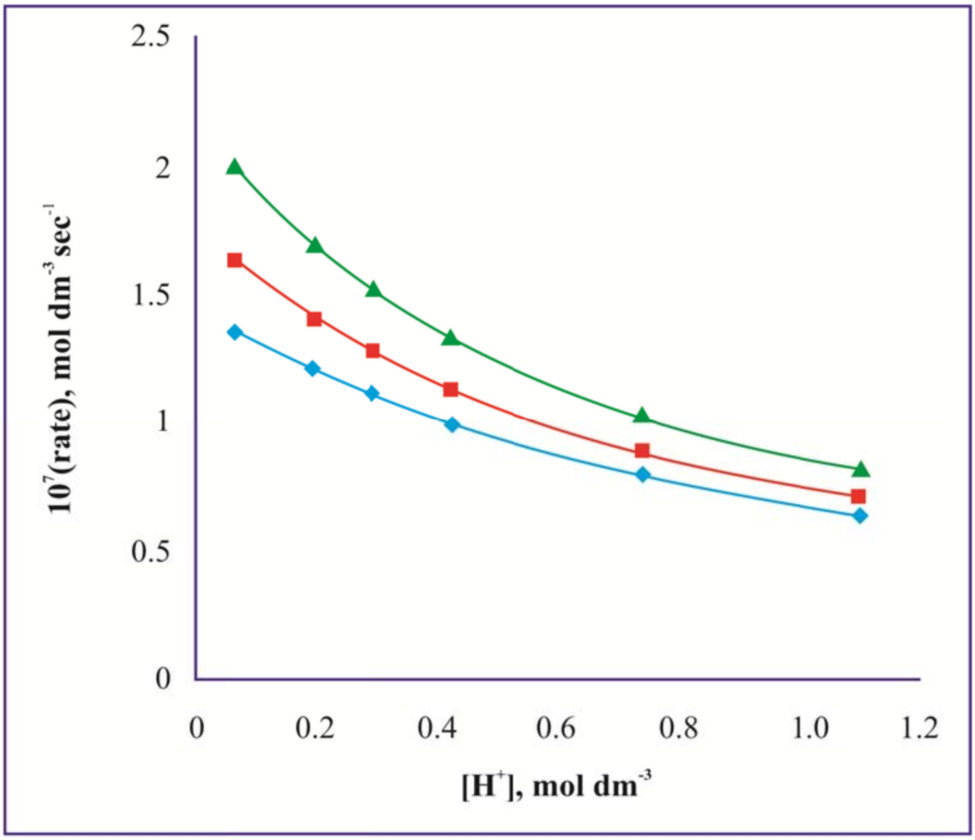


Figure 6.5: A plot of (rate) versus [H$^+$] at three different temperature

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}; [Asp] = 6.0×10^{-3} mol dm^{-3};

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

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

(Ref. Table 6.6, 6.7 and 6.8)

$$\mathrm{Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_2HSO_4^-} \tag{5}$$

$$\mathrm{Ce(SO_4)_2HSO_4^- + HSO_4^- + H^+ \overset{K_4}{\rightleftharpoons} H_3Ce(SO_4)_4^-} \tag{6}$$

The sum of the equations 2-6, gives the total cerium(IV) concentrations which is obtained by the cumulative equilibrium constants, K_{OH}, β_1, β_2, β_3 and β_4 as equation (7).

$$[\mathrm{Ce^{4+}}]_t = [\mathrm{Ce^{4+}}]_f \left\{ \begin{array}{l} 1 + \dfrac{K_{OH}}{[\mathrm{H^+}]} + \beta_1[\mathrm{SO_4^{2-}}] + \beta_2[\mathrm{SO_4^{2-}}]^2 + \beta_3[\mathrm{SO_4^{2-}}]^2[\mathrm{HSO_4^-}] \\ \quad + \beta_4[\mathrm{SO_4^{2-}}]^2[\mathrm{HSO_4^-}]^2[\mathrm{H^+}] \end{array} \right\} \tag{7}$$

Where, $K_{OH} = 15$, $\beta_1 = K_1 = 3.85 \times 10^2$, $\beta_2 = K_1 K_2 = 1.69 \times 10^2$, $\beta_3 = K_1 K_2 K_3 = 1.01 \times 10^2$ and $\beta_4 = K_1 K_2 K_3 K_4 = 2.03 \times 10^2$. The concentration of cerium sulphate complexes can be calculated from the concentration of Ce^{4+}, H^+, HSO_4^- and SO_4^{2-} **38-42**. The results show that the concentration of $Ce(OH)^{3+}$ is very less than other cerium species, so can be neglected. According to **Table 6.9** calculated results are plotted in **Figure 6.6** which indicates that only $Ce(SO_4)_2$ species is parallel with the variation of rate with H^+ concentration.

6.3.5 Effect of Initially Added Product

Added product Ce(III) was varied in the concentration range 5×10^{-5} to 5×10^{-4} mol dm^{-3} keeping other reactants concentration and conditions constant. The rate of reaction decreases with the addition of Ce(III), whereas other product malonic acid did not change the rate of reaction. The retarding effect of Ce(III) is shown in **Figure 6.7.** Results are given in **Table 6.10.**

6.3.6 Effect of Ionic Strength

At fixed concentration of [Ce(IV)] = 2×10^{-4} mol dm^{-3}, [Asp] = 6×10^{-3} mol dm^{-3}, [H_2SO_4] = 0.50 mol dm^{-3}, [Pd(II)] = 5×10^{-5} mol dm^{-3} and temperature 45°C, the ionic strength was varied from 0.60 to 1.60 mol dm^{-3} (ionic strength adjusted by Na_2SO_4), it is found that ionic strength did not affect the rate of reaction **(Figure 6.8)**. Results are given in **Table 6.11**.

Table 6.9: Variation of different Ce(IV) species with [H$^+$] on Pd(II) catalysed oxidation of aspartic acid by Ce(IV) in H_2SO_4 medium at 45°C

[H_2SO_4]	[H^+]	[HSO_4^-]	$10^3 \times \alpha_0$	α_{oH}	α_1	$10^2 \times \alpha_2$	$10^2 \times \alpha_3$	$10^2 \times \alpha_4$	$10^7 \times$ rate (mol dm^{-3} sec^{-1})
0.20	0.062	0.338	1.698	0.411	4.337	12.500	3.456	0.107	1.63
0.40	0.190	0.610	3.740	0.295	5.610	9.610	3.504	0.816	1.40
0.50	0.291	0.709	5.334	0.274	5.975	7.633	3.234	1.314	1.28
0.60	0.422	0.778	7.309	0.259	6.249	6.093	2.832	1.869	1.13
0.80	0.740	0.860	12.141	0.246	6.543	4.021	2.066	2.643	0.89
1.00	1.099	0.901	17.500	0.238	6.670	2.890	1.560	3.106	0.72

[Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3}, [Asp] = 6.0 × 10^{-3} mol dm^{-3}, [Pd(II)] = 5.0 × 10^{-5} mol dm^{-3}, I = 1.0 mol dm^{-3} α_0, α_{OH}, α_1, α_2, α_3 and α_4 are the fractions of total cerium(IV) of the species Ce^{4+}, $Ce(OH)^{3+}$, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$ and $H_3Ce(SO_4)_4^-$ respectively.

Table 6.10: Effect of cerium(III)

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3} **Temp. = 45°C**
[Asp] = 6.0×10^{-3} mol dm^{-3} **I = 1.0 mol dm^{-3}**
[Pd(II)] = 5.0×10^{-5} mol dm^{-3} **[H$^+$] = 0.50 mol dm^{-3}**

10^4[Ce(III)], mol dm^{-3}	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.418	0.423	0430	0.431	0.432	0.434
20	0.332	0.335	0.346	0.347	0.349	0.361
30	0.256	0.266	0.277	0.281	0.285	0.298
40	0.209	0.215	0.225	0.232	0.238	0.251
50	0.172	0.175	0.182	0.184	0.186	0.204
60	0.129	0.140	0.152	0.153	0.154	0.167
80	0.087	0.097	0.099	0.101	0.103	0.109
10^7 (rate), mol dm^{-3} sec^{-1}	**1.20**	**1.14**	**1.04**	**0.95**	**0.87**	**0.81**

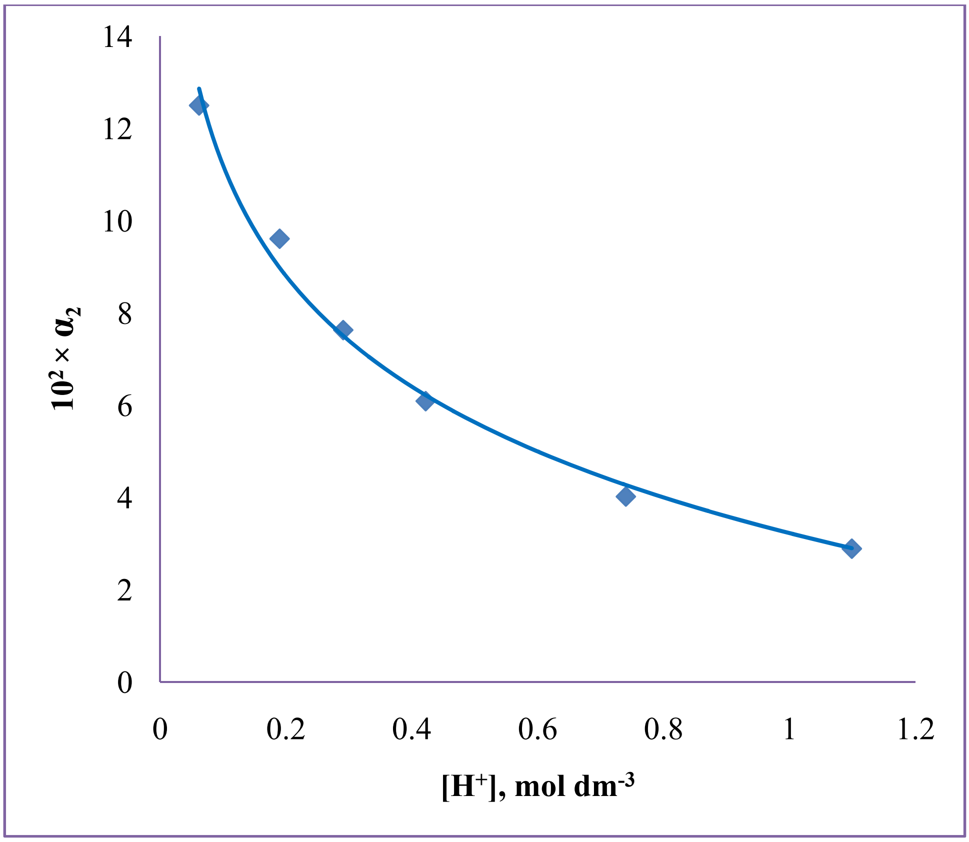


Figure 6.6: Effect of [H$^+$] concentration on different cerium(IV) species

(Ref. Table 6.9)

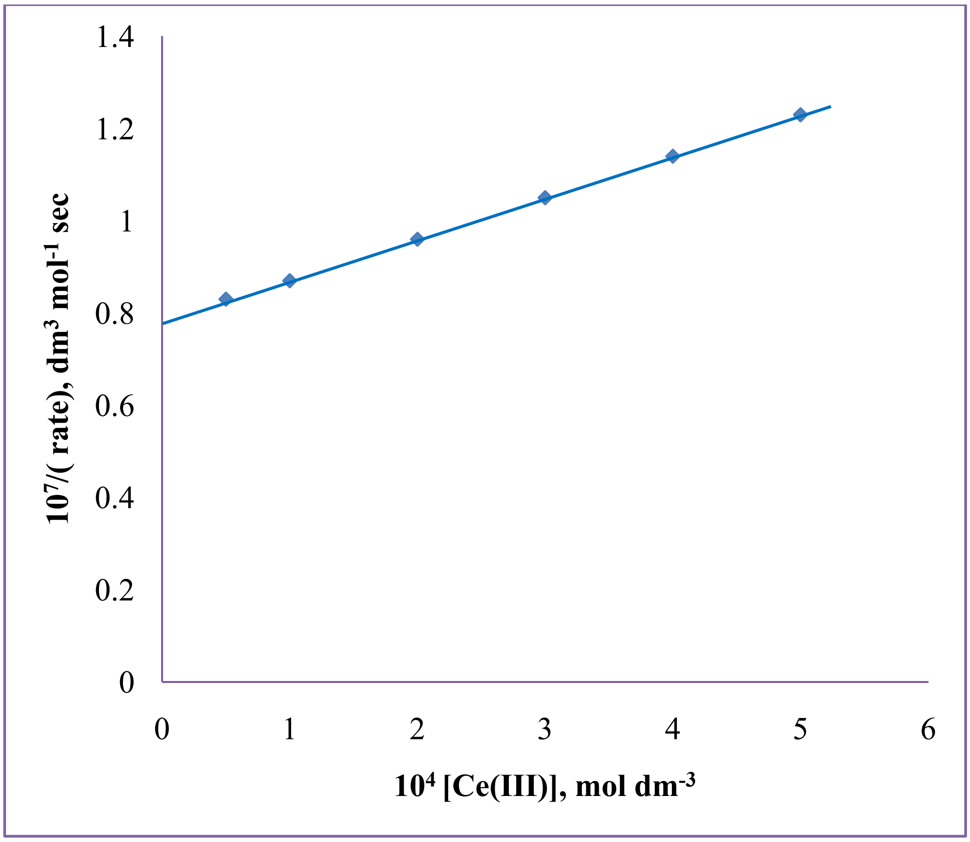


Figure 6.7: Effect of cerium(III)

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}; [Asp] = 6.0×10^{-3} mol dm^{-3};

[H$^+$] = 0.50 mol dm^{-3}; I = 1.0 mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; Temp. = 45° C

(Ref. Table 6.10)

Table 6.11: Variation of ionic strength

[Asp] = 6.0×10^{-3} mol dm^{-3}
[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

Temp. = 45°C
[H$^+$] = 0.50 mol dm^{-3}

I, mol dm^{-3}	**0.60**	**0.80**	**1.00**	**1.20**	**1.40**	**1.60**
Time in minutes			**Absorbance**			
0	0.528	0.528	0.528	0.528	0.528	0.528
10	0.414	0.413	0.413	0.416	0.414	0.413
20	0.325	0.323	0.325	0.326	0.325	0.323
30	0.252	0.250	0.252	0.253	0.252	0.250
40	0.205	0.203	0.205	0.206	0.205	0.204
50	0.168	0.166	0.168	0.169	0.168	0.167
60	0.127	0.125	0.127	0.130	0.126	0.125
80	0.083	0.081	0.083	0.086	0.083	0.081
10^7 (rate), mol dm^{-3}sec^{-1}	**1.28**	**1.29**	**1.28**	**1.27**	**1.28**	**1.29**

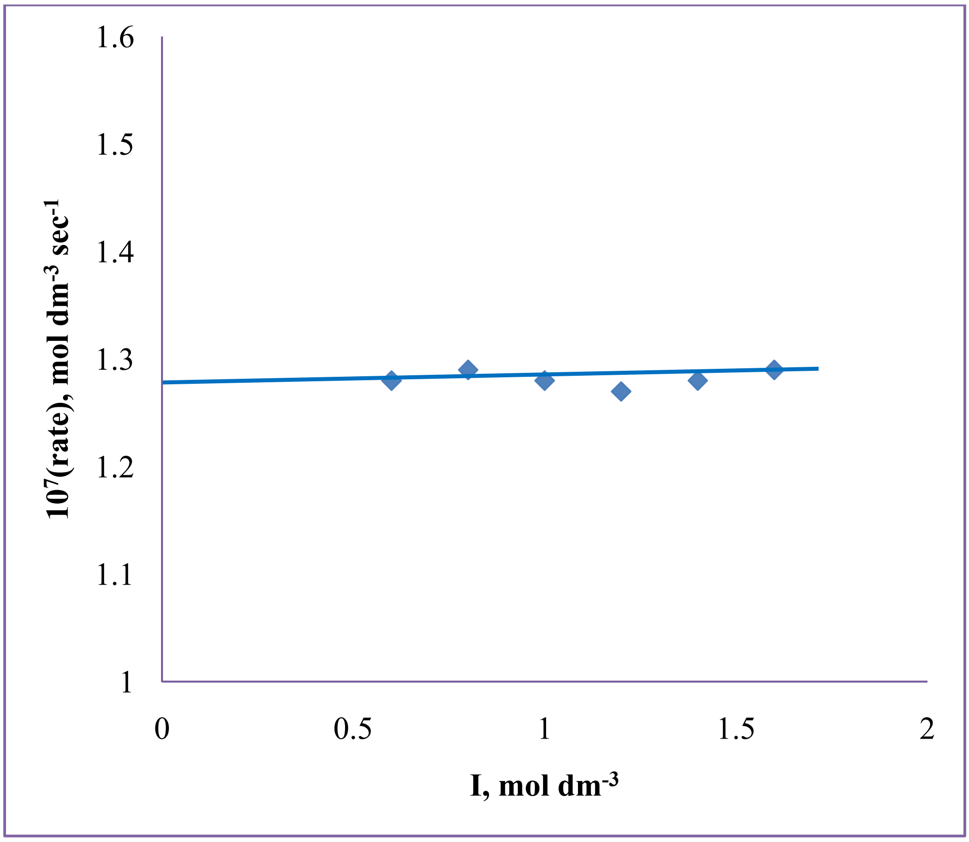


Figure 6.8: Variation of ionic strength

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}; [Asp] = 6.0×10^{-3} mol dm^{-3};

[Pd(II)] = 5.0×10^{-5} mol dm^{-3}; [H^+] = 0.50 mol dm^{-3}; Temp.= 45°C

(Ref. Table 6.11)

6.3.7 Effect of Chloride Ion

At fixed concentrations of [Ce(IV)] = 2.0×10^{-4} mol dm^{-3}, [Asp] = 6.0×10^{-3} mol dm^{-3}, [Pd(II)] = 5.0×10^{-5} mol dm^{-3}, [H_2SO_4] = 0.50 mol dm^{-3} and temperature 45°C, the concentration of NaCl was varied from 1×10^{-4} to 5×10^{-4} mol dm^{-3}. The rate was unaffected by the addition of Cl^- ions **(Figure 6.9)**. Results are given in **Table 6.12**.

6.4 Discussion

The uncatalysed cerium(IV) oxidation of aspartic acid is very slow in sulphuric acid under the present experimental conditions. However, the reaction is appreciably faster in the presence of small quantity of Pd(II) in sulphuric medium. The reaction is first order with respect to cerium(IV) and Pd(II) concentrations, and the order with respect to aspartic acid changes from first to zero order. Increasing [H^+] and [HSO_4^-] concentration results in a decrease in rate. As the sulphuric acid concentration increases, the H^+ ion concentration increases, corresponding HSO_4^- ion concentration also increases. The rate is inversely dependent on the HSO_4^- ion concentration, the overall effect of adding sulphuric acid would be to lower the rate of reaction[43-44] **(Table 6.9)**. Added product Ce(III) inhibits the rate of reaction due to formations of $Ce^{4+}.Ce^{3+}$ ion pair. The above results indicate that aspartic acid react with Pd(II) to form an adduct, which then react one mole of Ce(IV) in slow step and give Ce(III), a free radical derived from aspartic acid, carbon dioxide and Pd(II) catalyst regenerated. The free radical derived from aspartic acid then combine with another molecule of Ce(IV) in fast step and give cerium(III), malonic acid, ammonia. From the above kinetic results, the following mechanism has been proposed **(Scheme-6.1)**.

$$Ce^{4+} \cdot H^+ \overset{K_1}{\rightleftharpoons} Ce^{4+} + H^+$$

$$HOOCCH_2CH(NH_2)COOH + Pd(II) \overset{K_2}{\rightleftharpoons} \text{Adduct } (C_1)$$

$$\text{Adduct } (C_1) + Ce^{4+} \xrightarrow[\text{slow}]{k} Ce^{3+} + HOOCCH_2\overset{\bullet}{C}H(NH_2) + Pd(II) + H^+ + CO_2$$

Table 6.12: Effect of chloride ion

[Asp] = 6.0×10^{-3} mol dm^{-3}
[Ce(IV)] = 2.0×10^{-4} mol dm^{-3}
[Pd(II)] = 5.0×10^{-5} mol dm^{-3}

Temp. = 45°C
[H$^+$] = 0.50 mol dm^{-3}
I = 1.0 mol dm^{-3}

[Cl$^-$], mol dm^{-3}	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Time in minutes			**Absorbance**		
0	0.528	0.528	0.528	0.528	0.528
10	0.414	0.416	0.413	0.416	0.414
20	0.325	0.326	0.325	0.326	0.325
30	0.252	0.253	0.252	0.253	0.252
40	0.205	0.206	0.205	0.206	0.205
50	0.168	0.169	0.168	0.169	0.168
60	0.127	0.130	0.127	0.130	0.126
80	0.083	0.086	0.083	0.086	0.083
10^7 (rate), mol dm^{-3}sec^{-1}	**1.28**	**1.27**	**1.28**	**1.27**	**1.28**

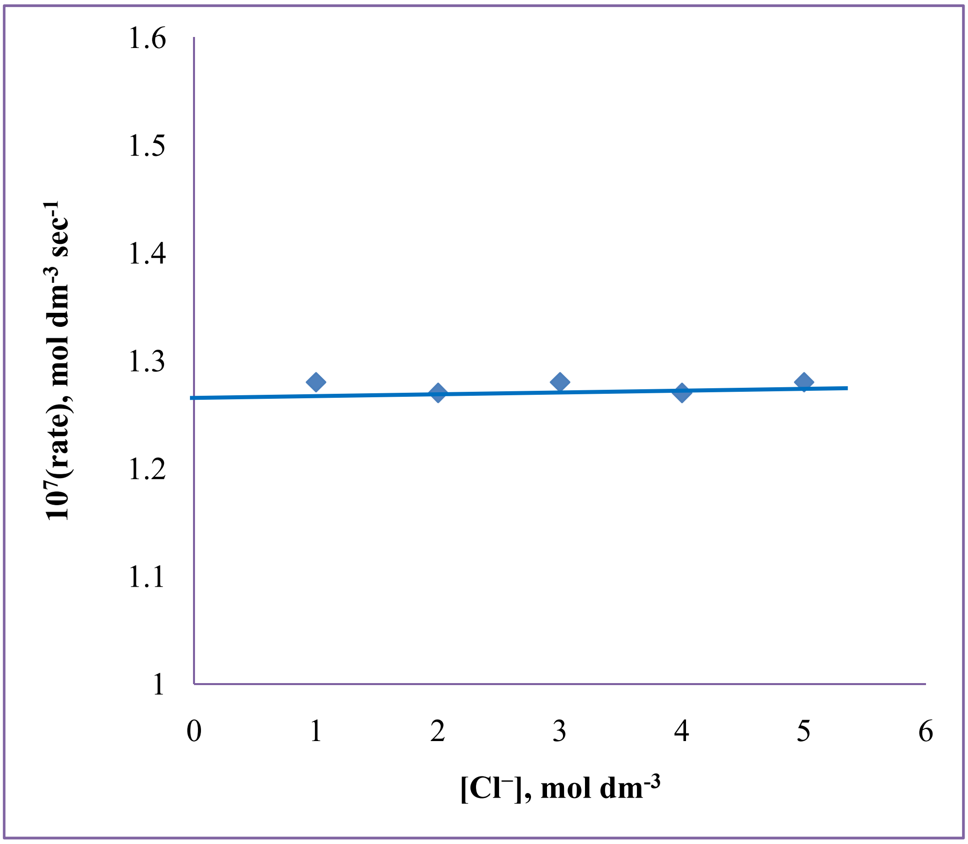


Figure 6.9: Effect of chloride ion

[Ce(IV)] = 2.0×10^{-4} mol dm^{-3};
[Asp] = 6.0×10^{-3} mol dm^{-3};
[Pd(II)] = 5.0×10^{-5} mol dm^{-3};
[H$^+$] = 0.50 mol dm^{-3};
I = 1.0 mol dm^{-3};
Temp. = 45°C

(Ref. Table 6.12)

$$\mathrm{HOOCCH_2\dot{C}H(NH_2) + Ce^{4+} \xrightarrow[H_2O]{fast} Ce^{3+} + HOOCCH_2CHO + NH_3 + H^+}$$

$$\mathrm{HOOCCH_2CHO + 2Ce^{4+} + H_2O \xrightarrow{fast} HOOCCH_2COOH + 2H^+ + 2Ce^{3+}}$$

Scheme-6.1

Scheme 6.1 leads to the following rate law from (9)

$$\text{(rate)} = k\,[\text{Adduct}]\,[\text{Ce(IV)}] \tag{8}$$

$$= \frac{kK_1K_2[\text{Ce(IV)}][\text{Asp}][\text{Pd(II)}]}{[\text{H}^+]} \tag{9}$$

The total concentration of aspartic acid is given by

$$\begin{aligned}[\text{Asp}]_t &= [\text{Asp}]_f + C_1\\ &= [\text{Asp}]_f + K_2\,[\text{Asp}]_f\,[\text{Pd(II)}]\\ &= [\text{Asp}]_f\,\{1 + K_2[\text{Pd(II)}]\}\end{aligned}$$

Therefore

$$[\text{Asp}]_f = \frac{[\text{Asp}]_t}{1 + K_2[\text{Pd(II)}]} \tag{10}$$

Where the subscripts ‘t’ and ‘f’ stand for total and free respectively.

In the present investigation the concentration of catalyst Pd(II) is very low, so term K_2[Pd(II)] can be ignored in comparison to unity in equation (10)

$$[\text{Asp}]_f = [\text{Asp}]_t \tag{11}$$

Similarly,

$$\begin{aligned}[\text{Pd(II)}]_t &= [\text{Pd(II)}]_f + K_2\,[\text{Asp}]\,[\text{Pd(II)}]_f\\ &= [\text{Pd(II)}]_f\,\{1 + K_2[\text{Asp}]\}\end{aligned}$$

So

$$[\text{Pd(II)}]_f = \frac{[\text{Pd(II)}]_t}{1 + K_2[\text{Asp}]} \tag{12}$$

and

$$\begin{aligned}[\text{Ce(IV)}]_t &= [\text{Ce(IV)}]_f + [\text{Ce(IV)}]_f\,[\text{H}^+]\\ &= [\text{Ce(IV)}]_f + K_1\frac{[\text{Ce(IV)}]_f}{[\text{H}^+]}\end{aligned}$$

$$= [\mathrm{Ce(IV)}]_f \left\{1 + \frac{K_1}{[\mathrm{H}^+]}\right\}$$

So

$$[\mathrm{Ce(IV)}]_f = \frac{[\mathrm{Ce(IV)}]_t}{1 + K_1/[\mathrm{H}^+]} \tag{13}$$

The value of $[\mathrm{Asp}]_f$, $[\mathrm{Pd(II)}]_f$, $[\mathrm{Ce}^{IV}]_f$ substituting in to equation (9) and omitting the subscripts, we have

$$\text{rate} = \frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{k\,K_1K_2\,[\mathrm{Ce(IV)}][\mathrm{Asp}][\mathrm{Pd(II)}]}{[\mathrm{H}^+] + K_1 + K_2[\mathrm{Asp}][\mathrm{H}^+] + K_1K_2[\mathrm{Asp}]} \tag{14}$$

The rate law (14) may be rearranged to equation (15)

$$\frac{[\mathrm{Ce(IV)}][\mathrm{Pd(II)}]}{\text{rate}} = \frac{[\mathrm{H}^+]}{k\,K_1K_2[\mathrm{Asp}]} + \frac{1}{kK_2[\mathrm{Asp}]} + \frac{[\mathrm{H}^+]}{k\,K_1} + \frac{1}{k} \tag{15}$$

According to equation (15) the plots of [Ce(IV)][Pd(II)] /rate versus 1/[Asp] and [Ce(IV)][Pd(II)]/rate versus $[\mathrm{H}^+]$ should be linear **(Figure 6.10 and 6.11)**. From the plot of [Ce(IV)][Pd(II)]/rate versus 1/[Asp]

$$(\mathrm{Slope})_1 = \frac{[\mathrm{H}^+]}{kK_1K_2} + \frac{1}{kK_2} \tag{16}$$

$$(\mathrm{Intercept})_1 = \frac{[\mathrm{H}^+]}{kK_1} + \frac{1}{k} \tag{17}$$

Where K_2 is the formation constant for adduct (C_1)

From the plot [Ce(IV)][Pd(II)]/ rate versus $[\mathrm{H}^+]$

$$(\mathrm{Slope})_2 = \frac{1}{kK_1K_2[\mathrm{Asp}]} + \frac{1}{kK_1} \tag{18}$$

$$= \frac{1}{kK_1}\left[\frac{1 + K_2[\mathrm{Asp}]}{K_2[\mathrm{Asp}]}\right]$$

$$(\mathrm{Intercept})_2 = \frac{1}{kK_2[\mathrm{Asp}]} + \frac{1}{k} \tag{19}$$

$$= \frac{1}{k}\left[\frac{1 + K_2[\mathrm{Asp}]}{K_2[\mathrm{Asp}]}\right] \tag{20}$$

Hence,

$$\frac{(\mathrm{Intercept})_2}{(\mathrm{Slope})_2} = K_1 \tag{21}$$

Where K_1 is the ionisation constant of $Ce^{4+}.H^+$.

Substituting the value of K_1 and $[H^+]$ in equation (17), we obtained the value of k, the rate constant with respect to slow step of scheme 6.1. The value of k, K_1 and K_2 are 24 ± 1 dm^3 mol^{-1} s^{-1}, 0.75 ± 0.02 mol dm^{-3} and $189 + 10$ dm^3 mol^{-1} respectively. The value of K_1 (0.72 mol dm^{-3}) is in good agreement with the literature**[45]**.

The rate of reaction was studied at 40°C, 45°C and 50°C with different concentrations of aspartic acid and sulphuric acid. The rate of reaction increases with increase in temperature. The rate constants (k) of slow step of scheme 6.1 were obtained from the intercepts and slopes of the plots of [Ce(IV)][Pd(II)]/rate versus1/[Asp] and [Ce(IV)][Pd(II)]/rate versus $[H^+]$ at three different temperatures **(Figure 6.10 and 6.11)**. The activation parameters were obtained from a plot of log k versus 1/T **(Figure 6.12)**. Results are given in **Table 6.13**. The ionisation constant (K_1) of the first step of scheme 6.1 was evaluated from $(\text{intercept})_2$ / $(\text{slope})_2$ of the plot of [Ce(IV)][Pd(II)]/rate versus $[H^+]$ at the three different temperatures. Similarly, the formation constant (K_2) of the complex of the second step of scheme 6.1 was obtained from $(\text{intercept})_1/(\text{slope})_1$ of the plot of [Ce(IV)][Pd(II)]/rate versus1/[Asp]. Thermodynamic quantities were calculated from the plots of log K_1 versus 1/T and log K_2 versus 1/T at three different temperature **(Table 6.13)**. It is a known fact**[46]** that for reaction between ions of opposite charges there is generally an increase in entropy is going from reactants to activated complex and for ions of like charges, there is an entropy decrease. In the present study, efforts were made to study the catalyst role of Pd(II) in oxidation of aspartic acid by Ce(IV) in acidic medium. Observed negative entropy of activation **(Table 6.13)** in oxidation of aspartic acid is clearly supports reaction scheme 6.1, where in the rate determining step the interaction between two similarly charged species results in the formation of very reactive adduct (C_1).

In the present study $Ce(SO_4)_2$ is most likely to be the active species of the oxidant cerium(IV). Therefore the terms of active species in the the rate law (14) changes in the below form.

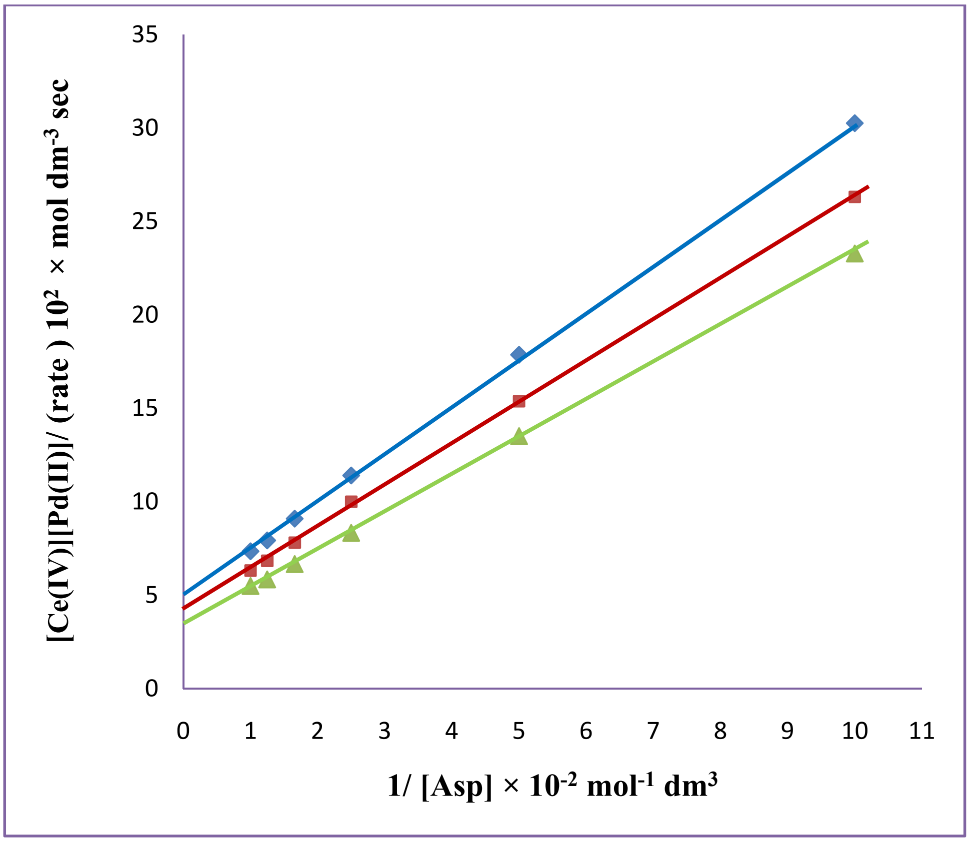


Figure 6.10: Plot of [Ce(IV)][Pd(II)] / (rate) versus 1 / [Asp] at three temperatures

[Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3};   [H^+] = 0.50 mol dm^{-3};

[Pd(II)] = 5.0 × 10^{-5} mol dm^{-3};   I = 1.0 mol dm^{-3},

Temp. = (◆) 40°C, (■) 45°C, (▲) 50°C.

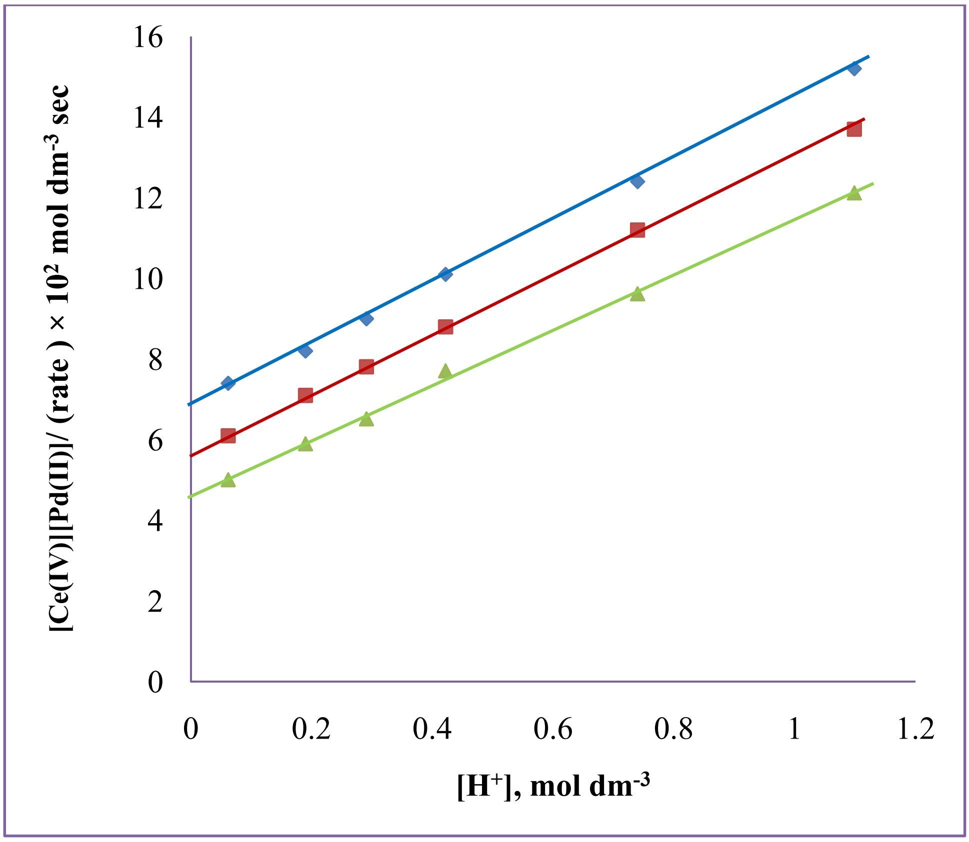


Figure 6.11: Plot of [Ce(IV)][Pd(II)] /(rate) versus $[H^+]$ at three temperatures

[Ce(IV)] = 2.0 × 10^{-4} mol dm^{-3}; [Asp] = 6.0 × 10^{-3} mol dm^{-3};

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

Temp. = (◆) 40° C; (■) 45° C; (▲) 50° C

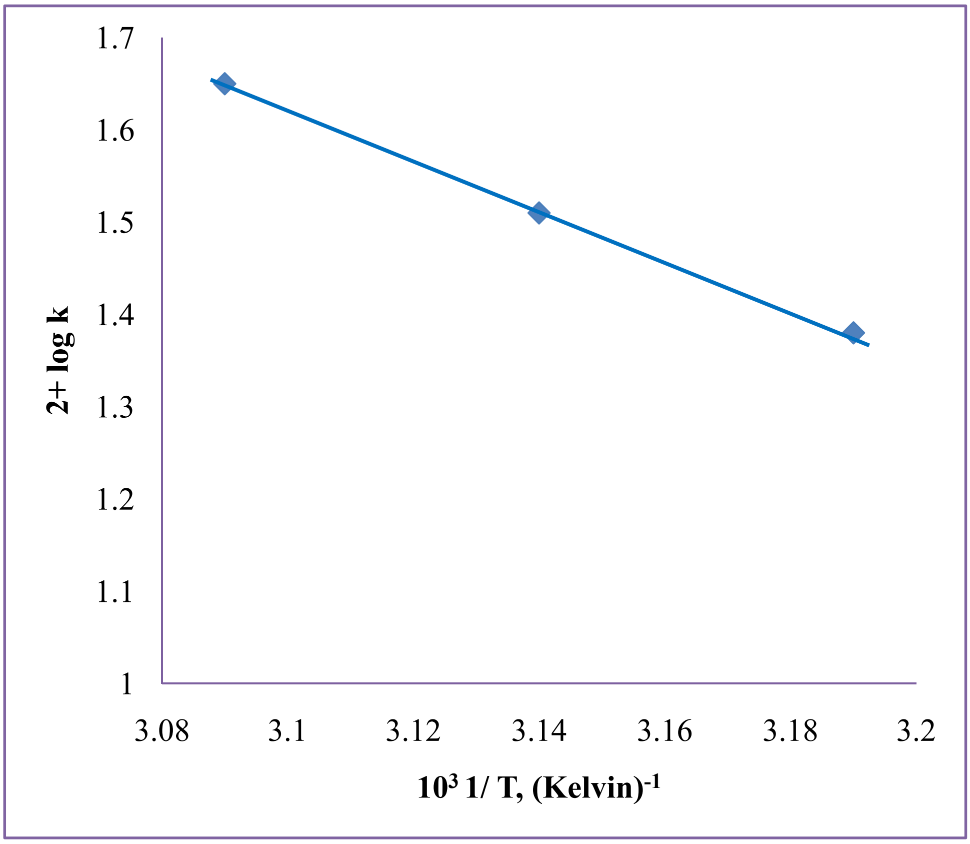


Figure 6.12: A plot of log k versus 1/T

Table 6.13: Effect of temperature on Pd(II) catalysed oxidation of aspartic acid by cerium(IV) in aqueous sulphuric acid medium

Temperature (K)	**K_1(mol dm^{-3})**	**K_2 (dm^3 mol^{-1})**
313	0.90	219
318	0.75	189
323	0.65	153
Thermodynamic Quantities	**Values from K_1**	**Values from K_2**
ΔS (J K^{-1} mol^{-1})	−161.08	−117.66
ΔG (k J mol^{-1})	23.65	10.61
ΔH (k J mol^{-1})	−27.57	−26.80
Temperature (K)	**10^2 k (mol^{-1} dm^{3}sec^{-1})**	**Activation Parameters**
313	24.50	E_a (k J mol^{-1}) = 49.78
318	33.04	$\Delta H^{\#}$ (k J mol^{-1}) = 47.86
323	45.24	$\Delta S^{\#}$ (J K^{-1} mol^{-1}) = −59.85
		$\Delta G^{\#}$ (k J mol^{-1}) = 66.89

$$\text{rate} = \frac{k\, K_1 K_2\, [\text{Ce(SO}_4)_2][\text{Asp}][\text{Pd(II)}]}{[\text{H}^+] + K_1 + K_2[\text{Asp}][\text{H}^+] + K_1 K_2[\text{Asp}]} \tag{22}$$

But,

$$[\text{Ce(SO}_4)_2] = \beta_2[\text{Ce}^{4+}][\text{SO}_4^{2-}]^2 \tag{23}$$

$[\text{Ce}^{4+}]_f$ from equation (7) in equation (22)

$$[\text{Ce(SO}_4)_2] = \frac{\beta_2[\text{Ce}^{4+}][\text{SO}_4^{2-}]^2}{\begin{array}{l}1 + (K_{\text{OH}}/[\text{H}^+]) + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^2[\text{HSO}_4^-] \\ + \beta_4[\text{SO}_4^{2-}]^2[\text{HSO}_4^-]^2[\text{H}^+]\end{array}} \tag{24}$$

Substituting equation (24) in to equation (22) and omitting subscripts.

$$\text{rate} = \frac{\beta_2\, k\, K_1 K_2\, [\text{Ce}^{4+}][\text{SO}_4^{2-}]^2[\text{Pd}^{2+}]}{[\text{H}^+] + K_1 + K_2[\text{H}^+] + K_1 K_2} \times \frac{1}{[X]}$$

Where,

$$\begin{aligned}[X] = {} & 1 + (K_{\text{OH}}/[\text{H}^+]) + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^2[\text{HSO}_4^-] \\ & + \beta_4[\text{SO}_4^{2-}]^2[\text{HSO}_4^-]^2[\text{H}^+]\end{aligned}$$

the rate of reaction is unaffected by the ionic strength is consistent with the reaction between neutral and charged species as in scheme 6.1, which confirms $\text{Ce(SO}_4)_2$ as the kinetically active species in present study.

6.5 Conclusion

The oxidation of aspartic acid by cerium(IV) experienced a slow reaction rate in acidic media, but increased in rate in the presence of the Pd(II) catalyst. The reactive species for the oxidation of cerium(IV) in acidic medium was $\text{Ce(SO}_4)_2$, although other species might be active to a much lesser extent. The rate constant of a slow step and other equilibrium constants involved in the mechanism were evaluated. Mechanism consistent with observed rate laws have been suggested. The results were explained by plausible mechanism and the related rate law was deduced. It can be stated that palladium(II) acts as an efficient catalyst for the oxidation of aspartic acid by cerium(IV) in acidic media.

6.6 References

1. A. Fawzy, ***Carbohydr. Polym.,*** **138,** 356, 2016.
2. M. Bolattin, M. Meti, S. T. Nandibewoor and S. A. Chimatadar, ***J. Sol. Chem.,*** **44,** 152, 2015.
3. D. V. Naik, K. S. Byadagi, S. T. Nandibewoor and S. A. Chimatadar, ***Monatsh. Chem.,*** **144,** 1307, 2013.
4. A. Fawzy, I. A. Zaafarany, F. A. Tirkistani, A. Al-Bonayan and F. A. Aljiffrey, ***Am. J. Phys. Chem.,*** **5,** 10, 2016.
5. M. K. Ghosh and S. K. Rajput, ***Am. Chem. Sci. J.,*** **4,** 383, 2014.
6. P. K. Tondon, M. Srivastava, S. Kumar and S. Singh, ***J. Mol. Catal. A: Chemical,*** **304,** 101, 2009.
7. S. A. Chimatdar, S. T. Nandibewoor, S. I. Mahatesh and J. R. Raju, ***J. Chem. Soc., Dalton Trans.,*** **573**, 1987.
8. S. T. Nandibewoor, S. B. Koujalagi and S. T. Nandibewoor, ***Trans. Met. Chem.,*** **26,** 241, 2001.
9. J. Kiwi, M. Gratzel and G. Blondeel, ***J. Chem. Soc., Dalton Trans.,*** **2215,** 1983.
10. R. V. Nadh, B. S. Sundar and P. S. Radhakrishnamurti, ***Asian J. Chem.,*** **9,** 515, 1997.
11. T. Sumathi, P. S. Sundaram, G. Chandarmohan, D. Deepa and R. Renganathan, ***Int. J. Chem. Sci., Tech.,*** **2,** 44, 2012.
12. P. K. Tandon, S. Sahgal, A. K. Singh and M. Dushia, ***J. Mol. Catal. A: Chemical,*** **258,** 320, 2009.
13. R. Shukla, S. Rani and I. C. Tewari, ***Int. J. Chem. Res.,*** **4,** 122, 2012.
14. R. L. Carroll and L. B. Thomas, ***J. Am. Chem. Soc.,*** **88,** 1376, 1966.
15. M. Sanjana, A. K. Patnaik, S. K. Badamali and P. Mohanty, ***J. Chem.,*** 7, 2013.
16. H. J. Bibert, ***"Basic Concepts in Biochemistry",*** Beijing, Perking University Medical Press, 188, 2002.
17. R. Sailani, M. Sharma, D. Pareeek, C. L. Khandewal and P. D. Sharma, ***React. Kinet. Mech. Catal.,*** **105,** 249, 2012.

18. B. S. Sherigara, K. I. Bhat, I. Pinto and N. M. M. Gowda, ***Int. J. Chem. Kinet.,*** **27,** 675, 1995.
19. S. Y. Hua, J. H. Shan, C. Y. Song, S. G. Shen and H. W. Sun, ***J. Iran.Chem. Soc,*** **4,** 414, 2007.
20. I. Sharma, V. Devra, D. Gupta, C. M. Gangwal and P. D. Sharma, ***Int. J. Chem. Kinet.,*** **27,** 1995.
21. A. K. Singh, ***Asian J. Chem.,*** **15,** 1313, 2003.
22. A. Fawzy and I. Althagafi, ***Am. J. Chem, Eng.,*** **4,** 23, 2016.
23. S. Mathur, M. B. Yadav and V. Devra, ***Int. J. Innov. Bio. Chem. Sci.,*** **6,** 23, 2015.
24. R. V. Nadh and M. Sireesha, ***Bul. Chem. Commun.,*** **47,** 13, 2015.
25. D. Bilehal, R. Kulkarni and S. Nandibewoor, ***J. Mol. Catal., A: Chemical,*** **232,** 21, 2005.
26. A. Goel, R. Sharma and R. Lasyal, ***Int. J. Sci. Eng. Res.,*** **4,** 1978, 2013.
27. J. Tsuji**, *"Palladium Reagents and Catalysis-New Perspective for the 21st century",*** John Wiley & Sons Ltd, Chichester**,** 2, 2004.
28. C. E. Garrett and K. Prasad, ***Adv. Synth. Catal.,*** 346, 889, 2004.
29. A. Zapf and M. Beller, ***Top. Catal.,*** **19,**101, 2002.
30. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, ***Ind. J. Chem.,*** **41A,** 316, 2002.
31. A. K. Singh, J. Jaiswal, R. A. Singh and K. Singh, ***Asian J. Chem.,*** **21,** 858, 2009.
32. K. M. Gligorich and M .S. Sigman, ***Chem. Commun.,*** 3854, 2009.
33. G. S. Zenbach, and H. Flaschka, ***"Complexometric titrations"*** (Methuen and Co., Landon), 250, 1969.
34. S. A. Chimatadar, S. V. Madawale and S. T. Nandibewoor, ***Transit. Met. Chem.,*** **32,** 634, 2007.
35. K. J. Laidler, ***"Chemical kinetics",*** 3rd edn., Pearson Education Pvt. Ltd., New Delhi, 19, 2004.
36. J. Casdo, M. A. Quintella and F. M. Barral, ***J.Chem. Edu.,*** **63,** 450.

37. G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denney, "***Vogel's Text Book of Quantitative Organic Analysis,*** 5th edn., ELBS, Longman, Essex, England", 381, 1996.
38. S. A. Chimatadar, S. T. Nandibewoor and J. R. Raju, ***Ind. J. Chem.,*** **28A,** 902, 1989.
39. R. K. Patil, S. A. Chimatadar and S. T. Nandibewoor, ***Transit. Met. Chem.,*** **33,** 625, 2008.
40. F. Y. Kulba, B. Y. Yakovlev and V. E. Mironov, ***Russ. J. Inorg. Chem.,*** **10,** 1113, 1965.
41. K. T. Bugaenko and K. Huang, ***Russ. J. Inog. Chem.,*** **8,** 1299, 1963.
42. S. E. Kharzeoua and V. V. Serebrennikou, ***Russ. J. Inorg. Chem.,*** **12,** 1601, 1967.
43. K. K. Sengupta, ***J. Ind. Chem. Soc.,*** **42,** 725, 1965.
44. R. N. Mehrotra and S. Ghosh, ***Z. Phys. Chem.,*** **231,** 91, 1966.
45. A. P. Savanur, S. T. Nandibewoor and S. A. Chimatadar, ***Transit. Met. Chem.,*** **34,** 711, 2009.
46. A. Frost and R. G. Pearson, ***"Kinetics and Mechanism",*** 2nd edn, John Wiley and Son's, Inc., 143, 1961.

Research Publications

Research Papers

1. "Kinetics and Mechanism of Chromium (VI) Oxidation of Threonine in Aqueous Perchloric Acid Medium", Shanu Mathur, **Dhan Raj**, Manju Bala Yadav, Vijay Devra, International Journal of Innovative Research in Science, Engineering and Technology, 3 (11), 17468-17474, 2014.

2. "Oxidation of Leucine by Cerium(IV) in Presence of Manganese(II) as a Catalyst in Sulphuric Acid Medium", **Dhan Raj,** Shanu Mathur, Manju Bala Yadav, Vijay Devra, International Journal of Research in Physical Chemistry, 5 (2), 11-16, 2015.

3. "Kinetics and Mechanism of the Reaction of Valine with Ceric Ion in the Presence of Palladium(II) Catalyst in Acid Media", **Dhan Raj,** Shanu Mathur, Manju Bala Yadav, Vijay Devra, International Journal of Research in Physical Chemistry, 5 (2), 11-16, 2015.

4. "Kinetic and Mechanistic Study of Oxidation of Serine by Cerium(IV) in Presence of Manganese(II) as Catalyst in Aqueous Acid Medium" **Dhan Raj**, Manju Bala Yadav, Vijay Devra, International Journal of Current Research in Chemistry and Pharmaceutical Sciences, 2(11), 1-8, 2015.

5. "A Kinetics and Mechanistic Study of Palladium(II) Catalysed Oxidation of Arginine by Cerium(IV) in Acid Media", **Dhan Raj,** Manju Bala Yadav, Vijay Devra, International Journal of Innovative Research in Science, Engineering and Technology, 4 (7), 5283-5291, 2015.

Participated/Papers Presented in National/International Conferences

1. "Kinetics and Mechanism of Oxidation of L-Valine by Osmium(VIII) in Aqueous Alkaline Medium", **Dhan Raj,** Shanu Mathur, Manju Bala Yadav, Vijay Devra. Presented a Research Paper in **3rd International Conference on Advance Trends in Engineering and Technology and Research (ICATETTR-2014)** at Bal Krishna Institute of Technology, Ranpur, Kota, Rajasthan during 22nd to 24th December, 2014.

2. **Dhan Raj,** S. K. Meena. Presented a paper in **National Conference on Modern Trends in Chemical Sciences" (MTCS-2016)** at Mohan Lal Sukhadia University, Udaipur during 30th -31th January 2016.

3. **Dhan Raj** Participated in **National Conference on Sustainable Chemical and Material Science (SCMS-2016)** held at S. S. Jain Subodh P. G. (Autonomous) College, Jaipur on 5th-6th August 2016.

4. "Mn(II) Catalysed Oxidation of Arginine by Ce(IV) in aqueous acidic medium: a kinetic and mechanistic study". **Dhan Raj,** Rashmi Gupta and Manju Bala Yadav. Presented a Poster in **National Conference on (ACEBS-2016)** at Merra Girls College Udaipur, held on 10th September 2016.

5. **Dhan Raj** Participated in **Symposium on Physical Methods in Chemical Sciences (RSC)** held at Pacific Academy of Higher Education and Research University, Udaipur on 2nd – 3rd October 2016.

6. **Dhan Raj** Presented a poster in **National Conference on Frontier in Chemical Sciences** held at Pacific Academy of Higher Education and Research University, Udaipur on 2nd – 3rd October 2016.