

KINETICS AND MECHANISM OF THE REACTION OF VALINE WITH CERIC ION IN THE PRESENCE OF PALLADIUM(II) CATALYST IN ACID MEDIA

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ABSTRACT

The reaction of valine 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 [H₂SO₄] 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.

Keywords : Kinetics, Mechanism, Cerium(IV), Valine, Palladium(II) catalysis, Sulphuric acid medium.

INTRODUCTION

Cerium(IV), an unusually strong one electron oxidant has been frequently used from the synthetic point of view¹. 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 chemistry²⁻⁵. The oxidation of variety of organic and inorganic compounds by cerium(IV) in acidic media has been the subject of several studies²⁻⁴. 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 produced⁶⁻⁷.

L-Valine is an essential, non-polar, aliphatic amino acid used to hold proteins 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 reactions⁸⁻¹², but the nature of its active form in reactions remain obscure. This prompted us to indicate systematic study of kinetics of palladium(II) catalysed oxidation of valine by acidic solution of cerium(IV) with a view to formulate the mechanistic steps and to know the active form of palladium(II) and cerium(IV) in acidic medium.

MATERIAL AND METHOD

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. Palladium(II) chloride was prepared in HCl (0.20 mol dm⁻³) and assayed by complexometric titration¹³. Other chemicals and

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reagents such as sodium sulphate, sulphuric acid, acetonitrile used were of analytical grade.

Table 1. EFFECT OF CERIUM(IV), VALINE, [H⁺] AND Pd(II) ON Pd(II) CATALYSED OXIDATION OF VALINE BY Ce(IV) IN AQUEOUS SULPHURIC ACID MEDIUM AT 45°C

10^4 [Ce(IV)] mol dm ⁻³	10^3 [Val] mol dm ⁻³	10^5 [Pd(II)] mol dm ⁻³	[H ⁺] mol dm ⁻³	10^4 k _{obs} , sec ⁻¹
0.50	5.0	5.0	1.0	4.43
1.0	5.0	5.0	1.0	4.41
2.0	5.0	5.0	1.0	4.41
3.0	5.0	5.0	1.0	4.45
4.0	5.0	5.0	1.0	4.41
5.0	5.0	5.0	1.0	4.41
5.0	1.0	5.0	1.0	1.72
5.0	2.0	5.0	1.0	2.78
5.0	3.0	5.0	1.0	3.45
5.0	4.0	5.0	1.0	4.17
5.0	5.0	5.0	1.0	4.41
5.0	6.0	5.0	1.0	4.79
5.0	7.0	5.0	1.0	4.98
5.0	8.0	5.0	1.0	5.18
5.0	9.0	5.0	1.0	5.37
5.0	10.0	5.0	1.0	5.46
5.0	5.0	1.0	1.0	0.86
5.0	5.0	2.0	1.0	1.63
5.0	5.0	3.0	1.0	2.68
5.0	5.0	4.0	1.0	3.45
5.0	5.0	5.0	1.0	4.41
5.0	5.0	6.0	1.0	5.37
5.0	5.0	7.0	1.0	6.04
5.0	5.0	8.0	1.0	7.00
5.0	5.0	9.0	1.0	7.86
5.0	5.0	10.0	1.0	8.82
5.0	5.0	5.0	0.20	1.82
5.0	5.0	5.0	0.40	2.78
5.0	5.0	5.0	0.60	3.26
5.0	5.0	5.0	0.80	3.83
5.0	5.0	5.0	1.0	4.41

Table 2. EFFECT OF TEMPERATURE ON THE REACTION BETWEEN CERIUM(IV) AND VALINE CATALYSED BY PALLADIUM(II) IN SULPHURIC ACID MEDIUM

Temp (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	ΔS [#] (JK ⁻¹ mol ⁻¹) = -84.55	215	ΔS(J K ⁻¹ mol ⁻¹) = -65.03
323	10.0	ΔG [#] (kJ mol ⁻¹) = 72.83	243	ΔG(kJ mol ⁻¹) = 62.79
		log A = 8.45		

Kinetic measurements

The kinetics were followed at 45 ± 1°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 in a 1 cm cell placed in the thermostated compartment of a Systronics(166) UV-Visible spectrophotometer. 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 ε = 2622 dm³mol⁻¹cm⁻¹. k_{obs} were obtained from the plot of log absorbance versus time.

RESULTS AND DISCUSSION

Effect of cerium(IV)

The reaction rate was measured with various [Ce(IV)] = 5 × 10⁻⁵ to 5 × 10⁻⁴ mol dm⁻³ at fixed [Val] = 5 × 10⁻³ mol dm⁻³, [H⁺] = 1.0 mol dm⁻³, [Na₂SO₄] = 0.5 mol dm⁻³, [Pd(II)] = 5 × 10⁻⁵ mol dm⁻³ and temp. = 45°C. The plot of log absorbance versus time was linear (Fig. 1) indicating that the reaction is first order with respect to [Ce(IV)]. The pseudo first order rate constant k_{obs} are independent of the [Ce(IV)].

Effect of valine

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, [Na₂SO₄] = 0.5 mol dm⁻³, [Pd(II)] = 5 × 10⁻⁵ mol dm⁻³ and temp. = 45°C, k_{obs} increases with the increase of [Val]. 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 excellent linearity (Fig. 2) with

positive intercept and slope.

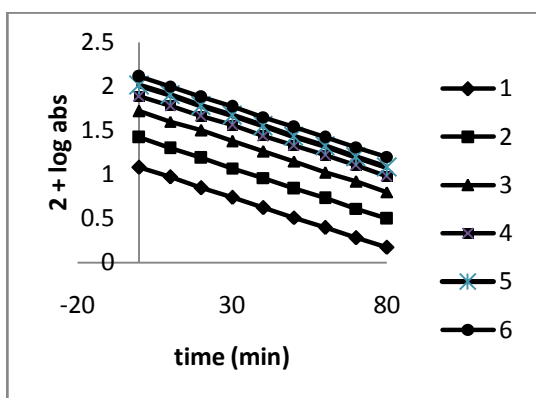


Fig. 1 Pseudo First Order Plots for The Variation Of Cerium(IV)

[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, [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.

Effect of [H⁺]

The reaction rate were measured with various [H⁺] = 0.2 to 1.0 mol dm⁻³ at fixed [HSO₄⁻], ([HSO₄⁻] = 1.0 mol dm⁻³ from H₂SO₄ and NaHSO₄), [Val] =

Effect of [HSO₄⁻]

[HSO₄⁻] was varied in the range of 0.2 to 1.0 mol dm⁻³ at fixed [H⁺] = 0.2 mol dm⁻³, [Ce(IV)], [Val], [Pd(II)], [I] and temperature. Here HSO₄⁻ ≈ [NaHSO₄] + [H₂SO₄], ignoring the dissociation of [HSO₄⁻] in strongly acidic medium. k_{obs} decreases with increase of [HSO₄⁻]. Therefore HSO₄⁻ shows a rate retarding effect (Fig. 3).

Effect of Pd(II) dependence

At fixed [Ce(IV)], [Val], [H₂SO₄] and [I], 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. k_{obs} increases with the increase of [Pd(II)]. Observed reaction order of palladium(II) can be obtained from the plot of log k_{obs} versus log [Pd(II)] is 1.0, indicates that the reaction is of first order with respect to [Pd(II)]. $1/k_{obs}$ versus $1/[Pd(II)]$ yielded good linear plots (Fig. 4) passing through the origin.

Effect of ionic strength

At fixed concentration of [Ce(IV)], [Val], Pd(II), [H₂SO₄] and temperature, the ionic strength was varied from 1.2 to 2.0 mol dm⁻³, it is found that ionic strength has slightly affected the rate of reaction.

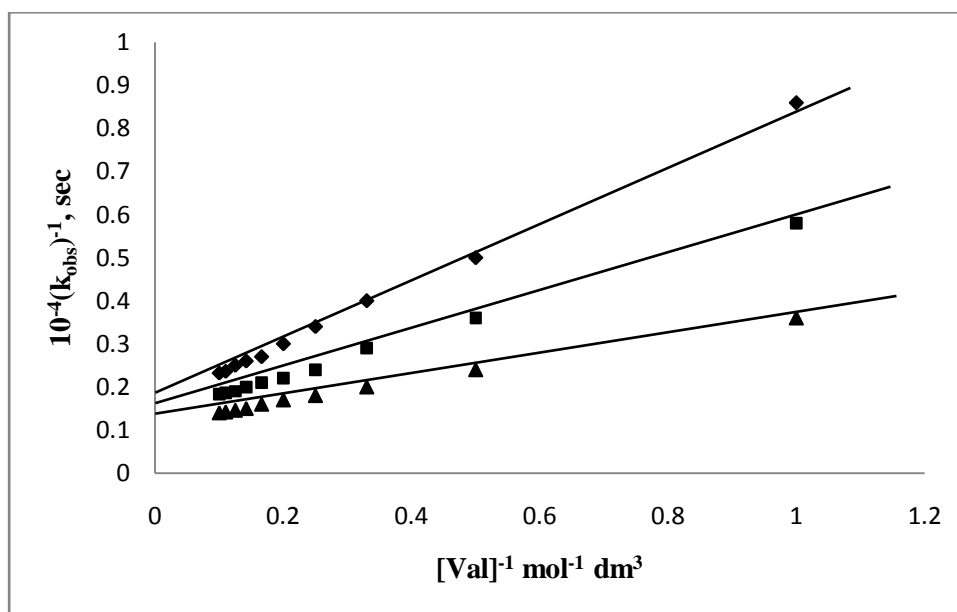


Fig. 2 A Plot of $(k_{obs})^{-1}$ versus $[Val]^{-1}$

[Ce(IV)] = 5.0×10^{-4} 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. = (◆) 40°C, (■) 45°C, (▲) 50°C.

5×10^{-3} mol dm⁻³, [Ce(IV)] = 5×10^{-5} 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⁺], 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⁺].

Effect of Cl⁻

At fixed concentrations of [Ce(IV)], [Val], [Pd(II)], [H₂SO₄] and temperature, the concentration of Cl⁻ was varied from 1×10^{-4} to

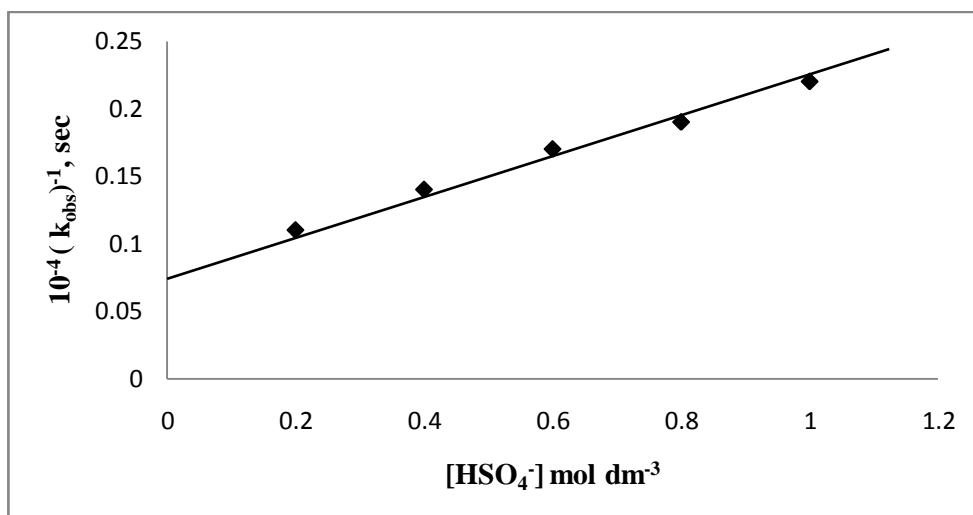


Fig. 3 A Plot of $(k_{\text{obs}})^{-1}$ versus $[\text{HSO}_4^-]$

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Pd(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Val}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, Temp = 45 °C

$5 \times 10^{-4} \text{ mol dm}^{-3}$. The rate was unaffected by the addition of Cl^- ions.

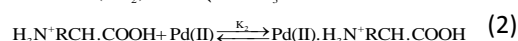
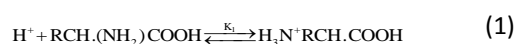
Mechanism

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. In most of the studies using palladium(II) as homogenous catalyst, it has been employed in the form of palladium(II) chloride. Palladium(II) chloride is rather insoluble in aqueous solution but is soluble in hydrochloric acid and exists¹⁴⁻¹⁵ as $[\text{PdCl}_4]^{2-}$, according to the equilibrium¹⁶.



The existence of PdCl_2 exclusively in the form of $[\text{PdCl}_4]^{2-}$ is also supported by¹⁷, 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), $[\text{PdCl}_4]^{2-}$. Since throughout the experiments, ratio of Cl^- ion to palladium(II) chloride concentration i.e. $\text{Cl}^- / [\text{PdCl}_4]^{2-}$ was maintained more than 2, it is reasonable to assume that the species $[\text{PdCl}_4]^{2-}$ is the sole palladium(II) species in HCl ¹⁸⁻¹⁹.

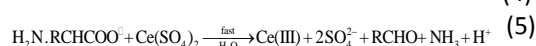
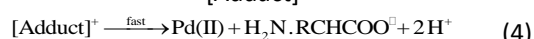
The observed fractional order with respect to valine indicate that there is possibility of complex formation between $[\text{PdCl}_4]^{2-}$ and valine in the first pre-equilibrium step. Valine is easily protonized in acid media, indicating the involvement of H^+ in the reaction in the pre-equilibrium step. $\text{Ce}(\text{SO}_4)_2$ has been found kinetically active in this study with generation of free radicals in the reaction. On the basis of above kinetic results, a probable reaction mechanism has been proposed. (Scheme-1)



[Adduct]



[Adduct]⁺



Scheme 1

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

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

Where $K = K_1 K_2$

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

Rearrangement of eqⁿ (7)

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

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

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

Equation (7) suggest that order with respect to palladium(II) is 1.0, less than one in valine and less than one in $[\text{H}^+]$, which is consistent with the result of our experiments. Equation (8) suggest that $1/k_{\text{obs}}$ versus $1/[\text{Pd(II)}]$ at constant $[\text{Val}]$, $[\text{H}^+]$ should yield good linear plots through the origin (Fig. 4). Eqⁿ (9) suggests that $1/k_{\text{obs}}$ versus $1/[\text{Val}]$ at fixed

[Pd(II)] and [H⁺] should be linear plots with positive intercept (Fig. 2). Eqⁿ (10) suggests that the plot of 1/ k_{obs} versus 1/ [H⁺] at constant [Pd(II)] and [Val] should also be linear.

Equation (16) may be written as

$$k_{\text{obs}} = \frac{C}{1 + Q_3[\text{HSO}_4^-]} \quad (16)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{C} + \frac{Q_3[\text{HSO}_4^-]}{C} \quad (17)$$

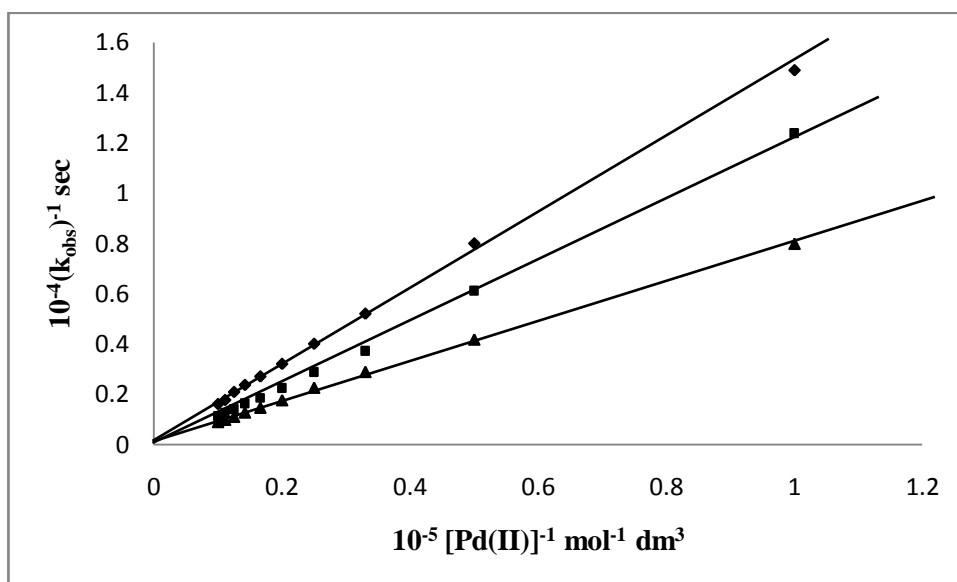
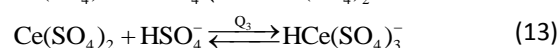
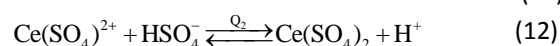
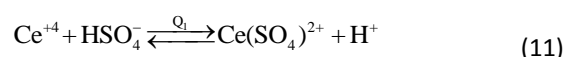


Fig. 4 A Plot of $(k_{\text{obs}})^{-1}$ versus $[\text{Pd(II)}]^{-1}$
 $[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Val}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, $I = 1.50 \text{ mol dm}^{-3}$,
 Temp. = (♦) 40°C, (■) 45°C, (▲) 50°C

Under the experimental conditions in aqueous sulphuric acid medium, the important Ce(IV) sulphato complexes are $\text{Ce}(\text{SO}_4)^{2+}$, $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3^-$ and relevant equilibria are²⁰



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 (Fig. 3) can be explained by assuming $\text{Ce}(\text{SO}_4)_2$ as the reactive species. The concentration of this active species is given by equation (14)

$$[\text{Ce}(\text{SO}_4)_2] = \frac{[\text{Ce(IV)}]_{\text{T}}}{1 + Q_3[\text{HSO}_4^-]} \quad (14)$$

$$= f [\text{Ce(IV)}]_{\text{T}}$$

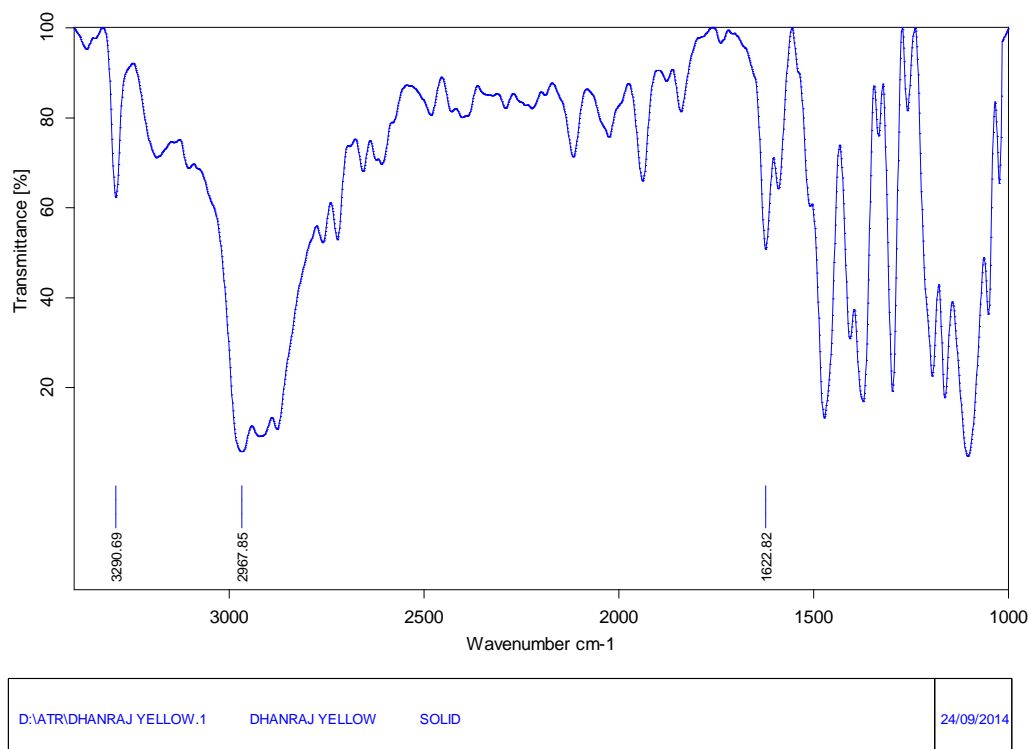
Thus equation (7) can be written as

$$k_{\text{obs}} = \frac{2kK[\text{Pd(II)}][\text{Val}][\text{H}^+]}{[K[\text{Val}][\text{H}^+] + 1][1 + Q_3[\text{HSO}_4^-]} \quad (15)$$

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

Equation (17) suggest that $1/k_{\text{obs}}$ versus $[\text{HSO}_4^-]$ 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 $1/k_{\text{obs}}$ versus $[\text{HSO}_4^-]$ (Fig. 3), 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 value²⁰⁻²¹. All the above results show that $\text{Ce}(\text{SO}_4)_2$ 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 $\text{Ce}(\text{SO}_4)_2$ as the kinetically active species in present study.

From equation (9), it can be seen that the intercept of the linear plot of $1/k_{\text{obs}}$ versus $1/[\text{Val}]$ is $1/2k[\text{Pd(II)}]$ and the slope is $1/2kK[\text{Pd(II)}][\text{H}^+]$. From the intercept and slope in Fig.-2, rate constants (k) and formation constants (K) at different temperature have been evaluated. Data in Table-2 shows that formation constants (K) increases with increase of temperature, indicating that the reaction is an endothermic reaction, which is consistent with $\Delta H^\ddagger > 0$. This supports the proposed mechanism. Activation parameters of rate determining step have been evaluated as $E_a^\ddagger = 45.95 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 42.12 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -84.55 \text{ JK}$



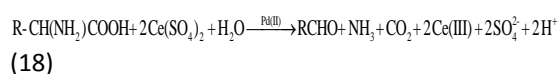
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Fig. 5 FT-IR spectra of the final product

mol^{-1} and $\Delta G^\ddagger = 72.83 \text{ kJ mol}^{-1}$, $\log A = 8.45$ from the linear plot of $\log k$ versus $1/T$.

Stoichiometry and product analysis

Different reaction mixture with different sets of concentrations of reactants where $[\text{Ce(IV)}]$ was in excess over $[\text{Val}]$ at constant conditions of ionic strength, acidity and catalyst were kept at 24h at 45°C . The unreacted $[\text{Ce(IV)}]$ was measured by absorbance at 360 nm. The main products are Ce(III) , 2-methylpropanal, ammonia and CO_2 . 2-methylpropanal was confirmed by the IR spectrum of the corresponding hydryzone (Fig. 5). The reaction mixture was treated with acidified 2,4-dinitrophenyl hydrazine solution, which yielded a hydryzone. Further, aldehyde group was confirmed with qualitative test such as Tollen's reagent²² and Schiff's reagent. Nitrile test was negative, the product generally reported in the oxidation of amino acids. Ammonia was confirmed with Nessler's test. Therefore the stoichiometry of the reaction positive with test of aldehyde can be represented by eqⁿ (18)



Where $\text{R} = (\text{CH}_3)_2\text{CH-}$

ACKNOWLEDGEMENT

The authors are thankful to DST Sponsored FIST lab, Govt. College Kota for providing research facilities.

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