

# A Kinetic and Mechanistic Study of Palladium (II) Catalysed Oxidation of Arginine by Cerium (IV) in Acid Media

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**ABSTRACT:** Kinetics of palladium(II) catalysed oxidation of arginine has been studied by Ce(IV) in acidic medium at 45°C. The reaction show first order kinetics with respect to Ce(IV) and Pd(II) in the oxidation of arginine. The first order kinetics with respect to arginine obtained at its lower concentration changes to zero order at its higher concentration. It is found that pseudo first order rate constant,  $k_{obs}$  decreases with increase of  $[HSO_4^-]$  and increases with the increase of  $[H^+]$ . Various activation parameters have been calculated with the pseudo first order rate constant values observed at three different temperatures. A plausible mechanism has been proposed from the results of kinetic studies, reaction stoichiometry and product analysis.

**KEYWORDS:** Kinetics, Oxidation, Mechanism, Arginine, Palladium(II), Cerium(IV), Sulphuric acid.

## 1. INTRODUCTION

Amino acids residues are the main constituents of proteins and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modifications [1]. A number of uncatalysed [2] and catalysed [3] kinetic studies have been reported on the oxidation of amino acid by different oxidants. The oxidation of biologically important amino acid arginine is very significant because it may reveal the mechanism of amino acid metabolism.

Ce(IV) is a powerful oxidizing agent in acidic medium with the reduction potential in  $HClO_4$  as 1.75 Volts [4]. The oxidizing potentialities of Ce(IV) in  $H_2SO_4$  medium have conclusively been established [5] and oxidant is reported to exist in the form of sulphato species. The oxidation of organic compounds by Ce(IV) usually proceeds via an intermediate complex [6-8].

Transition metals in the higher oxidation state generally can be stabilized by chelation with suitable complex agent. Metal complexes [9-12] such as Ag(III), Cu(II), Ni(IV) and Ce(IV) ions are good oxidants in acid or alkaline media under appropriate reaction condition. However, our preliminary observations indicate that oxidation of some organic compounds by Ce(IV) in aqueous sulphuric acid is kinetically sluggish, and the process can be efficiently catalyzed by various metal ion even at trace concentration. Different metal ion catalysts like palladium(II) [13-14], chromium [15], ruthenium(III) [16], iridium(III) [17], silver(I) [18] etc., have been used in the oxidation by cerium(IV).

Most studies using palladium(II) as catalyst have employed it in the form of palladium(II) chloride and the nature of its active form in such reaction remain obscure. We have investigated the effect of chloride as well as acid on palladium(II) catalysed oxidation of arginine to determine the active species of catalyst and oxidant, and to arrive at a plausible mechanism.

## II. MATERIAL AND METHOD

In the present work, double distilled water used for preparing the solutions. A stock solution of arginine (E. Merck) was prepared by dissolving it in water. The Ce(IV) stock solution was obtained by dissolving cerium(IV) ammonium

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sulphate (E. Merck) in 1.0 mol dm<sup>-3</sup> 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<sup>-3</sup>) and assayed by complexometric titration with EDTA [19]. Dilute solution of palladium(II) were made from the stock solution as required. Other chemical and reagents such as sodium sulphate, sulphuric acid, acetonitrile used were of analytical grade.

Kinetics of oxidation of arginine using Pd(II) as catalyst have been investigated at 45°C. The reaction was initiated by mixing reactant solution thermally equilibrated at the desired temperature. Kinetic studies were carried out in sulphuric acid medium under pseudo first order conditions with a large excess over Ce(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. The observed rate constants were reproducible within the experimental error ±5%.

### III. RESULT AND DISCUSSION

#### Stoichiometry and product analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [Arginine] 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 by absorbance at 360 nm. The main reaction products are Ce(III), 1-(4-oxobutyl) guanidine, ammonia and CO<sub>2</sub>. 1-(4-oxobutyl) guanidine 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. Further, aldehyde group was confirmed with qualitative test such as Tollen's reagent [20] and Schiff's reagent. Nitrile test was negative, the product usually reported in the oxidation of amino acids. Ammonia was confirmed with Nessler's test. Therefore, the stoichiometry of the reaction with positive test of aldehyde represented by eq<sup>n</sup>



Where R = -(CH<sub>2</sub>)<sub>3</sub>NH-C-H<sub>2</sub>N



In the first set of kinetic experiment, [Ce(IV)]<sub>T</sub> was varied from 0.5×10<sup>-5</sup> to 5×10<sup>-4</sup> mol dm<sup>-3</sup> at fixed concentration of [arginine] = 5×10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, [Pd(II)] = 5×10<sup>-5</sup> mol dm<sup>-3</sup>, ionic strength [I] = 1.50 mol dm<sup>-3</sup> and temp. = 45°C. The pseudo first order plots are found to be linear in each case (Fig.-1) giving k<sub>obs</sub>×10<sup>4</sup> (sec<sup>-1</sup>). The constant value of k<sub>obs</sub> is in agreement with first order dependence in [Ce(IV)]<sub>T</sub> (Table-1).

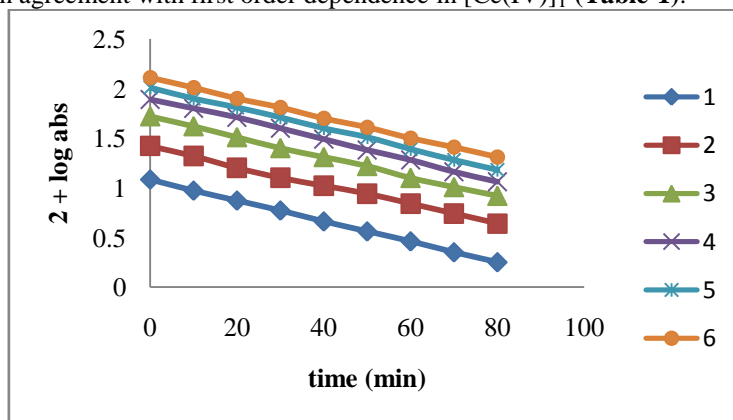


Fig. 1 Pseudo First Order Plots for The Variation Of Cerium(IV)

[Arg] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [Pd(II)] = 5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, I = 1.50 mol dm<sup>-3</sup>, Temp. = 45°C, [Ce(IV)] = (1) 0.50 × 10<sup>-4</sup> mol dm<sup>-3</sup>, (2) 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, (3) 2.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, (4) 3.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, (5) 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, (6) 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>.

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At a fixed  $[Ce(IV)] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Pd(II)] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \text{ mol dm}^{-3}$  ionic strength  $[I] = 1.50 \text{ mol dm}^{-3}$ , the effect of  $[Arginine]$  on the rate was studied in the  $1 \times 10^{-3}$  to  $1 \times 10^{-2} \text{ mol dm}^{-3}$  range at  $45^\circ\text{C}$ . The rate of the reaction is found to increase with increase in  $[Arginine]$  (**Table-1**).

**Table 1. Effect of cerium(IV), arginine and Pd(II) on Pd(II) catalysed oxidation of arginine by Ce(IV) in aqueous sulphuric acid medium at  $45^\circ\text{C}$   $[H^+] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 1.50 \text{ mol dm}^{-3}$**

$10^4 [Ce(IV)]$ $\text{mol dm}^{-3}$	$10^3 [Arg]$ $\text{mol dm}^{-3}$	$10^5 [Pd(II)]$ $\text{mol dm}^{-3}$	$10^4 k_{obs}$ $\text{sec}^{-1}$
0.50	5.0	5.0	3.96
1.0	5.0	5.0	3.92
2.0	5.0	5.0	3.91
3.0	5.0	5.0	3.95
4.0	5.0	5.0	3.96
5.0	5.0	5.0	3.96
5.0	1.0	5.0	1.42
5.0	2.0	5.0	2.31
5.0	3.0	5.0	3.01
5.0	4.0	5.0	3.52
5.0	5.0	5.0	3.96
5.0	6.0	5.0	4.48
5.0	7.0	5.0	4.72
5.0	8.0	5.0	4.81
5.0	9.0	5.0	4.90
5.0	10.0	5.0	4.93
5.0	5.0	1.0	0.81
5.0	5.0	2.0	1.62
5.0	5.0	3.0	2.43
5.0	5.0	4.0	3.24
5.0	5.0	5.0	3.96
5.0	5.0	6.0	4.92
5.0	5.0	7.0	5.73
5.0	5.0	8.0	6.54
5.0	5.0	9.0	7.32
5.0	5.0	10.0	8.12

Observed reaction order of arginine is 0.64 obtained from the linear regression of  $\log k_{obs}$  versus  $\log$  arginine, indicating fractional order with respect to arginine. The plot of  $1/k_{obs}$  versus  $1/\text{arginine}$  excellence linearity (**Fig.-II**) with positive intercept and slope.

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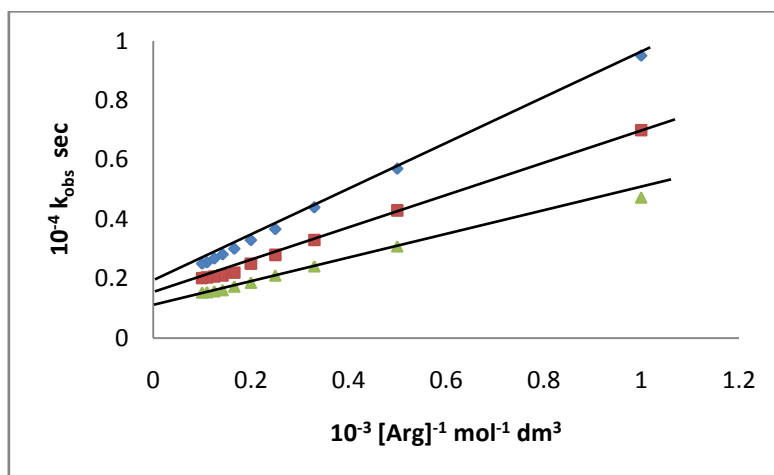


Fig. II. A Plot of  $(k_{\text{obs}})^{-1}$  versus  $[\text{Arg}]^{-1}$   
 $[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{Pd(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 1.50 \text{ mol dm}^{-3}$ ,  
 Temp:  $\blacklozenge$  ( ) 40°C,  $\blacksquare$  ( ) 45°C,  $\blacktriangle$  ( ) 50°C.

The reaction has been carried out in  $[\text{H}^+]$  range 0.20 to 1.0 mol dm<sup>-3</sup>. Hydrogen ion concentration was varied at three different concentration of arginine i.e.  $2.5 \times 10^{-3}$ ,  $5 \times 10^{-3}$  and  $7.5 \times 10^{-3}$  mol dm<sup>-3</sup> at fixed concentration of  $[\text{Ce(IV)}] = 5 \times 10^{-4}$  mol dm<sup>-3</sup>,  $[\text{Pd(II)}] = 5 \times 10^{-5}$  mol dm<sup>-3</sup> and  $[I] = 1.50$  mol dm<sup>-3</sup>. With the increase in  $[\text{H}^+]$  from 0.20 to 1.0 mol dm<sup>-3</sup>, the rate constants  $k_{\text{obs}}$  also increase (**Table-II**).

**Table II. Observed rate constant ( $k_{\text{obs}}$ ) for the reaction of Ce(IV) and arginine at different arginine and hydrogen ion concentration at 45°C**

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{Pd(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $I = 1.50 \text{ mol dm}^{-3}$

$10^3 [\text{Arginine}]$ mol dm <sup>-3</sup>	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$				
	0.2 <sup>a</sup>	0.4 <sup>a</sup>	0.6 <sup>a</sup>	0.8 <sup>a</sup>	1.0 <sup>a</sup>
2.5	0.98	1.53	2.12	2.64	2.98
5.0	1.52	2.41	3.12	3.73	3.96
7.5	2.32	3.51	4.34	4.83	5.22

<sup>a</sup> $[\text{H}^+] \text{ mol dm}^{-3}$ .

The plots of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  at different  $[\text{Arg}]$  and at 45°C are shown in (**Fig.-III**). Observed reaction order of  $\text{H}^+$  is 0.61 obtained from plot of  $\log k_{\text{obs}}$  versus  $[\text{H}^+]$  indicating that reaction is of positive fractional order with respect to  $[\text{H}^+]$ .

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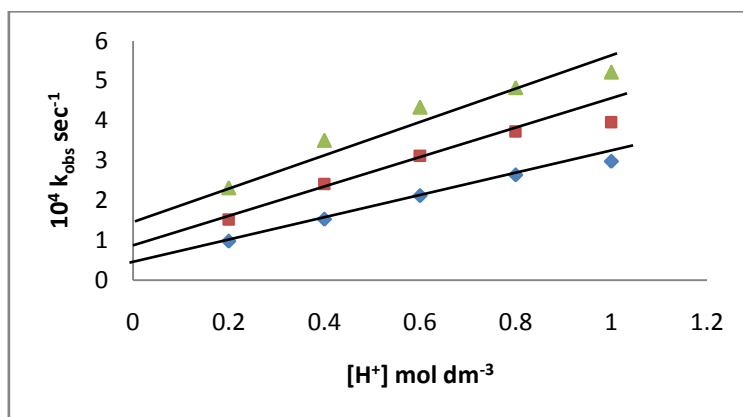


Fig. III. A Plot of  $k_{obs}$  versus  $[H^+]$  at different [Arginine]

$[Ce(IV)] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Pd(II)] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $I = 1.50 \text{ mol dm}^{-3}$ ,  
Temp. =  $45^\circ\text{C}$ , [Arg] (  $\blacklozenge$  ) =  $2.5 \text{ mol dm}^{-3}$ , (  $\blacksquare$  ) =  $5.0 \text{ mol dm}^{-3}$ , (  $\blacktriangle$  ) =  $7.5 \text{ mol dm}^{-3}$

At fixed  $[Ce(IV)]$ ,  $[Arg]$ ,  $[H_2SO_4]$  and [Ionic strength],  $Pd(II)$  was varied from  $1 \times 10^{-5}$  to  $1 \times 10^{-4} \text{ mol dm}^{-3}$  at  $40^\circ\text{C}$ ,  $45^\circ\text{C}$  and  $50^\circ\text{C}$  respectively.  $K_{obs}$  increase with increase of  $Pd(II)$ . Observed reaction order of  $Pd(II)$  is one that can be obtained from the plot of  $\log k_{obs}$  versus  $\log Pd(II)$ , indicating that the reaction is first order with respect to  $Pd(II)$ .  $1/k_{obs}$  versus  $1/Pd(II)$  yielded good linear plots (Fig.-IV) passing through the origin.

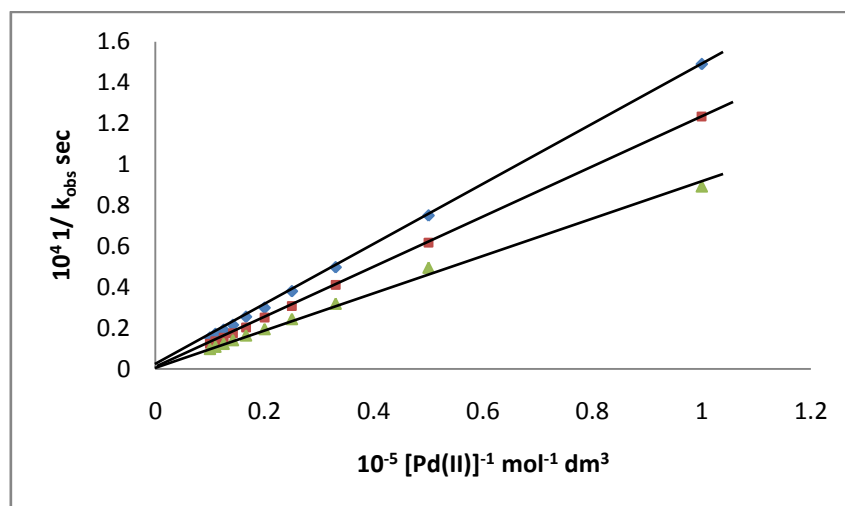


Fig. IV. A Plot of  $(k_{obs})^{-1}$  versus  $[Pd(II)]^{-1}$

$[Ce(IV)] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[Arg] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 1.50 \text{ mol dm}^{-3}$ , Temp. = (  $\blacklozenge$  )  $40^\circ\text{C}$ , (  $\blacksquare$  )  $45^\circ\text{C}$ , (  $\blacktriangle$  )  $50^\circ\text{C}$ .

At fixed concentration of other reactants and temperature, the ionic strength was varied from 1.2 to 2.0  $\text{mol dm}^{-3}$  (ionic strength adjusted by the  $\text{Na}_2\text{SO}_4$ ), it is found that ionic strength has slightly affected the rate of reaction.

At fixed concentration of other reactant and temperature, the concentration of  $\text{NaCl}$  varied from  $1 \times 10^{-4}$  to  $5 \times 10^{-4} \text{ mol dm}^{-3}$ . The rate was unaffected by the addition of  $\text{Cl}^-$  ion.

The reaction rate were measured with various  $[\text{HSO}_4^-] = 0.2$  to  $1.0 \text{ mol dm}^{-3}$  at  $[\text{Arginine}] = 5 \times 10^{-3}$ ,  $[Ce(IV)] = 5 \times 10^{-4}$ ,  $[H^+] = 0.2 \text{ mol dm}^{-3}$  and  $[Pd(II)] = 5 \times 10^{-5} \text{ mol dm}^{-3}$ . The rate of the reaction decrease with increase in  $[\text{HSO}_4^-]$  which indicates that the order with respect to  $[\text{HSO}_4^-]$  was negative. This is confirmed by linear plot of  $1/k_{obs}$  versus  $[\text{HSO}_4^-]$ . Therefore  $[\text{HSO}_4^-]$  shows rate retarding effect (Fig.-V).

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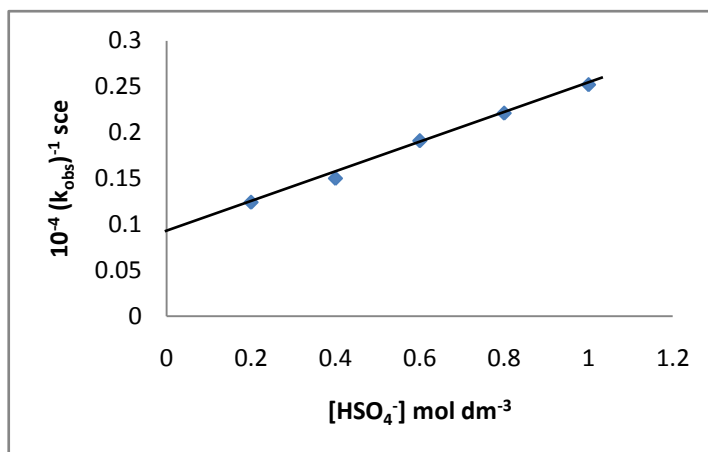
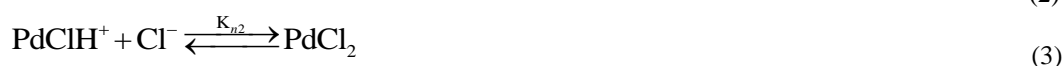
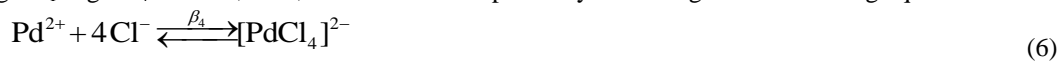


Fig. V. A Plot of  $1/k_{\text{obs}}$  versus  $[\text{HSO}_4^-]$   
 $[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{Pd(II)}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{Arg}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , Temp = 45°C

The complexes of platinum or palladium group metals are well known. The different possible mononuclear complexes of palladium(II) viz.  $[\text{PdCl}_3\text{L}]^-$ ,  $[\text{PdCl}_2\text{L}_2]$ ,  $[\text{PdClL}_3]^+$  and  $[\text{PdL}_4]^{2+}$  (where L represent a ligand like amine, phosphine, sulphide) are reported [21]. In most of studies using Pd(II) as homogeneous catalyst, it has been employed in the form of Pd(II) chloride. Palladous chloride [22] is insoluble in aqueous solution but it is dissolved in the presence of  $\text{Cl}^-$ . Elding [23] reported that in the presence of chloride ion, palladium chloride exists as  $[\text{PdCl}_4]^{2-}$  and in the aqueous solution, it may be further hydrolyzed to  $[\text{PdCl}_3(\text{H}_2\text{O})]^-$ . The equilibrium constant corresponding to the following equilibrium has been determined by several workers, and all are in good agreement with a value of  $\log \beta_4$  between 11 and 12 at 25°C [24].



It is reported [25] that  $K_{n4}$  is probably the most important stability constant for catalytic chemistry. The reported value of  $\log K_{n1}$ - $\log K_{n4}$  are 4.47, 3.29, 2.41 and 1.37 respectively according to the following equilibria



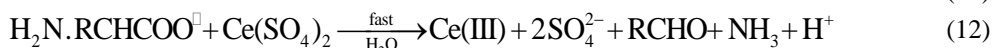
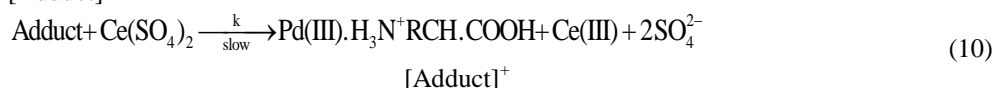
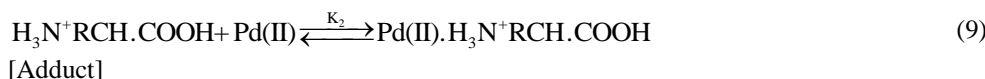
The reported value of  $\log \beta_4$  is 11.54 [26] ( $\beta_4$  is the equilibrium constant) and value of hydrolytic constant ( $K_h$ ) is  $2.50 \times 10^{-3}$ . The existence of Pd(II) chloride exclusive in the form of complex  $[\text{PdCl}_4]^{2-}$  is also reported [27].

Arginine is easily protonized in acidic media, indicating the involvement of  $\text{H}^+$  in the reaction in the pre equilibrium step. The observed fractional order with respect to arginine indicate that there is possibility of complex formation between  $[\text{PdCl}_4]^-$  and arginine in the first 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 result, a probable mechanism has been proposed. (Scheme-1)

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### Scheme 1

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

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2kK[\text{Pd(II)}][\text{Ce(IV)}][\text{Arg}][\text{H}^+]}{K[\text{Arg}][\text{H}^+] + 1} \quad (13)$$

Where  $K = K_1 K_2$

$$\frac{-d[\text{Ce(IV)}]/dt}{[\text{Ce(IV)}]} = k_{\text{obs}} = \frac{2kK[\text{Pd(II)}][\text{Arg}][\text{H}^+]}{K[\text{Arg}][\text{H}^+] + 1} \quad (14)$$

Rearrangement of eq<sup>n</sup> (14)

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

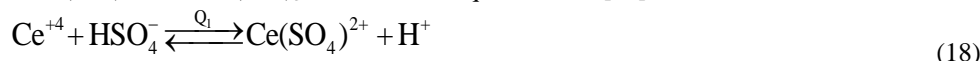
$$= \frac{1}{2k[\text{Pd(II)}]} + \frac{1}{2kK[\text{Arg}][\text{H}^+]} \cdot \frac{1}{[\text{Pd(II)}]} \quad (15)$$

$$= \frac{1}{2k[\text{Pd(II)}]} + \frac{1}{2kK[\text{Pd(II)}][\text{H}^+]} \cdot \frac{1}{[\text{Arg}]} \quad (16)$$

$$= \frac{1}{2k[\text{Pd(II)}]} + \frac{1}{2kK[\text{Pd(II)}][\text{Arg}]} \cdot \frac{1}{[\text{H}^+]} \quad (17)$$

Equation (14) suggest that order with respect to palladium(II) is 1.0, less than one in arginine and less than one in  $[\text{H}^+]$ , which is consistent with the result of our experiments. Equation (15) suggest that  $1/k_{\text{obs}}$  versus  $1/[\text{Pd(II)}]$  at constant  $[\text{Arg}]$ ,  $[\text{H}^+]$  should yield good linear plots through the origin (**Fig. IV**). Eq<sup>n</sup> (16) suggests that  $1/k_{\text{obs}}$  versus  $1/[\text{Arg}]$  at fixed  $[\text{Pd(II)}]$  and  $[\text{H}^+]$  should be linear plots with positive intercept (**Fig. II**). Eq<sup>n</sup> (17) suggests that the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{H}^+]$  at constant  $[\text{Pd(II)}]$  and  $[\text{Arg}]$  should also be linear with positive intercept.

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 are [28]



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 (18-20), inverse bisulphate dependence (**Fig. V**) can be explained by assuming  $\text{Ce}(\text{SO}_4)_2$  as the reactive

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species. The concentration of this active species is given by equation (21)

$$\text{Ce}(\text{SO}_4)_2 = \frac{[\text{Ce}(\text{IV})]_{\text{T}}}{1 + Q_3[\text{HSO}_4^-]} \quad (21)$$

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

Thus equation (14) can be written as

$$k_{\text{obs}} = \frac{2kK[\text{Pd}(\text{II})][\text{Arg}][\text{H}^+]}{[K[\text{Arg}][\text{H}^+] + 1][1 + Q_3[\text{HSO}_4^-]]} \quad (22)$$

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

Equation (23) may be written as

$$k_{\text{obs}} = \frac{C}{1 + Q_3[\text{HSO}_4^-]} \quad (23)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{C} + \frac{Q_3[\text{HSO}_4^-]}{C} \quad (24)$$

Equation (24) 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. V**), the ratio of slope to intercept was calculated to be 1.71 i. e.  $Q_3$  which is in good agreement with the previously reported value [29-30]. 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.

According to equation (16) and **fig-II** the rate constants ( $k$ ) and formation constants ( $K$ ) calculated from intercept and slope. Data in **Table-III** 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  $E_a^\ddagger = 31.78 \text{ kJ mol}^{-1}$ ,  $\Delta H^\ddagger = 28.72 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -129.13 \text{ JK mol}^{-1}$  and  $\Delta G^\ddagger = 72.84 \text{ kJ mol}^{-1}$  from the linear plot of  $\log k$  versus  $1/T$ .

**Table III. Effect of temperature on the reaction between cerium(IV) and arginine catalysed by palladium(II) in sulphuric acid medium**

Temp (K)	k ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	Activation parameters	K ( $\text{dm}^3 \text{ mol}^{-1}$ )	Thermodynamic quantities
313	5.55	$E_a(\text{kJ mol}^{-1}) = 35.03$	230	$\Delta H(\text{kJ mol}^{-1}) = 30.63$
318	6.66	$\Delta S^\ddagger(\text{JK}^{-1} \text{ mol}^{-1}) = -119.49$	267	$\Delta S(\text{J K}^{-1} \text{ mol}^{-1}) = -102.76$
323	8.33	$\Delta G^\ddagger(\text{kJ mol}^{-1}) = 68.62$	333	$\Delta G(\text{kJ mol}^{-1}) = 63.30$

#### IV. CONCLUSION

The oxidation of arginine 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  $\text{Ce}(\text{SO}_4)_2$ , 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 mechanisms and the related rate laws were deduced. It can be stated that palladium(II) acts as an efficient catalyst for the oxidation of arginine by cerium(IV) in acidic media.



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