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## **Kinetics and Mechanism of Palladium (II) Catalyzed Oxidation of D-(+) Galactose by Cerium(IV) in Aqueous Acidic Medium**

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### **Authors' contributions**

*This work was carried out in collaboration between both authors. This experimental work was carried out by author MKG. Author SKR supervised the work. Author MKG collected the data from practical work and write down the whole manuscript. Both authors read and approved the final manuscript.*

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### **ABSTRACT**

Kinetics of palladium (II) catalyzed oxidation of D-(+) galactose by cerium (IV) have been studied titrimetrically in aqueous acidic medium in the temperature range 308-333 K. The reaction has been found to be first order with respect to D-(+) galactose in catalyzed reactions. The rate of reaction decreases with increasing sulphuric acid. The reaction proceeded through formation of an intermediate complex, which was proved by kinetic method. The observed stoichiometric ratio was 1:2 in the oxidation of D-(+) galactose. From the effect of temperature on the rate of reaction, the Arrhenius equation and various activation parameters have been computed. Arabinose and formic acid have been identified as main oxidation products of the reaction. A plausible mechanism from the results of kinetic studies, reaction stoichiometry and product analysis has been proposed.

**Keywords:** *Catalyzed; Oxidation; D-(+) galactose; Palladium(II); Cerium(IV); Acidic medium.*

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## 1. INTRODUCTION

Milk sugar are the fuel of life, being the main energy source for living organisms and the central pathway of energy storage and supply for most cells. In research, many researchers have investigated the oxidative degradation of monosaccharides and their derivatives [1-3]. The study of carbohydrates is one of the exciting fields of organic chemistry. They are the primary source of energy in plants, animals and human beings. Energy is stored in the complex molecular structure of the carbohydrates. The atoms arrange themselves back into simple compounds during the metabolism of complex compounds and in this process, release their stored energy for our uses.

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 0.532 V. Most of the studies employed the palladium (II) as in the form of palladium (II) chloride [4]. 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 [5]. Indeed, palladium redox chemistry seems to be essentially limited to organic compounds, only a few studies of redox reactions with inorganic species being available [6]. The mechanism may be quite complicated due to the formation of different intermediates, including various oxidation states of palladium, etc. In recent years, platinum group metal ions including Ruthenium (III), Osmium (VIII), Iridium (III), Rhodium (III), and Palladium (II) are widely used as catalysts due to their strong catalytic influences in various reactions. Palladium (II) chloride is the most important salt in the catalytic chemistry of palladium. Several authors have performed studies using palladium (II) because of the commercial importance of reactions catalyzed by palladium (II) [7]. The mechanism of reaction depends upon the nature of the oxidant, nature of the substrate and the ways in which transition metal complex ions play their role in order to promote the reactant molecules to the activated state before changing into final products under experimental conditions [8-9]. However a large number of literature is available on the kinetics oxidation of carbohydrate by various inorganic and organic oxidants, such as rhodium (III) [10], formic acid [11], glycol [12], dialkyl-sulphoxide [13], tellurium (IV), toluene, benzene, cyclic ketones with ruthenium (III) catalyzed [14-19], cyclic alcohol [20] and iridium (III) [21-23].

The primary aim of this paper is to ascertain the catalyzed molecular reaction of D-(+) galactose, by titrimetric method in view of the synthetic and biological importance. In this present work, we report kinetics and mechanism of oxidation of galactose by cerium (IV) in presence of palladium (II) in aqueous acidic medium at 308 K. Preliminary experimental results indicate that the reaction of galactose with cerium (IV) in the acidic medium becomes facile in the presence of micro-amount of palladium (II) catalyst. Therefore, palladium (II) has been selected as a catalyst in the present investigations [24]. The objectives of the study are (i) to identify the oxidation products, (ii) to determine the plausible mechanism, (iii) to deduce rate law, (iv) to calculate the activation parameters and (v) to ascertain the reactive species of the oxidant.

## 2. EXPERIMENTAL WORK

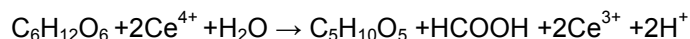
### 2.1 Materials and Methods

The chemical reaction between cerium (IV) and D-(+) galactose in aqueous acidic medium is studied in the following manner: An aqueous solution of cerium (IV) and D-(+) galactose (E.

Merck) was prepared afresh by dissolving a weighted amount in double distilled water. The solution was standardized iodometrically against standard solution of sodium thiosulphate (AR grade) using starch as an indicator. The solution of palladium (II) chloride (Johnson Matthey, India Pvt. Ltd., Kanpur) was prepared by dissolving the sample in sulfuric acid of known strength. Cerium(IV) [0.1M] acidified with sulphuric acid in the presence of palladium(II) and a known concentration of KHSO<sub>4</sub>(salts) solution is also taken in a 250 ml iodine flasks and placed in a thermostat for an hour to maintain the desired temperature within  $\pm 0.1^\circ\text{C}$ . Cerium (IV) is stable in acidic solution and do not show photochemical decomposition or undergo dimerisation. Hence, the rates could be measured in daylight [25]. Afterwards, the requisite volume of the carbohydrate solution is sucked out with the help of a pipette and poured into a reaction flask. A stop watch is started when approximately half of carbohydrate solution drained out of the pipette into the reaction vessel [26-28]. Aliquots of the reaction mixture were withdrawn quickly at known intervals of time and poured into another iodine flask containing a drop of 4% potassium iodide (Merck) solution to arrest the reaction. Liberated iodine was titrated against standard sodium thiosulphate solution till the starch end point. A micro burette was used for this purpose. From the titer value, the amount of cerium (IV) present in the aliquot could be easily determined.

## 2.2 Determination of Stoichiometry and Product Analysis

Qualitative analysis of the oxidized reaction mixture with the excess of carbohydrate with cerium (IV) in presence of H<sub>2</sub>SO<sub>4</sub> was performed. After completion of kinetic experiment, a part of oxidized reaction mixture was treated with alkaline hydroxylamine solution and the presence of lactones in the reaction mixture was tested by FeCl<sub>3</sub>.HCl blue test [29-30]. Formic acid formation and respective arabinose were confirmed by the help of spot test [31], by paper chromatography and high performance liquid chromatographic method. Formation of intermediate carbon centered arabinose free radicals were confirmed by EPR spin method [32].



D-(+)galactose Arabinose Formic acid

## 2.3 Test for Free Radicals

The formation of free radicals as an intermediate in the redox reaction between the reactants, the reaction mixture was mixed with an aqueous acrylonitrile monomer solutions and kept for 24 hours in an inert atmosphere. On addition of methanol, a white precipitate was formed, showing the presence of free radicals. The control experiments were also performed under the same reaction conditions.

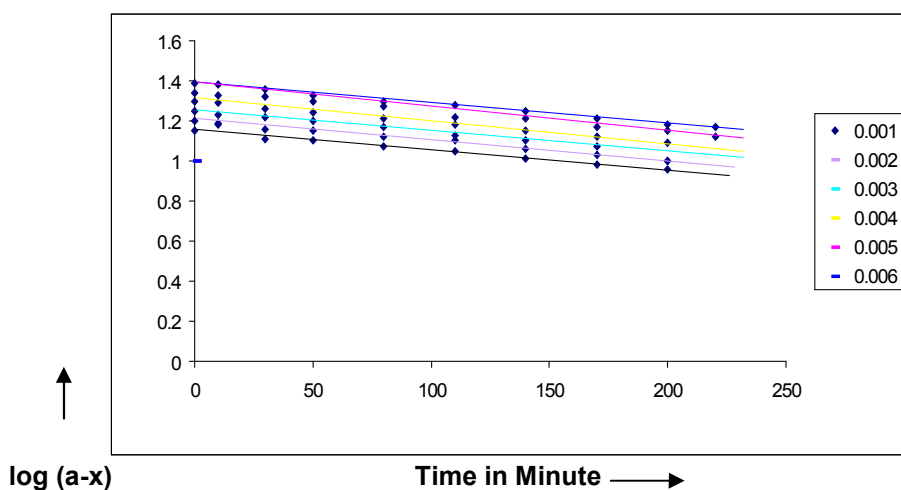
## 3. KINETIC RESULTS AND DISCUSSION

All the reagents were under the conditions of [Substrate] $\gg$ [Ce(IV)] $\gg$ [Pd(II)], the reaction is studied at different concentrations of oxidant at constant concentrations of other reactants. The order of reaction with respect to oxidant cerium (IV) is determined at constant concentration of substrate D-(+) galactose for different concentration of cerium (IV) [2]. The results are given in Table 1. The results show that the rate constant is inversely proportional to the concentration of cerium (IV) for catalyzed system. In presence of catalyst palladium (II) the plot of  $\log(a-x)$  v/s time was found to be linear (Fig. 1). This indicates the first order kinetics with respect to oxidant.

**Table 1. Effect of variation of [Ce(IV)], on the reaction rate, at 308 K**

Run No.	$10^3 \times [\text{Ce(IV)}] \text{ mol dm}^{-3}$	$10^4 \times k_1 \text{ sec}^{-1}$
1	1.00	7.62
2	2.00	7.10
3	3.00	6.43
4	4.00	5.79
5	5.00	5.04
6	6.00	4.37

$10^2 \times [\text{D-(+)} \text{ galactose}] = 5.00 \text{ mol dm}^{-3}$ ;  $10^5 \times [\text{Pd(II)}] = 5.00 \text{ mol dm}^{-3}$ ;  $10^2 \times [\text{H}_2\text{SO}_4] = 3.00 \text{ mol dm}^{-3}$ ;  
 $10^3 \times [\text{KHSO}_4] = 5.00 \text{ mol dm}^{-3}$



**Fig. 1. Plot of log (a-x) v/s time**

In order to study the behavior of substrate D-(+) galactose reaction rates, different sets of the experiments were carried out at different concentration of D-(+) galactose keeping concentration of other reactants constant. The observations are given in Table 2. The result shows that the graphical plot for the pseudo first order rate constant  $k_1$  v/s D-(+) galactose concentration is found to be a straight line for catalyzed system (Fig. 2), which indicates that the rate of the reaction is directly proportional to the substrate concentration. This indicates that the order with respect to substrate D-(+) galactose is one.

**Table 2. Effect of variation of [D-(+) galactose] on the reaction rate at 308 K**

Run No.	$10^2 \times [\text{D-(+)} \text{ galactose}] \text{ mol dm}^{-3}$	$k_1 \times 10^4 \text{ sec}^{-1}$
1	1.00	3.72
2	2.00	5.62
3	4.00	8.91
4	7.00	12.58
5	9.00	15.13
6	10.00	16.21
7	12.00	18.72

$10^3 [\text{Ce(IV)}] = 3.00 \text{ mol dm}^{-3}$ ;  $10^5 \times [\text{Pd(II)}] = 5.00 \text{ mol dm}^{-3}$ ;  $10^2 [\text{H}_2\text{SO}_4] = 3.00 \text{ mol dm}^{-3}$ ;  
 $10^3 [\text{KHSO}_4] = 5.00 \text{ mol dm}^{-3}$

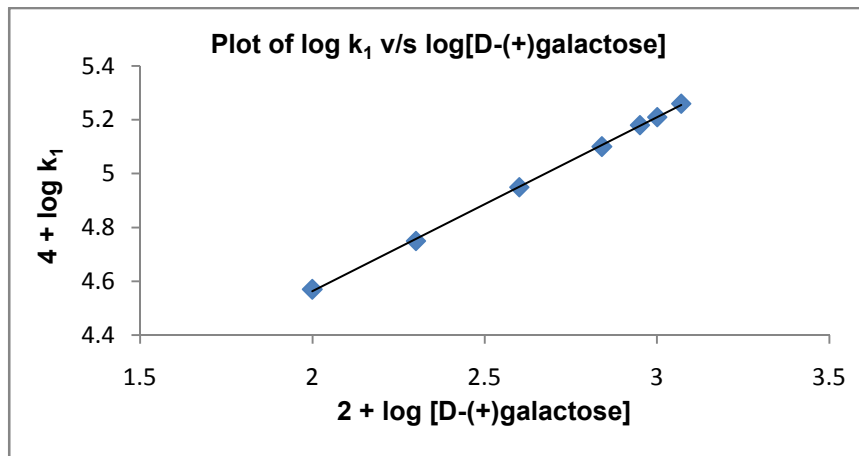


Fig. 2. Plot of  $\log k_1$  v/s  $\log[D-(+) \text{ galactose}]$

In order to see the effect of  $[H^+]$  ion concentration on the reaction velocity, it has been found that the reaction rate decrease with increase of sulphuric acid concentration for catalyzed oxidation. The reaction has been carried out at various initial concentration of sulphuric acid, while other reactants are constant. The results so obtained are represented in Table 3. It has been observed that rate of reaction decreases with increase of sulphuric acid concentration in palladium (II) catalyzed oxidation. The inhibition of reaction rate by the addition of sulphuric acid may be due to the removal of reactive species of cerium (IV). The results indicate the involvement of cerium (IV)-sulphato species. The plot of  $\log k_1$  v/s  $\log [H^+]$  are found to be decreasing the rate constant on increasing  $[H^+]$  ion as shown in Fig. 3.

Table 3. Effect of variation of  $[H^+]$  ion on the reaction rate at 308 K

Run No.	$10^2 \times [H_2SO_4]$ mol $dm^{-3}$	$k_1 \times 10^4 \text{ sec}^{-1}$
1	2.00	5.62
2	4.00	4.62
3	6.00	4.21
4	8.00	3.86
5	10.00	3.63
6	12.00	3.47
7	14.00	3.42

$10^{-3} [Ce(IV)] = 3.00 \text{ mol } dm^{-3}$ ;  $10^{-5} \times [Pd(II)] = 5.00 \text{ mol } dm^{-3}$ ;  $10^2 [D-(+) \text{ galactose}] = 5.00 \text{ mol } dm^{-3}$ ;  
 $10^3 [KHSO_4] = 5.00 \text{ mol } dm^{-3}$

In order to see the effect of catalyst palladium (II) on the reaction rate, the reaction has been carried out at various initial concentration of palladium (II) chloride, while keeping all other variables constant. The result so obtained are given in Table 4. The above data indicates that the rate is dependent on the catalyst concentration. When a graph is plotted between palladium (II) concentration and the rate constant, a linear curve is obtained indicating that the rate is linearly related to palladium (II) concentration. The plot of  $\log k_1$  v/s  $\log [Pd(II)]$  is linear in Fig. 4. The reaction rate increases with increase in palladium (II), suggesting that rate is directly proportional to the catalyst [palladium (II)].

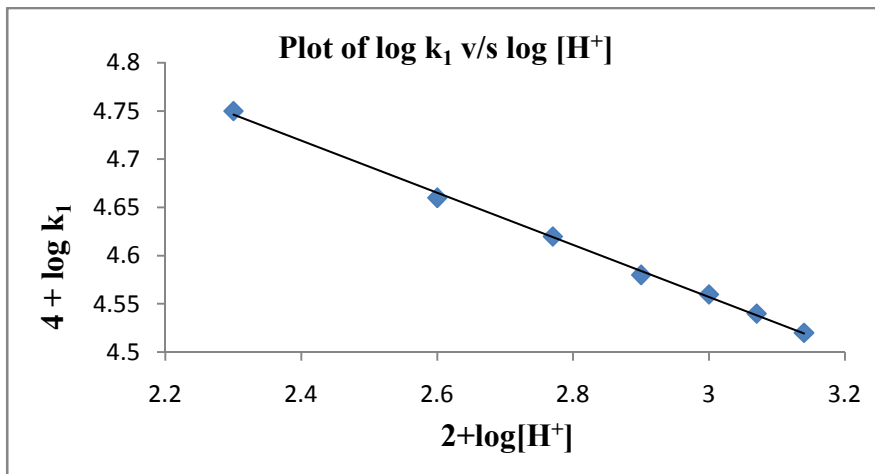


Fig. 3. Plot of  $\log k_1$  v/s  $\log [H^+]$

Table 4. Effect of variation of [catalyst] on the reaction rate at 308 K

Run No.	$10^5 \times [Pd(II)] \text{ mol dm}^{-3}$	$k_1 \times 10^4 \text{ sec}^{-1}$
1	5.00	5.62
2	7.00	6.76
3	9.00	7.76
4	11.00	8.70
5	13.00	9.50
6	15.00	10.23
7	17.00	11.22
8	19.00	11.74

$10^3 [Ce(IV)] = 3.00 \text{ mol dm}^{-3}$ ;  $10^2 \times [H_2SO_4] = 3.00 \text{ mol dm}^{-3}$ ;  $10^2 [D-(+) \text{ galactose}] = 5.00 \text{ mol dm}^{-3}$ ;  
 $10^3 [KHSO_4] = 5.00 \text{ mol dm}^{-3}$ .

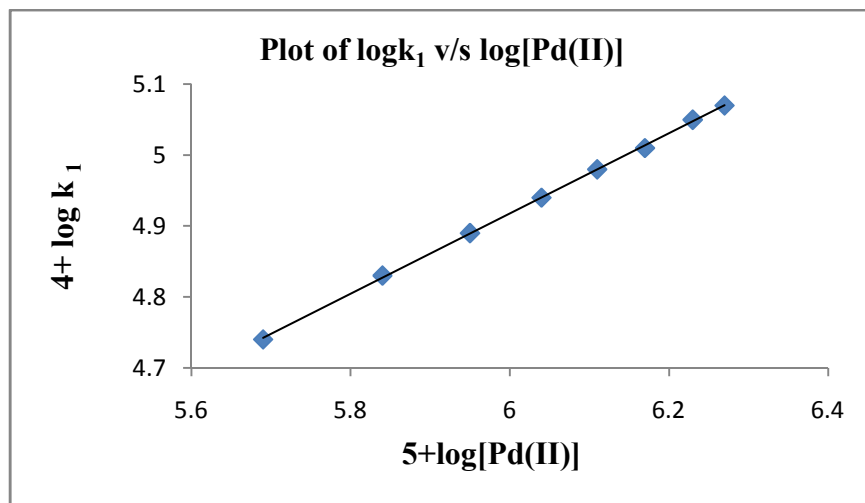


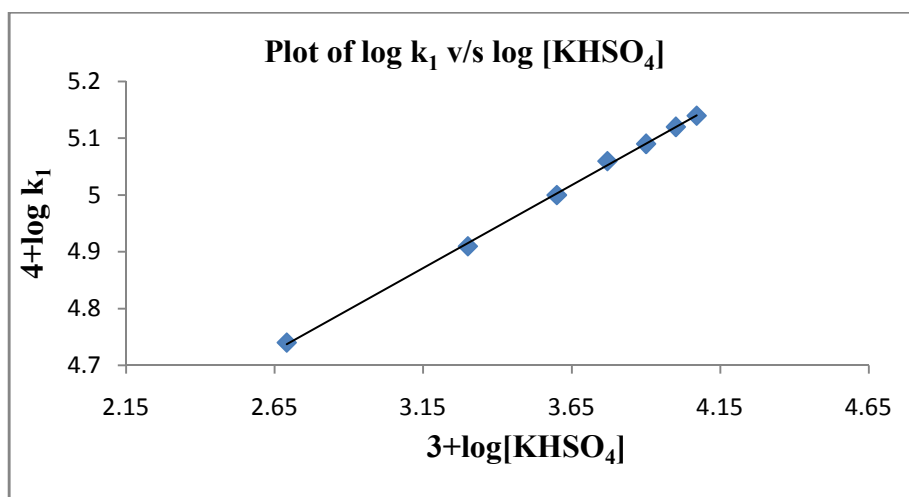
Fig. 4. Plot of  $\log k_1$  v/s  $\log [Pd(II)]$

The reactions were studied at different concentrations of salt [KHSO<sub>4</sub>], while other reactants are constant. The observations of salt effect are given in the Table 5. The graphical plot of log k<sub>1</sub> v/s log [KHSO<sub>4</sub>] for catalyzed oxidation was found to be a straight line shown in Fig. 5, which indicates that the rate of reaction is directly proportional to the HSO<sub>4</sub><sup>-</sup> ion concentration. Here the concentration of this electrolyte increase, the concentration of cerium(IV) at the reaction site decreases due to the salting-out effect [39]. Thus the [HSO<sub>4</sub><sup>-</sup>] dependence can be represented as equation(1). The following equation, which is similar to Michaelis-Menten type, can be used to explain the catalytic part of the observed results.

**Table 5. Effect of variation of [KHSO<sub>4</sub>] on the reaction rate at 308 K**

Run No.	10 <sup>3</sup> × [KHSO <sub>4</sub> ] mol dm <sup>-3</sup>	k <sub>1</sub> × 10 <sup>4</sup> sec <sup>-1</sup>
1	0.50	5.62
2	2.00	8.13
3	4.00	10.00
4	6.00	11.49
5	8.00	12.31
6	10.00	13.19
7	12.00	13.91

*10<sup>3</sup>[Ce(IV)]=3.00 mol dm<sup>-3</sup>; 10<sup>2</sup> × [H<sub>2</sub>SO<sub>4</sub>]=3.00 mol dm<sup>-3</sup>; 10<sup>2</sup>[D-(+) galactose]=5.00 mol dm<sup>-3</sup>; 10<sup>5</sup> × [Pd(II)] = 5.00 mol dm<sup>-3</sup>*



**Fig. 5. Plot of log k<sub>1</sub> v/s log [KHSO<sub>4</sub>]**

$$k' = \frac{a}{b + c[HSO_4^-]} \tag{1}$$

Where a, b and c are constants under the experimental conditions.

Here the k' increases obviously with the increase of [H<sup>+</sup>]. On the plotting of graph log k<sub>1</sub> v/s log [KHSO<sub>4</sub>] at 303 K is found to be a straight line. The results are given in the Table 5.

To observe the effect of temperature on the reaction rate, the reaction was studied at different temperatures from 308K to 333K, while keeping all other reactants are constant in Table 6. The kinetic data shows that the velocity of reaction increases with rise in temperature. The kinetic data shows the validity of the Arrhenius equation in Fig. 6. The plot of  $\log k_1$  vs  $1/T$  is linear for the catalyzed oxidation. So, an attempt has been made to correlate the various activation parameters on the reaction mechanism.

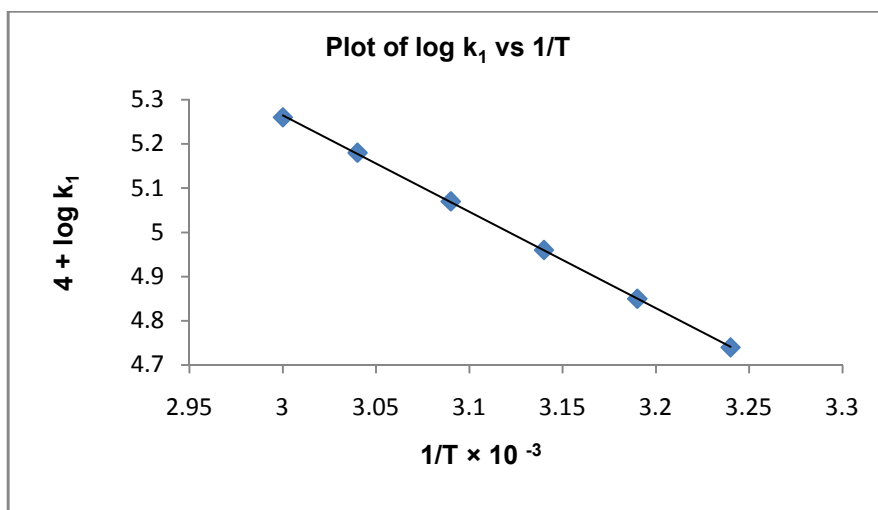
**Table 6. Variation of [temperature] on the reaction rate**

Temperature in K	$1/T \times 10^{-3}$	$k_1 \times 10^4 \text{sec}^{-1}$
308	3.24	5.62
313	3.19	7.08
318	3.14	9.12
323	3.09	11.75
328	3.04	15.14
333	3.00	18.27

**Kinetic and activation parameters for Pd(II) catalysed reaction**

Parameter	D-(+)galactose
$E_a^*$ (kJ mol <sup>-1</sup> )	40.22
$\Delta H^*$ (kJ mol <sup>-1</sup> )	37.57
$\Delta S^*$ (JK <sup>-1</sup> mol <sup>-1</sup> )	-100.61
$\Delta G^*$ (kJ mol <sup>-1</sup> )	69.57
log A	7.56

$10^3 \times [\text{Ce(IV)}] = 3.00 \text{ mol dm}^{-3}; 10^2 \times [\text{H}_2\text{SO}_4] = 3.00 \text{ mol dm}^{-3}; 10^2 \times [\text{D-(+)galactose}] = 5.00 \text{ mol dm}^{-3}; 10^5 \times [\text{Pd(II)}] = 5.00 \text{ mol dm}^{-3}; 10^3 \times [\text{KHSO}_4] = 5.00 \text{ mol dm}^{-3}$



**Fig. 6. Plot of  $\log k_1$  vs  $1/T$**



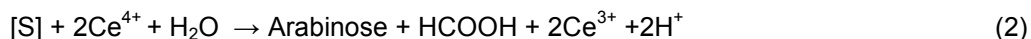
### 3.1 Energy and Entropy of Activation

From the linear Arrhenius plot of  $\log k_1$  versus  $1/T$ , the activation energy was calculated. With the help of the energy of activation, values of the other activation parameters such as enthalpy of activation, entropy of activation, Gibbs free energy of activation and Arrhenius factor (A), were calculated and these values are given in Table 6. The result shows that the average value of energy of activation energy ( $E_a$ ) was found to be  $40.22 \text{ kJmol}^{-1}$  for palladium (II) catalyzed oxidation. The value of frequency factor at 318K is  $7.56 \text{ min}^{-1}$  and entropy of activation at 318K is  $-100.61 \text{ JK}^{-1}\text{mol}^{-1}$  and free energy of activation ( $\Delta G^*$ ) is  $69.57 \text{ kJmol}^{-1}$  but the value of enthalpy of activation ( $\Delta H^*$ ) is  $37.57 \text{ kJmol}^{-1}$ . The value of entropy of activation is found to be negative. The high negative value of  $\Delta S^*$  suggests that the formation of more activated complex, whereas the high positive value of the free energy of the activation ( $\Delta G^*$ ) and enthalpy of activation ( $\Delta H^*$ ) indicate that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that palladium (II) forms the activated complex more easily compared to the other catalyst. Mechanism consistent with observed rate laws have been suggested.

### 3.2 Reaction Mechanism and Derivation of Rate Law

The kinetic data fit well with the Michaelis-Menten model, suggesting that 1:1 type complex of substrate D-(+) galactose and palladium(II) catalyzed is formed in the first equilibrium step. The kinetics of this reaction were studied and showed that the D-(+) galactose, cerium(IV) and catalyst palladium (II) ion interact in two equilibrium steps to form an intermediate complex [33-35] which is assumed to disproportionate forming a free radical and reduced to  $\text{Ce}^{+3}$  ion. It is believed to involvement of both  $\text{C}_1$  and  $\text{C}_2$  hydroxyls [36] in a complex. Substrate is easily protonated in acidic medium in the presence of catalyst, indicating involvement of  $\text{H}^+$  in the pre equilibrium step. Cerium (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 (Scheme 1).

The oxidation of D-(+) galactose in presence of palladium chloride at different temperatures from 308K to 333K was studied. It is consistent with the findings reported for the degradative oxidation of monosaccharide by Ce(IV). The observed stoichiometry of the reaction corresponds to the reaction as represented by the equation (2)



In this reaction one mole of  $[\text{S}] = \text{D-(+) galactose}$  oxidized by two mole of cerium(IV).

The rate law of consumption of Ce(IV) is,

$$\frac{-d[\text{Ce(IV)}]}{dt} = 2k_s[\text{complex}] \quad (3)$$

Based on mechanism as mentioned in the above, the rate law can be deduced as follows,

$$\frac{-d[\text{Complex}]}{dt} = k_1[\text{Ce(IV)}][\text{Pd(II)}] - k_2[\text{complex}] - k_3[\text{complex}][\text{S}] \quad (4)$$

At steady state condition,

$$\frac{-d[\text{Complex}]}{dt} = 0 \quad (5)$$

Hence,

$$k_1[\text{Ce(IV)}][\text{Pd(II)}] = k_2[\text{complex}] + k_3[\text{complex}][\text{S}] \quad (6)$$

Therefore, the concentration of the complex becomes

$$[\text{Complex}] = \frac{k_1[\text{Ce(IV)}][\text{Pd(II)}]}{\{k_2 + k_3[\text{S}]\}} \quad (7)$$

At steady state condition, the rate of disappearance of [Ce(IV)] as given as in eq.(8)

$$\frac{-d[\text{Ce(IV)}]}{dt} = 2k_s[\text{complex}]_1 \quad (8)$$

or

$$\frac{-d[\text{Ce(IV)}]}{dt} = 2k_s k_3 [\text{S}][\text{complex}] \quad (9)$$

{where,  $[\text{complex}]_1 = k_3[\text{S}][\text{complex}]$ }

Putting the value of [complex] we have

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2k_s k_1 k_3 [\text{S}][\text{Ce(IV)}][\text{Pd(II)}]}{\{k_2 + k_3 [\text{S}]\}} \quad (10)$$

Now, the total [Ce(IV)] may be considered as:

$$[\text{Ce(IV)}]_T = [\text{Ce(IV)}]_e + [\text{complex}] \quad (11)$$

Putting the value of [complex] we have,

$$[\text{Ce(IV)}]_T = [\text{Ce(IV)}]_e + \frac{k_1[\text{Ce(IV)}][\text{Pd(II)}]}{\{k_2 + k_3[\text{S}]\}} \quad (12)$$

$$[\text{Ce(IV)}]_T = \frac{[\text{Ce(IV)}]_e \{k_2 + k_3[\text{S}]\} + [k_1[\text{Ce(IV)}][\text{Pd(II)}]]}{\{k_2 + k_3[\text{S}]\}} \quad (13)$$

The value of [Ce(IV)] comes out to be, since  $[\text{Ce(IV)}]_e \approx [\text{Ce(IV)}]$

$$[Ce(IV)] = \frac{[Ce(IV)]_T \{k_2 + k_3[S]\}}{\{k_2 + k_3[S]\} + \{k_1[Pd(II)]\}} \quad (14)$$

From equation (10) and (14), the final rate law comes out to be,

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 k_3 [S][Pd(II)]}{\{k_2 + k_3[S]\}} \times \frac{[Ce(IV)]_T \{k_2 + k_3[S]\}}{\{k_2 + k_3[S]\} + \{k_1[Pd(II)]\}} \quad (15)$$

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 k_3 [S][Pd(II)][Ce(IV)]_T}{\{k_2 + k_3[S]\} + \{k_1[Pd(II)]\}} \quad (16)$$

Under the present experimental condition, one might assume the following inequality :

$$\{k_2 + k_3[S]\} \gg \{k_1[Pd(II)]\} \quad (17)$$

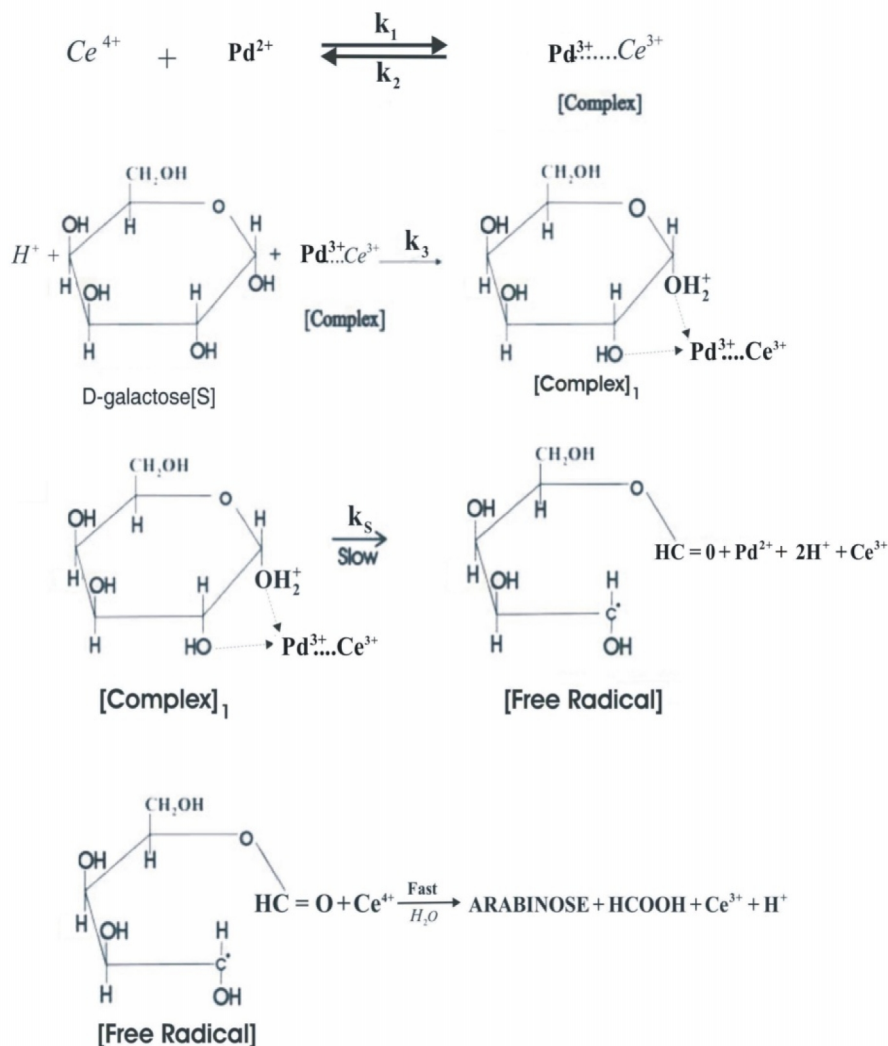
and hence, equation (16) becomes as:

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 k_3 [S][Pd(II)][Ce(IV)]_T}{k_2 + k_3[S]} \quad (18)$$

$$k' = \frac{-d[Ce(IV)]}{[Ce(IV)]_T dt} = \frac{2k_s k_1 k_3 [S][Pd(II)]}{k_2 + k_3[S]} \quad (19)$$

$$\frac{1}{k'} = \frac{1}{2k_s k_1 [Pd(II)]} + \frac{k_2}{2k_s k_1 k_3 [S][Pd(II)]} \quad (20)$$

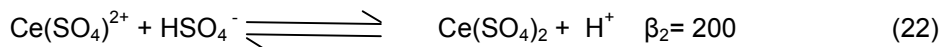
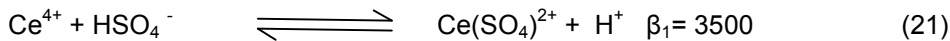
The plot of  $1/k'$  against  $1/[S]$  is made from which the constants  $1/k_s k_1$  and  $k_2/k_s k_1 k_3$  are determined from the slope and intercept respectively. According to the equations mentioned in the above; when plots are made between  $1/k'$  and  $1/[S]$ , a positive intercept would be observed which confirms the validity of the mechanism and also the rate law. Equation (20) also suggests that the plot of  $1/k'$  versus  $1/[H^+]$  at constant  $[Pd(II)]$  and  $[S]$  should also be linear.  $1/k'$  versus  $1/[Pd(II)]$  at constant  $[S]$  and  $[H^+]$  should yield good linear plots through the origin. The values of  $k_s k_1 k_3$  and  $k_2$  for  $[S]$  can also be calculated from the double reciprocal plots as shown in the graphs.



**Scheme 1. Mechanism of oxidation of D-(+) galactose in the presence of Pd (II) catalyst**

### 3.3 Reactive Species of Cerium (IV)

Here, under the experimental conditions in aqueous acidic medium, the important Ce(IV)-sulfato complexes are  $\text{Ce}(\text{SO}_4)_4^{2+}$ ,  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{HCe}(\text{SO}_4)_3^-$  and the relevant equilibria are [37-38]



The equilibrium constants  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  for steps(22) to(23) are reported to be 3500, 200 and 3.4 at 25°C respectively.

Now, among the different sulphate species, the kinetically active species should be inferred on the basis of kinetic data, and not according to the magnitude of concentration [40]. From the above relationship between  $\text{HSO}_4^-$  and  $\text{Ce}(\text{SO}_4)_2$  has been found as the kinetically active species in the present study. The concentration of  $\text{Ce}(\text{SO}_4)_2$  can be approximately obtained. As we know from the mass balance, equation (24) is obtained [41].

$$[\text{Ce(IV)}]_T = [\text{Ce}^{4+}] + \text{Ce}(\text{SO}_4)^{2+} + [\text{Ce}(\text{SO}_4)_2] + [\text{HCe}(\text{SO}_4)_3] \quad (24)$$

From equations (21)-(23), the following equations can be derived as,

$$\text{Ce}^{4+} = \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]^2}{\beta_1\beta_2[\text{HSO}_4^-]^2}$$

$$[\text{Ce}(\text{SO}_4)^{2+}] = \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]}$$

$$[\text{Ce}(\text{SO}_4)_2] = \frac{[\text{HCe}(\text{SO}_4)_3^-]}{\beta_3[\text{HSO}_4^-]}$$

$$[\text{HCe}(\text{SO}_4)_3] = \beta_3[\text{HSO}_4^-][\text{Ce}(\text{SO}_4)_2]$$

On substituting the above equations into Eq. (24),

$$[\text{Ce(IV)}]_T = \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]^2}{\beta_1\beta_2[\text{HSO}_4^-]^2} + \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]} + [\text{Ce}(\text{SO}_4)_2] + \beta_3[\text{Ce}(\text{SO}_4)_2][\text{HSO}_4^-] \quad (25)$$

By considering the relative magnitudes of the successive formation equilibrium constants which are in the order:  $\beta_1 \gg \beta_2 \gg \beta_3$ , the value of  $\frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]^2}{\beta_1\beta_2[\text{HSO}_4^-]^2}$  and  $\frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]}$  are much less than two terms present in the equation (25). Thus it can be neglected.

Therefore, we get Equation (26) from Equation(25),

$$[\text{Ce(IV)}]_T \approx [\text{Ce}(\text{SO}_4)_2] + \beta_3[\text{HSO}_4^-][\text{Ce}(\text{SO}_4)_2] = [\text{Ce}(\text{SO}_4)_2](1 + \beta_3[\text{HSO}_4^-]) \quad (26)$$

$$\text{So, } [\text{Ce}(\text{SO}_4)_2] = \frac{[\text{Ce(IV)}]_T}{1 + \beta_3[\text{HSO}_4^-]} = f[\text{Ce(IV)}]_T$$

$$f = \frac{1}{1 + \beta_3[\text{HSO}_4^-]} \quad (27)$$

Where,  $f$  denotes the fraction of kinetically active species to the total cerium (IV). According to the present mechanism, applying the steady-state condition to the free radicals [37].

$$k' = \frac{2fk_s k_1 k_3 [Pd(II)]_T [S][H^+]}{k_3 [S][H^+] + k_2} \quad (28)$$

where subscript T stands for total concentration.

Substituting Equation (27) into Eq. (28) we get,

$$k' = \frac{2k_s k_1 k_3 [Pd(II)]_T [S][H^+]}{\{k_3 [S][H^+] + k_2\} \{1 + \beta_3 [HSO_4^-]\}} \quad (29)$$

Assuming that,  $m = \frac{2k_s k_1 k_3 [Pd(II)]_T [S][H^+]}{k_3 [S][H^+] + k_2}$

Equation (29) may be written as,

$$k' = \frac{m}{1 + \beta_3 [HSO_4^-]} \quad (30)$$

Equation (30) is same as equation(1) which can explain well the negative order dependence on  $[HSO_4^-]$ . Eq. (30) suggests that  $1/k'$  v/s  $[HSO_4^-]$  should be linear and agrees with the experimental data. All the above result shows that  $Ce(SO_4)_2$  is the kinetically active species in the present study.

#### 4. CONCLUSIONS

The oxidation of D-(+) galactose by cerium(IV) experienced a slow reaction rate in acidic media, but increased in rate in the presence of the palladium (II) catalyst. The reactive species for the oxidation of cerium (IV) in an acidic medium was  $Ce(SO_4)_2$ , 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 and activation parameters with respect to the slow step of the reaction were estimated. The high negative value of  $\Delta S^*$  suggests the formation of more activated complex, whereas, the positive value of free energy of activation ( $\Delta G^*$ ) and enthalpy of activation ( $\Delta H^*$ ) indicates that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that it forms the activated complex. It is seen that the complex formed between cerium(IV) and D-(+) galactose in first equilibrium step gives another complex in the presence of catalyst which ultimately gives rise to products. The reaction follows first order kinetics with respect to catalyst concentrations. Mechanism consistent with observed rate laws have been suggested. The observed 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 D-(+) galactose by cerium(IV) in acidic media.

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## COMPETING INTERESTS

Authors do not have any competing interests with the publication of this work.

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