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Study of Palladium (II) Catalysed Oxidation of D-(+) Ribose by Cerium (IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Approach

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ABSTRACT

The kinetic investigation of palladium (II) catalysed oxidation of D-(+) ribose by cerium (IV) have been studied in acidic medium in the temperature range 308-333 K. The reaction has been found to be first order with respect to D-(+) ribose in the presence of palladium (II) catalysed. The rate follow first order kinetics in palladium (II) catalysed oxidation reaction. The effect of $[HSO_4^-]$ *has also been observed. The 1:2 Stoichiometry is observed in the oxidation. From the effect of temperature on the rate of reaction, various activation parameters have been computed. The various thermodynamic parameters were calculated form rate measurements at 308, 313, 318, 323 and 333 K respectively. A suitable mechanism has been proposed and a rate law explaining the experimental observations.*

Keywords: Catalysed, D-(+) ribose, Cerium (IV), Oxidation and Palladium (II).

INTRODUCTION

There are numerous mechanistic studies of oxidation of organic compounds apart from useful synthetic studies in which cerium (IV) has been employed as an oxidant in acid sulphate medium. The kinetics of oxidation of various carbohydrate compounds has received considerable attention in recent years. The primary aim is to ascertain the catalysed reaction of D-(+) ribose by titrimetric method in view of the analytical, synthetical and biological importance of this sugars. This was done by different oxidants such as rhodium (III)[1], palladium(II)[2],lanthanum(III)[3], ruthenium (III)[4-9] and iridium (III)[10-12] etc. have been used in the oxidation by cerium (IV). Among the different metal ions, ruthenium (III) and iridium (III) are highly efficient. Palladium (II) catalysis in oxidation reactions by Ce (IV) in aqueous acid media has been reported in a very few cases. So we were convinced to show our adept and studies on the oxidation of some sugar by Ce (IV) in acidic medium.

Palladium(II) most probably acts as either a catalyst or as a reductant having the reduction potential[13-14]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 [15]. 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 [16]. Indeed, palladium redox chemistry seems to be essentially limited to organic compounds, only a few studies of redox reactions with inorganic species being available [17]. The mechanism may be quite complicated due to the formation of different intermediates, including various oxidation states of palladium, etc. Hence 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 such media and to arrive at a possible mechanism.

MATERIALS AND METHODS

An aqueous solution of cerium (IV) and D-(+) ribose (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 using starch as an indicator. The solution of palladium (II) chloride (Johnson Matthey) was prepared by dissolving the sample in sulfuric acid of known strength. Cerium(IV) [0.1M] acidified with sulfuric acid in the presence of palladium(II) and a known concentration of $KHSO_4$(salts) solution is also taken in a 250 ml iodine flask and placed in a thermostat for an hour to attain the temperature of the bath. Cerium (IV) is stable in acidic solution and does not show photochemical decompose. Hence, the rates could be measured in daylight [18]. 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 solution to arrest the reaction. Librated iodine was titrated against standard sodium thiosulphate solution upto a 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.

Product Identification: Qualitative analysis of the oxidized reaction mixture with excess of carbohydrate with cerium (IV) in presence of H_2SO_4 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 $FeCl_3$.HCl blue test[19].Formic acid formation and respective aldotetrose were confirmed by spot test[20] and also by paper chromatography and high performance liquid chromatographic method. Formation of intermediate carbon centered aldotetrose free radicals were confirmed by induced polymerization reaction with acrylonitrile and EPR spin method [21].

RESULTS AND DISCUSSION

Under the conditions [S]>>[Ce(IV)]>>[Pd(II)], the reaction was 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 fixed concentration of substrate D-(+) ribose. The results are given in table 1.

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

Run No	10^3x[Ce(IV)] mol dm^{-3}	$10^4 \times k_1$ sec^{-1}
1	1.00	9.55
2	2.00	9.08
3	5.00	8.19
4	7.00	7.52
5	9.00	6.94
6	11.00	6.31
7	13.00	5.75

$10^2\times$ [D-(+)ribose]=5.00 mol dm^{-3}; $10^5\times$[Pd(II)]=5.00 mol dm^{-3};

$10^2\times$ [H_2SO_4]=3.00 mol dm^{-3}; $10^3\times$ [$KHSO_4$]= 5.00 mol dm^{-3}.

The results show that the rate constant is inversely proportional to the concentration of cerium (IV) for catalysed system. In the presence of catalyst Pd (II) the plot of k_1 v/s Ce(IV) concentration are found to be linear(figure 1). This indicates the first order kinetics with respect to cerium (IV).

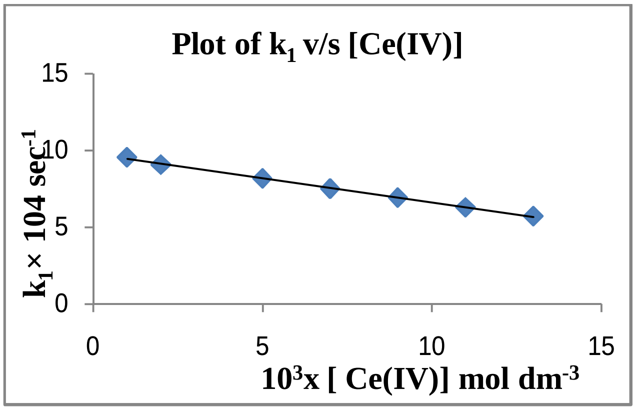


Figure 1; Plot of k_1 v/s [Ce(IV)]

In order to study the behavior of substrate D-(+) ribose reaction rates, different sets of the experiments were carried out at different concentration of D-(+) ribose keeping concentration of other reactants constant. The observations are given in table 2.

Table 2; Effect of variation of [D-(+) ribose] on the reaction rate at 308K

Run No	10^2x[D-(+)ribose]mol dm^{-3}	k_1x10^4 sec^{-1}
1	1.50	5.94
2	3.50	9.34
3	5.00	11.22
4	7.50	14.13
5	9.00	15.49
6	10.50	16.99
7	12.00	18.44

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

$10^2\times$ [H_2SO_4]=3.00 mol dm^{-3}; $10^3\times$ [$KHSO_4$]= 5.00 mol dm^{-3}.

The result shows that the graphical plot for the pseudo first order rate constant k_1 v/s ribose concentration is found to be a straight line (Figure 2a), which indicates that the rate of the reaction is directly proportional to the substrate concentration. The plot of log k_1 v/s log [D-(+) ribose] is linear (Figure 2b). This indicates that the order with respect to substrate D-(+) ribose is one.
In order to see the effect of H^+ ion concentration on the reaction velocity, the reaction has been carried out at various initial concentration of sulphuric acid, while fixed concentration of other reactants constant. The results so obtained are represented in table 3.

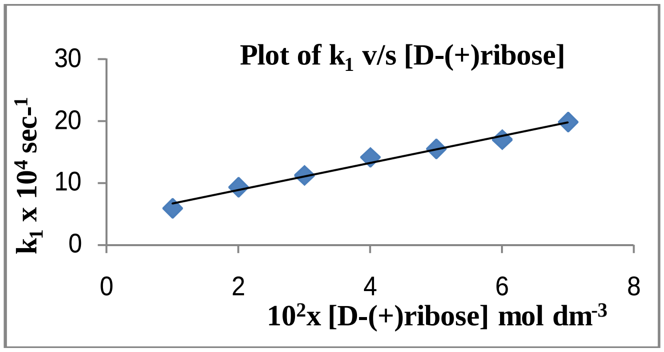


Figure 2(a). Plot of k_1 v/s [D-(+) ribose]

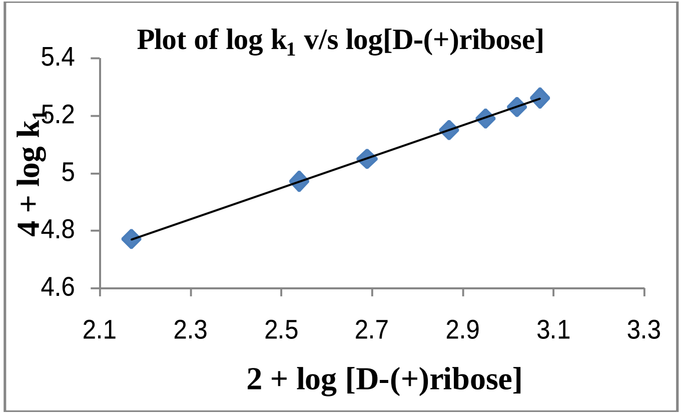


Figure 2(b) Plot of log k_1 v/s log [D-(+) ribose]

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

Run No	10^2x[H_2SO_4]mol dm^{-3}	k_1x10^4 sec^{-1}
1	3.50	9.34
2	4.50	8.51
3	5.50	7.95
4	6.50	7.50
5	7.50	7.18
6	8.50	6.99
7	9.50	6.69

10^3× [Ce (IV)] =3.00 mol dm^{-3}; 10^5×[Pd(II)]=5.00 mol dm^{-3};
10^2× [D-(+) ribose] =5.00 mol dm^{-3}; 10^3× [$KHSO_4$]= 5.00 mol dm^{-3}.

From the table 3 it was found that the rate of reaction decreases with the increase of sulphuric acid concentration in Pd (II) catalysed oxidation. The plot of k_1 v/s 1/[H^+] and log k_1 v/s log [H^+] are linear Figure 3(a) and Figure 3(b). The result indicates that the order with respect to [H^+] is inverse first.

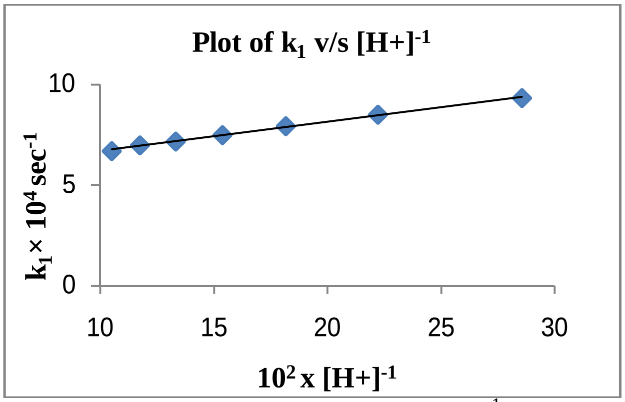


Figure 3(a). Plot of k_1 v/s $[H+]^{-1}$

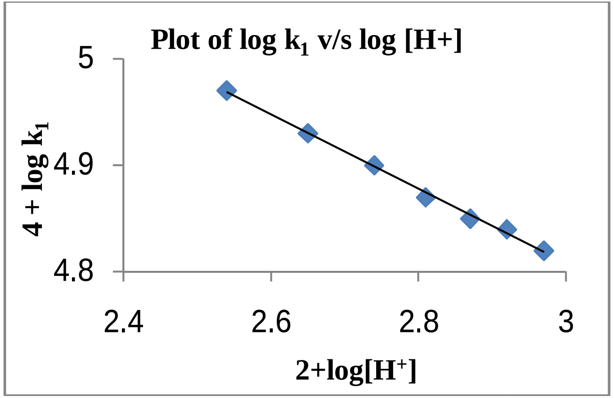


Figure 3(b). Plot of log k_1 v/s log $[H^+]$

Table 4. Effect of variation of [Pd(II)]on the reaction rate at 308K

Run No	10^5 **x [Pd(II)] mol dm^{-3}**	**k_1x10^4 sec^{-1}**
1	5.00	9.34
2	6.00	10.97
3	7.00	12.59
4	8.00	14.12
5	9.00	15.48
6	10.00	16.99
7	11.00	18.62
8	12.00	20.21

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

In order to see the effect of catalyst palladium (II) on the reaction velocity, 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 logk_1 v/s log [Pd(II)] is linear (figure 4). The reaction rate increases with increase in Pd (II), suggesting that rate is directly proportional to the Pd (II).

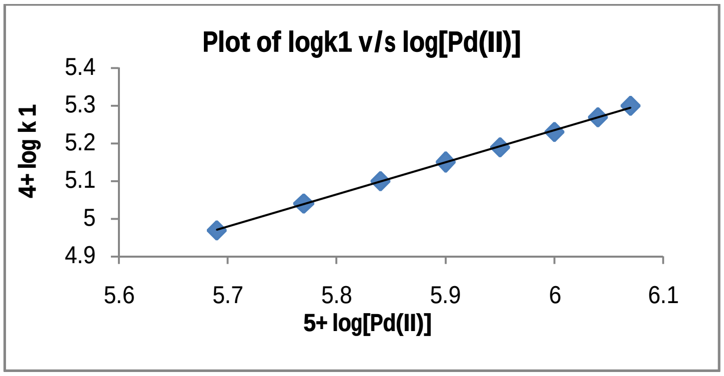


Figure 4. Plot of logk$_1$ v/s log[Pd(II)]

The reactions were studied at different concentration of [$KHSO_4$], while keeping all reactants constant. The observations are given in table 5.

Table 5. Effect of variation of [$KHSO_4$] on the reaction rate at 308K

Run No	**10^3x[$KHSO_4$] mol dm^{-3}**	**k_1x10^4 sec^{-1}**
1	0.50	9.34
2	1.00	10.48
3	3.00	12.02
4	5.00	12.88
5	7.00	13.49
6	9.00	13.81
7	10.00	14.12
8	12.00	19.50

$10^3\times$ [Ce(IV)]=3.00 mol dm^{-3}; $10^2\times$[H_2SO_4]=3.00 mol dm^{-3};

$10^2\times$ [D-(+) ribose]=5.00 mol dm^{-3}; $10^5\times$[Pd(II)] = 5.00 mol dm^{-3}.

The graphical plot of logK$_1$ v/s log [$KHSO_4$] is found to be a straight line (figure 5), which indicates that the rate of the reaction is inversely proportional to the HSO_4^- ion concentration. To observe the effect of temperature on the reaction rate, the reaction was studied at six different temperatures from 308K to 333K, while keeping all other reactants are constant. The observations are given in table 6.

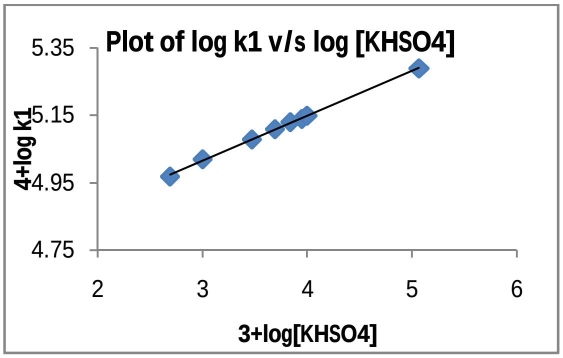


Figure 5 Plot of log k$_1$ v/s log [$KHSO_4$]

Table 6. Effect of variation of [Temperature] on the reaction

Temperature in K	**1/T x10^{-3}**	**K_1x10^4 sec^{-1}**
308	3.24	9.34
313	3.19	10.72
318	3.14	12.30
323	3.09	14.46
328	3.04	16.60
333	3.00	18.65

Kinetic and activation parameters for Palladium(II) catalysed reaction

Parameter	**D-(+)ribose**
E_a* (kJ mol^{-1})	23.57
ΔH* (kJ mol^{-1})	20.93
ΔS* (J mol^{-1})	-150.48
ΔG* (kJ mol^{-1})	68.78
log A	4.96

$10^3\times$ [Ce(IV)]=3.00 mol dm^{-3};$10^2\times$ [H_2SO_4]=3.00 mol dm^{-3};$10^2\times$ [D-(+)ribose]=5.00 mol dm^{-3}; $10^5\times$[Pd(II)] = 5.00 mol dm^{-3}; $10^3\times$ [$KHSO_4$]= 5.00 mol dm^{-3}.

The kinetic data shows that the velocity of reaction increases with rise in temperature, showing the validity of the Arrhenius equation in figure 6. The plot of logk_1 vs. 1/T is linear. So an attempt has been made to correlate the various activation parameters on the reaction mechanism.

Energy and Entropy of Activation: The result shows that the average value of energy of activation energy (E_a) was found to be 23.57 kJ/mol for palladium (II) catalysed oxidation. The value of frequency factor(A) at 318K is 4.96 min^{-1} and entropy of activation at 318K is -150.48 J mol^{-1} and free energy of activation(ΔG*) 68.78 kJmol^{-1}.The value of entropy of activation is found to be negative. The fairly high value of negative ΔS*suggests the formation of more order activated complex, whereas the high positive value of the free energy of the activation (ΔG*) and enthalpy of activation (ΔH*) indicate that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that Pd(II) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

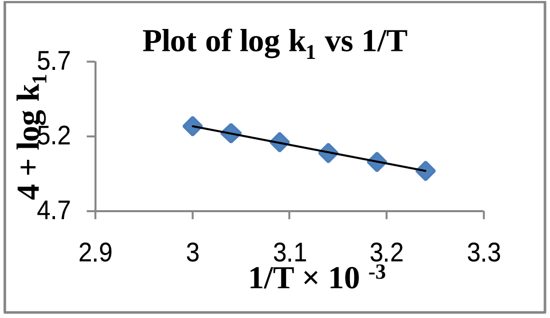
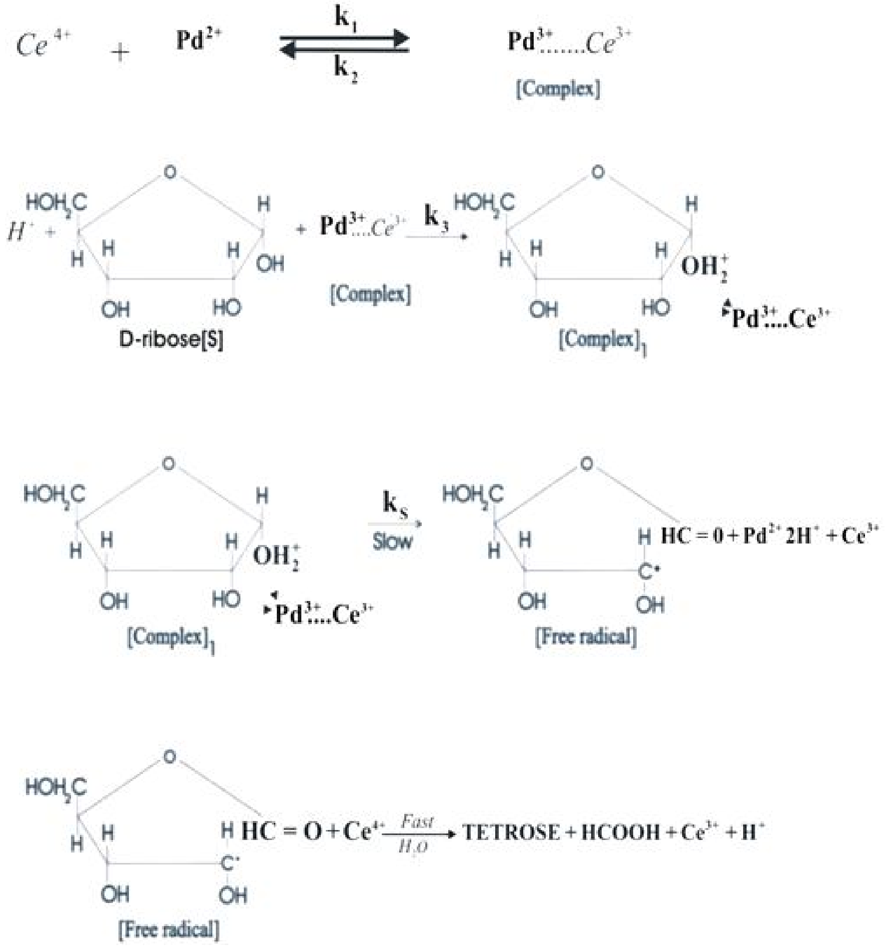


Figure 6 Plot of log k_1 vs. 1/T

Reaction Mechanism: The kinetic data fits well with the Michaelis-Menten model, suggesting that 1:1 type complex of substrate D-(+) ribose and Pd (II) is formed in the first equilibrium step. The plots of the data are linear indicating that the catalysed oxidation reactions are acid dependent [22-25]. The kinetics of this reaction were studied and showed that the sugars, Ce (IV) and catalyst ion Pd (II) interact in two equilibrium steps to form an intermediate complex [26-27] which is assumed to disproportionate forming a free radical and reduced to Ce(III). It is believed to involvement of both C_1 and C_2 hydroxyls [28] in a complex. Substrate is easily protonised in acid media in the presence of catalyst, indicating involvement of H^+ ion 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).

Rate Law: The oxidation of D-(+) ribose 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).



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

The observed Stoichiometry of the reaction corresponds to the reaction as represented by the equation (1)

$$[S] + 2Ce^{4+} \rightarrow \text{Aldotetrose} + HCOOH + 2Ce^{3+} + 2H^+ \qquad (1)$$

In this reaction one mole of [S] = D-(+) ribose oxidized by two mole of cerium (IV).

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

$$\frac{-d\left[Ce(IV)\right]}{dt} = 2k_S[complex] \qquad (2)$$

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

$$\frac{-d\left[Complex\right]}{dt} = k_1[Ce(IV)][Pd(II)] - k_2[complex] - k_3[complex][S] \qquad (3)$$

At steady state condition,

$$\frac{-d\left[Complex\right]}{dt}=0 \qquad (4)$$

Hence,

$$k_1[Ce(IV)][Pd(II)]=k_2[complex]+k_3[complex][S] \qquad (5)$$

Therefore, the concentration of the complex becomes

$$[Complex]=\frac{k_1[Ce(IV)[Pd(II)]}{\{k_2+k_3[S]\}} \qquad (6)$$

At steady state condition, the rate of disappearance of [Ce(IV)] as given as in equation (7)

$$\frac{-d\left[Ce(IV)\right]}{dt}=2ks[complex]_1 \qquad (7)$$

or,

$$\frac{-d\left[Ce(IV)\right]}{dt}=2k_S\,k_3\left[S\right]\left[complex\right] \qquad (8)$$

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

Putting the value of [complex] we have

$$\frac{-d\left[Ce(IV)\right]}{dt}=\frac{2k_S\,k_1\,k_3[S][Ce(IV)][Pd(II)]}{\left\{k_2+k_3\left[S\right]\right\}} \qquad (9)$$

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

$$[Ce(IV)]_T = [Ce(IV)]_e + [complex] \qquad (10)$$

Putting the value of [complex] we have,

$$[Ce(IV)]_T=[Ce(IV)]e+\frac{k_1[Ce(IV)][Pd(II)]}{\{k_2+k_3[S]\}} \qquad (11)$$

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

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

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

From equation (9) and (13), the final rate law comes out to be,

$$\frac{-d\left[Ce(IV)\right]}{dt}=\frac{2k_Sk_1k_3[S][Pd(II)]}{\{k_2+k_3[S]\}}\times\frac{[Ce(IV)]_T\{k_2+k_3[S]\}}{\{k_2+k_3[S]\}+k_1[Pd(II)]} \qquad (14)$$

$$\frac{-d\left[Ce(IV)\right]}{dt}=\frac{2k_Sk_1k_3[S][Pd(II)][Ce(IV)]_T}{\{k_2+k_3[S]\}+\{k_1[Pd(II)]\}} \qquad (15)$$

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

$$\{k_2+k_3[S]\} >> \{k_1[Pd(II)]\} \qquad (16)$$

and hence ,equation (7.3.13) becomes as

$$\frac{-d\left[Ce(IV)\right]}{dt}=\frac{2k_Sk_1k_3[S][Pd(II)][Ce(IV)]_T}{k_2+k_3[S]}$$

(17)

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

$$\frac{1}{k_{obs}} = \frac{1}{2k_S k_1 [Pd(II)]} + \frac{k_2}{2k_S k_1 k_3 [S][Pd(II)]} \quad (19)$$

The plot of $1/k_{obs}$ against 1/[S] is made from which the constants1/ $k_s k_1$ 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 between1/k_{obs} and 1/[S], a positive intercept would be observed which confirms the validity of the mechanism and also the rate law. Equation (9) also suggests that the plot of $1/k_{obs}$ versus $1/[H^+]$ at constant[Pd(II)] and [S] should also be linear. $1/k_{obs}$ 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.

Since Pd (II) is inert [4] in the proposed mechanism, it may bond to $[Ce^{+4}]$ to form an outer-sphere complex $[Pd^{+3}\ldots Ce^{+3}]$, which is rapidly reduced into an inner sphere complex by D-(+) ribose. As Pd^{+3} is unstable, the free radicals can be generated through an inner-sphere electron transfer process between $Pd^{+3}$and D-(+) ribose. Meanwhile, $Pd^{+3}$and the partially oxidized product can be obtained. Thus, the oxidation of D-(+) ribose occurs through the Pd^{+2}/ Pd^{+3} catalytic cycle.

APPLICATIONS

Oxidation of cerium (IV) in presence of metal ion catalysis in the presence of acidic medium was found several synthetic applications to cerate oxidimetry reactions and determining the organic compounds. Cerium (IV) react with D-(+) ribose to form a complex in first equilibrium step which on further gives the products of oxidation in presence of catalyst palladium chloride. The reaction follows first order kinetics. Rate of reaction is directly proportional to catalyst concentrations.

CONCLUSIONS

The oxidation of D-(+) ribose by cerium (IV) in sulfuric acid medium is to take place between the positively charged species of cerium (IV) and pyranose form of the monosaccharide. The reaction occurs through the formation of an intermediate complex, which undergoes slowly unimolecular decomposition to yield a free radical. The free radical then reacts with cerium (IV) species to form the product. The high negative value of ΔS^* suggests the formation of more activated complex whereas, the positive value of free energy of activation (ΔG^*) and enthalpy of activation (ΔH^*) indicate that the transition state is highly solvated. Energy of activation, free energy of activation and entropy parameters suggest that Pd (II) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

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