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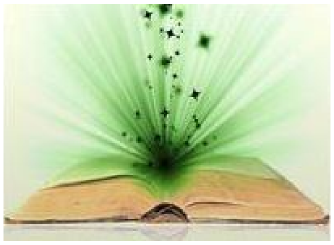

Kinetics and Mechanism of Rh(III) Catalysed Oxidation of D-ribose by Cerium(IV) in Aqueous Acidic Medium

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ABSTRACT

A Kinetics investigation of 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 ribose in the presence of Rh(III) catalysed .The rate follow first order kinetics in Rh(III)catalysed oxidation reaction. The effect of [HSO_4^-] has also been observed. A 1 : 2 stoichiometry is observed in the oxidation. From the effect of temperature on the rate of reaction , the Arrhenius equation and various activation parameters have been computed. A suitable mechanism has been proposed and a rate law explaining the experimental observations is derived.

Keywords: Kinetics, Reaction mechanism, Oxidation, Rhodium, Cerium (IV), Arrhenius equation.

INTRODUCTION

Kinetic studies have been used as a tool to know the mechanism of a reaction. In this paper the primary aim is to ascertain the catalysed molecular reaction of D-(+)ribose by titrimetric method in view of the analytical, synthetical and biological importance of reducing sugar. The kinetics and mechanism of rhodium(III) catalysed oxidation of dextrose is very important tool in medicinal and organic chemistry. Therefore it is beneficial to explore the kinetics oxidation of ribose by cerium(IV).

Rhodium(III) is an efficient catalyst in many redox reactions involving different complexities due to the formation of intermediate complex, free radicals and multiple oxidation state of rhodium. Rhodium complexes are reported[1] to have chemical reactivity, antitumor activity, electronic structure and catalytic functions with potential industrial application. Rhodium(III) chloride is reported to form a variety of complexes such as $(RhCl)^{2+}$, $(RhCl_2)^{+}$, $(RhCl_3)$, $(RhCl_4)^{-}$,$(RhCl_5)^{2-}$, and $(RhCl_6)^{3-}$ in the presence of HCl with varying concentration[2].Rhodium complexes are reported as versatile catalysts, which can be used for several oxidation reactions[3-5].Recently, use of chloro complex of Rh(III) as homogeneous catalyst has been reported for the oxidation of reducing sugars by N-bromoacetamide[6-8] and N-bromosuccinimide[9] in acidic medium. Literature survey indicates that, there are few reports[10-12] on the rhodium(III) mediated oxidation of sugars in presence of acidic medium by cerium(IV). Hence we have investigated the rhodium mediated oxidation of D-(+) ribose by cerium(IV) in order to understand the behavior of active species of oxidant in sulphuric acid media and to propose a suitable plausible 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 Rh(III) chloride(E. Merck) was prepared by dissolving the sample in sulfuric acid of known strength. Cerium(IV) [0.1M] acidified with sulfuric acid in the presence of $RhCl_3$ and a known concentration of $KHSO_4$salt solution is also taken in a 250 ml iodine flask and placed in a thermostat for two hours to attain the temperature. Cerium(IV) is stable in acidic solution and do not show any photochemical decompose. Hence, the rates could be measured in daylight[13]. 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. Liberated iodine was titrated against standard sodium thiosulphate solution using starch indicator . 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[21].Formic acid formation and respective aldotetrose were confirmed by spot test[14] 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 trapping method[15].

RESULTS AND DISCUSSION

Under the conditions [S]>>[Ce(IV)]>>[Rh(III)], 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 Table1.

Table 1. Effect of variation of Oxidant[Cerium(IV)] on the reaction rate at 308K
10^2[ribose]=5.00 mol dm^{-3}; 10^6[Rh(III)]=1.90 mol dm^{-3}; $10^2[H_2SO_4]$=3.00 mol dm^{-3}; $10^3[KHSO_4]$= 5.00 mol dm^{-3}.

Run No.	10^3[Ce(IV)] mol dm^{-3}	$10^4\times k_1$ sec^{-1}
1	1.00	5.92
2	3.00	5.86
3	5.00	5.80
4	7.00	5.73
5	9.00	5.69
6	11.00	5.62
7	13.00	5.57

The results show that the rate constant is inversely proportional to the concentration of cerium(IV) for catalysed system. In the presence of catalyst Rh(III) 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).

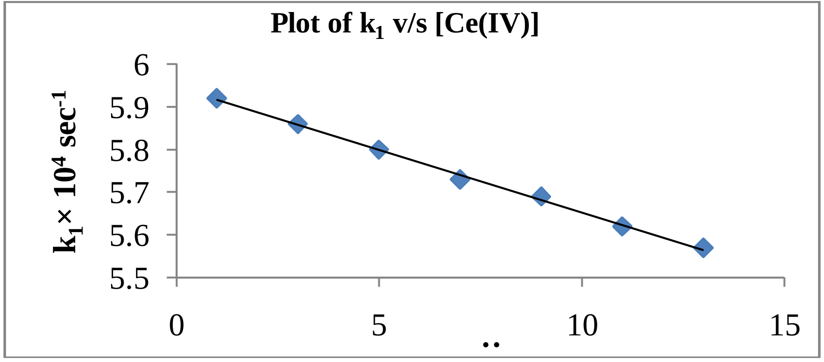


Figure-1 Plot of k_1 v/s [Ce(IV)]

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
10^3[Ce(IV)]=3.00 mol dm^{-3}; 10^6[Rh(III)]=1.90 mol dm^{-3}; 10^2[H_2SO_4]=3.00 mol dm^{-3}; 10^3[$KHSO_4$]= 5.00 mol dm^{-3}.

Run No.	10^2x[D-ribose]mol dm^{-3}	k_1x10^4 sec^{-1}
1	0.50	4.40
2	1.50	5.38
3	2.50	6.03
4	3.50	6.50
5	4.50	7.00
6	5.50	7.20
7	6.50	7.41

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 in 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[ribose] is linear in Figure 2b. This indicates that the order with respect to substrate D-(+)ribose is one.

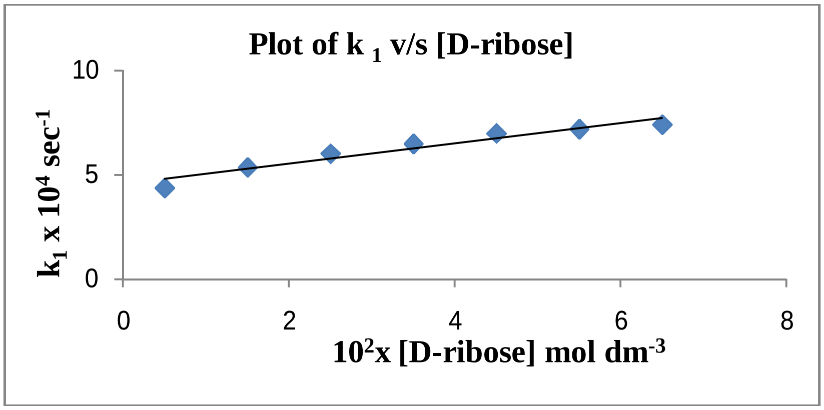


Figure 2(a). Plot of k_1 v/s [D-ribose]

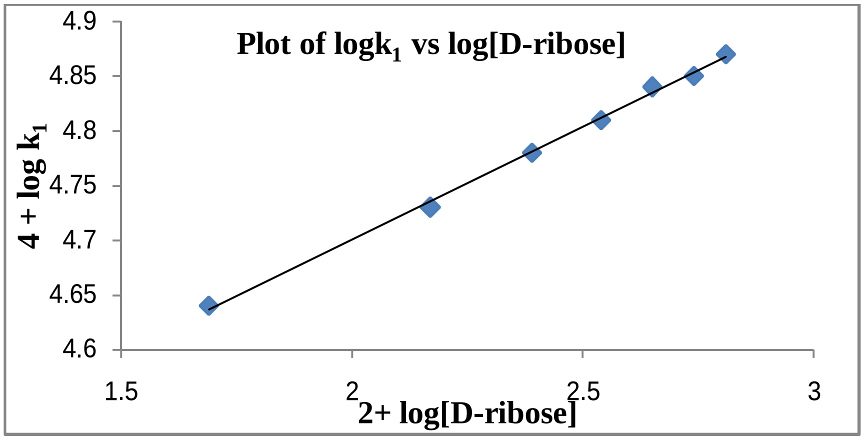


Figure 2(b). Plot of k_1 v/s [D-ribose]

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.

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

10^3[Ce(IV)]=3.00 mol dm^{-3}; 10^6×[Rh(III)]=1.90 mol dm^{-3}; 10^2[D-ribose]=5.00 mol dm^{-3}; 10^3[$KHSO_4$]= 5.00 mol dm^{-3}.

Run No.	**10^2x[H_2SO_4] mol dm^{-3}**	**k_1x10^4sec^{-1}**
1	3.50	6.50
2	5.00	5.56
3	7.00	4.72
4	9.00	4.34
5	11.00	4.12
6	13.00	3.78
7	15.00	3.68

Form the Table 3 it was found that the rate of reaction decreases with the increase of sulphuric acid concentration in Rh(III) 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.

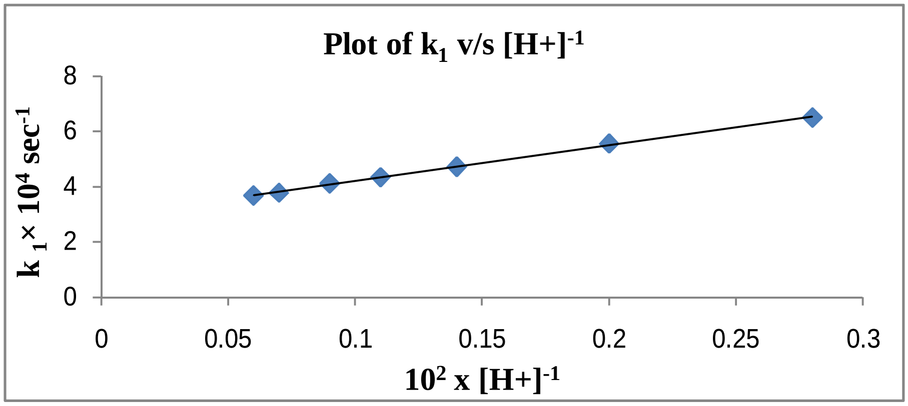


Figure 3(a) . Plot of k_1 v/s $[H^+]^{-1}$

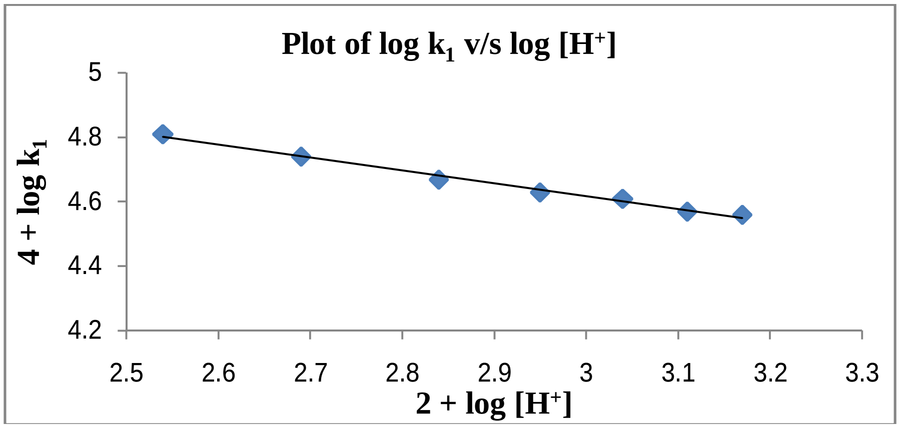


Figure 3(b). Plot of log k_1 v/s log $[H^+]$

In order to see the effect of catalyst $RhCl_3$ on the reaction velocity, the reaction has been carried out at various initial concentration of rhodium trichloride. The result so obtained are given in Table 4.

Table 4. Effect of variation of [Rh(III)]on the reaction rate at 308K
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}.

Run No.	10^6 x [Rh(III)] mol dm^{-3}	k_1x10^4 sec^{-1}
1	1.90	6.50
2	3.00	7.80
3	5.00	9.55
4	7.00	10.98
5	9.00	12.40
6	11.00	13.19
7	13.00	14.41

The above data indicates that the rate is dependent on the catalyst concentration. When a graph is plotted between $RhCl_3$ concentration and the rate constant, a linear curve is obtained indicating that the rate is linearly related to $RhCl_3$ concentration. The plot of logk_1 v/s log[Rh(III)] is linear (Figure 4). The reaction rate increases with increase in Rh(III), suggesting that rate is directly proportional to the Rh(III).

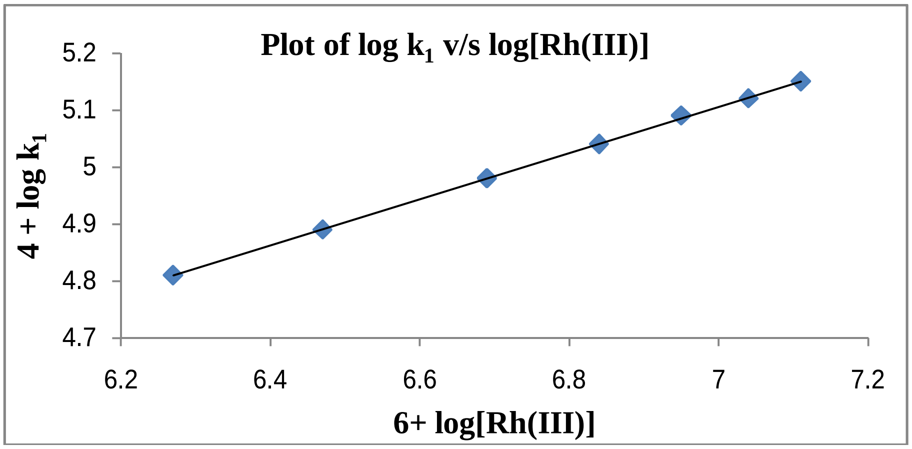


Figure 4. Plot of log k_1 v/s log[Rh(III)]

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
10^3[Ce(IV)]=3.00 mol dm^{-3}; $10^2\times$[H_2SO_4]=3.00 mol dm^{-3}; 10^2[D-ribose]=5.00 mol dm^{-3}; $10^6\times$[Rh(III)]] = 1.90 mol dm^{-3}.

Run No.	10^3x[$KHSO_4$] mol dm^{-3}	k_1x10^4 sec^{-1}
1	0.00	6.50
2	2.00	7.80
3	4.00	10.30
4	6.00	10.98
5	8.00	12.04
6	10.00	13.19
7	12.00	14.35

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.

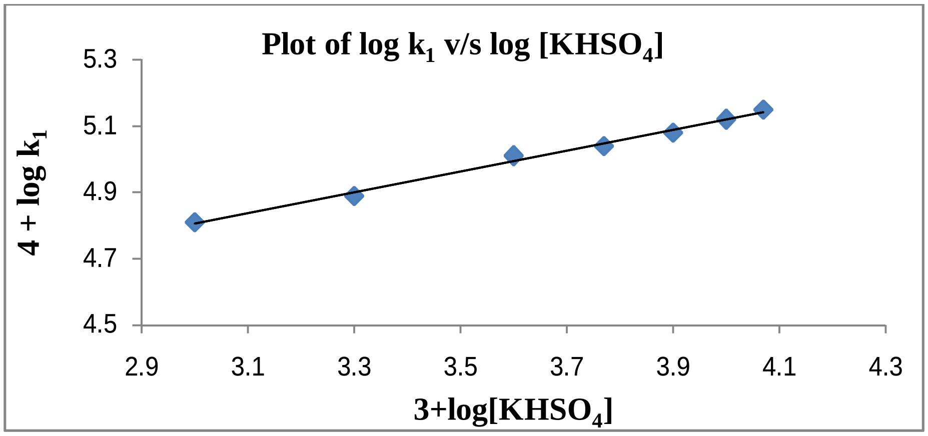


Figure 5. Plot of log k_1 v/s log [KHSO4]

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.

Table 6. Effect of variation of [Temperature]on the reaction
10^3[Ce(IV)]=3.00 mol dm^{-3}; $10^2\times$[H_2SO_4]=3.00 mol dm^{-3};10^2[D-ribose]= 5.00 mol dm^{-3}; $10^6\times$[Rh(III)]] = 1.90 mol dm^{-3}; 10^3[$KHSO_4$]= 5.00 mol dm^{-3}

Temperature in K	1/T x 10^{-3}	k_1x$10^4$$sec^{-1}$
308	3.24	6.50
313	3.19	7.80
318	3.14	9.34
323	3.09	10.97
328	3.04	13.19
333	3.00	15.42

Kinetic and activation parameters for Rh(III) catalysed reaction

Parameter	**D-ribose**
E_a* (kJ mol^{-1})	29.47
ΔH* (kJ mol^{-1})	26.82
ΔS* (J mol^{-1})	-134.22
ΔG* (kJ mol^{-1})	69.51
log A	5.81

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.

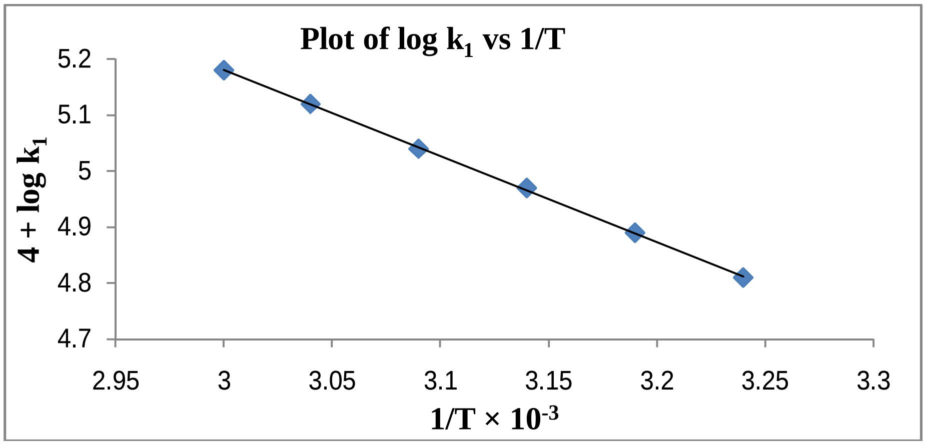
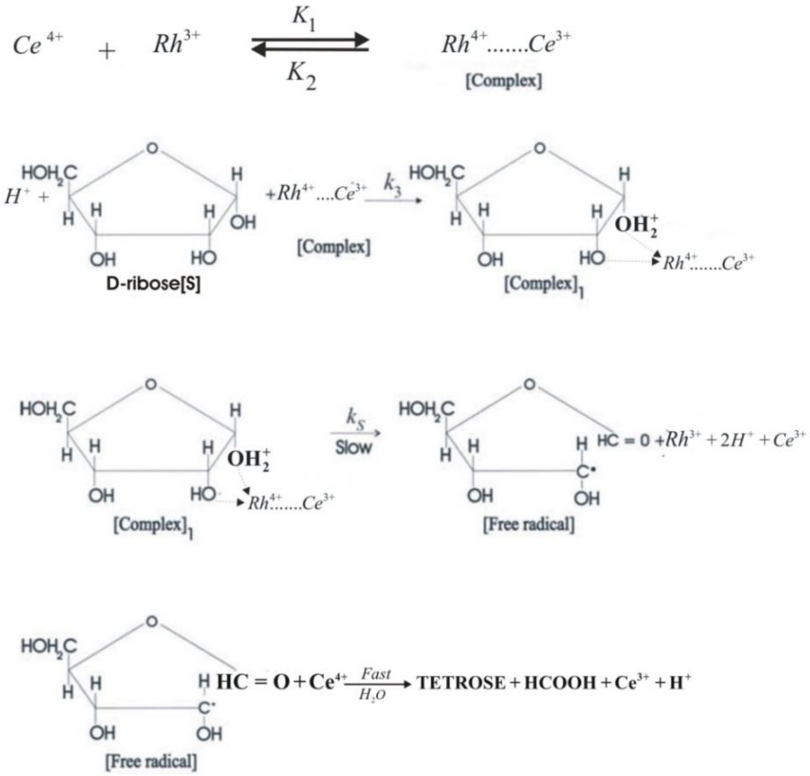


Figure 6. Plot of log k_1 vs. 1/T

Energy and Entropy of Activation: The result shows that the average value of energy of activation energy (E_a) was found to be 29.47 kJ/mol for rhodium(III) catalysed oxidation. The value of frequency factor at 318K is 5.81 min^{-1} and entropy of activation at 318K is -134.22 J mol^{-1} and free energy of activation(ΔG*) 69.51 $kJmol^{-1}$.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 Rh(III) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

Reaction Mechanism: The kinetic data fit well with the Michaelis-Menten model, suggesting that 1:1 type complex of substrate D-(+)ribose and Rh(III) catalysed is formed in the first equilibrium step. The kinetics of this reaction were studied and showed that the D-(+)ribose, cerium(IV) and catalyst Rh^{3+} ion interact in two equilibrium steps to form an intermediate complex[16-18] which is assumed to disproportionate forming a free radical and reduced to Ce^{+3} ion. It is believed to involvement of both C_1 and C_2 hydroxyls [19] in a complex.

Substrate is easily protonated in acid media in the presence of catalyst, indicating involvement of 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).



Scheme 1 Mechanism of oxidation of D-(+)ribose in the presence of Rh(III) catalyst

Rate Law: The oxidation of D-(+) ribose in presence of rhodium 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 (1)

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

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,

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

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

$$\frac{-d\left[Complex\right]}{dt} = k_1[Ce^{IV}][Rh^{III}] - k_2[complex] - k_3[complex][S] \text{---(3)}$$

At steady state condition,

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

Hence, $$k_1[Ce^{IV}][Rh^{III}] = k_2[complex] - k_3[complex][S] \qquad \text{-------(5)}$$

Therefore, the concentration of the complex becomes

$$[Complex] = \frac{k1[Ce^{IV}][Rh^{III}]}{\{k2 + k3[S]\}} \qquad \text{-------(6)}$$

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

$$\frac{-d\left[Ce^{IV}\right]}{dt} = 2ks[complex]_{1} \qquad \text{-------(7)}$$

or,

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

Putting the value of [complex] we have

$$\frac{-d\left[Ce^{IV}\right]}{dt} = \frac{2k_s\, k_1\, k_3[S][Rh^{III}][Ce^{IV}]}{\left\{k_2 + k_3\left[S\right]\right\}} \qquad \text{------- (9)}$$

Now, the total [Ce ^{IV}] may be considered as :

$$[Ce^{IV}]_T = [Ce^{IV}]_e + [complex] \qquad \text{-----(10)}$$

Putting the value of [complex] we have,

$$[Ce^{IV}]_T = \frac{[Ce^{IV}]e + k_1[Rh^{III}][Ce^{IV}]}{\{k_2 + k_3[S]\}} \qquad \text{-----(11)}$$

$$[Ce^{IV}]_T = \frac{[Ce^{IV}]e\{k_2 + k_3[S]\} + [k_1[Rh^{III}][Ce^{IV}]]}{\{k_2 + k_3[S]\}} \qquad \text{----(12)}$$

The value of [Ce ^{IV}]$_T$ comes out to be,

$$[Ce^{IV}]_T = \frac{[Ce^{IV}]_T\{k_2 + k_3[S]\}}{\{k_2 + k_3[S]\} + \{k_1[Rh^{III}]\}} \qquad \text{-----(13)}$$

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

$$\frac{-d\left[Ce^{IV}\right]}{dt} = \frac{2k_S k_1 k_3[S][Rh^{III}]}{\{k_2 + k_3[S]\}} \times \frac{[Ce^{IV}]_T\{k_2 + k_3[S]\}}{\{k_2 + k_3[S]\} + k_1[Rh^{III}]} \qquad \text{-----(14)}$$

$$\frac{-d\left[Ce^{IV}\right]}{dt} = \frac{2k_S k_1 k_3[S][Rh^{III}][Ce^{IV}]_T}{\{k_2 + k_3[S]\} + \{k_1[Rh^{III}]\}} \qquad \text{----(15)}$$

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

$$\{k_2 + k_3[S]\} >> \{k_1[Rh^{III}]\} \qquad \text{-------(16)}$$

And hence equation (13) becomes as

$$\frac{-d\left[Ce^{IV}\right]}{dt} = \frac{2k_S k_1 k_3[S][Rh^{III}][Ce^{IV}]_T}{k_2 + k_3[S]} \qquad \text{------(17)}$$

$$k_{obs} = \frac{\frac{-d[Ce^{IV}]}{dt}}{[Ce^{IV}]_T} = \frac{2k_s k_1 k_3[S][Rh^{III}]}{k_2 + k_3\left[S\right]} \qquad \text{------(18)}$$

$$\frac{1}{k_{obs}} = \frac{1}{2k_S k_1 [Rh^{III}]} + \frac{k_2}{2k_S k_1 k_3 [S][Rh^{III}]} \qquad \text{------(19)}$$

On the plot of $1/k_{obs}$ against 1/[S] is made from which the constants$1/\ k_sk_1$ and $k_2/k_sk_1k_3$ are determined from the slope and intercept respectively. According to the equations mentioned in the above; when plots are made between $1/k_{obs}$ 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$[Rh^{\ III}]$ and [S] should also be linear. $1/k_{obs}$ versus $1/[Rh^{\ III}]$ at constant [S] and $[H^+]$ should yield good linear plots through the origin. The values of $k_sk_1k_3$ and k_2 for [S] can also be calculated from the double reciprocal plots as shown in the graphs.

Since $Rh^{\ III}$ is inert [20] in the proposed mechanism, it may bond to$[Ce^{4+}]$ to form an outer-sphere complex$(Rh^{4+}…..Ce^{3+})$, which is rapidly reduced into an inner-sphere complex by D-(+)ribose. As Rh^{4+} is unstable, the free radicals can be generated through an inner-sphere electron transfer process between Rh^{4+} and ribose. Thus the oxidation of dextrose occurs through the Rh^{3+}/Rh^{4+} catalytic cycle.

APPLICATIONS

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

CONCLUSIONS

The proposed mechanism is well supported by the moderate values of energy of activation and thermodynamic parameters. The high positive value of the energy of activation(E_a) and (ΔH^*) indicate that the transition state is highly solvated where as the negative value of entropy of activation (ΔS^*) indicated that the activated complex is cyclic nature. Based on the kinetic results and reaction stoichiometry , a suitable mechanism has been proposed.

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