RESEARCH ARTICLE

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Kinetics and Mechanism of Rhodium(III) Catalyzed Oxidation of Dextrose by Cerium(IV) in Aqueous Acidic Medium

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Abstract
A kinetics investigation of catalysed oxidation of D-(+)dextrose 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 dextrose in the presence of Rh(III) catalysed. The rate follows 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(III); Cerium(IV); Arrhenius.

1. 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-(+)dextrose 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 of oxidation of sugars 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 sugars by cerium(IV) in order to understand the behavior of active species of oxidant in sulphuric acid media and to propose a suitable mechanism.

2. Methods

An aqueous solution of cerium(IV) and D-(+)dextrose (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) trichloride (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 $KHSO_4$(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 do not show 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 up to 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.

2.1 Product identification

Formic acid formation and respective aldopentose were confirmed by spot test [14] and also by paper chromatography and high performance liquid chromatographic method. Formation of intermediate carbon centered aldopentose free radicals were confirmed by induced polymerization reaction with acrylonitrile and EPR spin trapping method [15].

3. Results and Discussion

Under the conditions [S]>>[CeIV]>>[RhIII], the reaction is studied at different concentrations of oxidant cerium(IV) at constant concentrations of other reactants. The order of reaction with respect to oxidant cerium(IV) is determined at constant concentration of substrate D-(+)dextrose for different concentration of cerium(IV). The results are given in Table 1.

Table 1: Effect of variation of [Cerium(IV)] on the reaction rate at 308K.
10^2[Dextrose]=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}	$k_1 \times 10^4$ sec^{-1}
1	1.00	5.22
2	2.00	5.18
3	3.00	5.15
4	4.00	5.10
5	5.00	5.06
6	7.00	4.98
7	9.00	4.91

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 were found to be linear (Figure 1). This indicates the first order kinetics with respect to cerium(IV).

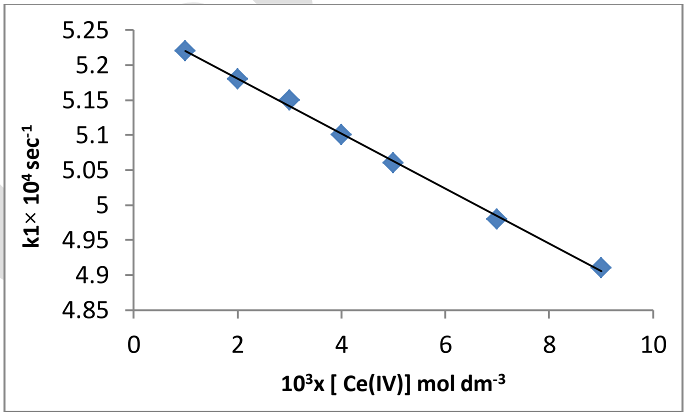


Figure 1: Plot of k_1 v/s [Ce(IV)].

In order to study the behavior of substrate D-(+)dextrose reaction rates, different sets of the experiments were carried out at different concentration of D-(+) dextrose 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 Dextrose 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[dextrose] is linear (Figure 2b). This indicates that the order with respect to substrate D-(+)dextrose is one.

Table 2: Effect of variation of [Dextrose] 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[Dextrose]mol dm^{-3}**	**k_1x10^4 sec^{-1}**
1	1.00	3.29
2	1.40	3.48
3	1.80	3.68
4	2.20	3.84
5	3.00	4.09
6	3.50	4.20
7	4.00	4.36

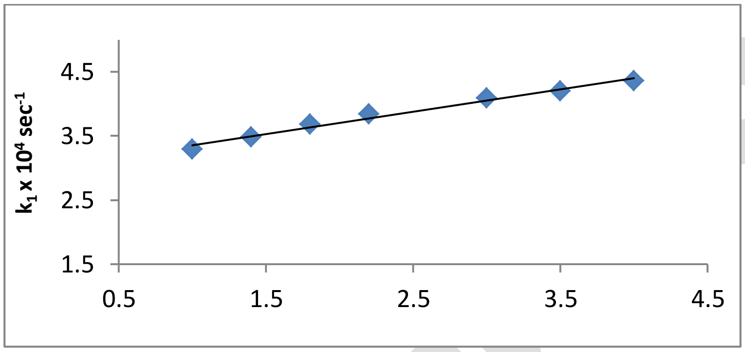


Figure 2(a): Plot of k_1 v/s [Dextrose].

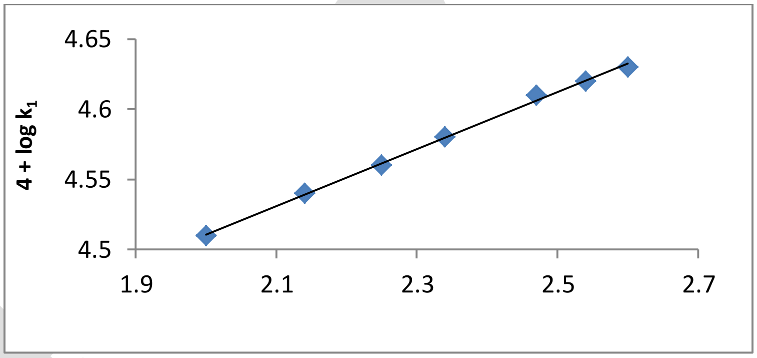


Figure 2(b): Plot of log k_1 v/s log[Dextrose].

In order to see the effect of H^+ ion concentration on the reaction velocity, the reaction has been carried out at various initial concentrations of sulphuric acid, while concentration of other reactants was constant. The results so obtained are represented in Table 3.

Table 3: Effect of variation of [H^+]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[Dextrose]=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	1.00	7.50
2	2.00	4.71
3	3.00	3.75
4	4.00	3.20
5	5.00	2.83
6	7.00	2.50
7	9.00	2.21
8	11.00	2.08

From 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 3(b). The result indicates that the order with respect to $[H^+]$ is inverse first.

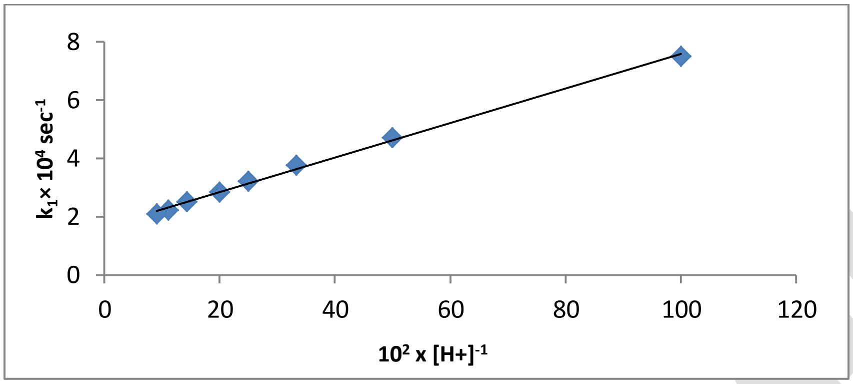


Figure 3(a): Plot of k_1 v/s $[H^+]^{-1}$.

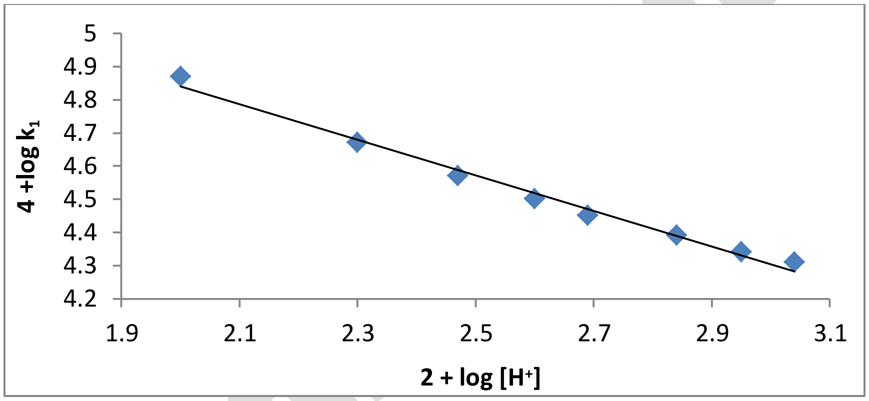


Figure 3(b): Plot of log k_1 v/s log $[H^+]$.

In order to see the effect of catalyst $RhCl_3$ on the reaction velocity, the reaction has been carried out at various initial concentrations of rhodium trichloride. The results 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[Dextrose]=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	1.00	2.22
2	1.40	2.63
3	1.90	3.05
4	2.90	3.72
5	3.90	4.41
6	4.90	5.15
7	5.90	5.87

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 $\log k_1$ 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).

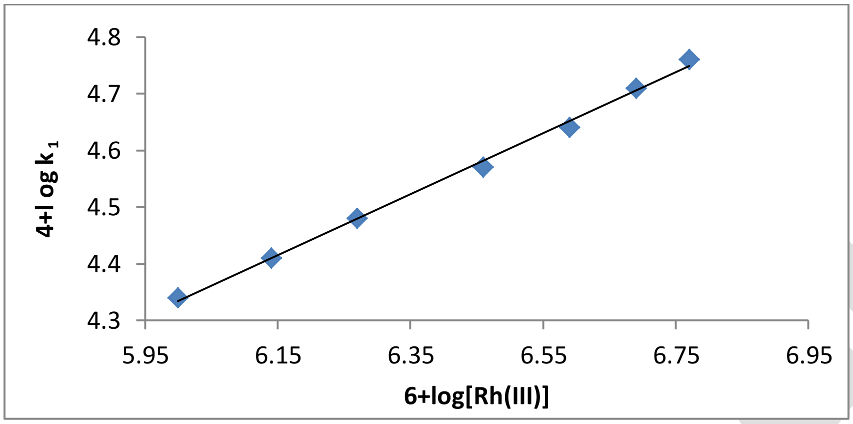


Figure 4: Plot of $\log k_1$ v/s log[Rh(III)].

The reactions were studied at different concentrations 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[Dextrose]=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	1.00	3.05
2	2.00	4.17
3	3.00	5.13
4	4.00	6.10
5	5.00	6.92
6	6.00	7.78
7	8.00	8.92

The graphical plot of $\log K_1$ 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.

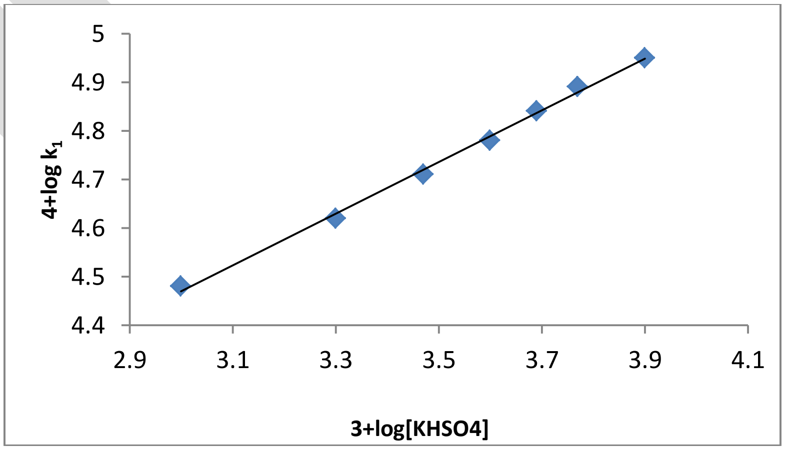


Figure 5: Plot of log k_1 v/s log $[KHSO_4]$.

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 constant. The observations are given in Table 6.

Table 6: Effect of variation of [Temperature] 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×[Dextrose]=5.00 mol dm^{-3}; 10^6×[Rh(III)]]=1.90 mol dm^{-3};
10^3×[$KHSO_4$]=5.00 mol dm^{-3}

<table>
<tr><th>Temperature in Kelvin</th><th>1/T $x10^{-3}$</th><th>K_1x10^4 sec^{-1}</th></tr>
<tr><td>308</td><td>3.24</td><td>3.05</td></tr>
<tr><td>313</td><td>3.19</td><td>3.90</td></tr>
<tr><td>318</td><td>3.14</td><td>5.14</td></tr>
<tr><td>323</td><td>3.09</td><td>6.61</td></tr>
<tr><td>328</td><td>3.04</td><td>8.32</td></tr>
<tr><td>333</td><td>3.00</td><td>10.25</td></tr>
<tr><th colspan="3">Kinetic and activation parameters for Rh(III) catalysed reaction</th></tr>
<tr><th>Parameter</th><th colspan="2">D-(+)dextrose</th></tr>
<tr><td>E_a* (kJ mol^{-1})</td><td colspan="2">41.355</td></tr>
<tr><td>ΔH* (kJ mol^{-1})</td><td colspan="2">38.711</td></tr>
<tr><td>ΔS* (J mol^{-1})</td><td colspan="2">-101.845</td></tr>
<tr><td>ΔG* (kJ mol^{-1})</td><td colspan="2">71.097</td></tr>
<tr><td>log A</td><td colspan="2">7.503</td></tr>
</table>

The kinetic data shows that the velocity of reaction increases with rise in temperature, showing the validity of the Arrhenius equation in Figure 5. The plot of log$k_1$vs 1/T is linear. So, an attempt has been made to correlate the various activation parameters on the reaction mechanism.

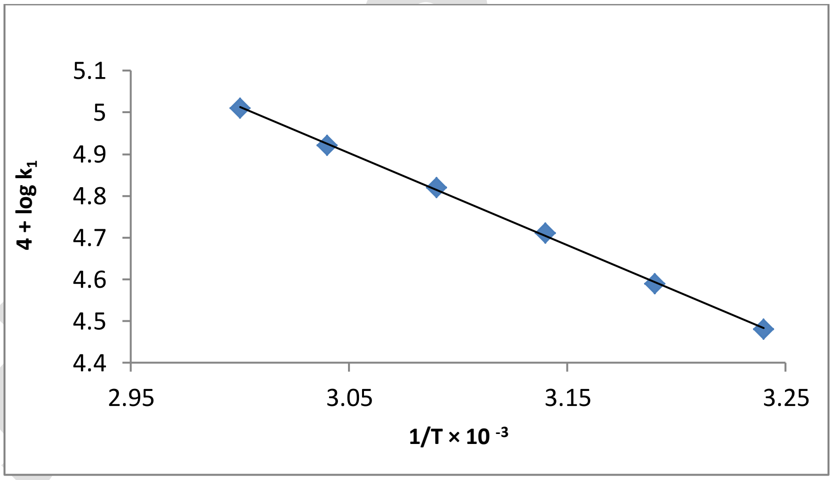


Figure 6: Plot of log k_1 vs 1/T.

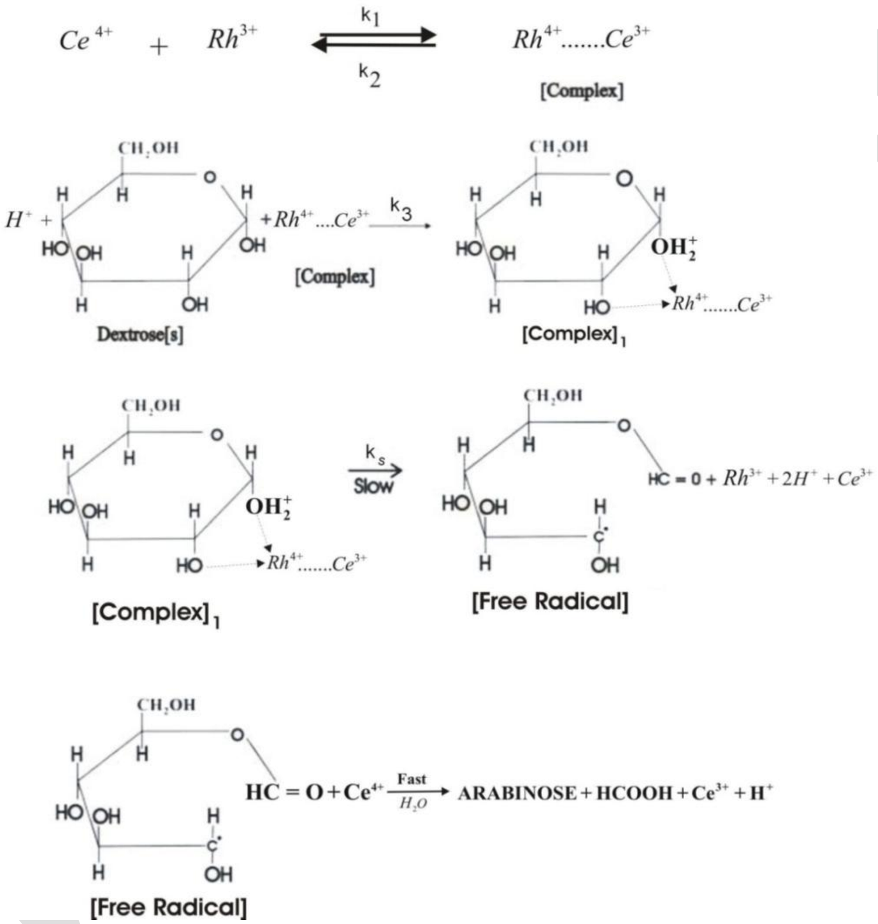
Energy and Entropy of Activation

The result shows that the average value of energy of activation (E_a) was found to be 41.35 kJ/mol for rhodium(III) catalysed oxidation. The value of frequency factor at 318K is 7.50 min^{-1} and entropy of activation at 318K is -101.84 J mol^{-1} and free energy of activation (ΔG*) 71.09 $kJmol^{-1}$. 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(+)dextrose and Rh(III) is formed in the first equilibrium step. The kinetics of this reaction were studied and showed that the D(+)dextrose, cerium(IV) and catalyst Rh^{3+} ion interact in two equilibrium steps to form an intermediate complex [16-18] which is assumed to be disproportionate forming a free radical and reduced to Ce^{+3} ion. It is believed to involve both C_1 and C_2 hydroxyls [19] in a complex.

Substrate is easily protonised 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 dextrose in the presence of Rh(III) catalyst.

Rate Law

The oxidation of D-(+) dextrose 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).

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

In this reaction, one mole of [S] = D(+)dextrose oxidized by two mole of cerium(IV). The rate law of consumption of Ce(IV) is,

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

Based on mechanism as mentioned 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,

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

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

Therefore, the concentration of the complex becomes

$$[Complex] = \frac{k_1[Ce^{IV}][Rh^{III}]}{\{k_2 + k_3[S]\}} \text{ ------- (6)}$$

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

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

1 ------- (7)

or,

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

Putting the value of [complex] we have

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

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

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

Putting the value of [complex] we have,

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

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

[Ce^{IV}] should be $[Ce^{IV}]_e$, since $[Ce(IV)]_e \approx [Ce(IV)]$

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

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

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

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

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

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

And hence, equation (13) becomes,

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

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

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

The plot of 1/k_{obs} 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 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 $k_s k_1 k_3$ and k_2 for [S] can also be calculated from the double reciprocal plots as shown in the graphs.

Since 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-(+)dextrose. As Rh^{4+} is unstable, the free radicals can be generated through an inner-sphere electron transfer process between Rh^{4+} and dextrose. Thus, the oxidation of dextrose occurs through the Rh^{3+}/Rh^{4+} catalytic cycle.

4. Conclusion

The oxidation of D-dextrose 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 slowly undergoes uni-molecular 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^*) indicates 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 has been suggested in this study.

Competing Interests

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

Authors' Contributions

Both authors contributed equally to this work.

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