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

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ABSTRACT

A kinetics investigation of catalysed oxidation of D-(+)galactose 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-(+)galactose in the presence of lanthanum(III) catalysed. The rate follow first order kinetics in lanthanum(III) 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 , the Arrhenius equation and various activation parameters have been computed. A suitable mechanism has been proposed. The reaction constants involved in the different steps of the mechanism have been calculated.

Keywords: Kinetics, Catalysed, D-(+)galactose, Cerium(IV) and Lanthanum(III).

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INTRODUCTION

In the carbohydrate field, many researchers have investigated the oxidative degradation of monosaccharides and their derivatives. This was done by different oxidants such as rhodium(III), chromium(VI),iridium(III),silver(I),ruthenium(III),vanadium(V), cerium (IV),palladium(II),cobalt (III) and iron (III) in aqueous sulfuric, perchloric acids and alkaline medium[1-13]. However, despite the extensive study made on the kinetics of the oxidation of monosaccharides by these oxidants, the use of surfactants in similar studies is not so common[14-18]. The primary aim is to ascertain the catalysed reaction of D-galactose by titrimetric method in view of the analytical, synthetical and biological importance of this sugars. Thus it is beneficial to explore the kinetics of oxidation of sugars by cerium(IV).

MATERIALS AND METHODS

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 using starch as an indicator. The solution of lanthanum 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 lanthanum(III) 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 [19]. 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: Formic acid formation and respective aldopentose were confirmed by spot test [20] 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 [21].

RESULTS AND DISCUSSION

Under the conditions [S]>>[Ce(IV)]>>[La(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-(+)galactose. The results are given in (Table-1).

Table-1. Effect of variation of Oxidant[Cerium(IV)] on the reaction rate at 308K
10^2[D-galactose]=5.00 mol dm^{-3}; $10^7 \times$[La(III)]=4.90 mol dm^{-3}; 10^2[H$_2$SO$_4$]=3.00 mol dm^{-3}; 10^3[KHSO$_4$]= 5.00 mol dm^{-3}

Run No	10^3x[Ce(IV)] mol dm^{-3}	$10^4 \times k_1$ sec^{-1}
1	2.00	5.82
2	4.00	5.23
3	6.00	4.64
4	8.00	4.12
5	10.00	3.51
6	12.00	2.87
7	14.00	2.31

The results show that the rate constant is inversely proportional to the concentration of cerium(IV) for catalysed system. In the presence of catalyst lanthanum(III) the plot of k_1 vs. Ce(IV) concentration are found to be linear(Figure1). This indicates that first order kinetics with respect to cerium(IV).
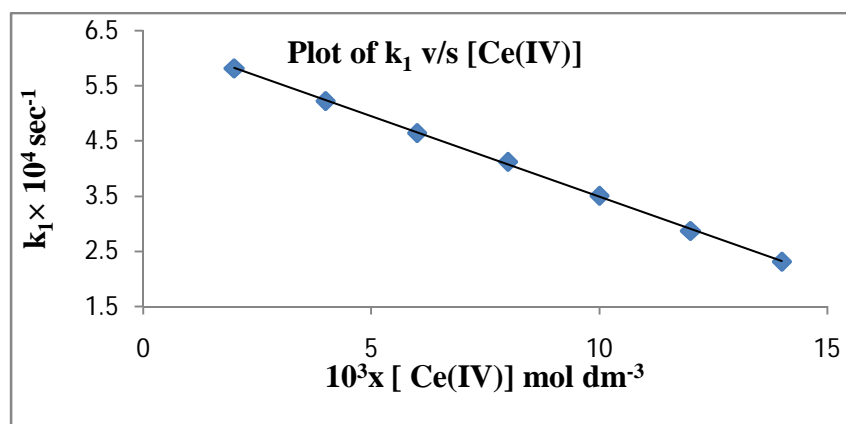

Figure1. Plot of k_1 vs [Ce(IV)]

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).

Table-2; Effect of variation of [D-galactose] on the reaction rate at 308K
10^3[Ce(IV)]=3.00 mol dm^{-3}; $10^7 \times$[La(III)]=4.90 mol dm^{-3}; 10^2[H$_2$SO$_4$]=3.00 mol dm^{-3}; 10^3[KHSO$_4$]= 5.00 mol dm^{-3}

Run No	10^2x[D-galactose]mol dm^{-3}	k_1x10^4sec^{-1}
1	1.50	2.72
2	3.00	5.76
3	5.00	8.79
4	7.00	11.53
5	9.00	14.64
6	11.00	17.58
7	13.00	21.02

The result shows that the graphical plot for the pseudo first order rate constant k_1 vs. D-galactose 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 vs. log[D-galactose] is linear (Figure 2b). This indicates that the order with respect to substrate D-(+)galactose is one.

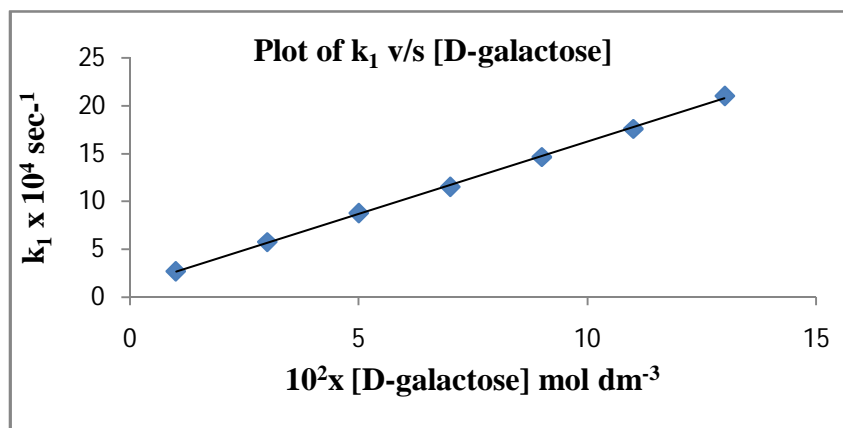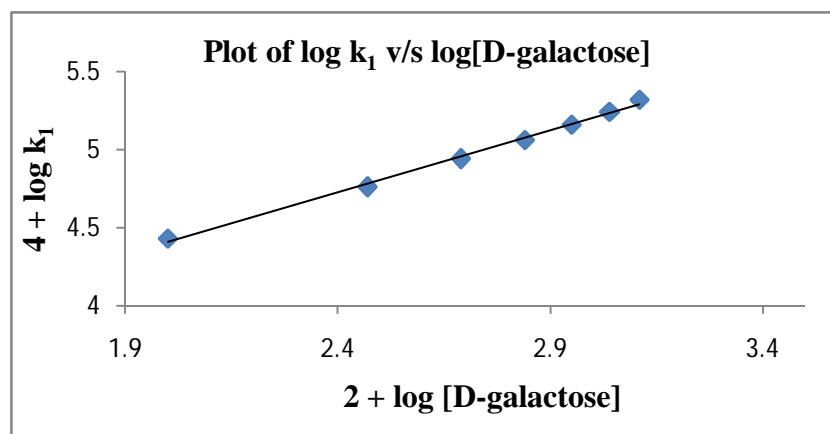**Figure 2(a) Plot of k_1 vs. [D-galactose]**

Figure 2(b) Plot of logk_1 vs. log[D-galactose]

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 308K

$10^3[Ce(IV)]$=3.00 mol dm^{-3}; $10^7 \times [La(III)]$=4.90 mol dm^{-3}; $10^2[D\text{-galactose}]$=5.00mol dm^{-3}; $10^3[KHSO_4]$= 5.00 mol dm^{-3}

Run No	10^2x[D-galactose]mol dm^{-3}	k_1x10^4 sec^{-1}
1	5.00	8.79
2	6.00	7.94
3	8.00	6.92
4	9.00	6.60
5	11.00	6.17
6	12.00	5.83
7	14.00	5.61

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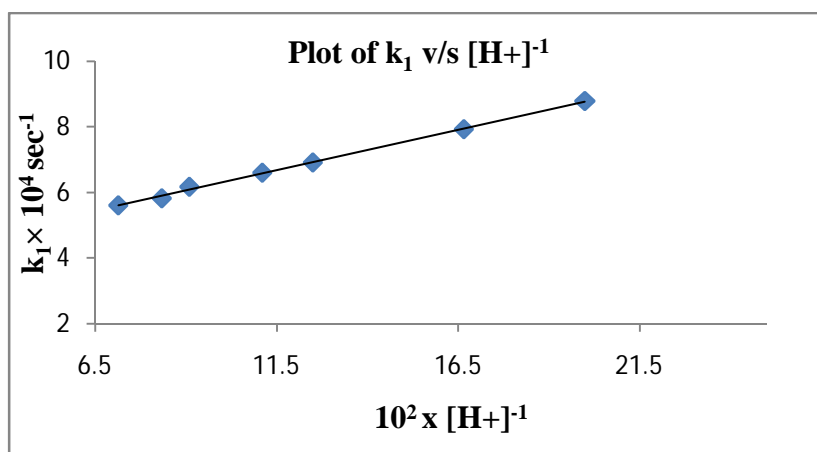

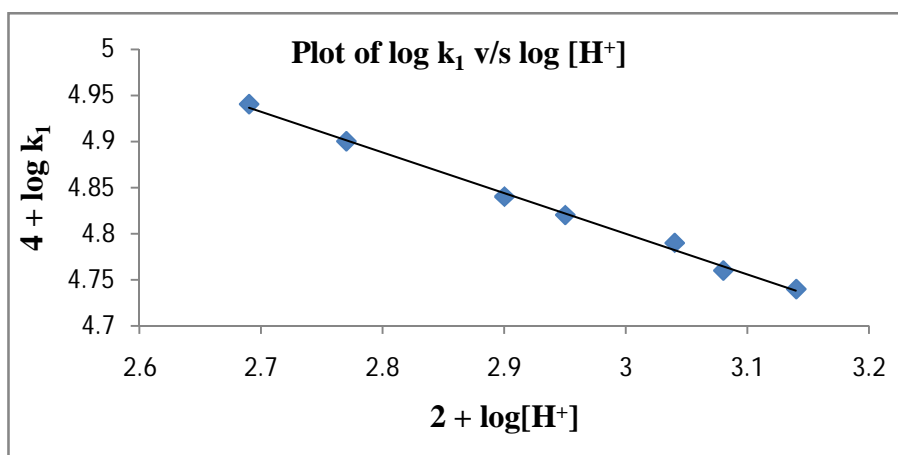**Figure 3(a).** Plot of k_1 vs. $[H+]^{-1}$

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

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In order to see the effect of catalyst lanthanum(III) on the reaction velocity, the reaction has been carried out at various initial concentration of lanthanum trichloride. The result so obtained are given in (Table-4). The table 4 indicates that the rate is dependent on the catalyst concentration.

Table-4. Effect of variation of [La(III)]on the reaction rate at 308K
$10^3 \times$ [Ce(IV)]=3.00 mol dm^{-3}; $10^2 \times$[H$_2$SO$_4$]=3.00 mol dm^{-3};$10^2 \times$ [D-galactose]=5.00mol dm^{-3};
$10^3 \times$ [KHSO$_4$]= 5.00 mol dm^{-3}

Run No	10^7 x [La(III)] mol dm^{-3}	k_1x10^4 sec^{-1}
1	4.90	8.79
2	5.90	7.08
3	6.90	8.51
4	7.90	9.33
5	8.90	10.00
6	9.90	11.48
7	10.90	12.30
8	11.90	17.74

When a graph is plotted between La(III) concentration and the rate constant, a linear curve is obtained indicating that the rate is linearly related to lanthanum(III) concentration. The plot of logk$_1$ v/s log[La(III)] is linear (Figure 4),which confirms first order kinetics with respect to [La(III)].

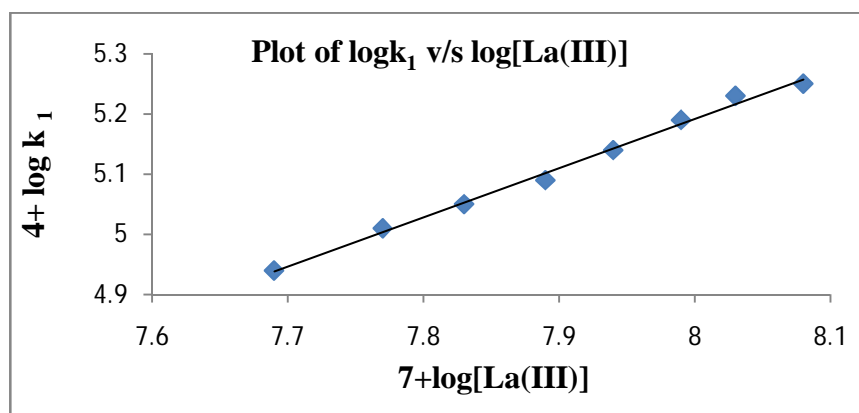**Figure 4.** Plot of logk$_1$ vs. log[La(III)]

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$_2$SO$_4$]=3.00 mol dm^{-3};10^2[D-galactose]=5.00 mol dm^{-3};$10^7 \times$ [La(III)]]=4.90 mol dm^{-3}

Run No	10^3x[KHSO$_4$] mol dm^{-3}	k_1x10^4 sec^{-1}
1	0.50	8.79
2	1.00	9.50
3	3.00	10.96
4	5.00	12.03
5	7.00	12.31
6	9.00	12.59
7	11.00	16.35

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.
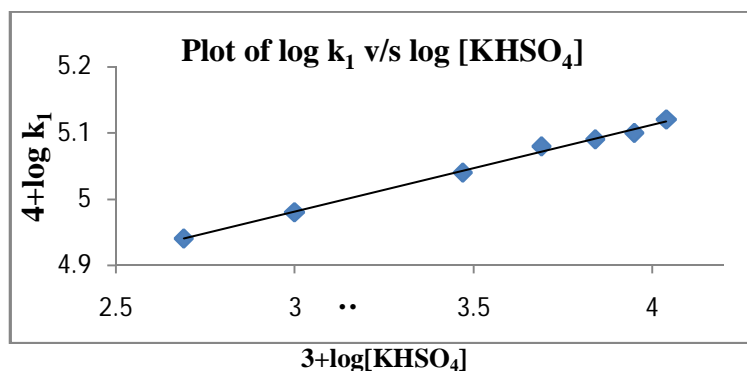
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Figure 5. Plot of log k_1 vs. log [KHSO$_4$]

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 are constant. The observations are given in(Table-6).

Table-6 . Effect of variation of [Temperature]on the reaction rate
$10^3 \times$ [Ce(IV)]=3.00mol dm^{-3};$10^2 \times$[H$_2$SO$_4$]=3.00mol dm^{-3};$10^2 \times$ [D-galactose]=5.00mol dm^{-3};
$10^7 \times$ [La(III)]=4.90 mol dm^{-3}; $10^3 \times$ [KHSO$_4$]= 5.00 mol dm^{-3}

Temperature in K	1/T x10^{-3}	K$_1$x10^4 sec^{-1}
308	3.24	8.79
313	3.19	10.72
318	3.14	13.49
323	3.09	16.22
328	3.04	19.50
333	3.00	23.31
Kinetic and activation parameters for lanthanum(III) catalysed reaction		
Parameter	**D-(+)galactose**	
E$_a$* (kJ mol^{-1})	33.27	
ΔH* (kJ mol^{-1})	30.62	
ΔS* (J mol^{-1})	-119.22	
ΔG* (kJ mol^{-1})	68.54	
log A	6.59	

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.
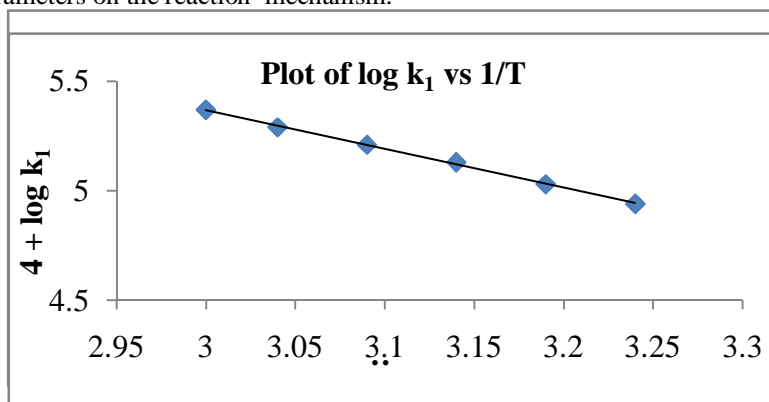

**Figure 6 .**Plot of log k_1 vs. 1/T

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Energy and Entropy of Activation: The result shows that the average value of energy of activation energy (E_a) was found to be 33.27 kJ/mol for lanthanum(III) catalysed oxidation. The value of frequency factor at 318K is 6.59 min^{-1} and entropy of activation at 318K is -119.22 J mol^{-1} and free energy of activation(ΔG^*) 68.54 kJ mol^{-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 La(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(+)galactose and lanthanum(III) catalysed is formed in the first equilibrium step. The kinetics of this reaction were studied and showed that the D-(+)galactose, cerium(IV) and catalyst La^{3+} ion interact in two equilibrium steps to form an intermediate complex[22-24]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 [25] 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).
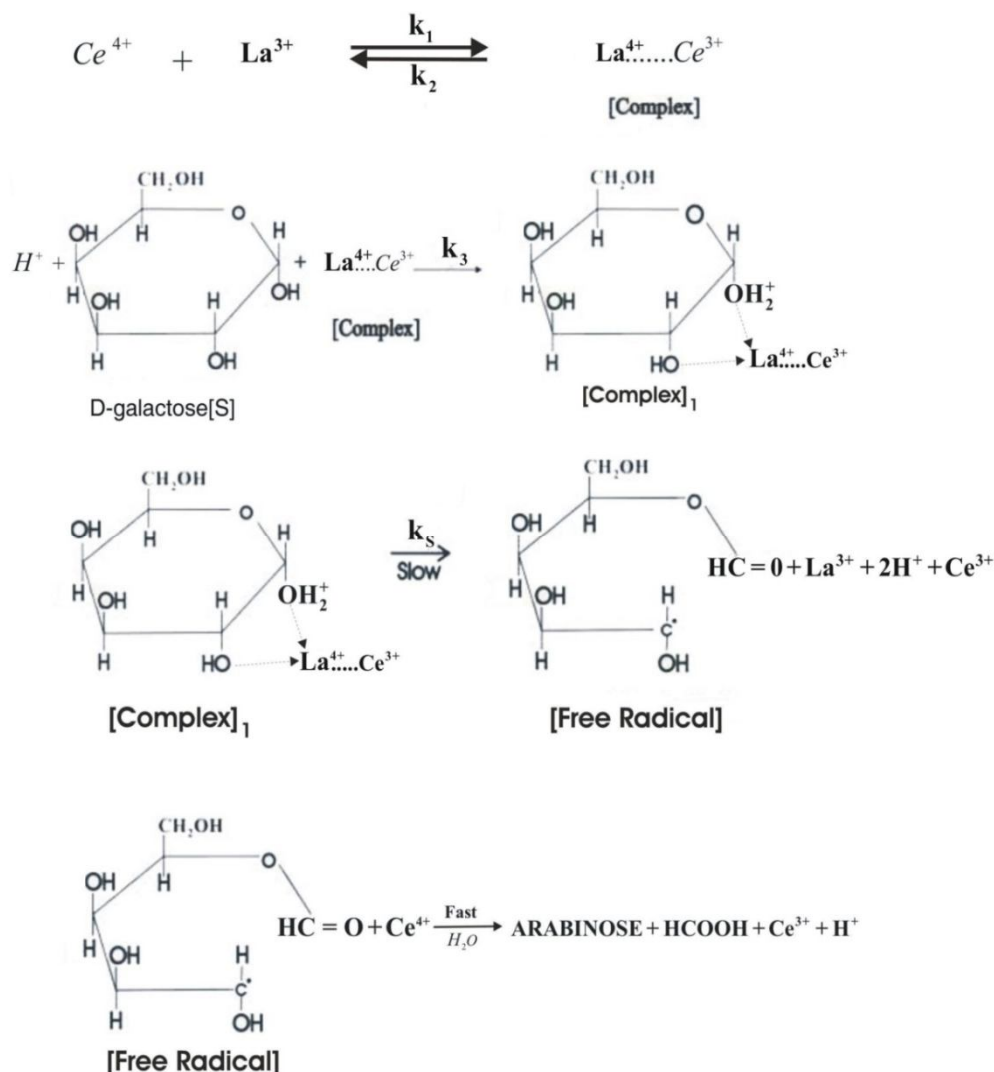
Scheme 1 Mechanism of oxidation of D-(+)galactose in the presence of lanthanum(III) catalyst

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Rate Law: The oxidation of D-(+)galactose in presence of lanthanum 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)

$$[S] + 2Ce^{4+} \rightarrow \text{Aldopentose} + HCOOH + 2Ce^{3+} + 2H^+ \qquad \text{------(1)}$$
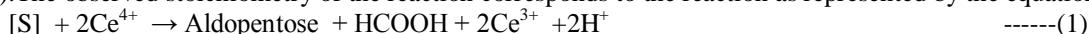
In this reaction one mole of [S] = D(+) galactose oxidized by two mole of cerium(IV).

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,

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

At steady state condition,

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

Hence,

$$k_1[Ce(IV)][La(III)] = k_2[complex] + k_3[complex][S] \qquad \text{-------(5)}$$

Therefore, the concentration of the complex becomes

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

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

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

or,

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

{where, [complex]$_1$ = k$_3$[S][complex]}

Putting the value of [complex] we have

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

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,

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

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

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

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

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

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

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

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

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

And hence ,equation (13) becomes as

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

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

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

On 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 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$[La(III)]$ and $[S]$ should also be linear. $1/k_{obs}$ versus $1/[La(III)]$ 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.

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 oxidation of D-galactose 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 La(III) forms the activated complex more easily compared to the others. Mechanism consistent with observed rate laws have been suggested.

ACKNOWLEDGEMENTS

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