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Reactivity of lactose towards Ce(IV) in sulphuric acid medium in presence of Ir^{3+} catalyst

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Lactose and cerium(IV) reacts in sulphuric acid medium in presence of Ir^{3+} catalyst. Lactose is oxidised to formic acid and cerium(IV) is reduced to cerium(III). One mole of lactose consumes twenty four moles of cerium(IV). The reaction is first order with respect to cerium(IV) as well as lactose. Increase in $[SO_4^{2-}]$ and $[HSO_4^-]$ decrease the rate. The reaction rate increases with increase in $[H^+]$. Ir^{3+} shows positive catalytic effect on reaction rate. The activation parameters have been determined. The rate law is conformity with the observed kinetic data have been derived as

$$\frac{-dln[Ce^{4+}]}{dt} = k_{obs} = \frac{k_1 k_2 k_3 [H_2O][Lactose][Ir^{3+}]}{k_{-1}k_{-2}+k_{-1}k_3[H_2O]+k_2 k_3[H_2O][Ir^{3+}]}$$

Keyword: Reactivity, lactose, Ce^{4+}, Iridium(III), catalyst.

1. Introduction

In acid media cerium(IV) is a strong oxidising agent and used for the oxidation of various organic and inorganic compounds[1-4]. Ru^{3+}, Os^{8+}, Ag^+ etc. have been used as catalyst [5-7]. P. N. Char [8], *et al.* studied a comparative kinetic study of iridium(III) catalysis in H_2SO_4 and $HClO_4$ media in the cerium(IV) oxidation of diacetone alcohol. They reported the formation of intermediate complex between Ir^{3+} and diacetone alcohol. Kinetics of oxidation of hexoses by cerium(IV) in presence of bromide catalyst in sulphuric acid medium have been studied[2,3] and reported the formation of intermediate complex between cerium(IV) and hexoses.

Lactose is soluble in water. Lactose, after the curdling process is not found in fat based portion, whereas it is found in water based portion. The fat free dairy product contains slightly higher lactose content. The presence of lactose in various source of milk from 4.6 to 9 % (approx.) gives rise to gastrointestinal symptoms, caused by a deficiency of the intestinal enzyme lactase that splits lactose into glucose and galactose and allows lactose to be absorbed from the intestine known as lactose intolerance. Lactose intolerance causes the symptoms which may include abdominal bloating, flatulence, diarrhoea, nausea, vomiting arise due to the consumption of significant amounts of lactose [9-11].

The aim of the present investigation is to find out the most probable path of the reaction between lactose and cerium(IV) in presence of Ir^{3+} catalyst in sulphuric acid medium. The investigation also aims to provide the kinetic orders with respect to each reactant of the reactions.

2. Experimental

2.1 Material: All chemicals used were of A.R. grade. Ceric ammonium sulphate solution was prepared by dissolving it in 2N H_2SO_4 and standardized by standard ferrous ammonium sulphate solution in presence of ferroin as an indicator. Ferrous ammonium sulphate solution was prepared by dissolving it in acid and diluted with distilled water and standardized by standard ceric ammonium sulphate solution in presence of ferroin as indicator. Stock solution of lactose was prepared by dissolving it in double distilled water. Stock solution of potassium sulphate, potassium bisulphate, sodium perchlorate and hydrated iridium(III) chloride were prepared by dissolving in double distilled water. Sulphuric acid and sodium perchlorate solutions were used to maintain required acidity and ionic strength respectively. Ferroin indicator was prepared iron(II) sulphate heptahydrate and 1,10-phenanthroline hydrate in double distilled water.

2.2 Methods: The measured amount of reagents i.e., solution of cerium(IV), $NaClO_4$, H_2SO_4 and Ir^{3+} were mixed in a conical flask and thermostated at 40 ^{0}C for thermal equilibrium. A known amount of lactose solution, also thermostated at 40 ^{0}C, was rapidly added to the reaction mixture. The kinetic studies were carried out by quenching an aliquot of the reaction mixture in measured excess of ferrous ammonium sulphate solution and back titrating the unreacted Fe^{2+} solution against standard cerium(IV) solution using ferroin as redox indicator[12].

3. Results and Discussion

3.1 Effect of variation of [Ce^{4+}]: The reaction was studied at various concentration of cerium(IV) varying from 2.5 × 10^{-3} mol dm^{-3} to 5.5 × 10^{-3} mol dm^{-3} but at constant [Lactose], [H_2SO_4], [Ir^{3+}], ionic strength and temperature of 2.5 × 10^{-2} mol dm^{-3}, 5.0 × 10^{-1} mol dm^{-3}, 5.0 × 10^{-3} mol dm^{-3}, 1.629 mol dm^{-3} and 313 K respectively. The average pseudo first order rate constant (55.97 ± 0.75) × 10^{-5} s^{-1} indicates that under the condition, when [Substrate] ≫ [Ce^{4+}], the reaction followed a first order with respect to cerium(IV).

$$\frac{-d[Ce^{4+}]}{dt} = k_{obs}\,[Ce^{4+}]$$

$$\frac{-d\ln[Ce^{4+}]}{dt} = k_{obs} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

3.2 Effect of variation of [Lactose]: To find out the rate constant with respect to substrate, the concentration of lactose was varied in the range 2.5 × 10^{-3} to 10.0 × 10^{-3} mol dm^{-3} at constant [Ce^{4+}], [H_2SO_4], [Ir^{3+}], ionic strength and temperature of 5.0 × 10^{-3} mol dm^{-3}, 5.0 × 10^{-1} mol dm^{-3}, 5.0 × 10^{-3} mol dm^{-3}, 1.62 mol dm^{-3} and 313 K respectively. The pseudo first order rate constants were determined at the different concentrations of lactose. Plot of log k_{obs} against log [lactose] are found to be linear (Figure 1) with slope equal to 0.99 showing first order with respect to [lactose]. In 5.0 × 10^{-1} mol dm^{-3} H_2SO_4, the values of k_s are calculated as (4.46 ± 0.44) × 10^{-1} dm^3 mol^{-1}s^{-1}, (8.68 ± 0.56) × 10^{-1} dm^3 mol^{-1} s^{-1}, (18.48 ± 0.48) × 10^{-1} dm^3 mol^{-1} s^{-1} and (32.44 ± 0.88) × 10^{-1} dm^3 mol^{-1} s^{-1} at 308 K, 313 K, 318 K and 323 K respectively.

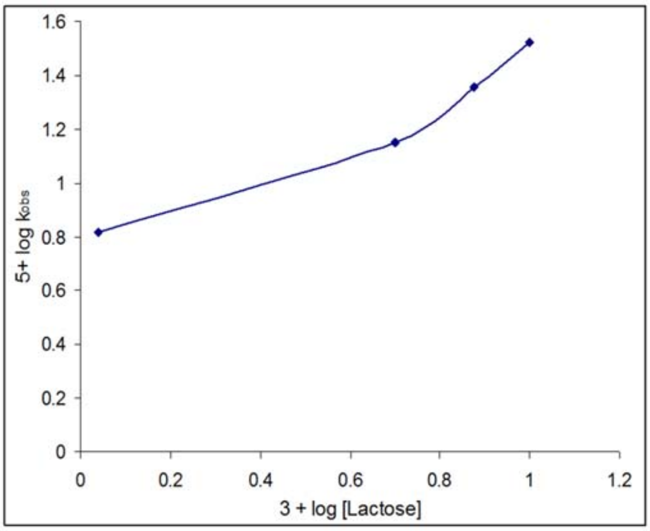

Figure 1. : Plot of log k_{obs} vs log [Lactose] at 313 K. [Ce^{4+}] = 5.0 × 10^{-3} mol dm^{-3}, [H_2SO_4] = 5.0 × 10^{-1} mol dm^{-3}, [Ir^{3+}] = 5.0 × 10^{-3} mol dm^{-3} and I = 1.62 mol dm^{-3}.

3.3 Effect of ionic strength: The effect of ionic strength was studied at different concentrations of sodium perchlorate from 3.0 × 10^{-3} mol dm^{-3} to 12.0 × 10^{-3} mol dm^{-3} but at fixed concentration of other reactants to establish the nature of intermediate species in the rate determining step. It was observed that the change in an ionic strength of the reaction medium does not change the rate constant (Table 1). The independent of rate constant on ionic strength of the medium indicates that both the reacting species are not ionic in nature. Hence, at least one of the reacting species was molecular or non ionic in nature at the rate determining step[13].

3.4 Effect of [Ir^{3+}]: The catalytic effect of [Ir^{3+}] was studied at different concentrations of [Ir^{3+}] varied from 9.0 × 10^{-3} mol dm^{-3} to 36.0 × 10^{-3} mol dm^{-3} at fixed concentrations of [Ce^{4+}], [lactose], [H_2SO_4], ionic strength and temperature of 5.0 × 10^{-3} mol dm^{-3}, 2.5 × 10^{-2} mol dm^{-3}, 5.0 × 10^{-1} mol dm^{-3}, 1.806 mol dm^{-3} and 313 K respectively. It was observed that the rate of reaction increases with increase in [Ir^{3+}], indicating catalytic effect of [Ir^{3+}] on the rate of reaction. The catalytic constant k_c were calculated (Table 1), are fairly constant, indicating the positive catalytic effect of [Ir^{3+}] on the rate of reaction. The catalytic ratios ($k_{cat.}/k_o$) were also calculated (Table 1), showing the catalytic effect of [Ir^{3+}] on the reaction rate.

$$\text{Catalytic ratio} = \frac{k_{cat.}}{k_{uncat.}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

From the experimental results it has been observed that the [Ir^{3+}], [Lactose] and [H_2O] decide k_{obs} of the reaction can be expressed as

$$k_{obs} = \frac{k_1 k_2 k_3^{\#}[Lactose][Ir^{3+}]}{k_{-1}k^{\#} + k_2 k_3^{\#}[Ir^{3+}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\frac{1}{k_{obs}} = \frac{k_{-1}k^{\#}}{k_1 k_2 k_3^{\#}[Lactose][Ir^{3+}]} + \frac{1}{k_1[Lactose]} \ldots\ldots\ldots\ldots.(4)$$

Where $k_3^{\#} = k_3$ [H_2O] and
$k^{\#} = k_{-2} + k_3^{\#}$

3.5 Effect of [SO_4^{2-}] and [HSO_4^-] on reaction rate: Reported [2,3,14] that in H_2SO_4 medium $Ce(SO_4)_2$ is the reactive species of cerium(IV). The rate of reaction decreases (Table 2) on increasing [SO_4^{2-}] and [HSO_4^-]. The inhibitory action of [SO_4^{2-}] and [HSO_4^-] ions are explained as due to conversion of the reactive species of cerium(IV), $Ce(SO_4)_2$ to the unreactive species according to the following equilibria

$Ce(SO_4)_2 + 2\,SO_4^{2-} \rightleftharpoons Ce(SO_4)_4^{4-}$ …(5)
$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^-$ …(6)
$HCe(SO_4)_3^- + HSO_4^- \rightleftharpoons H_2Ce(SO_4)_4^{2-}$ ..(7)

3.6 Effect of [H^+] on reaction rate: In H_2SO_4 medium the state of cerium(IV) is complicated by the fact that sulphate being a better ligand can combine with cerium(IV), forming various species. Reported [2,3,15,16] that in H_2SO_4 medium ceric sulphate exist mainly as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$ and $Ce(SO_4)_4^{4-}$ depending upon the concentration of sulphate. The rate of reaction increases on increasing the concentration of H_2SO_4 at constant ionic strength due to the conversion of unreactive species of cerium(IV) to reactive species of according to the following equilibria

$Ce(SO_4)^{2+} + H_2SO_4 \rightleftharpoons Ce(SO_4)_2 + 2\,H^+$ …….(8)

$Ce(SO_4)_3^{2-} + H^+ \rightleftharpoons Ce(SO_4)_2 + HSO_4^-$ ……...(9)

$Ce(SO_4)_4^{4-} + 2\,H^+ \rightleftharpoons Ce(SO_4)_2 + 2\,HSO_4^-$ …(10)

$Ce(SO_4)^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+$ …….(11)

From the plot of log k_{obs} versus log [H^+] (Figure 2), the order with respect to sulphuric acid concentration was determined and found to be less than unity (0.579). The plot of log k_{obs} versus $-H_o$ (Hammett acidity function) [17] are also found to be linear with slope equal to 0.193 in the H_2SO_4 concentrations ranging from 5.0 × 10^{-1} mol dm^{-3} to 25.0 × 10^{-1} mol dm^{-3} (Figure 3).

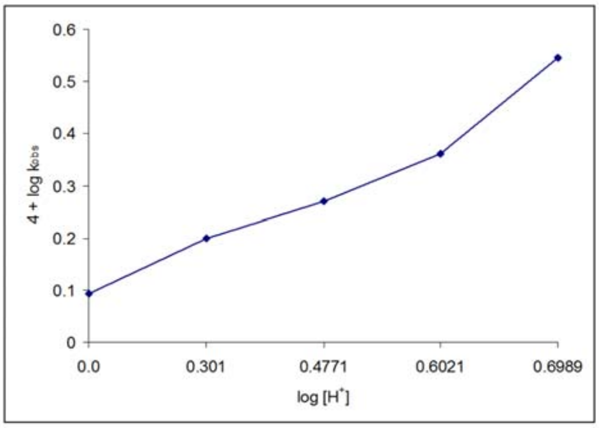

Figure 2. : Plot of log k_{obs} vs log [H^+] at 313 K. [Ce^{4+}] = 5.0 × 10^{-3} mol dm^{-3}, [Lactose] = 2.5 × 10^{-2} mol dm^{-3}, [Ir^{3+}] = 5.0 × 10^{-3} mol dm^{-3} and I = 7.62 mol dm^{-3}.

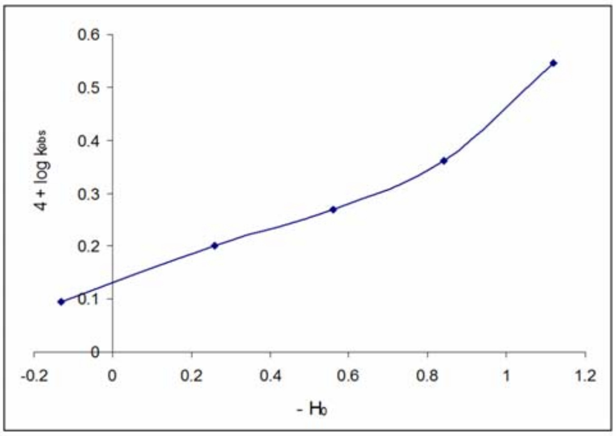

Figure 3. : Plot of log k_{obs} vs $-H_o$ at 313 K. $[Ce^{4+}] = 5.0 \times 10^{-3}$ mol dm^{-3}, [Lactose] $= 2.5 \times 10^{-2}$ mol dm^{-3}, $[Ir^{3+}] = 5.0 \times 10^{-3}$ mol dm^{-3} and $I = 7.62$ mol dm^{-3}.

3.7 Effect of temperature on reaction rate: The effect of temperature was studied at four different temperatures 308 K, 313 K, 318 K and 323 K at constant $[Ce^{4+}]$, [Lactose], $[H_2SO_4]$, $[Ir^{3+}]$ and ionic strength of 5.0×10^{-3} mol dm^{-3}, 2.5×10^{-2} mol dm^{-3}, 5.0×10^{-1} mol dm^{-3}, 5.0×10^{-3} mol dm^{-3} and 1.62 mol dm^{-3} respectively. As the results show, the rate of the catalysed reaction increases with increasing temperature. The pseudo first order rate constant, k_{obs} were used to calculate the activation parameters. The slope value of a plot between log k_{obs} versus 1/T i. e. Arrhenius plot has been used to calculate the energy of activation (E_a). The value of enthalpy of activation ($\Delta H^{\#}$) was calculated from the Eyring's plot, log (k_{obs}/T) versus 1/T (Figure 4) and from which entropy of activation ($\Delta S^{\#}$) and Gibbs energy of activation ($\Delta G^{\#}$) were calculated (Table 1). The negative value of entropy of activation and positive value of Gibbs free energy of activation suggest the formation of more ordered activated complex and transition state is highly solvated as compared to the reactive species [13,18]. The high energy of activation shows that the reaction is slow at rate determining step.

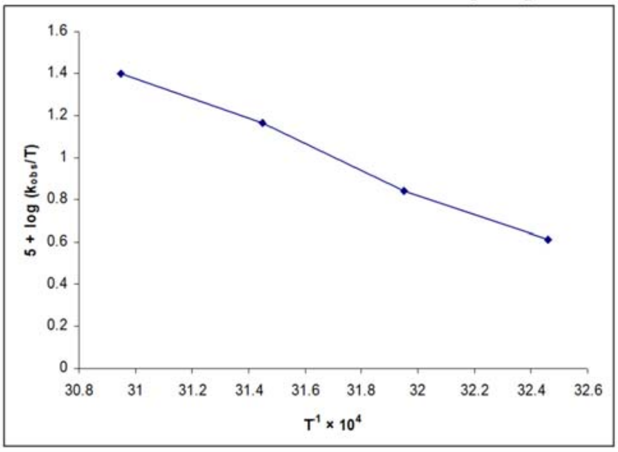

Figure 4. : Plot of log k_{obs}/T vs 1/T. $[Ce^{4+}] = 5.0 \times 10^{-3}$ mol dm^{-3}, [Lactose] $= 2.5 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 5.0 \times 10^{-1}$ mol dm^{-3}, $[Ir^{3+}] = 5.0 \times 10^{-3}$ mol dm^{-3} and $I = 1.62$ mol dm^{-3}.

Table 1. Effect of ionic strength on the rate of reaction and values of thermodynamic parameters, catalytic constants and catalytic ratios.

[Lactose] = 2.5×10^{-2} mol dm^{-3}, $[Ce^{4+}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[Ir^{3+}] = 5.0 \times 10^{-3}$ mol dm^{-3}, Temperature = 313 K, $[H_2SO_4] = 5.0 \times 10^{-1}$ mol dm^{-3}

$[NaClO_4] \times 10^3$/mol dm^{-3}	**4.0**	**8.0**	**12.0**	**16.0**
I/mol dm^{-3}	**1.624**	**1.628**	**1.632**	**1.636**
$k_{obs} \times 10^5$/s^{-1}	**24.81 ± 0.23**	**25.84 ± 0.48**	**24.91 ± 0.37**	**25.43 ± 0.54**

Thermodynamic parameters	**$\Delta H^{\#}$/kJ mol^{-1}**	**E_a/kJ mol^{-1}**	**$\Delta S^{\#}$/JK^{-1} mol^{-1}**	**$\Delta G^{\#}$/kJ mol^{-1}**
	58.98 ± 0.39	**61.59 ± 0.09**	**-94.36 ± 0.89**	**29.44 ± 0.27**

I = 1.806 mol dm^{-3}

$[Ir^{3+}] \times 10^3$/mol dm^{-3}	**0.0**	**9.0**	**18.0**	**27.0**	**36.0**
$k_{obs} \times 10^5$/s^{-1}	**4.067 ± 0.66**	**8.66 ± 0.78**	**14.33 ± 0.71**	**19.31 ± 0.85**	**23.033 ± 0.65**
$k_c \times 10^3$	**……**	**5.1**	**5.7**	**5.6**	**5.3**
$k_{cat.}/k_o$	**……**	**2.13**	**3.52**	**4.75**	**5.66**

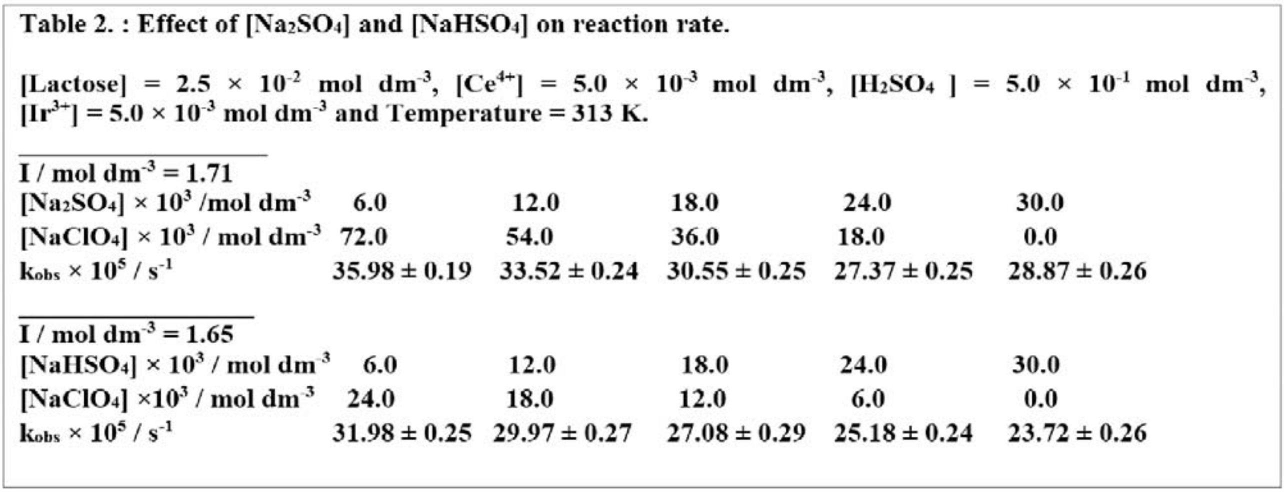

Table 2. : Effect of $[Na_2SO_4]$ and $[NaHSO_4]$ on reaction rate.

$[\text{Lactose}] = 2.5 \times 10^{-2}$ mol dm^{-3}, $[Ce^{4+}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 5.0 \times 10^{-1}$ mol dm^{-3}, $[Ir^{3+}] = 5.0 \times 10^{-3}$ mol dm^{-3} and Temperature = 313 K.

I / mol dm^{-3} = 1.71					
$[Na_2SO_4] \times 10^3$ /mol dm^{-3}	**6.0**	**12.0**	**18.0**	**24.0**	**30.0**
$[NaClO_4] \times 10^3$ / mol dm^{-3}	**72.0**	**54.0**	**36.0**	**18.0**	**0.0**
$k_{obs} \times 10^5$ / s^{-1}	**35.98 ± 0.19**	**33.52 ± 0.24**	**30.55 ± 0.25**	**27.37 ± 0.25**	**28.87 ± 0.26**

I / mol dm^{-3} = 1.65					
$[NaHSO_4] \times 10^3$ / mol dm^{-3}	**6.0**	**12.0**	**18.0**	**24.0**	**30.0**
$[NaClO_4] \times 10^3$ / mol dm^{-3}	**24.0**	**18.0**	**12.0**	**6.0**	**0.0**
$k_{obs} \times 10^5$ / s^{-1}	**31.98 ± 0.25**	**29.97 ± 0.27**	**27.08 ± 0.29**	**25.18 ± 0.24**	**23.72 ± 0.26**

3.8 Polymerisation test: Acrylonitrile was added in the reaction mixture. No gel formation was observed on addition of large excess of methanol, suggests the absence of free raical in the reaction mixture.

3.9 Mechanism: Based on the above experimental results of this investigation in acid medium in presence of Ir^{3+} catalyst, the reaction scheme consistent with the observed data proposed for the reaction is as below

$$\mathrm{R{-}CH_2{-}OH + Ce(SO_4)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Complex}_1}{\mathrm{R{-}CH_2{-}O{\rightarrow}Ce^{4+}(2SO_4)^{4-}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$\underset{\text{Complex}_1}{\mathrm{R{-}CH_2{-}HO{\rightarrow}Ce^{4+}(2SO_4)^{4-}}} + \mathrm{Ir^{3+}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{Complex}_2}{\mathrm{R{-}CH_2{-}HO{\rightarrow}Ce^{4+}(2SO_4)^{4-}{\rightarrow}Ir^{3+}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

$$\underset{\text{Complex}_2}{\mathrm{R{-}CH_2{-}HO{\rightarrow}Ce^{4+}(2SO_4)^{4-}{\rightarrow}Ir^{3+}}} + \mathrm{H_2O} \underset{\text{slow}}{\overset{k_3}{\longrightarrow}} \underset{\text{Complex}_3}{\mathrm{R{-}CH_2{-}O^{-}{\rightarrow}Ce^{4+}(2SO_4)^{4-}{\rightarrow}Ir^{3+}}} + \mathrm{H_3O^+} \ldots\ldots\ldots (14)$$

$$\underset{\text{Complex}_3}{\mathrm{R{-}CH_2{-}O^{-}{\rightarrow}Ce^{4+}(2SO_4)^{4-}{\rightarrow}Ir^{3+}}} \overset{\text{fast}}{\longrightarrow} \mathrm{RCHO + Ce(SO_4)_2^{-} + Ir^{3+}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

$$\mathrm{RCHO + H_2O \rightarrow RCH(OH)_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

$$\mathrm{RCH(OH)_2 + H_2O \rightarrow RCH(OH)O^{-} + H_3O^{+}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

$$\mathrm{RCH(OH)O^{-} + Ce(SO_4)_2 \rightarrow RCH(OH)O^{-} \rightarrow Ce^{4+}(2SO_4)^{4-}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

$$\mathrm{RCH(OH)O^{-} \rightarrow Ce^{4+}(2SO_4)^{4-} + H_2O \rightarrow RCOOH + Ce(SO_4)_2^{2-} + H_3O^{+}} \quad \ldots\ldots\ \ldots\ldots\ldots\ldots (19)$$

$Ce(SO_4)_2^{2-} + Ce(SO_4)_2 \rightarrow 2\ Ce(SO4)_2^{-}$ …………………… ………………………(20)

The oxidation of lactose by cerium(IV) takes place by the fission of C-C bond, through unstable intermediate complexes to form reaction product. The OH group of lactose combines with $Ce(SO_4)_2$, the reactive species[2,3,14] of cerium(IV) to form complex$_1$. Complex$_1$ combines with Ir^{3+} to form Complex$_2$. Complex$_2$ combines with H_2O to form Complex$_3$ and H_3O^+ is liberated. This is the slow and rate determining step. At this step H_2O molecule acts as a proton transfer agent. Highly unstable Complex$_3$ decomposes to form aldehyde, $Ce(SO_4)_2^-$ and Ir^{3+} is regenerated. The hydrated form of aldehyde combines with $Ce(SO_4)_2$, to form reaction product. There is no evidence in favour of the formation of proposed Complexes, but the proposed mechanism can not be invalidated, due to the very small steady state concentrations of the proposed complexes. The formation of intermediate complexes have also been reported between Ce^{4+}, Br^- and fructose [2] and $Ce(SO_4)_2$ and dextrose[3].
On the basis of above mechanism the rate law could be written as

$$\frac{-d[Ce^{4+}]}{dt} = \frac{k_1k_2k_3[H_2O][Lactose][Ir^{3+}][Ce^{4+}]}{k_{-1}k_{-2}+k_{-1}k_3[H_2O]+k_2k_3[H_2O][Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(21)$$

The above rate law (21) explains the first order dependence of rate on each in $[Ce^{4+}]$ and [Lactose] and fractional order on dependence on $[Ir^{3+}]$. The equation (21) could be written as

$$\frac{-dln[Ce^{4+}]}{dt} = k_{obs} = \frac{k_1k_2k_3[H_2O][Lactose][Ir^{3+}]}{k_{-1}k_{-2}+k_{-1}k_3[H_2O]+k_2k_3[H_2O][Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(22)$$

$$k_{obs} = \frac{k_1k_2k_3^{\#}[Lactose][Ir^{3+}]}{k_{-1}k_{-2}+k_{-1}k_3^{\#}+k_2k_3^{\#}[Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(23)$$

Where, $k_3^{\#} = k_3\ [H_2O]$

$$k_{obs} = \frac{k_1k_2k_3^{\#}[Lactose][Ir^{3+}]}{k_{-1}(k_{-2}+k_3^{\#})+k_2k_3^{\#}[Ir^{3+}]}$$

$$k_{obs} = \frac{k_1k_2k_3^{\#}[Lactose][Ir^{3+}]}{k_{-1}k^{\#}+k_2k_3^{\#}[Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(24)$$

Where, $k^{\#} = k_{-2} + k_3^{\#}$

$$k_{obs} = \frac{p\ [Lactose][Ir^{3+}]}{q + r\ [Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(25)$$

Where, $p = k_1k_2k_3^{\#}$, $q = k_{-1}k^{\#}$ and $r = k_2k_3^{\#}$

By taking reciprocal of equation (25)

$$\frac{1}{k_{obs}} = \frac{q + r\ [Ir^{3+}]}{p[Lactose][Ir^{3+}]} \quad \ldots\ldots\ldots\ldots(26)$$

$$\frac{1}{k_{obs}} = \frac{q}{p[Lactose][Ir^{3+}]} + \frac{r}{p\,[Lactose]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(27)$$

Where, p, q and r are constants and expressed in terms of different rate constants. The slope, intercept on $1/k_{obs}$ axis and extrapolated intercept on $1/[Ir^{3+}]$ axis, give the values of q/p[Lactose], r/p[Lactose] and -1/q respectively. At constant $[Ce^{4+}]$, a plot of $1/k_{obs}$ versus 1/[Lactose] was linear with small intercept (25.59) on $1/k_{obs}$ axis, offering support for complex formation.

4. Conclusion: The positive value of Gibbs free energy of activation ($\Delta G^{\#}$) and negative value of entropy of activation ($\Delta S^{\#}$) suggest the formation of activated complex. The positively charged $Complex_2$ reacts with H_2O to form $Complex_3$ in slow and rate determining step requires higher energy of activation (E_a). At rate determining step water molecule acts as a proton transfer agent. At constant $[Ce^{4+}]$, a plot of $1/k_{obs}$ versus 1/[Lactose] was linear with small intercept (25.59) on $1/k_{obs}$ axis, offering support for complex formation.

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