



## Uncatalysed Oxidation of Dextrose by Cerium(IV) in Aqueous Acidic Medium-A Kinetic and Mechanistic Study

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### Abstract

A Kinetics investigation of uncatalysed oxidation of dextrose by cerium(IV) have been studied in acidic medium in the temperature range 303-328K. The reaction has been found to be first order with respect to dextrose in an uncatalysed reactions. The effect of  $[HSO_4^-]$  has also been observed. The increase in ionic strength of the medium decreases the rate of uncatalysed reaction. A 1:2 stoichiometry is observed in the oxidation reaction. On the basis of the experimental results, a reasonable mechanism has been proposed. Rate equation derived from this mechanism can explain all the experimental results. From the effect of temperature on the reaction rate, the Arrhenius equation and various activation parameters have been computed.

**Keywords:** Kinetics, uncatalysed, dextrose, cerium (IV), arrhenius equation.

### Introduction

Kinetic studies have been used as a tool to know the mechanism of a reaction. Chemistry of cerium is a very broad area which has received considerable attention through the years, resulting in substantial advance both in the synthetic<sup>1-2</sup> and mechanistic categories. Cerium(IV) is a well known oxidant in acidic media<sup>3-5</sup> having reduction potential<sup>6-7</sup> of the couple  $Ce^{IV}/Ce^{III}$  (1.70V) and is stable only in high acid concentration. In sulphuric acid and sulphate media, several sulphate complexes<sup>6,9,10</sup> of cerium (IV) form, but their role has not received much attention so far. Kinetic provides the most important indirect evidence in the mechanism. The metal ion oxidants have been widely employed in the synthetic chemistry<sup>11,12</sup> including carbohydrates chemistry<sup>13-16</sup>. These are stable, in expensive and can readily be stored and handled. The kinetic method of analysis have been widely developed and accepted in chemical analysis of different samples<sup>17</sup> and kinetic study of Ru (III) catalysed oxidation of sucrose by sodium periodate in acidic medium have been studied by various scientists. Kinetic study has also been carried out using other oxidant<sup>20</sup>.

### Material and Methods

**Chemicals:** Chemicals of pure quality were used without further purification. Stock solution of dextrose and potassium bisulphate is prepared in double distilled water. Ce (IV) stock solution were prepared by dissolving ceric ammonium sulphate in aqueous sulphuric acid. sodium thiosulphate solution was standardized with standard iodine solution. All chemicals were purchased from E. Merck.

**Kinetic procedure:** Kinetic runs were performed in stopper glass vessels in a controlled temperature  $\pm 0.1^\circ C$  on water bath. Requisite volume ( $90cm^3$ ) of all reagents, including substrate, were introduced into a reaction vessel and thermally equilibrated to 308K. A measured volume ( $10cm^3$ ) of cerium solution, also at 308K was rapidly poured into the reaction vessel. The kinetics of the reaction was studied under the conditions  $[substrate] \gg [oxidant]$  in the case of Ce(IV). The kinetics were followed by estimating aliquots of the reaction mixture for cerium(IV) iodometrically, using starch indicator. Doubly recrystallised sugars (E.Merck) were used for the kinetic studies. Cerium solution was always made up and stored in black coated flask to prevent photochemical reaction. The solution was then standardized with sodium thiosulphate solution using starch indicator. Aqueous solution of dextrose were prepared fresh each day. All other reagent were of analytical grade. Conductivity water used throughout the study.

### Results and Discussion

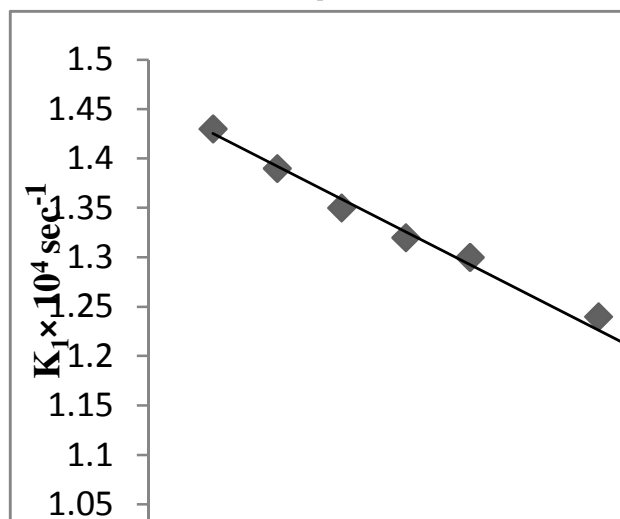
The order of reaction with respect to [oxidant] was determined in table 1. Result shows that the rate constant is directly proportional to the concentration of cerium (IV). Linear line is obtained in figure 1, when we plot of  $k_1$  v/s Ce(IV) concentration. This indicates the first order kinetics with respect to oxidant. The order of reaction was determined at different concentration of substrate and at fixed concentrations of other reactants in table 2. Plot of  $k_1$  v/s dextrose concentration is found to be a straight line figure 2(a), which indicates that rate of reaction is directly proportional to the concentration of the substrate. The plot of  $\log k_1$  v/s  $\log [dextrose]$  are linear. This indicates that the order with respect to [substrate] is one in figure 2(b).

**Table-1**

**Effect of variation of [Cerium(IV)] on the reaction rate**

$10^3 \times [\text{Ce(IV)}]$ mol dm <sup>-3</sup>	$K_1 \times 10^4$ sec <sup>-1</sup>
1.00	1.43
2.00	1.39
3.00	1.35
4.00	1.32
5.00	1.30
7.00	1.24
9.00	1.15

$10^2[\text{Dextrose}] = 5.00 \text{ mol dm}^{-3}$ ;  $10^2[\text{H}_2\text{SO}_4] = 3.00 \text{ mol dm}^{-3}$ ;  $10^3[\text{KHSO}_4] = 5.00 \text{ mol dm}^{-3}$ ; Temp. = 308K



**Figure-1**  
Plot of  $K_1$  v/s  $[\text{Ce(IV)}]$

The effect of  $\text{H}^+$  ion concentration on the reaction rate, the reaction has been carried out at various initial concentration of sulphuric acid tabulated in table 3. It has been observed that rate of reaction decreases with increase of sulphuric acid concentration as in figure 3. On the plot of  $k_1$  v/s  $1/[\text{H}^+]$  and  $\log k_1$  v/s  $\log [\text{H}^+]$  are found to be linear in nature as in figure 3 (a) and 3(b). This indicates that the order with respect to  $[\text{H}^+]$  is inverse first. The reactions were studied at different concentrations of salt  $[\text{KHSO}_4]$ , while other reactants are constant. The observations of salt effect are given in the table 4. The graphical plot of  $k_1$  v/s  $[\text{KHSO}_4]$  is found to be a straight line in figure 4, which indicates that the rate of the reaction is inversely proportional to  $\text{HSO}_4^-$  ion concentration. Thus the addition of salts viz.  $\text{KHSO}_4$  did not have much effect on the rate of reaction.

To observe the effect of temperature on the reaction rate, the reaction was studied at different temperatures, while keeping all

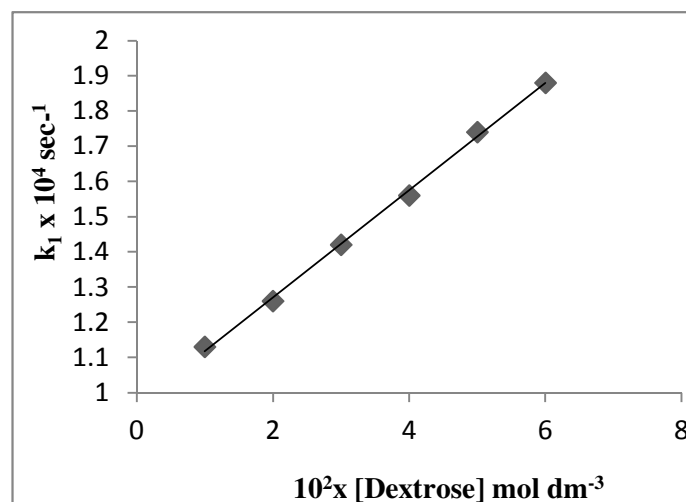
other reactants are constant in table 5. The kinetic data shows that the velocity of reaction increases with rise in temperature, showing the validity of the Arrhenius equation in figure 5. So an attempt has been made to correlate the various activation parameters on the reaction mechanism.

**Table-2**

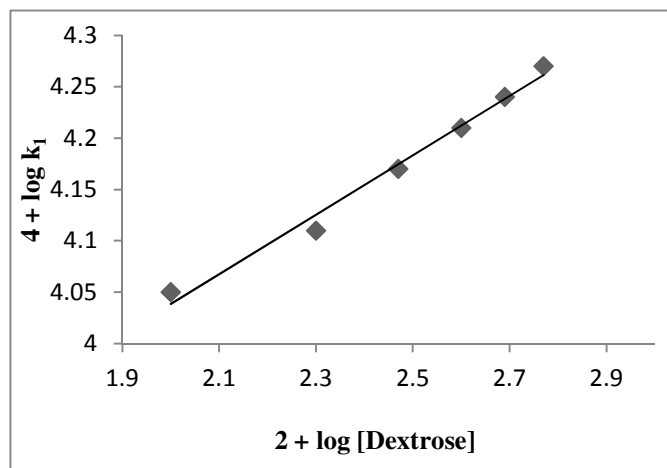
**Effect of variation of [Dextrose] on the reaction rate**

$10^2 \times$ [Dextrose] mol dm <sup>-3</sup>	$2 + \log$ [Dextrose]	$K_1 \times 10^4$ sec <sup>-1</sup>	$4 + \log$ [ $K_1$ ]
1.00	2.00	1.13	4.05
2.00	2.30	1.26	4.10
3.00	2.47	1.42	4.15
4.00	2.60	1.56	4.19
5.00	2.69	1.74	4.24
6.00	2.77	1.88	4.27

$10^3[\text{Ce(IV)}] = 3.00 \text{ mol dm}^{-3}$ ;  $10^2[\text{H}_2\text{SO}_4] = 3.00 \text{ mol dm}^{-3}$ ;  $10^3[\text{KHSO}_4] = 5.00 \text{ mol dm}^{-3}$ ; Temp. = 308K



**Figure-2(a)**  
Plot of  $K_1$  v/s [Dextrose]

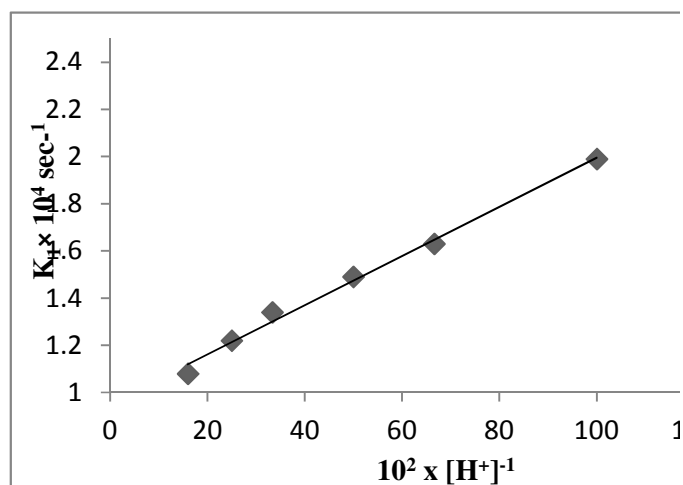


**Figure- 2(b)**  
Plot of  $\log K_1$  v/s  $\log[\text{Dextrose}]$

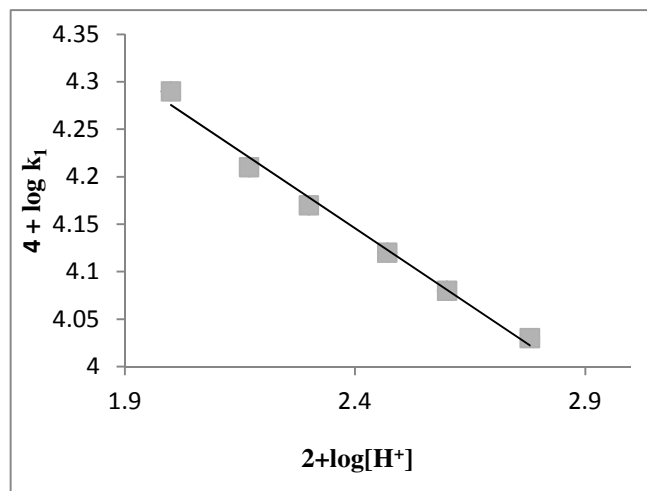
**Table-3**  
Effect of variation of  $[H^+]$  on the reaction rate

$10^2 \times [H_2SO_4]$ mol dm <sup>-3</sup>	$2 + \log[H^+]$	$K_1 \times 10^4$ sec <sup>-1</sup>	$4 + \log[K_1]$
1.00	2.00	1.99	4.29
1.50	2.17	1.63	4.21
2.00	2.30	1.49	4.17
3.00	2.47	1.34	4.12
4.00	2.60	1.22	4.08
6.00	2.77	1.08	4.03

$10^3 [Ce(IV)] = 3.00 \text{ mol dm}^{-3}$ ;  $10^2 [Dextrose] = 5.00 \text{ mol dm}^{-3}$ ;  $10^3 [KHSO_4] = 5.00 \text{ mol dm}^{-3}$ ; Temp. = 308K



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



**Figure-3(b)**  
Plot of  $\log K_1$  v/s  $\log [H^+]$

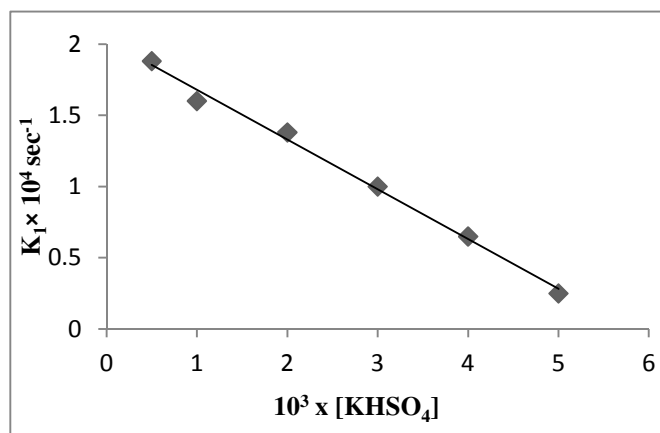
**Activation parameters:** The result shows the value of activation energy ( $E_a$ ) was found to be  $44.94 \text{ kJ mol}^{-1}$ . The value of enthalpy of activation ( $\Delta H^*$ ) at 313k is  $42.3 \text{ kJ mol}^{-1}$ , entropy ( $\Delta S^*$ ) at 313k is  $-17.9 \text{ J mol}^{-1}$ , frequency factor (A) at

313k is 11.8 and free energy ( $\Delta G^*$ )  $47.9 \text{ kJ mol}^{-1}$ . In order to seen that the high positive value of change in free energy ( $\Delta G^*$ ) indicates reaction is highly solvated transition state, while negative value of change in entropy ( $\Delta S^*$ ) suggested, the formation of an activated complex with reduction in the degree of freedom of molecules.

**Table-4**  
Effect of variation of  $[KHSO_4]$  on the reaction rate

$10^3 \times [KHSO_4]$ mol dm <sup>-3</sup>	$K_1 \times 10^4$ sec <sup>-1</sup>
0.50	1.88
1.00	1.60
2.00	1.38
3.00	1.00
4.00	0.65
5.00	0.25

$10^3 [Ce(IV)] = 3.00 \text{ mol dm}^{-3}$ ;  $10^2 [Dextrose] = 5.00 \text{ mol dm}^{-3}$ ,  $10^2 [H_2SO_4] = 3.00 \text{ mol dm}^{-3}$ ; Temp. = 308K



**Figure-4**  
Plot of  $K_1$  v/s  $[KHSO_4]$

**Reaction Mechanism:** The kinetics of the forgoing reactions were studied and showed that substrates and oxidant interact in an equilibrium step to form an intermediate complex which is assumed to disproportionate forming a free radical and reduced Ce(IV). It is believed that involvement of both  $C_1$  and  $C_2$  hydroxyls in a complex formation. On the basis of above statement and observed first order dependence on [oxidant] as well as [substrate] a probable mechanism (scheme-1) is proposed for the oxidation D-glucose such complex Formation between oxidant and substrate was observed in earlier studies.

**Rate Law:** The proposed mechanism involves the formation of complex in a reversible manner which reach with the substrate at rate determining steps to form  $[Ce(IV)-S]$  complex followed by a slow redox decomposition giving rise to aldoxide radical which oxidized by Ce(IV) rapidly.

The oxidation of dextrose at different temperatures from 303K to 328K was studied. The rate of disappearance of cerium(IV) in this reactions increases sharply with increasing concentration of dextrose. The plots of  $k_1$  against T were linear for uncatalyzed oxidation. The Arrhenius activation energy  $E_a$  for the uncatalyzed oxidation of dextrose was  $44.94 \text{ kJ mol}^{-1}$ .

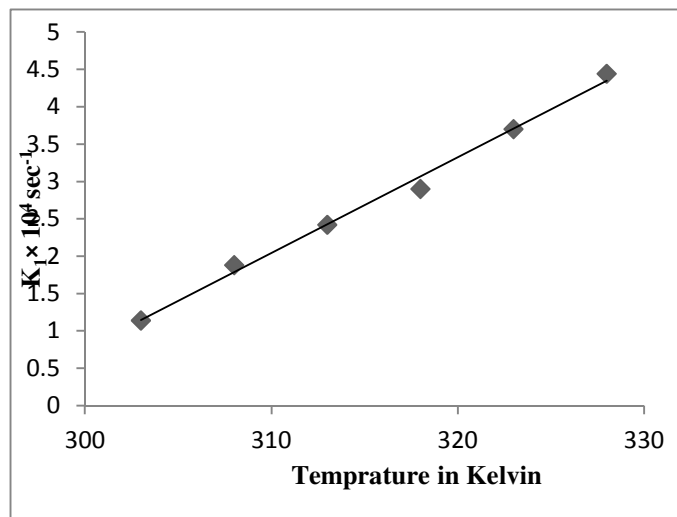


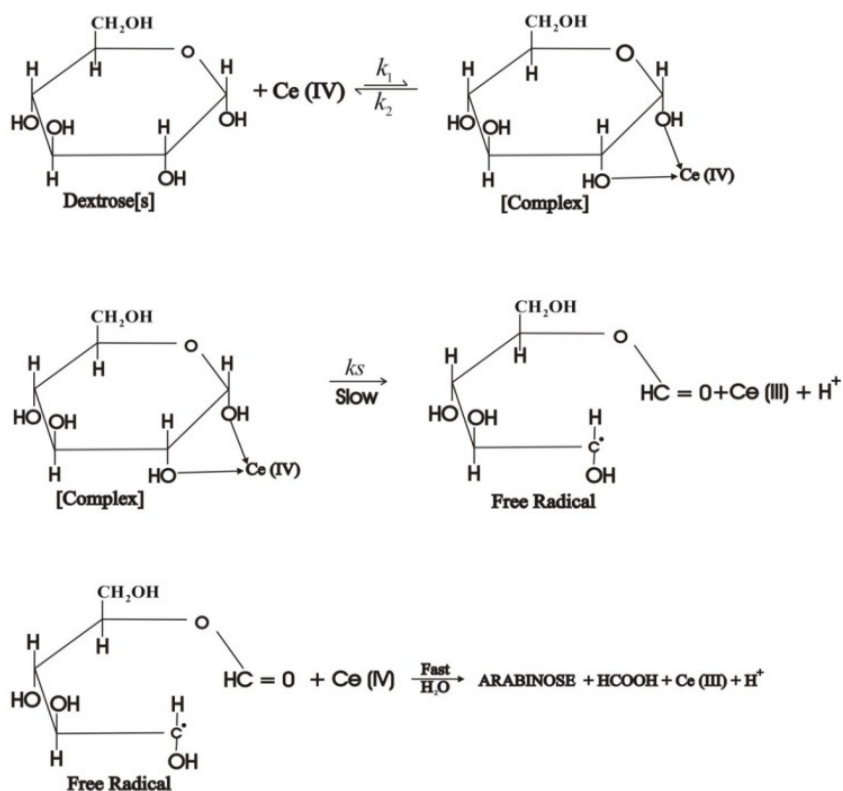
Figure-5  
 Plot of  $K_1$  v/s T

Table- 5  
 Effect of variation of Temperature on the reaction rate  
 $10^3[\text{Ce(IV)}]=3.00 \text{ mol dm}^{-3}; 10^2[\text{Dextrose}]=5.00 \text{ mol dm}^{-3}; 10^2[\text{H}_2\text{SO}_4]=3.00 \text{ mol dm}^{-3}; 10^3[\text{KHSO}_4]=5.00 \text{ mol dm}^{-3}$

Temperature in Kelvin	$1/T \times 10^3$	$K_1 \times 10^4 \text{ sec}^{-1}$
303	3.30	1.14
308	3.24	1.88
313	3.19	2.42
318	3.14	2.90
323	3.09	3.70
328	3.04	4.44

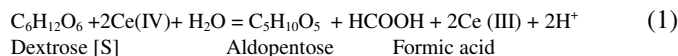
  

Kinetic and Activation parameters for uncatalysed reaction	
Parameter	Dextrose
$E_a^*$ ( $\text{kJ mol}^{-1}$ )	44.94
$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	42.34
$\Delta S^*$ ( $\text{J mol}^{-1}$ )	-17.90
$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	47.50
log A	11.88



Scheme-1

The observed<sup>18</sup> stoichiometry of the reaction corresponds to the reaction can be represented by the equation 1.



In this reaction one mole of substrate oxidized by two mole of cerium(IV). Formic acid formation and respective aldopentose were confirmed by spot test 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 acryle nitrile and EPR spin trapping method<sup>19</sup>.

The rate of consumption of Ce(IV) is,

$$\frac{-d[Ce(IV)]}{dt} = 2k_s[complex] \quad (2)$$

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

$$\frac{-d[Complex]}{dt} = k_1[Ce(IV)][S] - k_2[complex] \quad (3)$$

At steady state condition,

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

$$\text{Hence, } k_1[S][Ce(IV)] = k_2[complex] \quad (5)$$

Therefore, the concentration of the complex becomes,

$$[Complex] = \frac{k_1[S][Ce(IV)]}{k_2} \quad (6)$$

At steady state condition, the rate of disappearance of [Ce(IV)] as given as in equation (2)

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

Putting the value of [Complex] from equation (6) we have,

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 [S][Ce(IV)]}{k_2} \quad (7)$$

Now, the total Cerium(IV) may be considered as,

$$[Ce(IV)]_T = [Ce(IV)]_e + [complex] \quad (8)$$

Putting the value of [Complex] we have,

$$[Ce(IV)]_T = [Ce(IV)]_e + \frac{k_1[S][Ce(IV)]}{k_2} \quad (9)$$

$$[Ce(IV)]_T = \frac{[Ce(IV)]_e k_2 + [k_1[S][Ce(IV)]]}{k_2} \quad (10)$$

The value of [Ce(IV)]<sub>T</sub> becomes as, since [Ce(IV)]<sub>e</sub> ≈ [Ce(IV)]

$$[Ce(IV)] = \frac{[Ce(IV)]_T k_2}{k_2 + k_1[S]} \quad (11)$$

From the equation (7) and (11), rate law becomes as,

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 [S]}{k_2} \times \frac{[Ce(IV)]_T k_2}{k_2 + k_1[S]} \quad (12)$$

$$\frac{-d[Ce(IV)]}{dt} = \frac{2k_s k_1 [S][Ce(IV)]_T}{k_2 + k_1[S]} \quad (13)$$

$$k_{obs} = \frac{-d[Ce(IV)]/dt}{[Ce(IV)]_T} = \frac{2k_s k_1 [S]}{k_2 + k_1[S]} \quad (14)$$

$$\frac{1}{k_{obs}} = \frac{1}{2k_s} + \frac{k_2}{2k_s k_1 [S]} \quad (15)$$

On the plot of 1/k<sub>obs</sub> against 1/[S] is made from which the constants 1/k<sub>s</sub> and k<sub>2</sub>/k<sub>s</sub>k<sub>1</sub> are determined from the slope and intercept respectively. According to the equation mentioned in the above, when plot between 1/k<sub>obs</sub> and 1/[S], a positive intercept would be observed which confirms the validity of the mechanism and also the rate law.

## Conclusion

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 (ΔG<sup>\*</sup>) and (ΔH<sup>\*</sup>) indicate that the transition state is highly solvated where as the negative value of entropy of activation (ΔS<sup>\*</sup>) indicated that the activated complex is cyclic nature.

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