Pak. J. Chem. 5(1): 1-7, 2015
ISSN (Print): 2220-2625
ISSN (Online): 2222-307X

Full Paper
DOI: 10.15228/2015.v05.i01.p01

Comparative Kinetic and Mechanistic Study of Oxidation of β-Cyclodextrin by Potassium Dichromate

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ABSTRACT

A comparative kinetic and mechanistic study of oxidation of β-Cyclodextrin (β-CD) by Potassium Dichromate ($K_2Cr_2O_7$) in presence of aqueous H_2SO_4 medium was monitored at λ_{max} 350 nm spectrophotometrically. The oxidation reaction follows first order kinetics with respect to [β-CD] and [$Cr_2O_7^{-2}$] and markedly increased by increasing [H^+]. The slow reaction was accelerated with Fe (III) as a catalyst that enhances the rate significantly. The results of varying temperature were used to compute different activation parameters. The values of activation energy E_a were 37.70KJ mol^{-1} for catalysed and 50.183 KJ $mol^{-1}$for uncatalysed reactions. These clearly indicate that Fe (III) greatly reduced the activation barrier thereby increases the rate of reaction. Oxidation product results due to the oxidation of -CH_2OH group present on each glucose monomer of β-CD.A mechanism consistent with kinetic and thermodynamic data is also proposed that involves two-electron reduction of Cr (VI).

Keywords: β-Cyclodextrin, $K_2Cr_2O_7$, Fe (III) catalyst, E_a, two-electron reduction.

1. INTRODUCTION

Carbohydrates are the fuel of life, being the main energy source for living organisms and the central pathway of energy storage and supply for most cells. The study of the carbohydrates and their derivatives has greatly enriched chemistry, particularly with respect to the role of molecular shape and conformation in chemical reactions[1].β-Cyclodextrin (β-CD) is a naturally occurring carbohydrate, formed by α 1→4 linkage of seven D-glucopyranose units. Structurally, they are hollow truncated cones in which the inner cavity is lipophilic and exterior is hydrophilic due to the presence of primary hydroxyl groups. These days, applications of cyclodextrins have no limits from Industrial aspects because this outstanding constructional feature of cyclodextrins molecule makes them able to form inclusion complexes and becomes a great deal of interest in food, drugs, dyes and perfumery industries[2-9]. Numerous β-CD reaction studies involving selective modifications of primary and secondary alcoholic groups of cyclodextrin have been conducted through different organic oxidants[10-12] to improve their physiochemical behaviour (solubility, surface activity etc.). However the information about the reaction kinetics and mechanism is still lacking.

Only a very few reports are available with inorganic oxidant[13, 14]. Potassium Dichromate $K_2Cr_2O_7$, has been used to oxidize a variety of organic compounds[15-19] but still not reported for the oxidation of β-CD. Therefore, the object of this research is to perform the oxidation kinetics of β-CD by Potassium dichromate in H_2SO_4 medium and to study reaction kinetics by conventional spectrophotometric method in order to establish stoichiometry and reaction mechanism. The reaction kinetics is also studied in presence of Fe (III) as a catalyst and results are compared to that of uncatalysed reaction. The crucial information about thermodynamics and spectral evidences are gathered to develop mechanistic approach consistent with product analysis.

2. EXPERIMENTAL

The stock solutions for kinetics investigation were prepared in doubly distilled water. β-CD, Potassium dichromate, Iron (III) chloride, and sulfuric acid used were of AR quality (Merck and BDH). Required amount of all reagents were mixed in a beaker placed on thermostat bath DFS KW-1000DB. The rate of disappearance of $Cr_2O_7^{2-}$ was followed spectrophotometrically by monitoring the absorbance at known time intervals. Neither β-CD nor product showed any absorbance at 350 nm. Pseudo-first order rate constants (k_1) of these kinetic runs were obtained by slopes of the plot of ln (Absorbance) versus time.

3. RESULTS AND DISCUSSION

3.1 *Stoichiometry and Product Analysis*

The stoichiometry of oxidation of β-cyclodextrin (β-CD) was determined by adding a warm solution of β-CD ($3x10^{-3}$ mol dm^{-3}, 30°C) to a warm solution of $K_2Cr_2O_7$ ($3x10^{-4}$ mol dm^{-3}) having H_2SO_4 (1.6 mol dm^{-3}) until the decolorization of $K_2Cr_2O_7$ was completed. Different sets of experiments revealed that 1 mole of $K_2Cr_2O_7$ reacts with 7.5 mole of β-CD.The same procedure was repeated with reaction mixtures containing $1x10^{-5}$ mol dm^{-3} Iron (III) chloride. On successive experiments, it was found that 1 mole of $K_2Cr_2O_7$ reacts with 5 mole of β-CD. The obtained stoichiometric results were also confirmed by mole ratio method which produced same results.

To identify the oxidation product an experiment was setup, as reported earlier[14] in which all solutions β-CD ($3x10^{-3}$ mol dm^{-3}), $K_2Cr_2O_7$ ($3x10^{-4}$ mol dm^{-3}), and H_2SO_4 (1.6 mol dm^{-3}) were added to the reaction vessel. A separate

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Received 27th January 2015, Accepted 10th February 2015

reaction vessel was also prepared containing Iron (III) chloride (1x10^{-5} mol dm^{-3}) in addition to the other solutions. Both reactions were conducted at30°C.After the complete disappearance of color,100cm^3 saturated solution of 2, 4 dinitrophenyl hydrazine in 2M HCl were added to the 50 cm^3 reaction mixture taken from reaction flask. The resultant mixture was left overnight in a refrigerator. The precipitates of 2, 4 dinitrophenyl hydrazone were filtered, washed, and dried. The IR spectrum of 2, 4 dinitrophenyl hydrazone confirmed the presence of aldehyde; carbonyl stretching at 1645cm^{-1}, band of aldehyde stretching at 2926 cm^{-1}. It is obvious now that an aldehyde was formed after the oxidation of β-CD, as the spot test for acid was negative.

3.2 *Spectral evidences*

The reaction mixtures were also investigated by UV-Visible spectroscopy in the 300-600nm region. Spectral scan was performed for two reaction mixtures containing β-cyclodextrin (3x10^{-3} mol dm^{-3}), $K_2Cr_2O_7$ (3x10^{-4} mol dm^{-3}), and H_2SO_4 (1.6 mol dm^{-3}) and another mixture contained same amounts with Iron (III) chloride (1x10^{-5} mol dm^{-3}) respectively.

Both spectra showed the two peak maxima at 350nm that corresponds Cr (VI), and 450nm to Cr (III). Similar scans were taken after 2 hours of reaction (Fig. 1 and 2). It is evident from the spectra that as the reaction proceeds Cr (VI) consumes at 350nm and Cr (III) grows at around 450nm. Thus, it was confirmed that under present experimental conditions, Cr (III) ion formed as product.

3.3 *Kinetic measurements*

The kinetics of oxidation of β-cyclodextrin with potassium dichromate $K_2Cr_2O_7$is carried out in aqueous acidic medium. The reaction is also studied in presence of Iron (III) chloride as catalyst. Sulfuric acid (H_2SO_4) is used to maintain the pH throughout the reaction.The reactions were monitored spectrophotometrically by change in absorbance of $Cr_2O_7^{2-}$ at λ_{max} 350nm. The rate constants were calculated via slope of the plot of ln (A)versus time. The observed rate constants are obtained in form of pseudo-first order rate constants (k_1) under sustained kinetic conditions.

3.4 *Effect of [$Cr_2O_7^{-2}$]*

The reactions were carried out at various concentration of [$Cr_2O_7^{-2}$] ranging from 1x10^{-4} – 5x10^{-4} mol/dm^3 keeping other variables [β-CD], [H^+] and temperature constant. The values of k_1 (Tab.1) were independent of varying [$Cr_2O_7^{-2}$] showing a good agreement with a first order dependence on [$Cr_2O_7^{-2}$].It was noted that k_1 was significantly increased in presence of catalyst showing Fe (III) is accelerating rate of reaction.

3.5 *Effect of [β-CD]*

The effect of [β-CD] was also investigated by varying concentrations 1x10^{-3} – 5x10^{-3} mol/dm^3 at constant parameters. Tab. 1 shows the comparative values of rate constant which increases with increasing [β-CD], indicating first order kinetics. The values of n, order of reaction for both catalysed and uncatalysed reaction were 0.796 and 0.759 respectively (Fig. 3).

3.6 *Effect of [H^+]*

The variation in [H^+] (1.0, 1.2, 1.4, 1.6 and1.8 mol/dm^3) at other constant parameters showed the dependence of $k_1$for both catalysed and uncatalysedupon [H^+] (Tab. 1). Change in ionic strength maintained by K_2SO_4 had no effect. It was observed that rate of reaction increases as [H^+] increases i.e. the reaction is acid dependent. A plot of log $k_1$against log [H^+] (Fig. 4) gave the value of 2.2 and 1.8 for catalysed and uncatalysed reactions respectively.

3.7 *Effect of [Fe(III)]*

Effect of catalyst Fe(III) was evaluated by using different concentration at constant[$Cr_2O_7^{-2}$] (1x10^{-4} mol/dm^3), [β-CD] (1x10^{-4} mol/dm^3) and [H^+] (1.6 mol/dm^3). It was found that k_1 is independent of varying [Fe(III)]. The catalyst played a significant role in the reduction of activation energy from 50.183 to 37.70KJ mol^{-1}(Tab.2) and hence increased the rate of reaction.

3.8 *Effect of Temperature*

Dependence of temperature on rate of reaction was also studied at 30, 35, 40, 45 and 50 °C by keeping [β-CD], [$Cr_2O_7^{-2}$], and [H^+] constant (Tab. 2).The influence of temperature was also checked in presence of [Fe (III)]. Both reactions followed Arrhenius Plot (Fig. 5) from which activation energy $E_a$was calculated. The values of $E_a$were37.70 and 50.183 KJ mol^{-1} for catalysed and uncatalysed reaction respectively (Tab. 3). It is clear that the catalyst played a significant role in reducing Activation barrier. Tab. 3 also presents the values of other activation parameters that were computed by plotting Ln(k/T) against 1/T (Fig. 6). The high negative values of $\Delta S^{\#}$ (-181.96 &-215.922 J mol^{-1}) shows that the transition state is highly solvated.

Table-1: Observed pseudo-first order rate constants in the oxidation of β-Cyclodextrin by Dichromate ion, with and without addition of Catalyst Iron (III) Chloride

[$K_2Cr_2O_7$] ×10^{-4} mol/dm^3	**[β-Cyclodextrin] ×10^{-3} mol/dm^3**	**[H_2SO_4] mol/dm^3**	**[$FeCl_3$] ×10^{-5} mol/dm^3**	**k_1 ×10^{-5} s^{-1}**	
				Catalyzed	**Uncatalyzed**
1	3	1.6	1	2	0.8
2	3	1.6	1	2	0.8
3	3	1.6	1	2	0.9
4	3	1.6	1	2	0.9
5	3	1.6	1	3	0.8
3	1	1.6	1	1	0.6
3	2	1.6	1	2	2
3	3	1.6	1	2	3
3	4	1.6	1	3	2
3	5	1.6	1	4	2
3	3	1.0	1	0.8	0.5
3	3	1.2	1	1	0.7
3	3	1.4	1	1	0.6
3	3	1.6	1	2	0.7
3	3	1.8	1	3	2
3	3	1.6	1	2	-
3	3	1.6	2	2	-
3	3	1.6	3	2	-
3	3	1.6	4	3	-
3	3	1.6	5	3	-

Temperature = 303K

Table-2: Effect of temperature on the rate constant value for oxidation of β-Cyclodextrin, with and without addition of Iron (III) Chloride

Temperature (K)	**β-Cyclodextrin**	
	Uncatalysed k_1 ×10^{-5} s^{-1}	**Catalysed k_1 ×10^{-5} s^{-1}**
303	1	3
308	2	3
313	2	5
318	3	6
323	4	7

[$K_2Cr_2O_7$]= 3x10^{-4} mol/dm^3[β-Cyclodextrin] = 3×10^{-3} mol/dm^3 [H_2SO_4] =1.6M
[$FeCl_3$] = 1x10^{-5} mol/dm^3

Table-3: Arrhenius and thermodynamic activation parameters for oxidation of β-Cyclodextrin, with and without addition of Iron (III) Chloride.

Parameters	**Uncatalysed reaction**	**Catalysed reaction**
E_a (KJ mol^{-1})	50.183	37.70
$\Delta H^{\#}$ (KJ mol^{-1})	47.78	35.23
$\Delta S^{\#}$ (J mol^{-1})	-181.96	-215.922
$\Delta G^{\#}$ (KJ mol^{-1})	57	67.61

Temperature = 303K

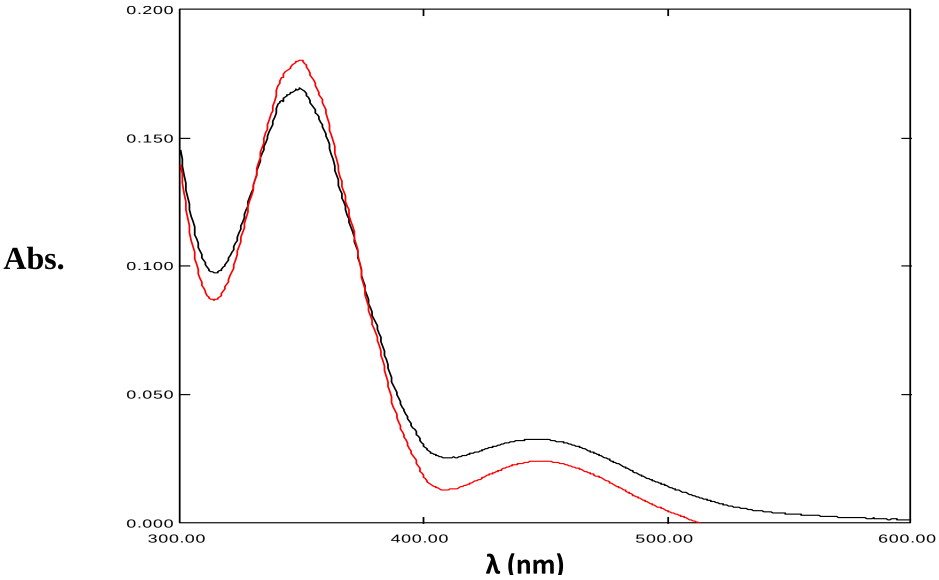


Fig-1: An overlay showing progress of reaction at Temp = 303K of [β-CD] = 3x10^{-3} mol dm^{-3}, [$K_2Cr_2O_7$] 3x10^{-4} mol dm^{-3}, and [H_2SO_4]1.6 mol dm^{-3}

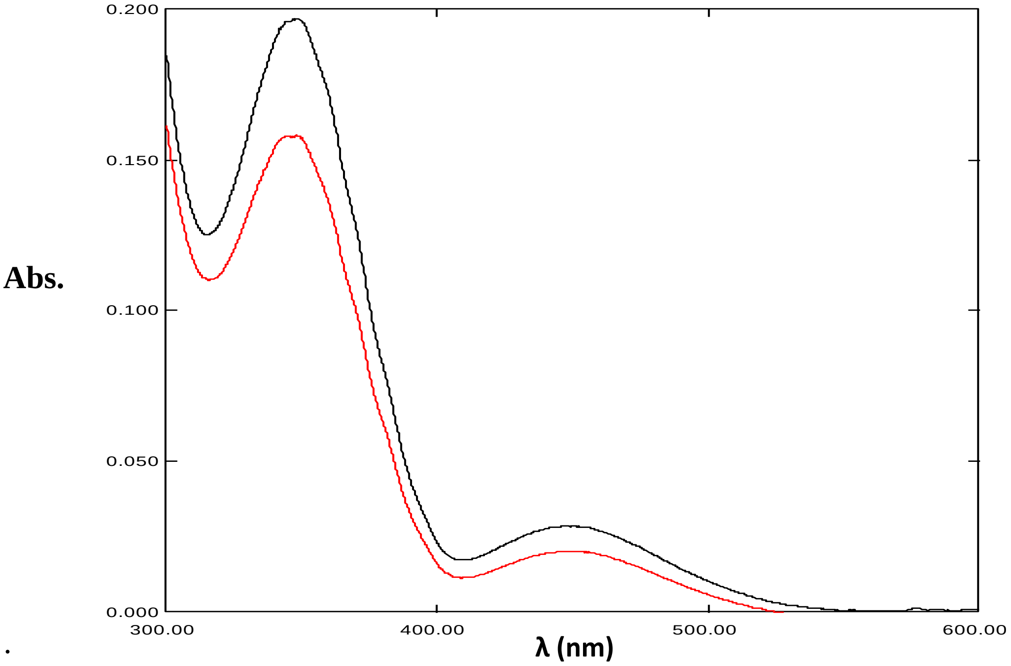


Fig-2: An overlay showing progress of reaction at Temp. = 303K. [β-CD] = 3x10^{-3} mol dm^{-3}, [$K_2Cr_2O_7$] 3x10^{-4} mol dm^{-3},[H_2SO_4] 1.6 mol dm^{-3}, and [$FeCl_3$] = 1x10^{-5} mol/dm^3

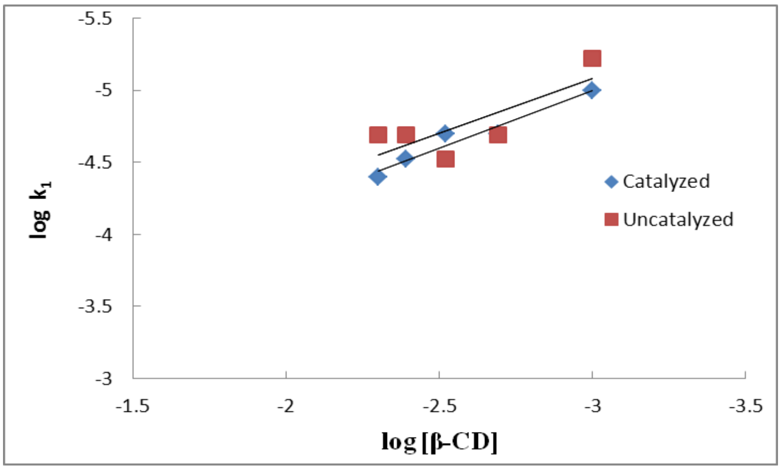


Fig-3: Plot of log [β-CD] versus log k_1

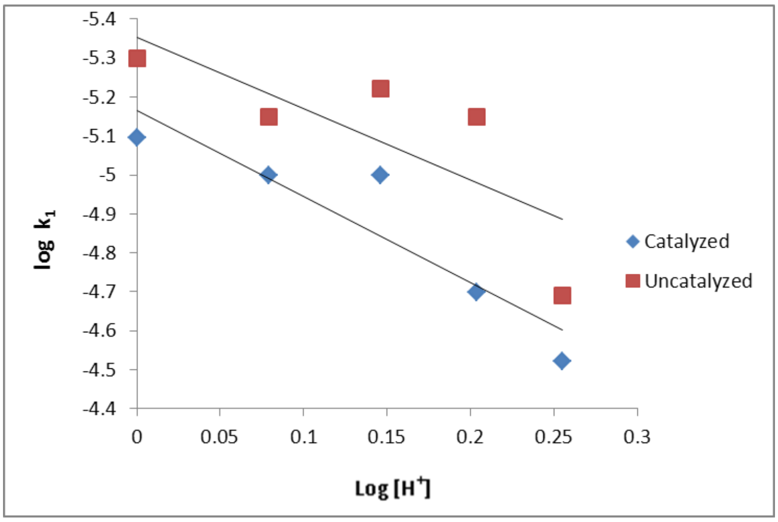


Fig-4: Plot of log [H_2SO_4] versus log k_1.

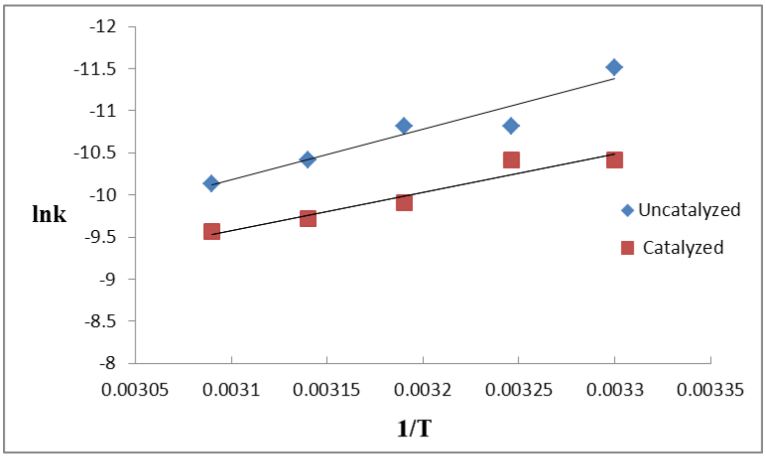


Fig-5: Plot of 1/T versus ln k

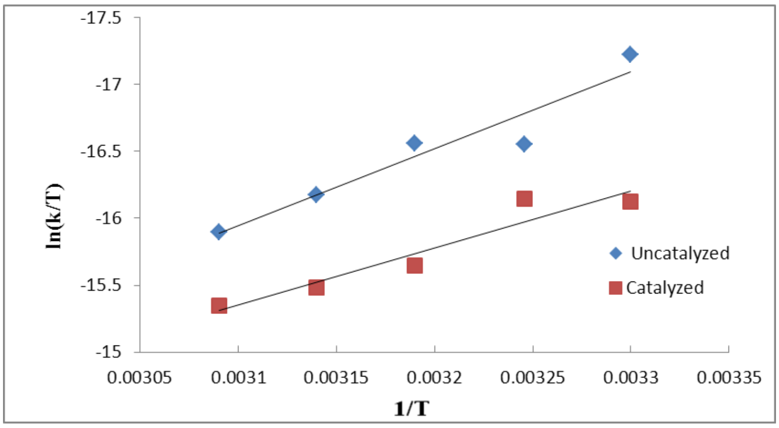
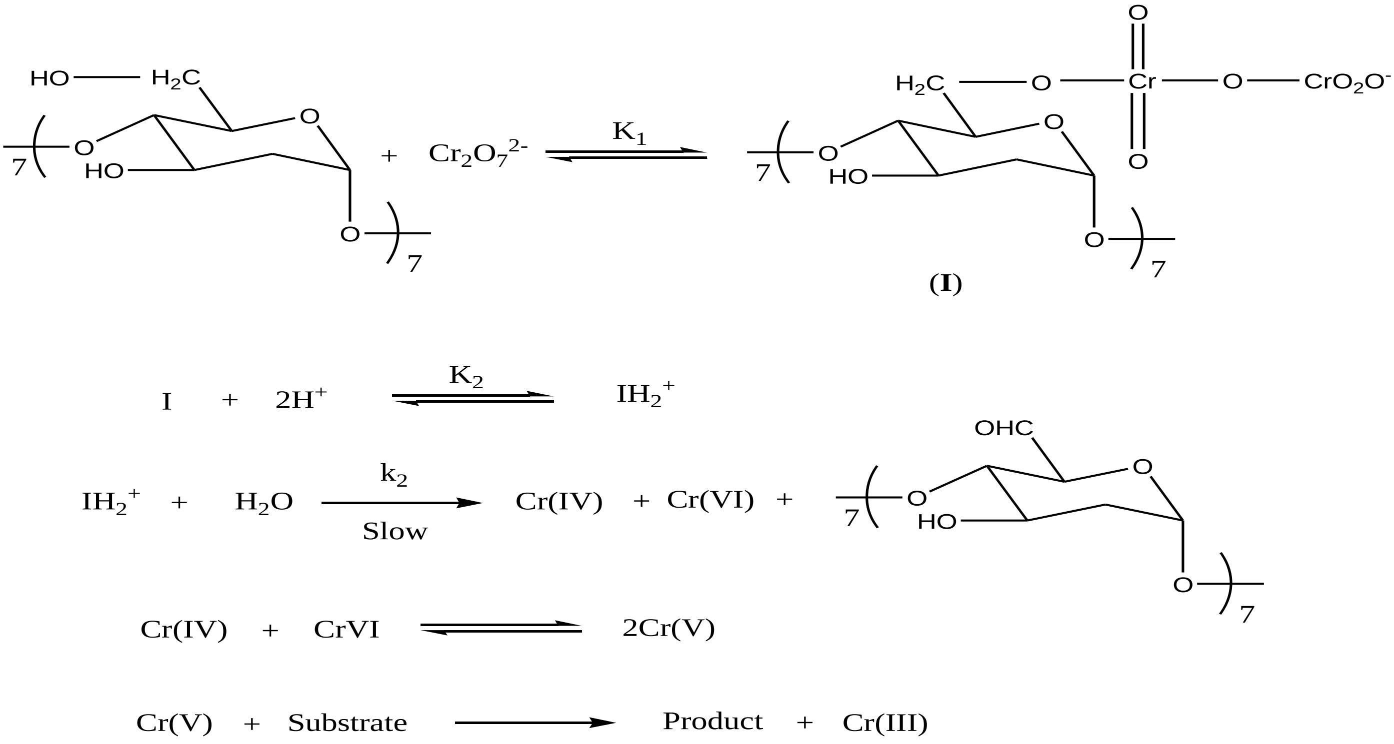


Fig-6: Plot of 1/T versus ln (k/T).

3.9 *Mechanism*

As β-CD comprises of seven α-D-glucopyranose units joined by α(1-4) bonds, OH-1 of each unit is blocked by glycosidic linkage[14]. This suggests that the reactive site is to be C-6 and -CH_2OH group is the one where oxidation takes place by Cr(VI).

In the light of all gathered experimental facts following mechanism is proposed:



Scheme 1.

Scheme 1 shows that first step involves the combination of Cr(VI) with β-CD to form an intermediate anionic complex (I) which becomes doubly protonated to form a new complex (IH_2^+)[16]. This resulting complex slowly decomposes in presence of water. Here in rate determining step water molecule abstracts proton resulting in the formation of product. In our proposed mechanism, redox reaction proceeds through two-electron steps and Cr (VI) is formed.Cr (VI) involves in fast steps, does not accumulate in the reaction [A] and finally Cr (III) is formed.

$$2H^+ + 15\beta\text{-CD} + 2Cr\,(VI) \longrightarrow 15\text{product} + 2Cr\,(III)$$

The rate law consistent with kinetic observations can be expressed as:

$$-d[Cr(VI)] / dt = k_2[IH_2^+] \qquad (1)$$

Since

$$[IH_2^+] = K_2\,[I]\,[H^+]^2 \qquad (2)$$

Therefore eq. 1 can become:

$$-d[Cr(VI)] / dt = k_2K_2\,[I]\,[H^+]^2 \qquad (3)$$

As,

$$[I] = K_1[Cr_2O_7^{-2}]\,[\beta\text{-CD}] \qquad (4)$$

Replacing [I] in eq. 3

$$-d[Cr(VI)] / dt = k_2K_1K_2[Cr_2O_7^{-2}]\,[\beta\text{-CD}][H^+]^2 \qquad (5)$$

As,

$$[Cr\,(VI)]_T = [Cr_2O_7^{-2}] + [I^-] \qquad (6)$$

Then,

$$[Cr\,(VI)]_T = [Cr_2O_7^{-2}]\,\{1 + K_1[\beta\text{-CD}]\} \qquad (7)$$

Or,

$$[Cr_2O_7^{-2}] = [Cr\,(VI)]_T/1 + K_1[\beta\text{-CD}] \qquad (8)$$

Therefore, eq. 5 becomes:

$$-d[Cr(VI)] / dt = \frac{k_2K_1K_2\,[\beta\text{-CD}][H^+]^2\,[Cr\,(VI)]_T}{1 + K_1[\beta\text{-CD}]} \qquad (9)$$

As catalyst also affects the rate of reaction, the rate law becomes:

$$-d[Cr(VI)] / dt = \frac{k_2K_1K_2\,[\beta\text{-CD}][H^+]^2\,[Cr\,(VI)]_T\,[Fe\,(III)]}{1 + K_1[\beta\text{-CD}]} \qquad (10)$$

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