

## Oxidation of $\beta$ -Cyclodextrin by Hexacyanoferrate(III) in Aqueous Alkaline Medium: a Kinetic and Mechanistic Study

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**Abstract**—The kinetics of redox reaction between  $\beta$ -cyclodextrin ( $\beta$ -CD) and hexacyanoferrate(III) has been studied spectrophotometrically in alkaline medium at 25°C and at an ionic strength of 1.10 mol dm<sup>-3</sup>. The order with respect to [Fe(CN)<sub>6</sub>]<sup>3-</sup> was found to be unity and order with respect to alkali and [ $\beta$ -CD] was found to be less than unity. Increasing alkali and ionic strength concentration accelerates the rate of the reaction. The reaction between  $\beta$ -CD and hexacyanoferrate(III) involves 1:2 stoichiometry. Oxidised products are confirmed by FT-IR and <sup>1</sup>H-NMR spectral technique. The main reaction product is identified as (3*S*,4*R*,5*S*,6*S*)-4,5-dihydroxy-3,6-dimethoxy-tetrahydro-2*H*-pyran-2-carbaldehyde. Based on the experimental results a suitable mechanism is proposed and the rate law is derived. The reaction in alkaline medium proceeds through the formation of oxidant–reductant complex that decomposes slowly in a rate determining step followed by fast step to give the product. The activation parameters with respect to the slow step of the mechanism are calculated. The reaction constants involved in the mechanism have been computed. There is a good agreement between the experimental and calculated rate constants under different experimental conditions.

**Keywords**—Kinetics; Oxidation;  $\beta$ -cyclodextrin; Hexacyanoferrate(III); Mechanism

### I. INTRODUCTION

$\beta$ -Cyclodextrin ( $\beta$ -CD), is composed of seven units of D(+)-glucopyranose units joined by  $\alpha$ -1, 4-glycosidic bonds arranged in a truncated cone-shaped structure [1]. In the pharmaceutical industry, it can be used as complexing agent for increasing the solubility of poorly soluble drug as well as increasing its bioavailability and stability. It can alleviate the gastrointestinal drug irritation, and prevent drug-drug and drug-excipient interactions [2]. It can also be used in food, pharmaceutical, drug delivery, and chemical industries, as well as agriculture and environmental engineering.

$\beta$ -CD is the most interesting of the cyclodextrins available due to its ease of production, price and attachment to textile surfaces and the size of the cavity which makes it suitable for hosting a range of guest molecules. Typical pharmaceutical drug release profiles are of four main types; immediate, prolonged, modified and delayed. Based on this knowledge, cyclodextrin derivatives are used in the pharmaceutical industry to modify drug release.

Apart from applications in the pharmaceutical industry,  $\beta$ -CD has found applications in the cosmetic industry in the controlled release of fragrances from inclusion products, such as from detergents, perfumes and room fresheners. In environmental sciences,  $\beta$ -CD is used in the removal of organic pollutants and heavy metals from water and soil

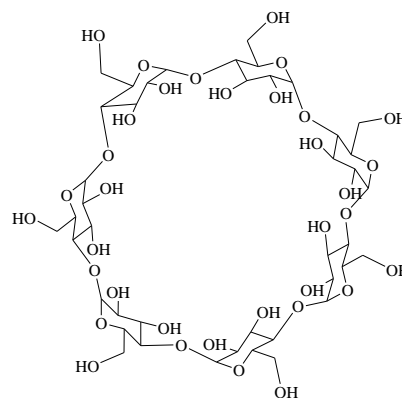


Figure 1. Structure of  $\beta$ -cyclodextrin

Hexacyanoferrate(III) has been widely used to oxidize numerous organic and inorganic compounds in alkaline media. The authors[3] have suggested that alkaline hexacyanoferrate(III) ion simply acts as an electron abstracting reagent in redox reactions. However, Speakman and Waters[4] have suggested different path of oxidation of aldehydes, ketones and nitroparaffins by hexacyanoferrate(III). Singh et.al.,[5] while discussing the oxidations of formaldehyde, acetone and ethyl methyl ketone by hexacyanoferrate(III) have suggested that the oxidation takes place via an electron transfer process

resulting in the formation of a free radical intermediate. In alkaline medium, the redox potential[6] of the couple  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  is +0.450V. It is one equivalent oxidant leading to its reduction to hexacyanoferrate(II), a stable product[7,8].

Rest of the paper is organized as follows, Section I contains the introduction of  $\beta$ -Cyclodextrin, hexacyanoferrate(III) and importance of the study, Section II contains the related work of experiment. Section III includes reagents/materials used, kinetic studies and stoichiometry and product analysis. Section IV contains result part in which order with respect to  $[\text{Fe}(\text{CN})_6^{3-}]$ ,  $[\beta\text{-CD}]$  and  $[\text{OH}^-]$ , effect of ionic strength and temperature on rate and test for free radicals are given. Along with this probable mechanism and rate law are discussed. Section V concludes research work with future directions.

## II. RELATED WORK

Reports are available on the oxidation of  $\beta$ -cyclodextrin by permanganate in the acidic medium[9] and as well as in the alkaline medium[10]. But no reports are found about the reaction of  $\beta$ -CD with hexacyanoferrate (III). Hence the study is undertaken to find out the reaction products of  $\beta$ -cyclodextrin with hexacyanoferrate(III) in alkaline medium. Such studies are of much significance in understanding the mechanistic profile of  $\beta$ -cyclodextrin in redox reaction, in different medium under different conditions and provide an insight into the interaction of metal ions with substrate.

## III. METHODOLOGY

### Materials and Reagents

The stock solution of the oxidant, hexacyanoferrate(III), was prepared by dissolving potassium hexacyanoferrate(III) (SISCO-CHEM) in distilled water and the concentration was ascertained by iodometric titration[11]. A stock solution of  $0.01 \text{ mol dm}^{-3}$   $\beta$ -cyclodextrin (Himedia) was prepared by dissolving  $\beta$ -cyclodextrin in distilled water. Potassium hydroxide was used as the source of  $\text{OH}^-$  ions to vary the alkali concentrations in the reaction media. The ionic strength was maintained using potassium nitrate. The stock solutions were diluted as required before use. All the solutions were freshly prepared before use.

### Kinetic Studies

Results were recorded at  $25 \pm 0.1^\circ \text{C}$  and at  $I = 1.10 \text{ mol dm}^{-3}$ . Reactions were initiated by mixing the solutions of hexacyanoferrate(III) and  $\beta$ -cyclodextrin which also contained the required amounts of KOH and  $\text{KNO}_3$ . The reaction was performed in pseudo-first order condition by taking  $\beta$ -cyclodextrin in excess. Progress of the reaction was followed by measuring the absorbance of hexacyanoferrate(III) in the reaction mixture at 420 nm placed in the thermostated compartment of a Systronics 1800 Bio UV- Vis spectrophotometer. Application of Beer's law under reaction conditions is verified between

$1.0 \times 10^{-4}$  to  $10 \times 10^{-4} \text{ mol dm}^{-3}$  of hexacyanoferrate(III) at 420 nm. The molar extinction coefficient of  $\text{Fe}(\text{CN})_6^{3-}$  at 420 nm was found to be  $\epsilon = 1050 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The spectral changes during the chemical reaction for standard condition at  $25^\circ \text{C}$  are shown in Fig. 2. It is evident from the figure that the concentration of  $\text{Fe}(\text{CN})_6^{3-}$  decreases at 420 nm. The kinetic studies indicate more than 70% completion of the reaction with first order kinetics. The first order rate constants,  $k_{\text{obs}}$  were obtained from the plot of  $\log [\text{Fe}(\text{CN})_6^{3-}]$  versus time.

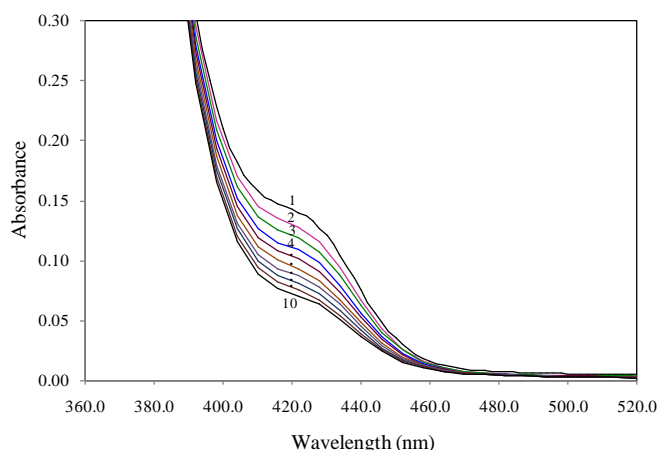
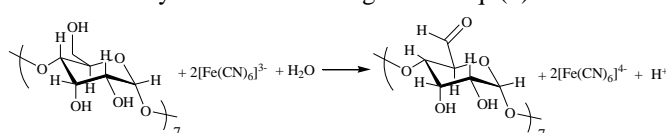


Figure 2. UV-vis, spectral changes observed during the oxidation of  $\beta$ -cyclodextrin by hexacyanoferrate(III) at  $25^\circ \text{C}$ ;  $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-4}$ ,  $[\beta\text{-CD}] = 3.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 0.70$  and  $I = 1.10 \text{ mol dm}^{-3}$  with scanning interval time of: 1.0 to 10.0 min

### Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratio of hexacyanoferrate(III) to  $\beta$ -CD in the presence of constant amount of  $\text{OH}^-$  and  $\text{KNO}_3$  were allowed to react for about 5 hours at  $25^\circ \text{C}$ . The remaining concentration of hexacyanoferrate(III) was assayed by measuring the absorbance at 420 nm. The results indicated 1:2 stoichiometry for conditions as given in Eq. (1).



Products were obtained by ether extraction and confirmed by FT-IR and  $^1\text{H-NMR}$  spectral studies. Since,  $\beta$ -cyclodextrin is a bulky molecule having seven  $\alpha$ -glucopyranose units, it is bit difficult to locate exact oxidation site. On the top, it has fourteen secondary  $-\text{OH}$  groups and seven primary  $-\text{OH}$  groups are located at the bottom of the molecule. Hence, outside the  $\beta$ -cyclodextrin has hydrophilic  $-\text{OH}$  groups. In the present case, it has been assumed that C-1 position is blocked by glycosidic linkage, the reactive site is to be sixth position (C-6). Thus, it is the  $\text{CH}_2\text{OH}$  group of  $\beta$ -cyclodextrin which was oxidized [12, 13] and generally after oxidation, sugars and carbohydrates yield aldehydes [9]. In the present study also  $\beta$ -cyclodextrin containing  $-\text{CH}_2\text{OH}$  group oxidizes to form aldehyde. FT-IR spectrum of product shows  $-\text{C}=\text{O}$  stretching at  $1715 \text{ cm}^{-1}$  and stretching for aromatic aldehydic  $-\text{C}-\text{H}$  appears at  $2785$  and  $2851 \text{ cm}^{-1}$  (Fig. S1).

Further the product was confirmed by  $^1\text{H-NMR}$  spectra which shows sharp peak at (DMSO): 9.70 (s, 1H, CHO) confirming the product (3*S*,4*R*,5*S*,6*S*)-4,5-dihydroxy-3,6-dimethoxy-tetrahydro-2*H*-pyran-2-carbaldehyde (Fig. S2). Along with this, the product was quantitatively estimated by its 2,4-DNP derivative[14].

#### IV. RESULTS AND DISCUSSION

##### Reaction Order

The reaction orders were evaluated from the slopes of the plots of  $\log k_{\text{obs}}$  versus  $\log(\text{concentration})$  by varying the concentrations of  $\beta$ -Cyclodextrin and alkali, keeping all other reactant concentrations and conditions constant.

##### Effect of [Hexacyanoferrate(III)]

At constant concentration of  $\beta$ -Cyclodextrin, alkali and at constant ionic strength,  $I = 1.10 \text{ mol dm}^{-3}$ , the hexacyanoferrate(III) concentration was varied from  $0.50 \times 10^{-4}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$  (Table 1). The constant rate constant ( $k_{\text{obs}}$ ) values, at different hexacyanoferrate(III) concentration indicates first order with respect to  $[\text{Fe}(\text{CN})_6]^{3-}$ .

##### Effect of [ $\beta$ -cyclodextrin]

The  $\beta$ -Cyclodextrin, concentration was varied in the concentration range of  $0.50 \times 10^{-3}$  to  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ , keeping all other conditions constant. The rate constant,  $k_{\text{obs}}$  increased with increase in the concentration of  $\beta$ -Cyclodextrin (Table 1). From the slope of the plot of  $\log k_{\text{obs}}$  versus  $\log[\beta\text{-CD}]$ , the order with respect to  $\beta$ -Cyclodextrin concentration was found to be less than unity (0.75).

##### Effect of [Alkali]

The effect of alkali concentration on the reaction was studied in the range  $0.10$  to  $1.0 \text{ mol dm}^{-3}$  at constant concentrations of  $\beta$ -Cyclodextrin, hexacyanoferrate(III) at constant ionic strength of  $1.10 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . The rate constants increased with increase in the alkali concentration (Table 1). From the slope of the plot of  $\log k_{\text{obs}}$  versus  $\log[\text{OH}^-]$ , the order with respect to alkali, concentration was found to be fractional (0.65).

##### Effect of Ionic strength

At constant concentration of reactants and other constant conditions, the ionic strength was varied in the range  $0.90$  to  $1.70 \text{ mol dm}^{-3}$  by varying the concentrations of potassium nitrate and the rate was found to be increase with increasing ionic strength. This indicates involvement of the similar charged species in the reaction. A plot of  $\log k_{\text{obs}}$  versus  $\sqrt{I}$  is linear with a positive slope.

##### Test for Free Radicals (Polymerization Study)

The involvement of free radicals was examined as follows. To the reaction mixture, a known quantity of acrylonitrile scavenger is added initially and it is kept in an inert atmosphere for two hours at room temperature. Upon diluting the reaction mixture with methanol, a white precipitate obtained, indicates the intervention of free

radicals in the reaction [15]. The blank experiments of either hexacyanoferrate(III) or  $\beta$ -CD alone with acrylonitrile does not induce the polymerization.

Table 1. Effect of variation of  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\beta$ -cyclodextrin and  $\text{OH}^-$  concentrations on the oxidation of  $\beta$ -cyclodextrin by hexacyanoferrate(III) in alkaline medium at  $25^\circ\text{C}$  and  $I = 1.10 \text{ mol dm}^{-3}$ .

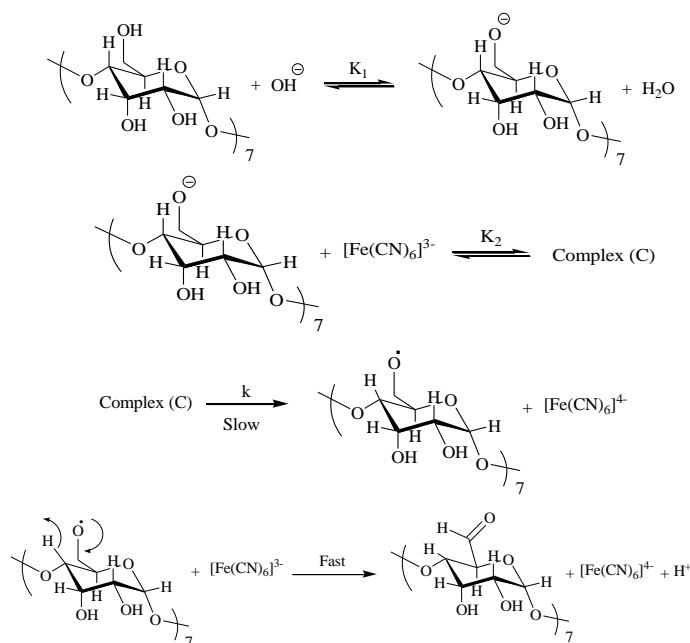
##### Effect of Temperature

$[\text{Fe}(\text{CN})_6^{3-}]$ $\times 10^4$ ( $\text{mol dm}^{-3}$ )	$[\beta\text{-CD}]$ $\times 10^3$ ( $\text{mol dm}^{-3}$ )	$[\text{OH}^-]$ ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}} \times 10^4$ ( $\text{s}^{-1}$ )	
			Exptl.	Calc.
0.5	3.0	0.70	6.12	5.60
1.0	3.0	0.70	6.61	5.60
2.0	3.0	0.70	6.25	5.60
3.0	3.0	0.70	6.81	5.60
4.0	3.0	0.70	6.10	5.60
5.0	3.0	0.70	6.40	5.60
1.0	0.5	0.70	1.04	0.92
1.0	1.0	0.70	2.39	1.86
1.0	2.0	0.70	4.05	3.70
1.0	3.0	0.70	6.61	5.60
1.0	4.0	0.70	7.52	7.40
1.0	5.0	0.70	9.57	9.21
1.0	3.0	0.10	2.18	2.08
1.0	3.0	0.30	3.14	4.05
1.0	3.0	0.50	4.45	4.98
1.0	3.0	0.70	6.61	5.60
1.0	3.0	1.00	8.57	6.00

The kinetics was studied at three different temperatures  $15$ ,  $25$ , and  $35^\circ\text{C}$  under varying alkali and  $\beta$ -cyclodextrin concentrations. The rate was found to increase with increasing temperature. The rate constant  $k$ , of slow step,  $K_1$  the value of first equilibrium step and  $K_2$ , the value of second equilibrium step of the Scheme 1 were obtained from the plots of  $[1]/k_{\text{obs}}$  versus  $1/[\beta\text{-CD}]$  and  $[1]/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  at three different temperatures and are given in Table 2.

The hexacyanoferrate (III) oxidation of  $\beta$ -cyclodextrin in alkaline medium occurs in measurable rate in  $0.70 \text{ mol dm}^{-3}$  alkali at  $25^\circ\text{C}$ . The reaction has a stoichiometry 1:2 with respect to  $\beta$ -cyclodextrin to the oxidant. No effect of added product was observed in most of the oxidation reactions. Hexacyanoferrate(III) resembles copper(II), which involves free radical formation and rapidly oxidizes the substrate hexacyanoferrate(III) – hexacyanoferrate(II) system, which has the higher redox potential the copper(II)-copper(I) system, substantiates a better possibilities for the rapid oxidation of free radical with hexacyanoferrate III and the rapid oxidation of free radicals might completely mask the polymerisation. On the basis of the experimental results, a mechanism can be proposed for which all the observed orders in each constituents i.e [oxidant], [reductant] and alkali may be well accounted.

The results suggest that, in the prior equilibrium step,  $\beta$ -cyclodextrin combines with alkali to give the anionic form of  $\beta$ -cyclodextrin which is supported by experimentally observed fractional orders in [alkali] and [ $\beta$ -cyclodextrin]. In the second equilibrium step the anionic form of  $\beta$ -cyclodextrin combines with hexacyanoferrate III to give complex (C) in a slow step decomposes to form a free radical intermediate and  $\text{Fe}(\text{CN})_6^{4-}$ . In a fast step the free radical intermediate combines with one more mole of hexacyanoferrate III to give product (3S,4R,5S,6S)-4,5-dihydroxy-3,6-dimethoxytetrahydro-2H-pyran-2-carbaldehyde and  $\text{Fe}(\text{CN})_6^{4-}$ . The results are accommodated in scheme 1.



**Scheme 1** mechanism for the oxidation of  $\beta$ -cyclodextrin by hexacyanoferrate(III) in alkaline medium

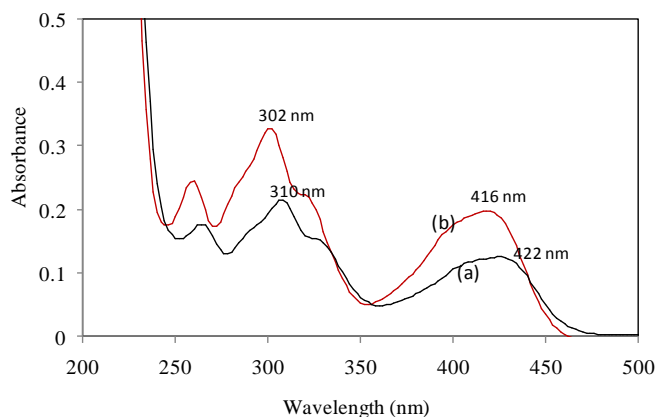
The results indicate the formation of a complex between oxidant and substrate. The spectral evidence for the complex formation between the oxidant and substrate was obtained from UV-vis spectra of oxidant and oxidant-substrate mixtures in which a hypsochromic shift of 6 nm from 422 nm to 416 nm was observed (Fig. 3). The formation of complex was also proved kinetically by Michaelis-Menten plot (Fig. 4). Such complex formation between oxidant and substrate was also observed in literature [16].

From Scheme 1, the rate law can be given as:

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{Fe}(\text{CN})_6^{3-}]} = \frac{k K_1 K_2 [\beta\text{-CD}] [\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{OH}^-] [\beta\text{-CD}]} \quad \dots(1)$$

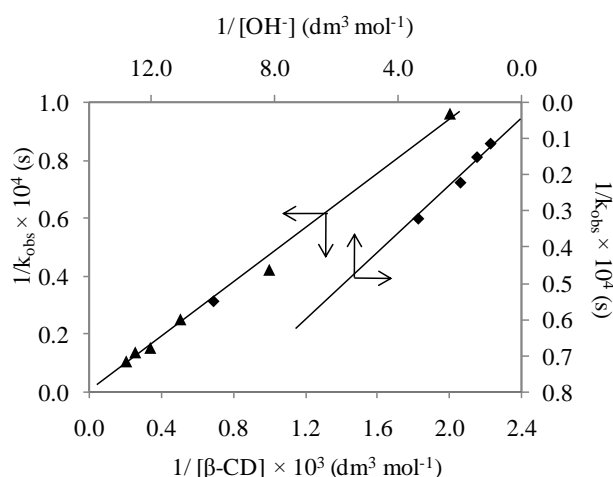
Eq. (1) can be rearranged in the form of the following Eq. (2), which is suitable for verification,

$$\frac{1}{k_{\text{obs}}} = \frac{\text{Rate}}{[\text{Fe}(\text{CN})_6^{3-}]} = \frac{1}{k K_1 K_2 [\beta\text{-CD}] [\text{OH}^-]} + \frac{1}{k K_2 [\beta\text{-CD}]} + \frac{1}{k} \quad \dots(2)$$



*Figure 3. UV- vis spectral evidence for the complex formation between hexacyanoferrate(III) and  $\beta$ -cyclodextrin [hexacyanoferrate(III)(422 nm) and hexacyanoferrate(III) +  $\beta$ -cyclodextrin (416 nm)].*

According to equation (12) the plots of  $1/k_{\text{obs}}$  versus  $1/[\beta\text{-CD}]$  and  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  is linear and found to be so (Fig. 4). The intercept and slope of such plot lead to the values of  $k$ ,  $K_1$  and  $K_2$ . Using these values, rates under different experimental conditions were calculated. The values of  $K_1$  and  $K_2$  at three different temperatures are given in Table 2.



*Figure 4. Verification of rate law (1) in the form of equation (2)*

The effect of ionic strength on the rate qualitatively explains the reaction between two negatively charged ions as in Scheme 1. The moderate values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favorable for electron transfer processes. The large negative value of  $\Delta S^\ddagger$  ( $-330 \text{ JK}^{-1} \text{ mol}^{-1}$ ) indicates that the complex is more ordered than the reactants and also indicates that,  $\Delta S^\ddagger$  observed in the decomposition of the intermediate complex is in accordance with the propositions suggested for oxidation reactions of an inner-sphere nature[17]. The positive value of free energy of activation ( $\Delta G^\ddagger = 138 \text{ kJ mol}^{-1}$ ) and enthalpy of activation ( $\Delta H^\ddagger = 40 \text{ kJ mol}^{-1}$ ) indicate that the transition state is highly solvated [18].

Table 2. (a) Effect of temperature on the oxidation of  $\beta$ -cyclodextrin by hexacyanoferrate(III) in aqueous alkaline medium and Activation parameters with respect to slow step of Scheme 1

Temperature (K)	$k \times 10^2$ ( $s^{-1}$ )	Activation Parameters	Values
288	8.05	$E_a$ ( $\text{kJ mol}^{-1}$ )	42.65
298	15.5	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	40.17
308	25.4	$\Delta S^\ddagger$ ( $\text{J K}^{-1}\text{mol}^{-1}$ )	-330.1
		$\Delta G^\ddagger_{298}$ ( $\text{kJ mol}^{-1}$ )	138.56
		$\log_{10} A$	6.70

(b) Effect of temperature on the first and second equilibrium step of Scheme 1

Temperature ( $^{\circ}\text{C}$ )	$K_1$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$K_2 \times 10^{-1}$ ( $\text{dm}^3 \text{mol}^{-1}$ )
15	1.020	3.021
25	2.462	1.823
35	3.521	0.902

## V. CONCLUSION AND FUTURE SCOPE

The redox reaction between  $\beta$ -cyclodextrin and hexacyanoferrate(III) has been studied spectrophotometrically in alkaline medium at  $I = 1.10 \text{ mol dm}^{-3}$ . The reaction revealed 1:2 stoichiometry with reductant to oxidant. The products were identified by IR and  $^1\text{H-NMR}$  spectral studies. The main reaction product was identified as (3*S*,4*R*,5*S*,6*S*)-4,5-dihydroxy-3,6-dimethoxy-tetrahydro-2*H*-pyran-2-carbaldehyde and it is also confirmed by 2,4-DNP test. Activation parameters were evaluated. Plausible mechanism and related rate law was proposed. The reaction between  $\text{Fe}(\text{CN})_6^{3-}$  and  $\beta$ -CD involves the formation of an oxidant-reductant complex which was confirmed by UV-vis spectral data. The overall sequence described here is consistent with all the experimental evidence including the product, spectral, mechanistic and kinetic studies.

## VI. ACKNOWLEDGEMENTS

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## REFERENCES

- [1]. J. Szejtli, *Cyclodextrine Technology*, Kluwer Academic Publishers, Dordrecht, Netherlands, 1988, pp. 143-154.
- [2]. S. Swain, C. Niranjana Patra, M. E. Bhanaji Rao, *Pharmaceutical Drug Delivery Systems and Vehicles*, CRC Press, 2016
- [3]. [3] E. P. Kelson, P. P. Phengsy, "Kinetic study of 2-propanol and benzyl alcohol oxidation by alkaline hexacyanoferrate(III)

- catalyzed by a terpyridyl ruthenium complex*", International Journal of Chemical Kinetics, Vol. 32, pp. 760-770, 2000.
- [4]. P. T. Speakman, W. A. Waters, "Kinetic features of the oxidation of aldehydes, ketones and nitroparaffins with alkaline ferricyanide", Journal of Chemical Society, pp. 40-45, 1955.
  - [5]. V. N. Singh, M. P. Singh, B. L. Saxena, M. P. Singh, "Kinetics and mechanism of the oxidation of formaldehyde by hexacyanoferrate(III) ion", Canadian Journal of Chemistry, Vol. 47, pp. 1051-1056, 1969
  - [6]. M. C. Day, Jr. and J. Selbin, Reinhold Publishing Corporation, New York (1964) p.226
  - [7]. A. Nowduri, K.K. Adari, N. Gollapalli, V. Parvataneni, "Kinetics and mechanism of oxidation of L-cystine by hexacyanoferrate (III) in alkaline medium", Journal of Chemistry, Vol.6 pp.93-98, 2009.
  - [8]. S. K. Upadhyay, M. C. Agrawal, J. Sci. Ind. Res., 1983, 508
  - [9]. S. M. Manmeet, M. Faqeer, Z. Khan, "A kinetic study of oxidation of  $\beta$ -cyclodextrin by permanganate in aqueous media", Colloids and Surfaces A: Physico Chemical Engineering Aspects, Vol. 295 pp.165-171, 2007.
  - [10]. M. B. Bolattin, S. T. Nandibewoor, S. A. Chimatadar, "Influence of micellar aggregates on oxidative degradation of  $\beta$ -cyclodextrin by alkaline permanganate: A kinetic and mechanistic study of inclusion complex", Journal of Environmental Chemical Engineering, Vol.5 pp.4344-4352, 2017.
  - [11]. G. H. Jeffery, J. Bassett, J. Mendham, R. C. Denny, Vogel's Text book of Quantitative Chemical Analysis, 5<sup>th</sup> edition BLBS, Longman, Essex, UK, (1996) (a) p.381, (b) p.406
  - [12]. I. L. Finar, Organic Chemistry, Longman, ELBS, UK, 1973, Vol. 1, pp. 505.
  - [13]. K. K. SenGupta, S. SenGupta, S. K. Mandal, Indian J. Chem., 1988, 27A, 23
  - [14]. F. Fiegel, Spot tests in Organic Analysis, Elsevier, New York, 1975.
  - [15]. G. G. Ariga, S. A. Chimatadar, "Spectrophotometric study of oxidation of fosfomycin by potassium permanganate in aqueous perchloric acid medium-a kinetic and mechanistic approach", International Journal of Scientific Research in Chemical Sciences, Vol. 5, Issue. 4, pp.1-7, 2018.
  - [16]. M. B. Bolattin, M. D. Meti, S. T. Nandibewoor, S. A. Chimatadar, "Oxidative degradation of the antihypertensive drug losartan by alkaline copper (III) periodate complex in the presence and absence of ruthenium (III) catalyst: a kinetic and mechanistic study of losartan metabolite", Monatshefte für Chemie, Vol. 146, pp.1649-1663, 2015.
  - [17]. M. B. Bolattin, S. T. Nandibewoor, S. A. Chimatadar, "Conclusive evidence for autocatalytic behaviour of manganese (II) ions in the oxidative degradation of ondansetron by permanganate in aqueous sulfuric acid medium-a kinetic and mechanistic approach", Journal of Environmental Chemical engineering, Vol. 3, pp. 1233-1242, 2015.
  - [18]. M. K. Ghosh, S. K. Rajput, "Kinetics and mechanism of lanthanum(III) catalyzed oxidation of dextrose by cerium(IV) in aqueous acidic medium", International Journal of Physical Chemistry, Vol. 2, pp.49-54, 2012.

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Meritorious Students (RFSMS) given by University Grant Commission (UGC), New Delhi, India. The research interest includes kinetics, catalysis and drug protein interaction studies. She has published 08 research papers in reputed international journals including Royal society of chemistry (RSC) and American chemical society (ACS). Currently she is working as an Assistant professor in P.G. Department of Chemistry, D.M.S Mandal's Bhaurao Kakatkar College, Belagavi.

Dr. Abhay Sakharam Kulkarni obtained his B.Sc, M.Sc and Ph.D degree from Karnatak University Dharawd. He joined Bhaurao Kakatkar College, Belguam in the year 1987. Presently he is working as Head of the Department of Chemistry. He has published 2 research publications in the international journals. He has got more than 30 years of teaching experince in the U.G. level. He worked as a NAAC Co-ordinator from the year 2010-2013. He is the member of BOE, Rani Channamma University, Belagavi.



Mr.Naim M. Mulla obtained his master's degree in 2018 from P.G. Department of Chemistry, D.M.S Mandal's Bhaurao Kakatkar College, Belagavi (affiliated to Rani Channamma University, Belagavi). He has cleared Karnatak State Eligibility Test (K-SET) for Lectureship in 2018. Currently he is working as a lecturer in S.M.A Trust's Shivanand College, Kagwad.



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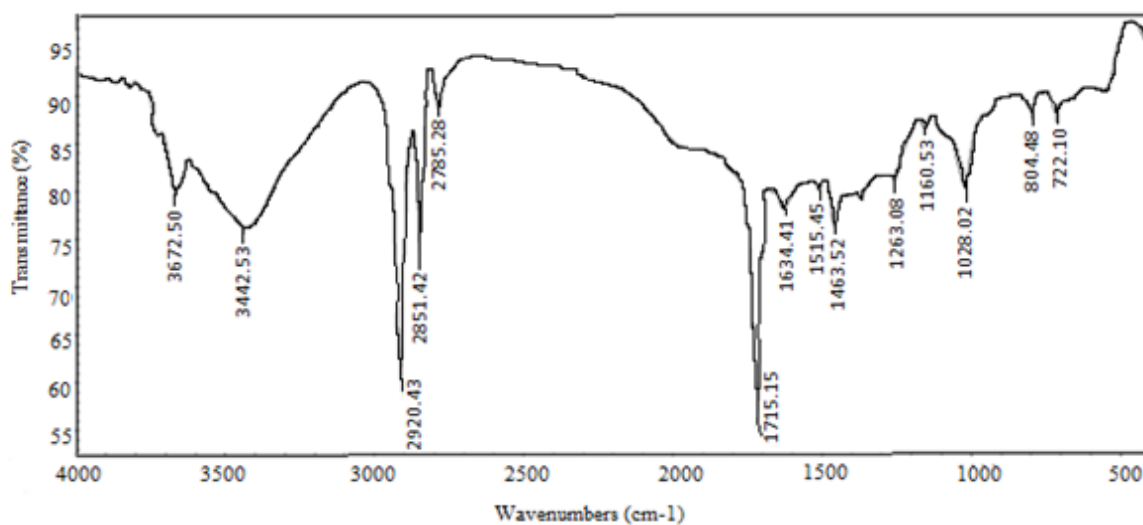
**Appendix: Supporting Information (SI)**

Figure SI 1. FT-IR spectrum of the product showing  $\text{C}=\text{O}$  stretching at  $1715\text{cm}^{-1}$ , stretching for aromatic aldehydic  $\text{C}-\text{H}$  appears at  $2785$  and  $2851\text{cm}^{-1}$ .

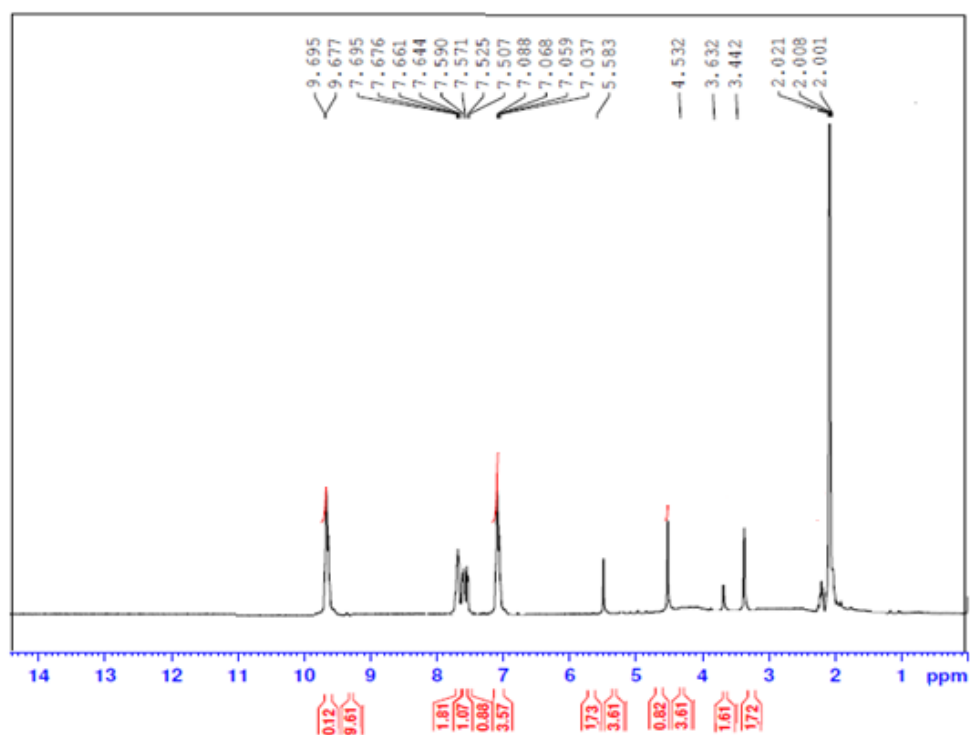


Figure SI 2. <sup>1</sup>H NMR spectrum of oxidation product obtained during reaction between  $\beta$ -cyclodextrin and hexacyanoferrate(III) in alkaline medium