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## The Kinetics of Rh(III)-Catalyzed Oxidation of D(+) Melibiose By Cu(II) Bipyridyl Complex In Alkaline Medium

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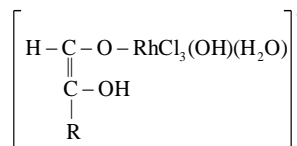
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### ABSTRACT

The kinetics of Rh(III)-catalyzed reaction between D(+)melibiose and  $(Cu(Bip)_2)^{2+}$  the reaction has been studied in the temperature range 35-50°C in alkaline medium. Kinetic data show that the rate of oxidation is independent of  $[Cu(II)]$  and follows first-order kinetics with respect to  $[Rh(III)]$ . Reaction shows fractional-positive order kinetics with respect to  $[OH^-]$  and  $[D(+)\text{melibiose}]$ . In the present kinetic study, bipyridyl (Bip) was used as complexing agent so that the reaction mixture remains homogeneous throughout the course of reaction. Variations of  $[Bip]$  and ionic strength of the medium show nil effect on the rate of oxidation. The pseudo-zeroth-order rate constant decreases with increase in the dielectric constant of the medium. Various activation parameters including energy of activation along with entropy of activation were also calculated. Sodium salts of arabinonic acid, lyxonic acid and formic acid were identified as oxidation products of reaction under investigation. On the basis of the experimental findings, spectrophotometric observations, stoichiometric evidence and product analysis, a suitable mechanism has been proposed.

**Graphical Abstract:** The kinetics of Rh(III)-catalyzed reaction between D(+)melibiose and Copper(II) complexed with bipyridyl has been studied spectrophotometrically, for the first time, at 40°C in alkaline medium. The rate determining step of the reaction involves the formation of most reactive activated complex, which disproportionate into the products via fast steps.



**Keywords:** Spectrophotometric study, D(+)melibiose, chlorocomplex of Rh(III), copper-bipyridyl complex, alkaline medium.

## INTRODUCTION

Carbohydrates serve as the chief fuel and metabolic intermediate in biological systems. Carbohydrates and their derivatives play key role in the immune system, fertilization, pathogenesis, blood clotting and development [1]. Carbohydrates are biologically important substances whose micro biological and physiological activities depend largely on their redox behavior [2]. Literature shows that catalyzed and non catalyzed oxidation of various sugars viz. mono and disaccharides have been widely studied using various organic as well as inorganic oxidants [3]. Cu(II) compounds among them occupy a major place in oxidation chemistry. Oxidation reactions that involve copper ion promoted activation are wide spread in nature and have numerous catalytic and synthetic applications [4,5]. Copper-carbohydrate complexes have potential efficiency in the treatment of rheumatoid arthritis [6]. Among various transition metals used as catalyst in the oxidation of sugars, Rh(III) has drawn considerable attention due to its chemical reactivity, antitumor activity and catalytic functions of its complexes with potential industrial applications [7,8]. Cis-dichloro -bis (1,10-phenanthroline) rhodium(III) chloride is reported[9] to form covalent linkage with DNA involving the attachment of the metal to a base. Rh (III) is frequently used as a catalyst in the oxidation of various organic substrates[10-15]. Although kinetic studies of sugars [6,16-21] involving Cu(II) as an oxidant have been made for a number of uncatalyzed reactions, there seems to be few reports [22,23] about its oxidation mode in catalyzed processes. Surprisingly attempts to probe its oxidation mode in catalyzed reaction with sugars are rather scanty. This prompted us to study the kinetics and mechanism of Rh (III)-catalyzed oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium, which may be very useful to understand the complicated biochemical and other medicinal problems in the living system. Main objectives of the present kinetic investigation are to : (i) elucidate a plausible mechanism (ii) deduce an appropriate rate law (iii) ascertain the various reactive species including the formation of complexes during the course of reaction and (iv) identify the oxidation products.

## MATERIALS AND METHODS

**Preparation of solutions and Instruments used:** The standard solutions of  $\text{CuSO}_4$ , bipyridyl, D(+)-melibiose, sodium carbonate and potassium chloride were made by dissolving the calculated amount of samples in double distilled water. Throughout the study the medium of the reaction was maintained alkaline with the help of sodium carbonate solution. Concentration of hydroxyl ions was calculated by measuring the pH of the reaction mixture at room temperature. In the present investigation, the solution of potassium chloride was used for maintaining constant ionic strength of the medium. 1000ml of Rhodium (III) chloride solution was prepared by dissolving 1g of sample in hydrochloric acid maintaining 3M HCl. The strength of Rh (III) chloride in the stock solution was determined as  $3.79 \times 10^{-3}$  M. For kinetic measurements, Varian Carry Win UV-VIS Spectrophotometer connected with Pettier Accessory and Computer was used. For pH measurement EUTECH Instrument pH 5.10 was used.

**Method of study:** Copper compounds in +1, +2 states absorbs in visible region and by making use of this property of oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium was studied spectrophotometrically using Rh (III) as homogeneous catalyst. The absorption spectra of  $\text{Cu}(\text{Bip})_2^+$  solutions were recorded between 380-800 nm and absorbance maximum was found at 425 nm (Fig.1) with molar absorptivity  $5.11 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (Fig.2). At 425 nm, the product i.e.  $\text{Cu}(\text{Bip})_2^+$  absorbs maximum while oxidant  $\text{Cu}(\text{Bip})_2^{2+}$  absorbs minimum.

One set of reaction mixture containing the reactants i.e. copper sulphate, sodium carbonate, Ru(III) chloride, potassium chloride and bipyridyl and another set having same reactants except copper sulphate, were taken in two separate conical flasks and placed in a thermostatic water bath at constant temperature of  $40^\circ \pm 0.1^\circ \text{C}$ . Solution of sugar was also kept in another conical flask. When the reaction mixture had attained the required temperature, calculated amount of the sugar solution was added in both sets of

reaction mixture. Immediately the reaction mixtures were transferred to quartz cell of 1cm width and placed to the sample compartment of the spectrophotometer.

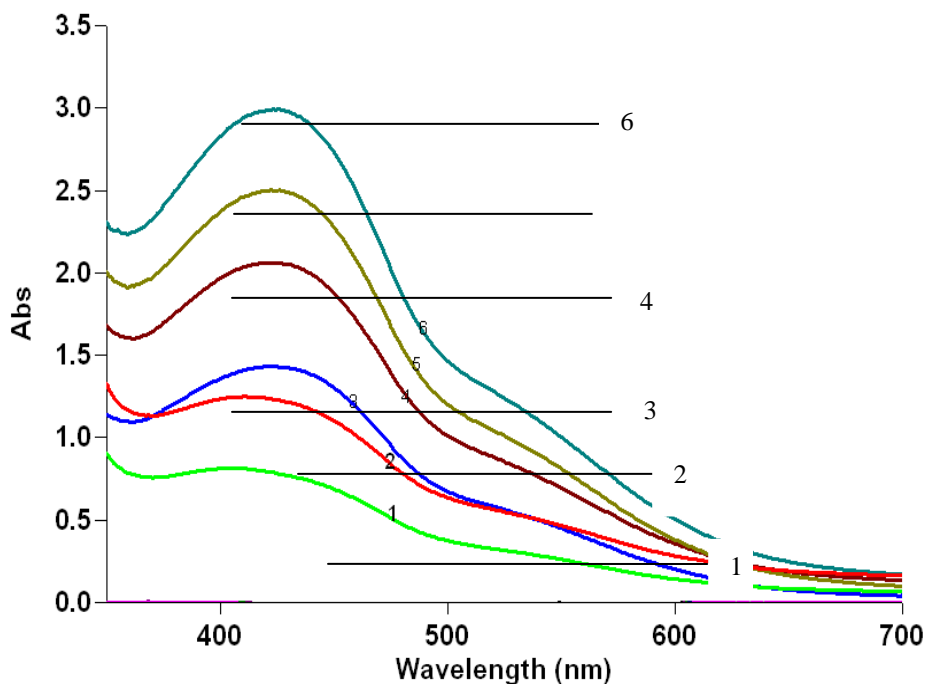


Fig. 1: Spectra of  $\text{Cu}(\text{Bip})_2^+$  solutions recorded at room temperature

(1) $[\text{Cu}(\text{II})^*] = 1.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$	(2) $[\text{Cu}(\text{II})^*] = 2.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$	(3) $[\text{Cu}(\text{II})^*] = 3.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$
(4) $[\text{Cu}(\text{II})^*] = 4.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$	(5) $[\text{Cu}(\text{II})^*] = 5.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$	(6) $[\text{Cu}(\text{II})^*] = 6.00 \times 10^{-4} \text{ M}$ [Free Bip] = $40.00 \times 10^{-4} \text{ M}$ [ $\text{Na}_2\text{CO}_3$ ] = $1.00 \times 10^{-2} \text{ M}$ [Sugar] = $1.50 \times 10^{-2} \text{ M}$

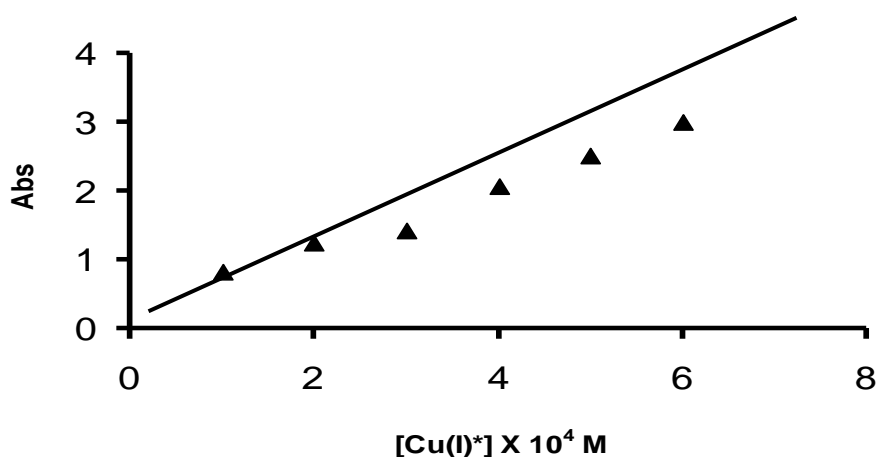


Fig. 2: Plot between  $[\text{Cu}(\text{I})^*]$  and Absorbance (Abs)

The mixture containing the solution of  $\text{CuSO}_4$  acts as absorbing sample and the mixture without  $\text{CuSO}_4$  solution acts as reference sample. The progress of the reaction was monitored spectrophotometrically by measuring the increase in absorbance at 425 nm. The absorbance versus time data over a defined time ranges were used to calculate the value of rate constant.

The zeroth-order rate constants for various kinetic runs were calculated by using the following formula, based on least square technique taken from the kinetic application of Varian Carry 300 Bio UV-VIS Spectrophotometer. The order for various species was determined from the slope of the plot of  $\log k$  vs. respective concentration of species.

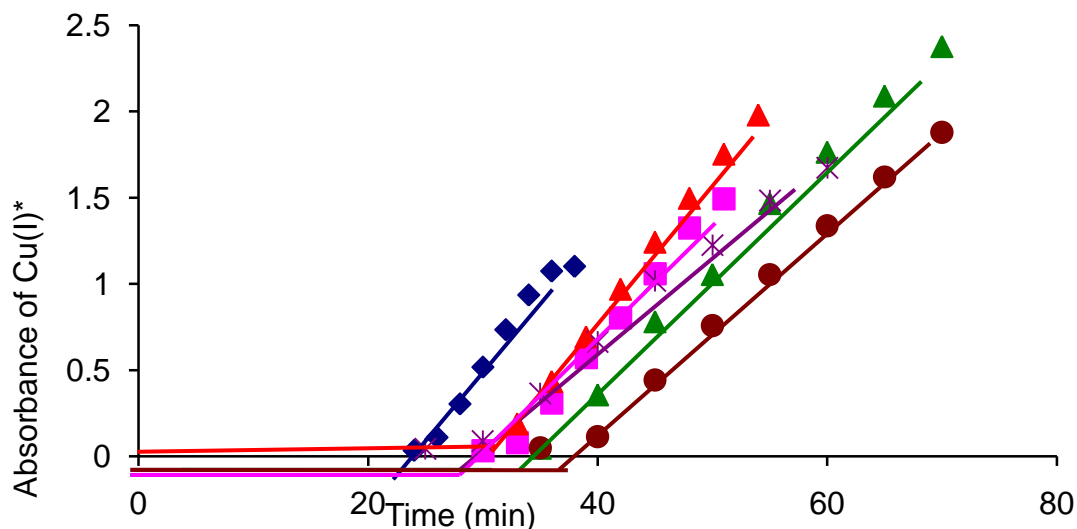
$$A = k t + A_0$$
$$\text{or } k = (A - A_0) / t$$

where  $A$  is the absorbance at time 't',  $A_0$  is the absorbance at zero time,  $k$  is pseudo-zeroth-order rate constant and  $t$  is the time in minute.

**Stoichiometry and products analysis:** Different sets of experiments were performed with different  $[\text{Cu(II)}]:[\text{D(+)melibiose}]$  ratios under the condition  $[\text{Cu(II)}] \gg [\text{D(+)melibiose}]$ . The estimation of unconsumed  $\text{Cu(II)}$  showed that one mole of  $\text{D(+)melibiose}$  is oxidized by four moles of  $\text{Cu(Bip)}_2^{2+}$ . On the basis of equivalence and kinetic studies and also the spot test [24] and thin layer chromatography [25] experiments performed for the confirmation of sodium salt of formic acid, it can be inferred that sodium salts of arabinonic acid and lyxonic acid are the other oxidation products of the reaction under investigation.

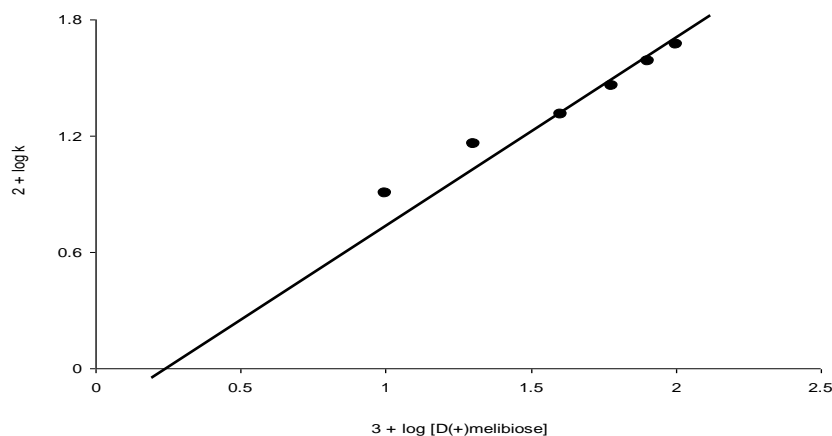
## RESULTS AND DISCUSSION

Kinetics of oxidation of  $\text{D(+)melibiose}$  by  $\text{Cu(Bip)}_2^{2+}$  in alkaline medium using  $\text{Rh(III)}$  as homogeneous catalyst have been studied at  $40^\circ\text{C}$ . Before formulating the most suitable mechanism, it is necessary to find out order of reaction with respect to each reactant involved in the reaction under investigation. For the determination of order of reaction, the help of Ostwald's Isolation method along with van't Hoff differential method has been taken. In the light of Ostwald's Isolation method, the concentration of  $\text{Cu(II)}$  was taken in a very small quantity as compared to the concentration of substrate throughout the study. To find out the order of reaction with respect to  $[\text{Cu(II)}]$  in  $\text{Rh(III)}$ -catalyzed oxidation of  $\text{D(+)melibiose}$  in alkaline medium, the concentration of  $\text{Cu(II)}$  was varied from  $1.00 \times 10^{-4} \text{ M}$  to  $10.00 \times 10^{-4} \text{ M}$  at constant temperature  $40^\circ\text{C}$  (Fig.3). The concentrations of all other reactants were maintained constant throughout the variation of  $\text{Cu(II)}$  concentration. Almost constant values of pseudo-zeroth-order rate constant,  $k$ , presented against varying concentration of  $\text{Cu(II)}$  in table 1 clearly show that the reaction follows zero-order kinetics with respect to  $\text{Cu(II)}$ . After ascertaining the order of reaction with respect to  $\text{Cu(II)}$  as zero, experiments with varying concentration of substrate were performed to determine the order of reaction with respect to  $[\text{D(+)melibiose}]$ . When a plot was made between  $\log k$  and  $\log [\text{D(+)melibiose}]$ , a straight line having positive intercept on  $\log k$ -axis was obtained (Fig.4). From the slope of the straight line the value of order of reaction with respect to  $[\text{D(+)melibiose}]$  was calculated as 0.71. Thus, it is clear that order of reaction with respect to  $[\text{D(+)melibiose}]$  throughout its ten-fold variation is fractional positive. Efforts were also made to find out the order of reaction with respect to  $\text{Rh(III)}$  concentration in the oxidation of  $\text{D(+)melibiose}$ . The variation in  $\text{Rh(III)}$  was made from  $0.50 \times 10^{-9} \text{ M}$  to  $5.0 \times 10^{-9} \text{ M}$  at constant concentrations of all other reactants. When a plot was made between pseudo-zeroth-order rate constant  $k$  and concentration of  $\text{Rh(III)}$ , a straight line passing through origin was obtained, indicating first-order kinetics with respect to  $\text{Rh(III)}$ .



**Fig.3:** Plots between Absorbance of  $\text{Cu(I)}^*$  and time at  $40^\circ\text{C}$

[Free Bip] =  $40.00 \times 10^{-4} \text{ M}$ , [D(+)-melibiose] =  $1.00 \times 10^{-2} \text{ M}$   
 [Ru(III)] =  $7.60 \times 10^{-7} \text{ M}$ , [Na<sub>2</sub>CO<sub>3</sub>] =  $1.00 \times 10^{-2} \text{ M}$ ,  $\mu$  =  $30.00 \times 10^{-2} \text{ M}$   
 (1) [Cu(II)\*] =  $1.00 \times 10^{-4} \text{ M}$  (2) [Cu(II)\*] =  $2.00 \times 10^{-4} \text{ M}$  (3) [Cu(II)\*] =  $4.00 \times 10^{-4} \text{ M}$   
 (4) [Cu(II)\*] =  $6.00 \times 10^{-4} \text{ M}$  (5) [Cu(II)\*] =  $8.00 \times 10^{-4} \text{ M}$  (6) [Cu(II)\*] =  $10.00 \times 10^{-4} \text{ M}$

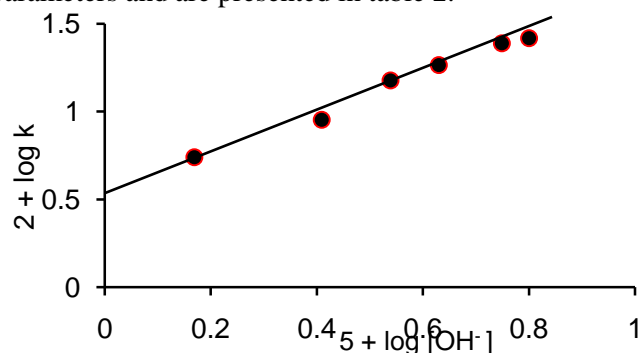


**Fig.4.** Plot between  $\log k$  and  $\log [\text{D(+)-melibiose}]$  at  $40^\circ\text{C}$

[Cu(II)\*] =  $6.00 \times 10^{-4} \text{ M}$ , [Free Bip] =  $48.00 \times 10^{-4} \text{ M}$   
 [Rh(III)] =  $2.00 \times 10^{-9} \text{ M}$ , [Na<sub>2</sub>CO<sub>3</sub>] =  $1.00 \times 10^{-2} \text{ M}$ ,  $\mu$  =  $30.00 \times 10^{-2} \text{ M}$

Next series of experiments with varying concentration of  $\text{OH}^-$  for the oxidation of D (+)melibiose were performed. The observed values of pseudo-zeroth-order rate constant for various kinetic runs are presented against varying concentration of  $\text{OH}^-$  (Table 1) which clearly shows fractional-positive order kinetics with respect to  $[\text{OH}^-]$  (Fig.5). Kinetic experiments were also performed for the effect of bipyridyl concentration on pseudo-zeroth-order rate constant, in the oxidation of D (+) melibiose. The concentration of bipyridyl was varied from  $1.50 \times 10^{-3} \text{ M}$  to  $9.0 \times 10^{-3} \text{ M}$ , and the observed values of pseudo-zeroth-order rate constant,  $k$ , for various kinetic runs clearly reveals that there is almost no change in the value of  $k$  with the change in bipyridyl concentration for the aforesaid redox reaction.

In order to find out the effect of temperature on the rate of  $\text{Cu}(\text{Bip})_2^{2+}$  oxidation of D(+)-melibiose using Rh(III) as catalyst in alkaline medium, the reaction was studied at four different temperatures i.e. 35°, 40°, 45°, 50°C at constant concentrations of the reactants and at constant ionic strength of the medium. Observed Pseudo-zeroth-order rate constant,  $k_o$  values were utilized to calculate energy of activation ( $E_a$ ) and various activation parameters and are presented in table 2.

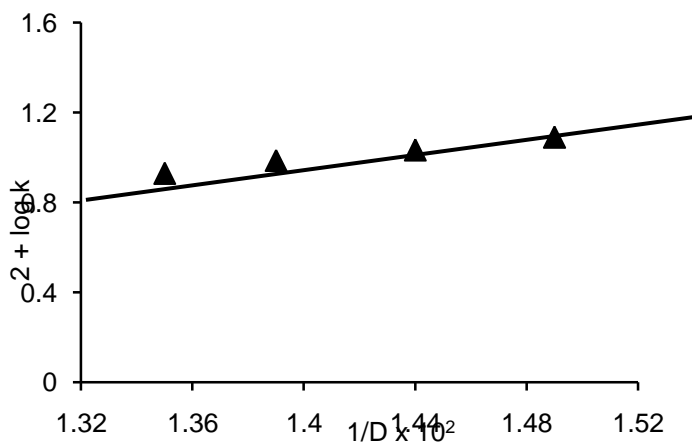


**Fig.5 :** Plot between  $\log k$  and  $\log[\text{OH}^-]$  at 400C

$$[\text{Cu}(\text{II})^*] = 6.00 \times 10^{-4} \text{M}, \quad [\text{Free Bip}] = 48.00 \times 10^{-4} \text{M}$$

$$[\text{D}(+)\text{melibiose}] = 1.00 \times 10^{-2} \text{M}, \quad [\text{Rh}(\text{III})] = 2.00 \times 10^{-9} \text{M}, \quad \mu = 30.00 \times 10^{-2} \text{M}$$

For the determination of the effect of dielectric constant of the medium on pseudo-zeroth-order rate constant,  $k$ , in the oxidation of D(+)-melibiose, several experiments with varying dielectric constant of the medium were conducted under uniform reaction condition. The change in dielectric constant of the medium was ensured by the addition of ethyl alcohol 5 - 20 % to the reaction mixture. On the basis of observed kinetic data it is concluded pseudo-zeroth-order rate constant increases with decrease in dielectric constant of the medium (Fig. 6). It is a known [35] fact that when reaction takes place between an ion and a molecule or dipole, there will be an increase in the rate with the decrease in dielectric constant ( $D$ ) of the medium.

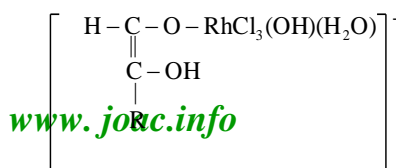


**Fig.6:** Plot between  $\log k$  and  $1/D$  at 40°C

$$[\text{Cu}(\text{II})^*] = 6.00 \times 10^{-4} \text{M}, \quad [\text{Free Bip}] = 48.00 \times 10^{-4} \text{M}, \quad [\text{D}(+)\text{melibiose}] = 1.00 \times 10^{-2} \text{M}, \quad [\text{Rh}(\text{III})] = 2.00 \times 10^{-9} \text{M}$$

$$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{M}, \quad \mu = 30.00 \times 10^{-2} \text{M}$$

On the basis of this observation it can be said that the reaction is taking place between a dipole and an ion. This is an additional support for the formation of a complex, in the rate determining step by the interaction of a dipole and an ion.



For the effect of ionic strength of the medium on the rate of oxidation of D(+)-melibiose several kinetic experiments were conducted at constant temperature 40°C, with different ionic strength of the medium under uniform reaction conditions. From the results of various kinetic runs for the oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium using Rh(III) as homogeneous catalyst, it is clear that there is almost no change in k with the change in ionic strength of the medium. This supports that the reaction is taking place between an ion and a dipole.

**Test for free radicals:** To test the presence of free radicals in the oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium using Rh(III) as homogeneous catalyst, various reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. When the reaction mixtures were diluted with methanol, the formation of a precipitate was not seen. These results confirm that there is no possibility of formation of free radicals in the reaction.

**Reactive species of Cu(II) in alkaline medium:** Literature reveals [6,16-22] that Cu(II) along with different complexing agent is used for the oxidation of various reducing sugars in acidic/alkaline medium. In the present study, Cu (II) has been used with bipyridyl as complexing agent in alkaline medium so that reaction mixture remains homogeneous throughout the course of reaction.

**Table 1.** Calculated values of zeroth-order rate constants for the variations of [Cu(II)], [Rh(III)], [D(+)-melibiose], and [OH<sup>-</sup>] in the oxidation of D(+)-melibiose using Rh(III) as catalyst at 40°C

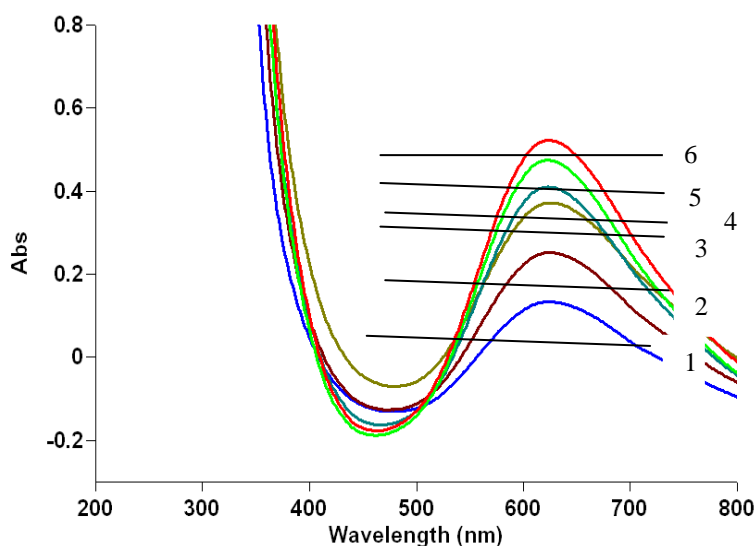
[Cu(II)] $\times 10^4$ (M)	[Rh(III)] $\times 10^9$ (M)	[D(+)-melibiose] $\times 10^2$ (M)	[OH <sup>-</sup> ] $\times 10^5$ (M)	k (Abs/min)
1.00	2.00	1.00	2.57	0.075
2.00	2.00	1.00	2.57	0.072
4.00	2.00	1.00	2.57	0.076
6.00	2.00	1.00	2.57	0.073
8.00	2.00	1.00	2.57	0.078
10.00	2.00	1.00	2.57	0.077
6.00	0.50	1.00	2.57	0.031
6.00	1.00	1.00	2.57	0.062
6.00	2.00	1.00	2.57	0.095
6.00	3.00	1.00	2.57	0.165
6.00	4.00	1.00	2.57	0.211
6.00	5.00	1.00	2.57	0.265
6.00	2.00	1.00	2.57	0.080
6.00	2.00	2.00	2.57	0.144
6.00	2.00	4.00	2.57	0.205
6.00	2.00	6.00	2.57	0.289
6.00	2.00	8.00	2.57	0.386
6.00	2.00	10.00	2.57	0.468
6.00	2.00	1.00	1.48	0.060
6.00	2.00	1.00	2.57	0.910
6.00	2.00	1.00	3.47	0.151
6.00	2.00	1.00	4.27	0.188
6.00	2.00	1.00	5.62	0.268
6.00	2.00	1.00	6.31	0.318

**Solution conditions-** For [Cu(II)] variation: [Free bipyridyl]= 40.00 $\times 10^{-4}$ M;  $\mu$ = 0.30M.  
For [Rh(III)], [sugar] and [OH<sup>-</sup>] variation: [Free bipyridyl]= 48.00 $\times 10^{-4}$ M;  $\mu$ = 0.30M

**Table 2.** Activation parameters for Rh (III)-catalyzed oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium at  $40^\circ\text{C}$ 

Reducing sugar	$k_r$ ( $\text{mol}^{-2}\text{dm}^6\text{sec}^{-1}$ )	$E_a$ ( $\text{kJmol}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJmol}^{-1}$ )	$\Delta G^\ddagger$ ( $\text{kJmol}^{-1}$ )	$\Delta S^\ddagger$ (eu)	A ( $\text{mol}^{-2}\text{dm}^6\text{sec}^{-1}$ )
D(+)-melibiose	$5.39 \times 10^8$	88.83	74.39	24.43	38.19	$3.3 \times 10^{21}$

In order to verify that the reactive species of  $\text{Cu}(\text{Bip})_2^{2+}$  but not free  $\text{Cu}(\text{II})$ , various spectra of solutions containing  $\text{Cu}(\text{II})$  and  $\text{Na}_2\text{CO}_3$  and also  $\text{Cu}(\text{II})$ ,  $\text{Na}_2\text{CO}_3$  and bipyridyl were collected with the help of Varian Carry 300 Bio UV-VIS Spectrophotometer (Fig.7). On the basis of kinetic results obtained and spectrophotometric evidence collected, it can be assumed that the reactive species of  $\text{Cu}(\text{II})$  is  $\text{Cu}(\text{Bip})_2^{2+}$ . Formation of  $\text{Cu}(\text{Bip})_2^{2+}$ , is confirmed by its absorption at  $\lambda_{\text{max}} = 670 \text{ nm}$  with molar extinction coefficient  $0.59 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  which is also supported by literature [26].

**Fig.7 :** Spectra of  $\text{Cu}(\text{Bip})_2^{2+}$  for solutions [1-6] recorded at room temperature  
Solution conditions:

- |   |   |   |
|---|---|---|
| (1) $[\text{Cu}(\text{II})^*] = 3.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ | (3) $[\text{Cu}(\text{II})^*] = 5.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ | (5) $[\text{Cu}(\text{II})^*] = 7.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ |
| (2) $[\text{Cu}(\text{II})^*] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ | (4) $[\text{Cu}(\text{II})^*] = 6.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ | (6) $[\text{Cu}(\text{II})^*] = 8.00 \times 10^{-3} \text{ M}$<br>$[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$<br>$[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ |

**Reactive species of Rh(III) chloride in alkaline medium:** Earlier Wolsey et.al. [27] were isolated various complex species i.e.  $\text{RhCl}_2^+$ ,  $\text{RhCl}_2^+$ ,  $\text{RhCl}_3$ ,  $\text{RhCl}_4^-$ ,  $\text{RhCl}_5^{2-}$ , and  $\text{RhCl}_6^{3-}$  of rhodium(III) and chloride ion in dilute hydrochloric acid (concentration of hydrochloric acid in the range 0.01 M to 2.00 M). Later James and Rempel [28] reported that only anionic complexes such as  $[\text{RhCl}_6]^{3-}$ ,  $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$  and  $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_4]^-$  will activate molecular hydrogen for the homogeneous reduction of ferric ion in aqueous acidic solution. They have also proposed that when Rh(III) chloride is prepared in 3-5 M HCl solutions, the 5:1 chloro species persists over this range of HCl concentration. This result is contrary to the findings of Harrord and Halpern [29] that when  $\text{RhCl}_3$  is the predominant species in 3.0 M - 5.0 M HCl solutions. James and Rempel [15] also reported that  $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$  is predominating species of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in the 3 M HCl medium. It is also reported [30] that on boiling aqueous solutions of the rhodium trichloride,  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  is formed and with excess HCl the rose pink hexachlororhodate ion,  $[\text{RhCl}_6]^{3-}$  is obtained.



Between these two species, there are several intermediates. On aquation  $[\text{RhCl}_6]^{3-}$  produces  $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ , cis  $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$  and fac- $\text{RhCl}_3(\text{H}_2\text{O})_3$ .

In the present investigation the solution of Rh(III) chloride was prepared in 3M HCl solution and its concentration was determined as  $3.7879 \times 10^{-3}$  M. This original solution was further diluted with the help of double distilled water and the concentration of the catalyst Rh (III) chloride in each kinetic run was fixed in the order of  $10^{-9}$  M. In view of the literature reports earlier and also in view of the conditions under which the experiments were performed for the effect of  $[\text{Cu}(\text{II})]$ , [reducing sugar],  $[\text{OH}^-]$  and  $[\text{Rh}(\text{III}) \text{ chloride}]$  on the rate of oxidation, it can safely be assumed that the starting species of Rh(III) chloride in the reactions is the neutral species i.e.  $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ . This assumption finds support from the report [14] where it has been assumed that  $[\text{RhCl}_3(\text{H}_2\text{O})_3]$  is the reactive species of Rh(III) chloride in the oxidation of styrene, stilbene and phenylacetylene by acid periodate.

**Reactive species of reducing sugar in alkaline medium:** It is reported [16,31] that reducing sugars in alkaline medium exist in the form of enediol anion and enediol. Of them which form is actually taking part in the reaction under investigation will be decided on the basis of observed kinetic data and also the effect of  $[\text{OH}^-]$  on the rate of oxidation. Taking into consideration the positive effect of  $\text{OH}^-$  concentration on the rate of reaction and giving due weightage to other relevant kinetic observations, it can be assumed that it is the enediol form of reducing sugars which is actually taking part in the reaction.

**Spectrophotometric evidence for the formation of various complexes during the course of reaction:**

It is reported [22],[32] in the literature that transition metal ions form a complex with sugar molecule. In order to verify the formation of a complex between reactive species of Rh(III)chloride and a sugar molecule, spectra for solutions containing Rh(III) and  $\text{OH}^-$  and Rh(III),  $\text{OH}^-$ , and reducing sugar were collected with the help of Varian Carry 300 Bio UV-VIS Spectrophotometer (Fig. 8). When spectrum of Rh(III) and  $\text{OH}^-$  solution was compared with the spectra of solutions containing Rh(III),  $\text{OH}^-$ , and three different concentrations of sugars, it was found that there is an increase in absorbance from 1.08 to 1.23, 1.33 and 1.73 at fixed wave length 223 nm (Fig.8:(4), (5) and(6)).

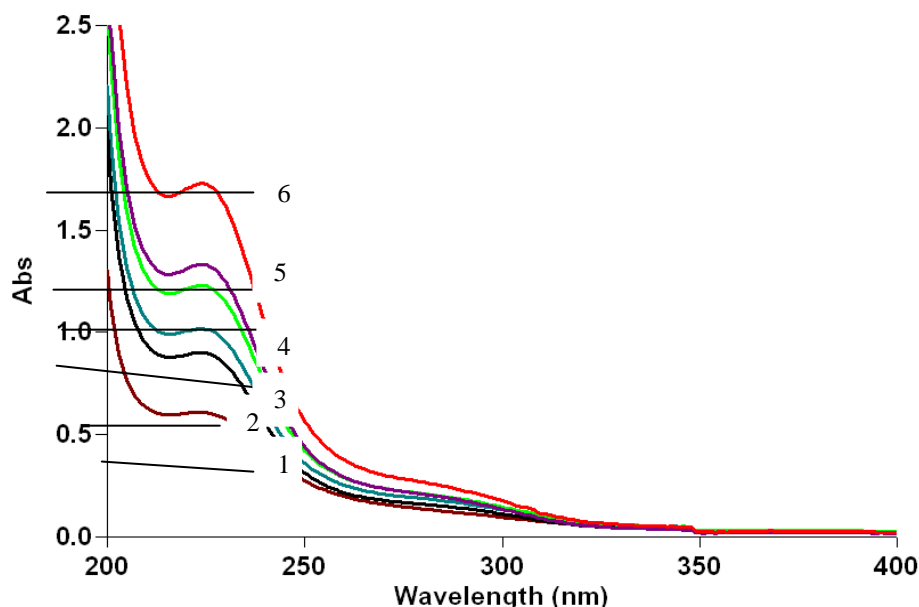
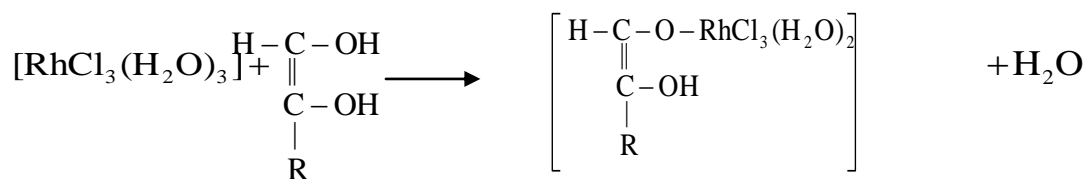


Fig.8: Spectra of solutions [1-6] recorded at room temperature

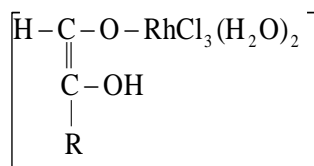
Solution conditions:

- |  |   |
|--|---|
| (1) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$     | (5) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$          |
| (2) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$     | $[\text{Na}_2\text{CO}_3] = 2.00 \times 10^{-2} \text{ M}$      |
| $[\text{Na}_2\text{CO}_3] = 1.00 \times 10^{-2} \text{ M}$ | $[\text{D}(+)\text{melibiose}] = 2.00 \times 10^{-2} \text{ M}$ |
| (3) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$     | (6) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$          |
| $[\text{Na}_2\text{CO}_3] = 2.00 \times 10^{-2} \text{ M}$ | $[\text{Na}_2\text{CO}_3] = 2.00 \times 10^{-2} \text{ M}$      |
| (4) $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$     | $[\text{D}(+)\text{melibiose}] = 5.00 \times 10^{-2} \text{ M}$ |
|  | $[\text{Na}_2\text{CO}_3] = 2.00 \times 10^{-2} \text{ M}$      |
|  | $[\text{D}(+)\text{melibiose}] = 1.00 \times 10^{-2} \text{ M}$ |

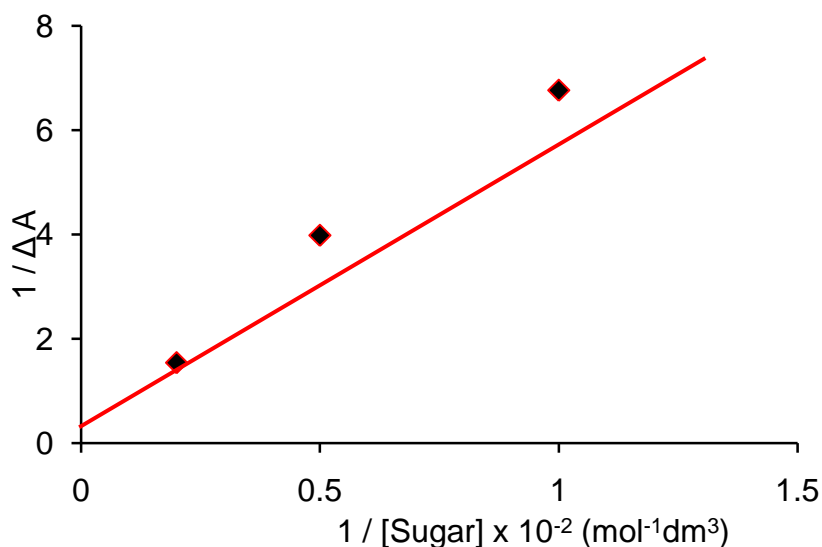
This observation led us to conclude that a complex of the type shown below is formed between reactive species of Rh (III)chloride and a sugar molecule (enediol).



Formation of 1:1 complex



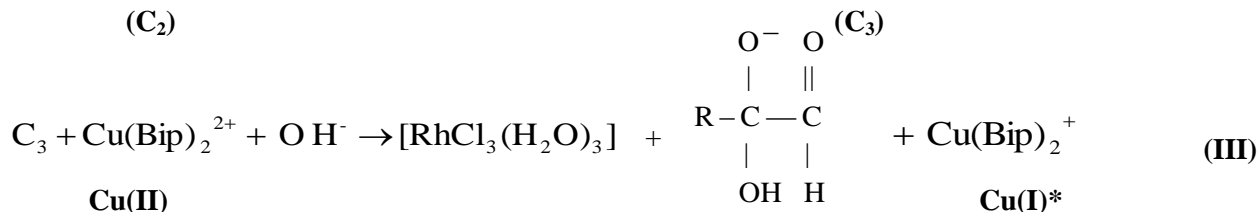
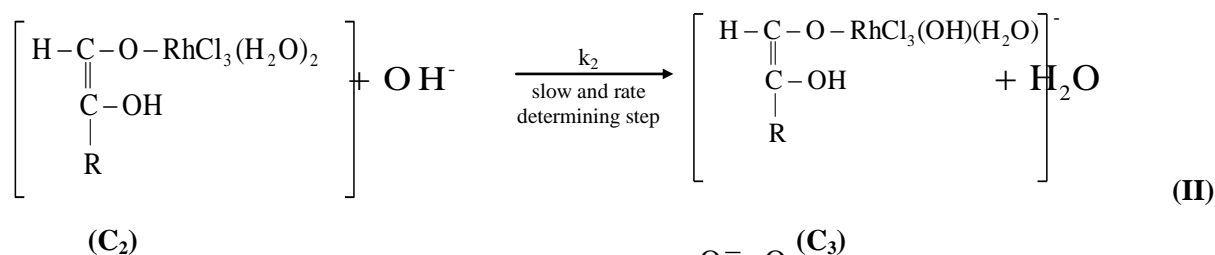
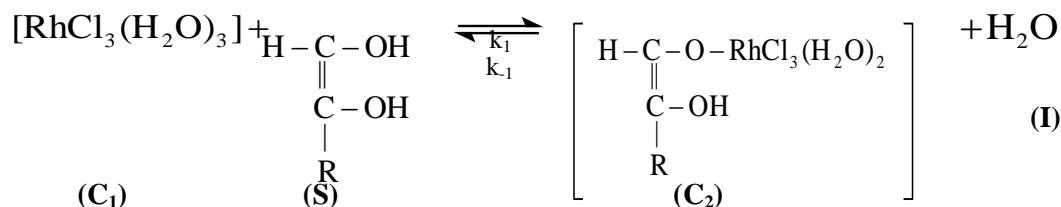
is supported by Job's plot [33-34] ( $1/\Delta A$  vs.  $1/[\text{S}]$ ) where straight line with positive intercept on y-axis was obtained (Fig. 9).  $\Delta A$  on y-axis indicates the difference in absorbance of the solution containing Rh(III), OH<sup>-</sup> and reducing sugar and the solution containing Rh(III) and OH<sup>-</sup>.



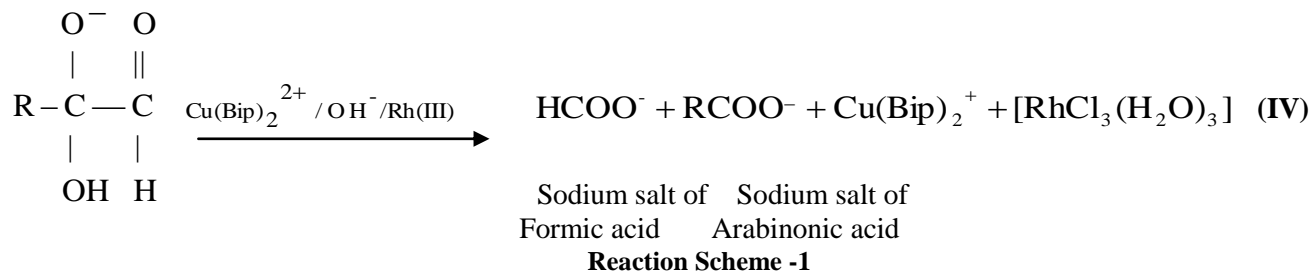
**Fig.9:** Plot between  $1/\Delta A$  and  $1/[\text{Sugar}]$   
 $[\text{Rh(III)}] = 3.80 \times 10^{-5} \text{ M}$ ,  $[\text{Na}_2\text{CO}_3] = 2.00 \times 10^{-2} \text{ M}$

**Mechanism and derivation of rate law:** On the basis of observed kinetic orders with respect to reactants involved in the reaction, spectrophotometric evidence collected for the formation of complexes, effect of dielectric constant of the medium on the rate of oxidation and the positive entropy of activation, a most

probable Reaction Scheme-1 in the following form can be proposed for the Rh(III) catalyzed oxidation of D(+)melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  in alkaline medium.



where R stands for  $\text{C}_4\text{H}_9\text{O}_4$



For the second unit of monosaccharide in D(+)melibiose, the same process shall be repeated.

On the basis of proposed Reaction Scheme-1, the rate in terms of formation of product i.e.  $\text{Cu}(\text{Bip})_2^+$  can be expressed as

$$\text{Rate} = \frac{d[\text{Cu}(\text{I})^*]}{dt} = 4k_2[\text{C}_2][\text{OH}^-] \quad (1)$$

where 4 indicates that one mole of D(+) melibiose is oxidized by 4 mole of Cu(II).

On applying steady state approximation to the concentration of  $\text{C}_2$  and taking help of the equation  $[\text{Rh(III)}]_{\text{T}} = [\text{Rh(III)}] + [\text{C}_2]$ , the rate in terms of appearance of  $\text{Cu}(\text{I})^*$  can be expressed as equation (2)

$$\text{Rate} = \frac{d[\text{Cu}(\text{I})^*]}{dt} = \frac{4k_1k_2[\text{Rh(III)}]_{\text{T}}[\text{S}][\text{OH}^-]}{k_{-1} + k_2[\text{OH}^-] + k_1[\text{S}]} \quad (2)$$

At very low concentrations of hydroxyl ion, the inequality  $k_{-1} + k_1[S] \gg k_2[OH^-]$  can be assumed as valid one and under this condition equation (2) will take the shape of equation (3)

$$\text{Rate} = \frac{d[Cu(I)^*]}{dt} = \frac{4k_1k_2[Rh(III)]_T[S][OH^-]}{k_{-1} + k_1[S]} \quad (3)$$

Equation (3) is the final rate law which is strictly in accordance with our experimental findings.

On reversing equation (3) we have equation (4)

$$\frac{1}{\text{Rate}} = \frac{k_{-1}}{4k_1k_2[S][OH^-][Rh(III)]_T} + \frac{1}{4k_2[OH^-][Rh(III)]_T} \quad (4)$$

By making plot between  $1/\text{Rate}$  and  $1/[OH^-]$ , the values of  $k_{-1}/k_1$  and  $k_2$  were calculated from the slope and the intercept of the straight line obtained for the oxidation of D(+)-melibiose (Fig.10). The values of  $k_{-1}/k_1$  and  $k_2$  for the oxidation of D(+)-melibiose were found as  $45.12 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \text{ sec}$  and  $8.33 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}$ , respectively. Utilizing these values of  $k_{-1}/k_1$  and  $k_2$  and taking help of rate law (3), the rates for the variation of  $[OH^-]$  in the oxidation of D(+)-melibiose have been calculated and are presented in Table-3. The close resemblance between the calculated and the experimental rates for the oxidation of D(+)-melibiose provides support to the rate law (3) valid at very low concentrations of D(+)-melibiose and Rh(III)chloride and hence the proposed mechanism.

**Table-3.** Calculated and Experimental values of zero-order rate constants for the variation of  $[OH^-]$  in the Rh(III)- catalyzed oxidation of D(+)-melibiose at  $40^\circ\text{C}$

$[OH^-] \times 10^5$ (M)	$k \times 10^7$ ( $\text{mol dm}^{-3} \text{ sec}^{-1}$ )	$k \times 10^7$ ( $\text{mol dm}^{-3} \text{ sec}^{-1}$ )
	Calculated	Experimental
1.48	2.12	1.96
2.57	3.59	3.58
3.47	4.76	4.93
4.27	5.76	6.00
5.62	7.38	8.06
6.31	8.18	8.58

Solution conditions:  $[Cu(II)^*] = 6.00 \times 10^{-4} \text{ M}$ ,  $[\text{Free Bip}] = 4.00 \times 10^{-3} \text{ M}$ ,  $[\text{Sugar}] = 1.00 \times 10^{-2} \text{ M}$ ,  $[\text{Rh(III)}] = 2.00 \times 10^{-9} \text{ M}$

**Calculation of the size of activated complex ( $d_{AB}$ ):** The effect of the dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well known equation

$$\log k = \log k_0 - \frac{z_A z_B e^2 N}{2.303(4 \pi \epsilon_0) d_{AB} RT D}$$

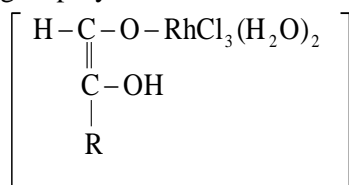
where  $k_0$  is the rate constant in a medium of infinite dielectric constant and  $z_A$  and  $z_B$  are the charges of reacting ions. In above equation,  $d_{AB}$  is for the size of activated complex, T is for absolute temperature and D is for dielectric constant of the medium. It is quite evident from equation mentioned above that if a plot is made between  $\log k$  and  $1/D$ , a straight line having an intercept on  $\log k$  axis will be obtained. From the slope of the straight line, the value of  $d_{AB}$  can be calculated in the following way

$$\text{Slope} = - \frac{z_A z_B e^2 N}{2.303(4 \pi \epsilon_0) d_{AB} RT}$$

$$\text{Or } d_{AB} = - \frac{z_A z_B e^2 N}{2.303(4 \pi \epsilon_0) RT} \cdot \frac{1}{\text{slope}}$$

By making a plot between  $\log k$  and  $1/D$ , the value of  $d_{AB}$  was calculated from the slope of the straight line obtained for the oxidation of D(+)-melibiose and found as  $3.05 \text{ \AA}^0$ .

**Role of Entropy of Activation:** It is a well known fact [36] that for reaction between ions of opposite charge there is generally an entropy increase in going from reactants to activated complex and for ions of like sign or charge there is an entropy decrease. In the present study of oxidation of D(+)-melibiose using chloro-complex of Rh(III) as catalyst, the observed positive entropy of activation provides support for the formation of complex, in rate determining step by the interaction of an ion,  $\text{OH}^-$ , and a dipole molecule,



In this case the activated state or transition state will be less polar than the initial state.

**Comparative studies:** Efforts were made to compare the findings of this paper with the results reported for Rh(III)-catalyzed [10] and Pd(II)-catalyzed [37] oxidation of D(+) melibiose by N-bromoacetamide (NBA) in acidic medium. When the present study in respect of the role of oxidant i.e.  $\text{Cu}(\text{Bip})_2^{2+}$  was compared with the earlier reported literature [10, 37], it was found that the observed zero order in Cu(II) is entirely different from the reported first order with respect to [NBA] in Rh(III)-catalyzed [10] and first to zero order in Pd(II)-catalyzed [37] oxidation of D(+) melibiose. As far as reactive species of oxidant is concerned it is  $\text{Cu}(\text{Bip})_2^{2+}$  in the present study and protonated NBA i.e.  $\text{NBAH}^+$  and  $\text{HOBr}$  in the reported Rh(III)-catalyzed [10] and Pd(II)-catalyzed [37] oxidation reactions respectively. The present study is similar to the reported two studies [10,37] as far as order with respect to catalyst is concerned. Fractional-positive order with respect to D(+)-melibiose in its  $\text{Cu}(\text{Bip})_2^{2+}$  oxidation is different from the unity order in the reported two studies [10,37]. The formation of a reactive complex between the reactive species of the Rh(III) chloride and reactive species of D(+)-melibiose in the present study on one hand shows similarity with the reported Pd(II)-catalyzed oxidation [37] where a complex between the reactive species of the Pd(II) chloride and reducing sugar molecule is formed and on the other hand it differs from the study [10] where the reactive species of the Rh(III) chloride combines with protonated NBA i.e.  $\text{NBAH}^+$  to form a reactive complex which in the rate determining step reacts with reducing sugar molecule to form the intermediate. The facts mentioned above clearly shows that the present study in many respect differs from the other two reported studies [10, 37].

## APPLICATIONS

Based on the observed kinetic data and spectroscopic evidence, a most probable reaction path for Rh(III)-catalyzed oxidation of D(+) melibiose by Copper(II) complexed with bipyridyl in alkaline medium has been proposed.

## CONCLUSIONS

Making basis to the observed kinetic data and spectrophotometric information, the following conclusions for the oxidation of D(+)-melibiose by  $\text{Cu}(\text{Bip})_2^{2+}$  using Rh(III) as catalyst in alkaline medium were derived-

(1). Cu(II) in the form of  $\text{Cu}(\text{Bip})_2^{2+}$  participates in the reaction after the rate determining step as the reaction follows zeroth-order kinetics with respect to  $[\text{Cu}(\text{II})]$

(2). The rate of reaction shows first-order kinetics with respect to  $[\text{Rh}(\text{III})]$  and fractional positive-order kinetics with respect to  $[\text{D}(+)\text{melibiose}]$  and  $[\text{OH}^-]$ .

(3). The species  $[\text{RhCl}_3(\text{H}_2\text{O})_3]$  has been assumed as the reactive species of Rh(III) chloride in alkaline medium for the oxidation of D(+)-melibiose.

(4). The formation of 1:1 complex,  $\left[ \begin{array}{c} \text{H}-\text{C}-\text{O}-\text{RhCl}_3(\text{H}_2\text{O})_2 \\ || \\ \text{C}-\text{OH} \\ | \\ \text{R} \end{array} \right]$  between reactive species of Rh(III) chloride

and enediol form of reducing sugar is supported by observed kinetic data, spectrophotometric evidence and the Job's plot.

(5). In step (II) of Reaction Scheme-1, an interaction between a charged species,  $\text{OH}^-$  and a dipolar molecule,  $\left[ \begin{array}{c} \text{H}-\text{C}-\text{O}-\text{RhCl}_3(\text{H}_2\text{O})_2 \\ || \\ \text{C}-\text{OH} \\ | \\ \text{R} \end{array} \right]$ , resulting in the formation of most reactive activated complex is

well supported by the observed positive entropy of activation and the effect of dielectric constant of the medium on the rate of oxidation.

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