Role of Ru(III) as Inhibitor in Oxidation of Arabinose and Ribose by [Cu(bipy)₂]²⁺ in Alkaline Medium: Spectrophotometric and Kinetic Studies

BHARATI BEHERA and JASHODA BEHERA[*]

Department of Chemistry, Utkal University, Bhubaneswar-751 004, India

*Corresponding author: E-mail: jbeherachemistry@gmail.com; jbehera2017@gmail.com

The kinetics and mechanism of oxidation of arabinose and ribose by $[Cu(bipy)_2]^{2+}$ in alkaline medium has been studied spectrophotometrically at 50 °C. The rate is first order in [oxidant] (*i.e.* $[Cu(bipy)_2]^{2+}$). From rate equation, the rate of reaction was found to be directly proportional to [sugar] and [OH⁻] and inversely proportional to [Ru(III)]. There is a substantial decrease in the pseudo first order rate constant with increase in the concentration of $RuCl_3$, indicating the role of $RuCl_3$ as an inhibitor. The reaction also shows slight decrease in rate by increasing dielectric constant of the medium. Ionic strength of the medium and [Cl⁻] have no effect on the rate of oxidation. The activation parameters for the rate determining step have been calculated. Based on kinetic data and spectrophotometric evidences, a suitable mechanism is proposed.

Keywords: Kinetics, Reaction mechanisms, Oxidations, Copper-bipyridyl complex, Ruthenium(III) chloride, Arabinose, Ribose.

INTRODUCTION

The importance of carbohydrates is due to their reactivities, biochemical and physiological properties. The reactivities and related properties depend largely on their redox behaviour. Their oxidation can provide new compounds and materials with interesting physico-chemical properties.

Copper(II) is a much needed element which is of course very toxic at elevated concentrations. By complexation with ligands its reactivity and biological effects are same time increased [1]. Copper complexes are reported to have potential use as antimicrobial, antiviral and antitumor agents [2]. Several authors have reported the kinetic study of Cu(II) complexed with bipyridyl in alkaline medium using Pd(II) and Rh(II) as homogeneous catalysts [3,4]. Copper(II) along with various complexing agents has been used for the oxidation of various reducing sugars in acidic as well as in alkaline media [5-9].

Many oxidation-reduction reactions take place using transition metals as catalyst for their multiple oxidation states. Ruthenium(III) acts as a catalyst in the oxidation of many organic and inorganic complexes [10,11]. Ruthenium(III) also shows a greater resistance to hydrolysis and more selective action on tumors unlike traditional platinum complexes [12], with its catalytic role [13]. Recently Ru(III) complexes are frequently used as catalysts for the oxidation of various organic compounds like sugars, alcohols, ketones in acidic and alkaline medium [14-20]. Kinetics and mechanism of redox reactions of some simple reducing sugars have been studied using various transition metals like Cr(VI), Cu(II), Fe(III), Ir(III), Rh(III), Pd(II), Ru(III) [21-26]. The kinetics of oxidation of sugars has been the most popular and interesting research in recent years [27-30].

The main objective of the present research work is to study the kinetics of oxidation of arabinose and ribose by copper(II) bipyridyl complex spectrophotometrically in alkaline medium under various operational parameters to establish the pathway of reaction on the basis of kinetic and spectroscopic analysis. Ruthenium(III) chloride in alkaline medium acted as a negative catalyst.

EXPERIMENTAL

Standard solutions of $CuSO_4$ (Qualigens, AR grade) and bipyridyl (AR grade) were prepared by dissolving their requisite amounts in double distilled water separately. Bipyridyl was used as complexing agent so that the reaction mixture remains homogeneous throughout the course of the reaction. The standard solution of reducing sugar, *i.e.*, arabinose and ribose (AR grade, CDH) were prepared daily by weighing the requisite amount and dissolving it in double distilled water. Ruthenium(III) chloride was dissolved in 1000 mL HCl (0.01 M) to get a stock solution of Ruthenium(III) chloride as 7.63×10^{-3} M. Throughout the study the medium of the reaction was maintained alkaline with the help of sodium carbonate solution. Standard solution of sodium carbonate (Merck) was prepared by dissolving the

appropriate amount in double distilled water. Concentration of hydroxyl ions were calculated by measuring the pH of the reaction mixture using $K_w = [H^+][OH^-]$ at 35, 40, 45 and 50 °C. Standard solution of potassium chloride (E.Merck) used for ionic strength adjustment which was prepared by weighing.

For kinetic measurements, Agilent UV-visible spectrophotometer and computer was used. For pH measurements, Electronics India pH-101 model was used.

General procedure: The absorption spectra of $[Cu(bipy)_2]^+$ solutions were recorded at 300-700 nm and at 425 nm maximum absorbance was chosen for rate measurement (Figs. 1 and 2). $\{[\varepsilon^{425}\ dm^3\ mol^{-1}\ cm^{-1};\ 0.021 \times 10^4$ for $[Cu(bipy)_2]^{2+}$ and 0.015×10^4 for $[Cu(bipy)_2]^+\}$.

One set of reaction mixture containing the reactants, *i.e.*, copper sulphate, sodium carbonate, ruthenium(III) chloride, potassium chloride and bipyridyl and another set having the same reactants except copper sulphate, were taken into two separate conical flasks and placed in a thermostatic water bath at constant temperature. When the reaction mixture had attained the required temperature, the calculated amount of sugar solution was added to both sets of the reaction mixture and immediately transferred to 1 cm quartz cell and placed in the sample compartment of the spectrophotometer. The mixture containing the solution of $CuSO_4$ was the absorbing sample while the mixture without $CuSO_4$ solution was the reference sample. The progress of the reaction was monitored spectrophotometrically by measuring the decrease in absorbance at 425 nm.

The pseudo-first order rate constants were calculated by least squares method using $\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt$, where A_t is the absorbance at time t, A_0 and A_∞ are the absorbances at
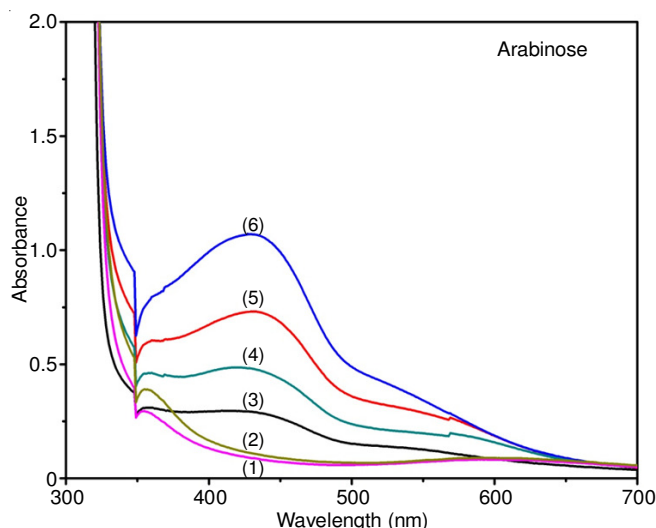

Fig. 1.   Spectra of Cu(bipy)₂⁺ for solutions [1-6] recorded at 50 °C for arabinose. **(1)** $[Cu(bipy)_2]^{2+} = 1.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(2)** $[Cu(bipy)_2]^{2+} = 2.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(3)** $[Cu(bipy)_2]^{2+} = 4.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(4)** $[Cu(bipy)_2]^{2+} = 6.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(5)** $[Cu(bipy)_2]^{2+} = 8.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(6)** $[Cu(bipy)_2]^{2+} = 10.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Arabinose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M

Fig. 2.   Spectra of Cu(bipy)₂⁺ for solutions [1-6] recorded at 50 °C for ribose. **(1)** $[Cu(bipy)_2]^{2+} = 1.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(2)** $[Cu(bipy)_2]^{2+} = 2.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(3)** $[Cu(bipy)_2]^{2+} = 4.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(4)** $[Cu(bipy)_2]^{2+} = 6.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(5)** $[Cu(bipy)_2]^{2+} = 8.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M **(6)** $[Cu(bipy)_2]^{2+} = 10.0 \times 10^{-4}$ M; [Ru(III)] = 7.60×10^{-7} M; [Ribose] = 1.00×10^{-2} M [Na₂CO₃] = 1.00×10^{-2} M

zero time and infinitive time respectively and k is the pseudo-first order rate constant.

The order of the reaction with respect to a component reactant and keeping other constant [reactants] was determined from the slope of the plot of log k *versus* log (conc.) of that reactant.

Stoichiometry and products analysis: Different sets of experiments were performed with different [Cu(II)]:[arabinose] and [Cu(II)]:[ribose] ratios under the condition [Cu(II)] >> [arabinose] and [Cu(II)] >> [ribose] respectively. The estimation of unconsumed Cu(II) showed that one mole of arabinose and ribose were oxidized by four moles of $[Cu(bipy)_2]^{2+}$.

RESULTS AND DISCUSSION

The oxidation reaction of arabinose and ribose by $[Cu(bipy)_2]^{2+}$ in alkaline medium has been investigated at 50 °C at different initial concentrations. The reaction was followed by the change in absorbance of $[Cu(bipy)_2]^{2+}$ for 10×10^{-4} M at different intervals of time keeping all other reactants constant at 50 °C (Figs. 3 and 4). The absorbance-time plots for the oxidation of arabinose and ribose were shown in (Figs. 5 and 6) which determines the pseudo-first order rate constant as a function time. The pseudo-first order rate constants obtained for various runs clearly reveal that there is a direct proportionality between pseudo-first order rate constant, k and concentration of arabinose and ribose.

Also, varying the concentrations of ruthenium(III) chloride, it was observed that there was a decrease in pseudo-first order rate constant with the increase in concentration of ruthenium(III) chloride (Tables 1 and 2). The plots of log k against log [Ru(III)] (Figs. 7 and 8) were straight lines. The slopes of which gave
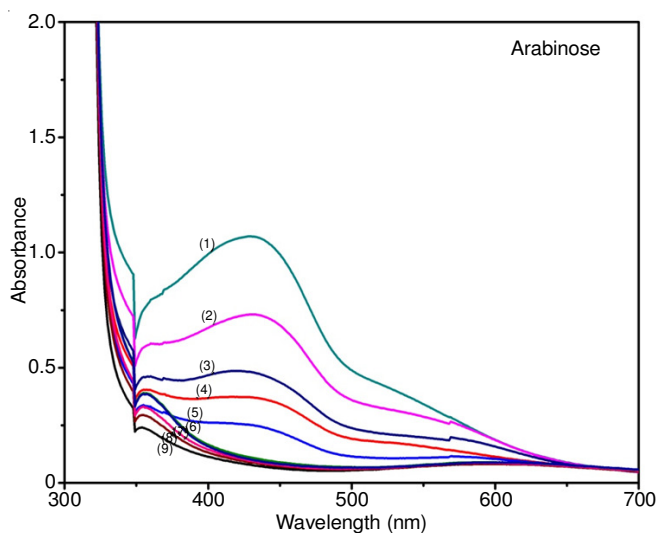
Fig. 3.   UV-visible time scan of Cu(bipy)$_2^+$ for arabinose at 50 °C. {[Cu(bipy)$_2$]$^{2+}$ = 10.0 × 10^{-4} M; [Ru(III)] = 7.60 × 10^{-7} M; [Arabinose] = 1.00 × 10^{-2} M [Na$_2$CO$_3$] = 1.00 × 10^{-2} M} Curve (1-9), Δt = 5 min
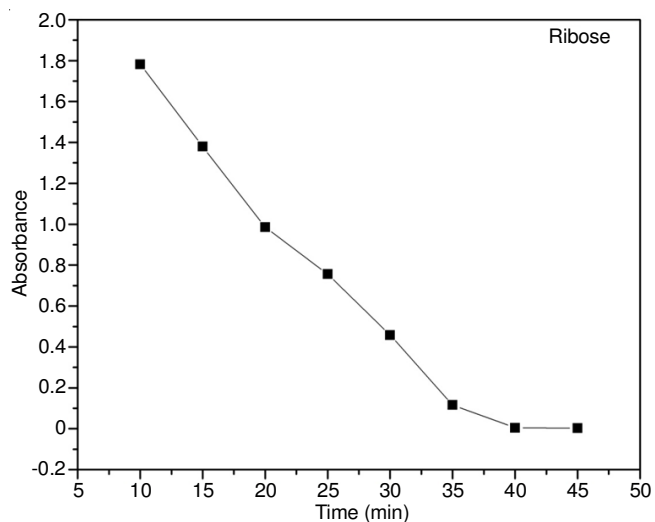
Fig. 6.   Plot between absorbance of Cu(bipy)$_2^+$ and time for ribose at 50 °C. [Cu(bipy)$_2$]$^{2+}$ = 10.0 × 10^{-4} M; [Ru(III)] = 7.60 × 10^{-7} M; [Ribose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M
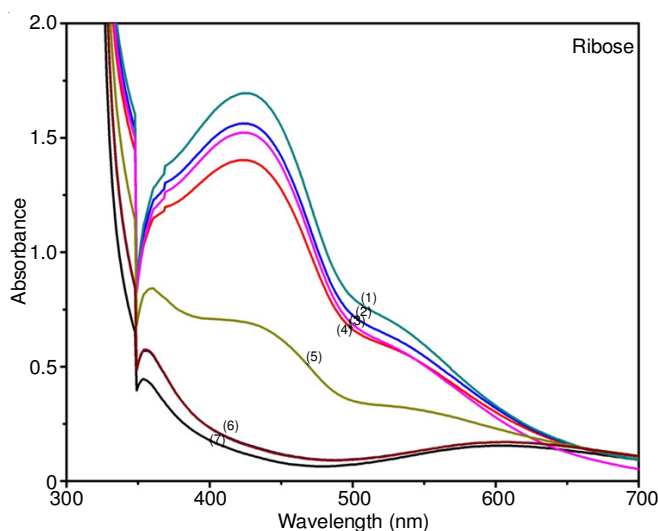
Fig. 4.   UV-visible time scan of Cu(bipy)$_2^+$ for ribose at 50 °C {[Cu(bipy)$_2$]$^{2+}$ = 10.0 × 10^{-4} M; [Ru(III)] = 7.60 × 10^{-7} M; [Ribose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M} Curve (1-7), Δt = 5 min
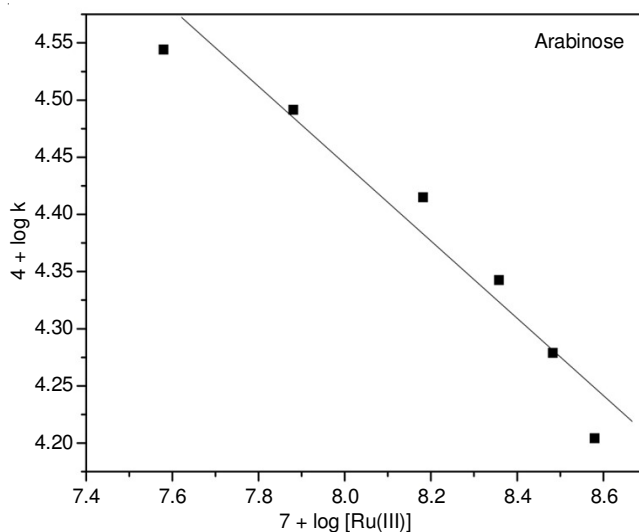
Fig. 7.   Plot between logk and log [Ru(III)] at 50 °C. {[Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Arbinose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M}
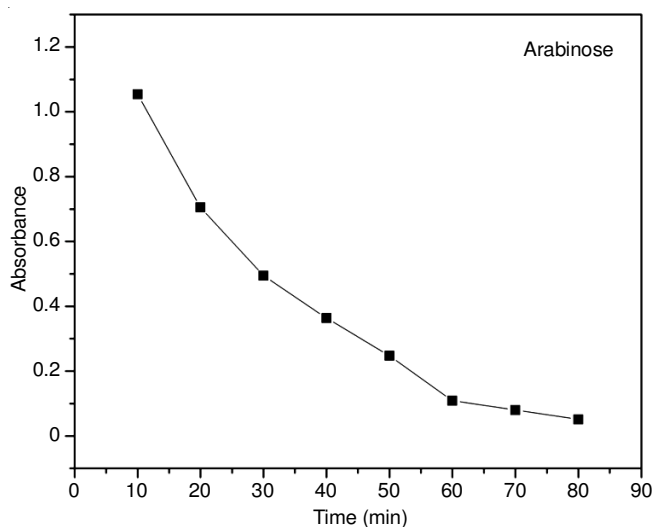
Fig. 5.   Plot between absorbance of Cu(bipy)$_2^+$ and time for arabinose at 50 °C. [Cu(bipy)$_2$]$^{2+}$ = 10.0 × 10^{-4} M; [Ru(III)] = 7.60 × 10^{-7} M; [Arabinose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M
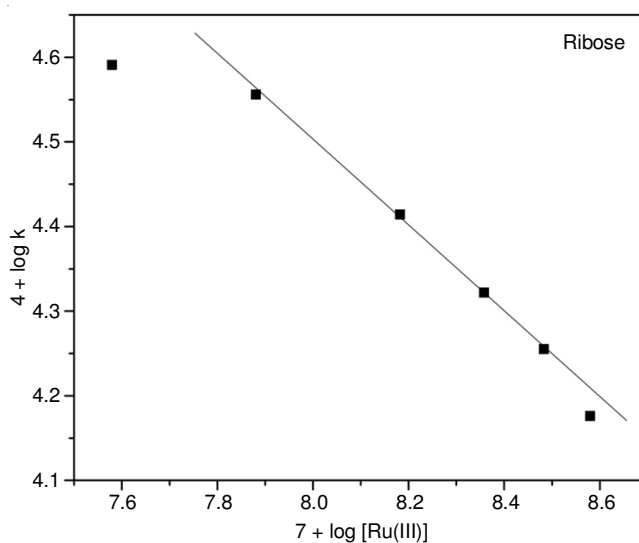
Fig. 8.   Plot between logk and log [Ru(III)] at 50 °C. {[Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Ribose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M}

TABLE-1
PSEUDO-FIRST ORDER RATE CONSTANTS IN
THE OXIDATION OF ARABINOSE USING Ru(III)
AS AN INHIBITOR AT 50 °C

| [Cu(bipy)$_2$]$^{2+}$ × 10^4 (M)	[Ru(III)] × 10^7 (M)	[Arabinose] × 10^2 (M)	[Na$_2$CO$_3$] × 10^2 (M)	K (sec)$^{-1}$ × 10^4
1.00	7.60	1.00	1.00	0.3
2.00	7.60	1.00	1.00	0.5
4.00	7.60	1.00	1.00	0.6
6.00	7.60	1.00	1.00	1.1
8.00	7.60	1.00	1.00	1.5
10.00	7.60	1.00	1.00	1.8
6.00	3.80	1.00	1.00	3.5
6.00	7.60	1.00	1.00	3.1
6.00	15.20	1.00	1.00	2.6
6.00	22.80	1.00	1.00	2.2
6.00	30.40	1.00	1.00	1.9
6.00	38.00	1.00	1.00	1.6
6.00	7.60	1.00	1.00	2.1
6.00	7.60	2.00	1.00	3.2
6.00	7.60	3.00	1.00	4.1
6.00	7.60	4.00	1.00	4.7
6.00	7.60	5.00	1.00	5.3
6.00	7.60	6.00	1.00	5.8
6.00	7.60	8.00	1.00	7.2
6.00	7.60	10.00	1.00	8.8
6.00	7.60	1.00	0.50	1.2
6.00	7.60	1.00	0.80	2.1
6.00	7.60	1.00	1.00	2.8
6.00	7.60	1.00	2.00	4.9
6.00	7.60	1.00	3.00	5.8
6.00	7.60	1.00	4.00	6.4
6.00	7.60	1.00	5.00	7.1

TABLE-2
PSEUDO-FIRST ORDER RATE CONSTANTS
IN THE OXIDATION OF RIBOSE USING Ru(III)
AS AN INHIBITOR AT 50 °C

| [Cu(bipy)$_2$]$^{2+}$ × 10^4 (M)	[Ru(III)] × 10^7 (M)	[Ribose] × 10^2 (M)	[Na$_2$CO$_3$] × 10^2 (M)	K (sec)$^{-1}$ × 10^4
1.00	7.60	1.00	1.00	1.9
2.00	7.60	1.00	1.00	2.6
4.00	7.60	1.00	1.00	3.8
6.00	7.60	1.00	1.00	5.1
8.00	7.60	1.00	1.00	6.4
10.00	7.60	1.00	1.00	7.2
6.00	3.80	1.00	1.00	3.9
6.00	7.60	1.00	1.00	3.6
6.00	15.20	1.00	1.00	2.6
6.00	22.80	1.00	1.00	2.1
6.00	30.40	1.00	1.00	1.8
6.00	38.00	1.00	1.00	1.5
6.00	7.60	1.00	1.00	3.1
6.00	7.60	2.00	1.00	4.9
6.00	7.60	3.00	1.00	5.8
6.00	7.60	4.00	1.00	6.5
6.00	7.60	5.00	1.00	7.3
6.00	7.60	6.00	1.00	8.2
6.00	7.60	8.00	1.00	8.8
6.00	7.60	10.00	1.00	9.2
6.00	7.60	1.00	0.50	1.9
6.00	7.60	1.00	0.80	4.5
6.00	7.60	1.00	1.00	5.1
6.00	7.60	1.00	2.00	8.1
6.00	7.60	1.00	3.00	9.8
6.00	7.60	1.00	4.00	11.2
6.00	7.60	1.00	5.00	14.3

order with respect to [Ru(III)], (-0.32 and -0.42 for arabinose and ribose respectively). From this it was confirmed that Ru(III) acts as an inhibitor.

Reactive species of Cu(II) in alkaline medium: Copper(II) has been used as an oxidant in various oxidation processes either in acidic or in alkaline medium. In the present study, Cu(II) has been used with bipyridyl as complexing agent in alkaline medium. On the basis of kinetic and spectrophotometric data, it is known that the reactive species is [Cu(bipy)$_2$]$^{2+}$.

Ruthenium(III) chloride in alkaline medium: From the literature it was observed that the [RuCl$_2$(H$_2$O)$_4$]$^+$ species is the most stable species present in solution under experimental conditions at pH 2 and is stabilized in its hydrolyzed form according to the equilibrium shown below:

$$[RuCl_2(H_2O)_4]^+ + H_2O \rightleftharpoons [RuCl_2(H_2O)_3OH] + H_3O^+$$
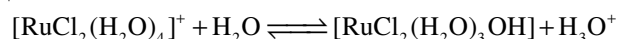
Ruthenium(III) chloride solution was prepared in 0.01 M HCl (pH = 2.0). In view of the above, the starting species may be assumed to be [RuCl$_2$(H$_2$O)$_3$OH]. Further, since the medium of the reaction was maintained alkaline throughout the study, it is necessary to take into account the effect of [OH$^-$] on the rate of oxidation. Considering the positive effect of [OH$^-$] on pseudo-zero order rate constant, the existence of the following equilibrium in the reaction may be assumed.

$$[RuCl_2(H_2O)_3 OH] + OH^- \rightleftharpoons [RuCl_2(H_2O)_2(OH)_2]^- + H_3O$$
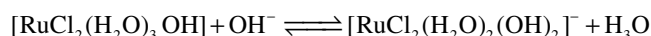
Between the two species, *i.e.*, [RuCl$_2$(H$_2$O)$_3$OH] and [RuCl$_2$(H$_2$O)$_2$(OH)$_2$]$^-$, the species [RuCl$_2$(H$_2$O)$_2$(OH)$_2$]$^-$ can be considered as the species of ruthenium(III) chloride in alkaline medium. This also finds support from the spectra observed for ruthenium(III) chloride alone and ruthenium(III) chloride with varying concentrations of OH$^-$, where increase in absorbance with the increasing [OH$^-$] is observed (Fig. 9).

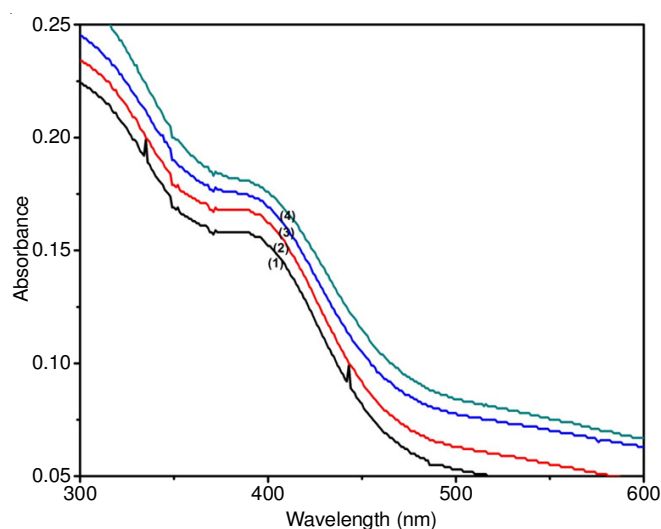Fig. 9. UV spectra of reaction solutions recorded at room temperature. {[Ru(III)] = 7.63 × 10^{-5} M (curve 1); [Ru(III)] = 7.63 × 10^{-5} M, [Na$_2$CO$_3$] = 10.00 × 10^{-2} M (curve 2); [Ru(III)] = 7.63 × 10^{-5} M, [Na$_2$CO$_3$] = 20.00 × 10^{-2} M (curve 3); [Ru(III)] = 7.63 × 10^{-5} M, [Na$_2$CO$_3$] = 50.00 × 10^{-2} M (curve 4)}

Reactive species of reducing sugar (arabinose and ribose) in alkaline medium: It is reported [31] that reducing sugars in alkaline medium exist in the form of enediol anion

and enediol. Out of these two forms 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 [OH⁻] on the rate of oxidation. Taking into consideration the positive effect of 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 sugar which is actually taking part in the reaction. The base catalyzed formation of enediol can be shown as follows:
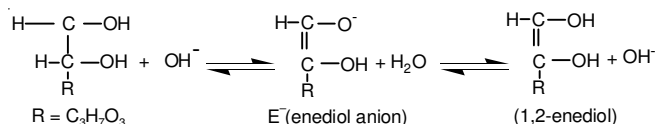
Spectrophotometric evidence for the formation of complex between reactive species of Cu(II) and reducing sugar molecules: Based on the observed kinetic data, there is a probability of formation of complex between reactive form of Cu(II) and also the reactive form of both arabinose and ribose. To study this four solutions are prepared. One of the solution contains $[Cu(bipy)_2]^{2+}$ and Na_2CO_3 and other three solutions contain $[Cu(bipy)_2]^{2+}$, Na_2CO_3 and different concentrations of arabinose and ribose (Figs. 10 and 11) respectively. With increase in sugar concentrations there is an increase in absorbance indicating formation of a complex between $[Cu(bipy)_2]^{2+}$ and reducing sugar molecules **(Scheme-I)**.
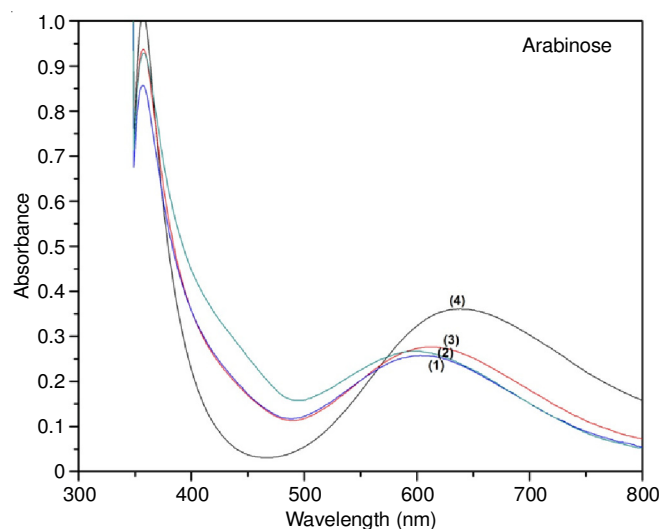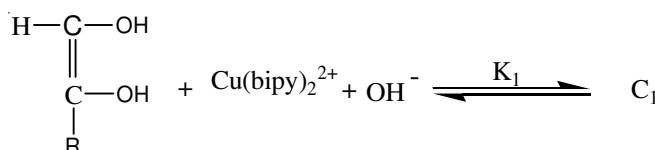

Fig. 10. Spectra of solutions [1-4] recorded at room temperature. {**(1)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M **(2)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Arabinose] = 1.00 × 10⁻² M **(3)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Arabinose] = 2.00 × 10⁻² M **(4)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Arabinose] = 4.00 × 10⁻² M}

Scheme-I
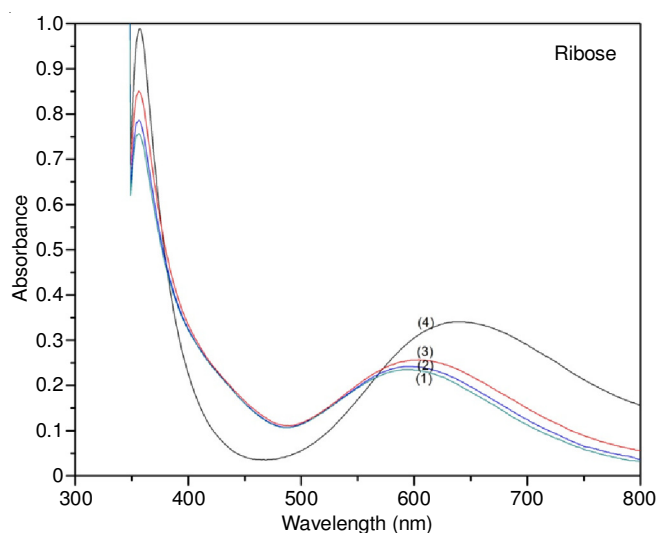
Fig. 11. Spectra of solutions [1-4] recorded at room temperature. {**(1)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M **(2)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Ribose] = 1.00 × 10⁻² M **(3)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Ribose] = 2.00 × 10⁻² M **(4)** $[Cu(bipy)_2]^{2+}$ = 4.0 × 10⁻³ M; [Free Bipy] = 4.0 × 10⁻³ M; [Na₂CO₃] = 1.00 × 10⁻² M; [Ribose] = 4.00 × 10⁻² M}

From the various kinetic data, there is a possibility of formation of complex between reactive species of ruthenium(III) chloride *i.e.* $[RuCl_2(H_2O)_2(OH)_2]^-$ and the complex (C_1) in alkaline medium **(Scheme-II)**.

$$C_1 \; + \; [RuCl_2(H_2O)_2(OH)_2]^- \xrightleftharpoons{K_2} C_2$$

Scheme-II
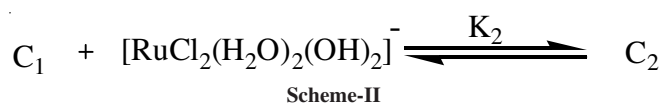
Derivation of rate law: On the basis of the observed kinetic orders with respect to the reactants, the spectrophotometric evidence collected for the formation of complexes and the negative entropy of activation, the most probable reaction path way is proposed for the oxidation of arabinose and ribose by $[Cu(bipy)_2]^{2+}$ in alkaline medium using Ru(III) as an inhibitor **(Scheme-III)**.

Scheme of reaction:
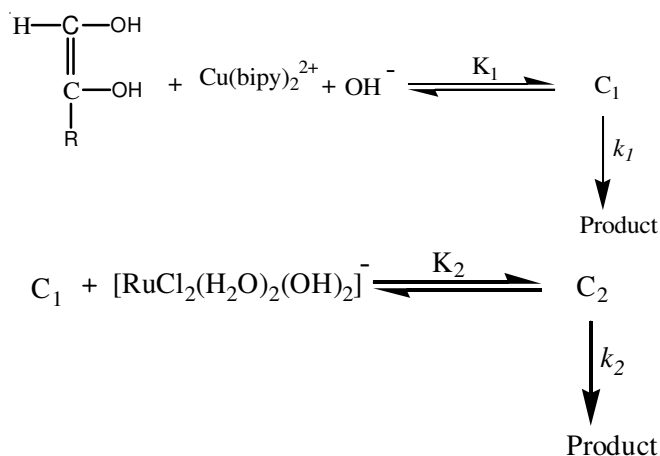
Scheme-III

where C$_1$ is [Cu(bipy)$_2$]$^{2+}$ complex with deprotonated arabinose and C$_2$ is the mixed Ru^{III}, [Cu(bipy)$_2$]$^{2+}$ complex formed with C$_1$.

On the basis of **Scheme-III**, the rate law for the formation of product is shown in eqn. 1.

$$\text{Rate} = -\frac{d[\text{Cu(II)}]_T}{dt} = k_{obs}[\text{Cu(II)}]_T = k_1[C_1] + k_2[C_2] \quad (1)$$

K$_1$ and K$_2$ can be expressed as

$$K_1 = \frac{C_1}{[S][\text{Cu(II)}][\text{OH}^-]}$$

$$K_2 = \frac{C_2}{[C_1][\text{Ru(III)}]}$$

Substituting for C$_1$ and C$_2$, we get

$$-\frac{d[\text{Cu(II)}]_T}{dt} = k_1 K_1[S][\text{Cu(II)}][\text{OH}^-] +$$

$$k_2 K_2 K_1[S][\text{Cu(II)}][\text{OH}^-][\text{Ru(III)}]$$

$$= \frac{\{k_1 K_1[S][\text{OH}^-] + k_2 K_2 K_1[S][\text{OH}^-][\text{Ru(III)}]\}}{\{1 + K_1[S][\text{OH}^-] + K_2 K_1[S][\text{OH}^-][\text{Ru(III)}]\}} \quad (2)$$

And [Cu(II)]$_T$ can be expressed as

$$[\text{Cu(II)}]_T = [\text{Cu(II)}]_f + C_1 + C_2$$
$$= [\text{Cu(II)}]_f + K_1[S][\text{Cu(II)}]_f[\text{OH}^-] + K_2[\text{Ru(III)}]$$
$$K_1[S][\text{Cu(II)}]_f[\text{OH}^-]$$
$$= [\text{Cu(II)}]_f\{1 + K_1[S][\text{OH}^-] + K_2 K_1[S][\text{OH}^-][\text{Ru(III)}]\}$$

Accordingly

$$k_{obs} = \frac{\{k_1 K_1 + k_2 K_2 K_1[\text{Ru(III)}]\}[S][\text{OH}^-]}{1 + K_1[S][\text{OH}^-]\{1 + K_2[\text{Ru(III)}]\}} \quad (3)$$

where acting that the assumption k$_2$K$_2$K$_1$[Ru(III)] <<< k$_1$K$_1$ is valid from the observed [Ru(III)] dependence as shown in eqn. 4.

$$k_{obs} = \frac{k_1 K_1[S][\text{OH}^-]}{1 + K_1[S][\text{OH}^-]\{1 + K_2[\text{Ru(III)}]\}} \quad (4)$$

Eqn. 4 can be rearranged to eqn. 5.

$$\frac{1}{k_{obs}} = \frac{1}{k_1 K_1[S][\text{OH}^-]} + \frac{1}{k_1} + \frac{K_2[\text{Ru(III)}]}{k_1} \quad (5)$$

The plots between 1/k$_{obs}$ and [Ru(III)], at constant [S] and [OH$^-$] were linear (Fig. 12) for both arabinose and ribose. Also the plots between 1/k$_{obs}$ and 1/[S] at constant [Ru(III)] and [OH$^-$] were linear (Fig. 13) for both arabinose and ribose. From the slope and intercept the values k$_1$, K$_1$ and K$_2$ were calculated. The values of k$_1$ at different temperature were used to calculate activation parameters (Table-3) using the relation:

$$\ln\frac{k_1}{T} = \ln\frac{k_b}{h} + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT}$$

Negative entropy of activation shows the electron transfer state is an ordered transition state. Equilibrium step involves a positive entropy change which shows that the desolvation of the intermediate complex (C$_1$ and C$_2$) contribute largely to the overall entropy change.

In the present study, the observed negative entropy of activation provides support for the formation of the neutral complex in the rate determining step by the interaction of
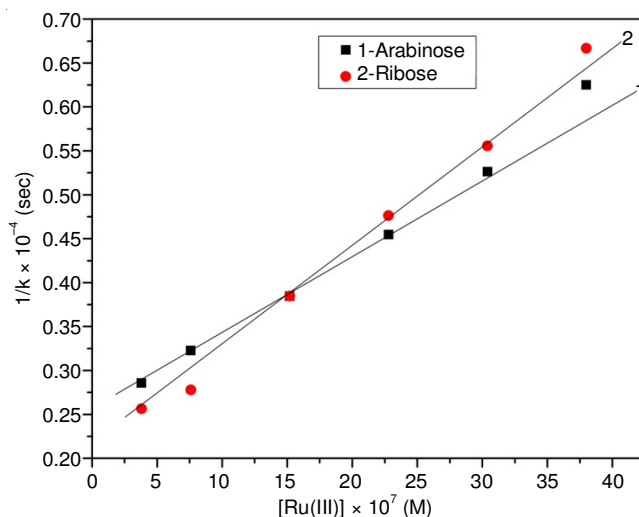

Fig. 12. Plot between 1/k and [Ru(III)]; (**1**) [Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Arabinose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M (**2**) [Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Ribose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M
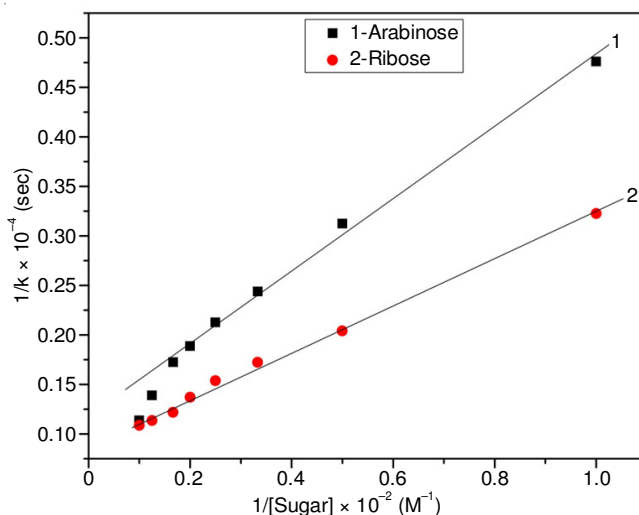
Fig. 13. Plot between 1/k and 1/[sugar]; (**1**) [Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M; [Ru(III)] = 7.60 × 10^{-7} M with variation of [arabinose] (**2**) [Cu(bipy)$_2$]$^{2+}$ = 6.0 × 10^{-4} M; [Ribose] = 1.00 × 10^{-2} M; [Na$_2$CO$_3$] = 1.00 × 10^{-2} M; [Ru(III)] = 7.60 × 10^{-7} M with variation of [ribose]

TABLE-3 ACTIVATION PARAMETERS FOR Ru(III)-CATALYZED OXIDATION OF ARABINOSE AND RIBOSE BY [Cu(bipy)$_2$]$^{2+}$			
Reducing sugar	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})
Arabinose	30.4	-197.9	60.98
Ribose	69.9	-69.7	21.54

complex (C$_1$) and [Ru(III)]. In this case the transition state will be less polar than the initial state.

Studies were carried out with varying dielectric constant of the medium under uniform reaction conditions. It was observed that with the decrease in the dielectric constant of the medium, there was an increase in pseudo-first order rate constant (k). This is an additional support for the formation of a neutral complex, (C$_2$) by the interaction of complex (C$_1$) and [RuCl$_2$(H$_2$O)$_2$(OH)$_2$]$^-$.

The results of the present investigation were in contrast with the results reported earlier for the oxidation of reducing sugars by alkaline sodium metaperiodate [15] and potassium iodate [16] using ruthenium(III) chloride as homogeneous catalyst. The pseudo-zero order kinetics in copper(II) concentration was reported earlier for IO_3^- and IO_4^- oxidation of sugars. However, in the present investigation, $[Cu(bipy)_2]^{2+}$ complex was found to be the reactive species of Cu(II) in alkaline medium. In the present case the role of Ru(III) was as an inhibitor in $[Cu(bipy)_2]^{2+}$ oxidation of arabinose and ribose, whereas Ru(III) was found to be a positive catalyst in iodate and periodate oxidation of reducing sugars in alkaline medium. As a positive catalyst, Ru(III) combined with the reactive species of IO_3^- and IO_4^- to form complex species of the type $[RuCl_2(H_2O)(OH)_2(OIO_2)]^{3-}$ and $[RuCl_2(H_2O)(OH)_2(IO_4)]^{2-}$, respectively and enhanced the oxidative capacity of oxidants. However, in the present investigation, Ru(III) in the form of $[RuCl_2(H_2O)_2(OH)_2]^-$ combined with (C_1) to form the complex, (C_2) and played the role of an inhibitor. The complex C_1 and C_2 can be assumed like:
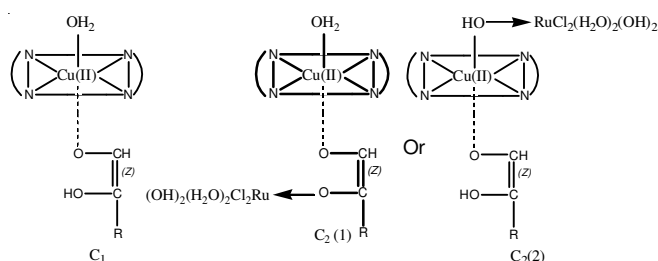
when Ru(III) reacts with the complex (C_1) there are possibility of two structures of complex (C_2). In the structure $C_2(1)$, Ru(III) withdraws electrons from sugar towards itself and decreases the electron density of the Cu(II) complex. *i.e.* ruthenium(III) will retard the rate of reaction. Hence, it will act as an inhibitor. But in the structure $C_2(2)$, the OH^- function coordinated to Cu(II) donates electrons to Ru(III) species. This causes favourable electron supply to Cu(II) from the sugar moiety and should enhance the oxidation of sugar. This is contrary to our observation. Hence, $C_2(1)$ is considered to be the preferable structure of the intermediate involved in the oxidation reaction.

Conclusion

The present study shows that $RuCl_3$ in the oxidation of arabinose and ribose by $[Cu(bipy)_2]^{2+}$ acts as an inhibitor in alkaline medium. The formation of the reactive complex of $[Cu(bipy)_2]^{2+}$ with enediol anion (E^-) of sugar in the first step is equilibrium controlled. The species, $[RuCl_2(H_2O)_2(OH)_2]^-$ in alkaline medium plays the role of an inhibitor in the oxidation of arabinose and ribose. An inactive complex is formed between $[RuCl_2(H_2O)_2(OH)_2]^-$ and the reactive complex of $Cu^{II}(bipy)_2$ with sugar prior to the rate determining step. This unreactive complex is responsible for the inhibitory action of $RuCl_3$ in the $[Cu(bipy)_2]^{2+}$ oxidation of arabinose and ribose in alkaline medium.

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