



## Kinetic And Mechanistic Studies of Ir<sup>3+</sup> Catalysed Oxidation of D-Ribose By Vanadium (V) In Perchloric Acid Medium

Maheshwar Prasad Sah

P. G. Department of Chemistry, S. M. College, Bhagalpur-812001, **INDIA**

Email: [reach2lecturermps@gmail.com](mailto:reach2lecturermps@gmail.com)

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### ABSTRACT

*D-ribose and vanadium(V) reacts in perchloric acid medium at 313 K, vanadium(V) is reduced to vanadium(IV) and D-ribose oxidised to formic acid. In this reaction 1 mol of D-ribose consumes 10 mol of vanadium (V). The reaction follows complex kinetics, being first order each in D-ribose and vanadium (V). The rate of reaction increases on increasing perchloric acid concentration. Variation of ionic strength of the medium on addition of various amounts of sodium perchlorate had no effect on the rate, indicates that at least one of the reacting species in rate determining step was molecular in nature. The activation parameters have been determined. The rate law has been evaluated as*

$$\frac{-d\ln [V^{5+}]}{dt} = k_{\text{obs}} = \frac{k_1 k_2 k_3 [D\text{-ribose}] [Ir^{3+}]}{k_{-1} k_{-2} + k_{-1} k_3 + k_2 k_3 [Ir^{3+}]}$$

**Keywords:** D-ribose, vanadium (V), perchloric acid, catalysis, oxidation, kinetics, mechanism.

### INTRODUCTION

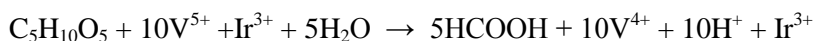
D-ribose is a source of energy that the body makes from food, but it is not like any other sugars. Sugar such as table sugar (sucrose), corn sugar (glucose), milk sugar (lactose), honey (predominantly fructose) and others are used by the body as fuel. Ribose on the other hand, is special and when the human consume, the body recognises and preserves it for making energy molecule that powers human hearts, muscles, brains and every other tissue in the body [1-4]. Ribose provides the key building block of ATP (adenosine triphosphate) and presence of ribose in the cell stimulates the metabolic pathway of human bodies. Ribose also stores ATP to normal or near normal levels after the heart muscle injury seen in the heart attack [5-13]. Vanadium is a metallic element that occurs in seven oxidation states [14] in various compounds. Vanadium in extremely small amount is a nutritional requirement for many types of organism including higher animals, but can be toxic at higher concentrations [15-17]. In environmental systems, vanadium (V) is more toxic than vanadium (IV) and can be produced by the several industrial redox processes. In body, it can undergo changes in oxidation state from vanadium (V) to vanadium (IV) and can also bind with blood protein [18]. Insulin like activities and anti-cancer properties of vanadium containing compounds have been reported [19-26]. The reduction of the level of hyperglycemia in diabetic rate has been reported by the treatment of vanadium, serious signs of its toxicity were also reported [16,17]. Vanadium is used extensively in metallurgy, the atomic energy industry, space technology, pharmaceutical industrial

processes, making vanadium one of the most important metals for modern technology. The aim of the present investigation is to provide the most probable reaction mechanism for the  $\text{Ir}^{3+}$  catalysed oxidation of biological important D-ribose by vanadium (V) in perchloric acid medium as well as to determine the kinetic orders with respect to each reactant of the reactions.

## MATERIALS AND METHODS

All chemicals used were of analytical reagent grade. The stock solution of vanadium (V) was prepared in double distilled water by dissolving appropriate amount of ammonium metavanadate and perchloric acid and standardised by ferrous ammonium sulphate solution using barium diphenylamine sulphonate as redox indicator [33]. Stock solution of D-ribose was prepared by dissolving it in double distilled water. Stock solutions of sodium sulphate, sodium bisulphate, sodium perchlorate and hydrated iridium (III) chloride were prepared in double distilled water. Sodium perchlorate and perchloric acid were used to maintain the required ionic strength and acidity respectively. The measured amount of reagents, i.e., vanadium (V), sodium perchlorate and  $\text{Ir}^{3+}$  were mixed in a conical flask and thermostated at 40 °C, was rapidly added to the reaction mixture. The kinetic studies were carried out by quenching an aliquot of the reaction mixture in measured excess of ferrous ammonium sulphate and back titrating the unreacted  $\text{Fe}^{2+}$  solution against standard vanadium (V) solution using barium diphenylamine sulphonate as redox indicator [34].

**Stoichiometry:** The stoichiometry of the reaction was determined by mixing a known concentrations of substrate, acid and  $\text{Ir}^{3+}$  with a known excess of vanadium (V). After completion of the reaction, the unconsumed vanadium (V) was determined by titration with standard  $\text{Fe}^{2+}$  solution using barium diphenylamine sulphonate as redox indicator [35]. The stoichiometry thus determined was found to be 10 mol of vanadium (V) to 1 mol of D-ribose. Formic acid was detected by Fehling's solution.



## RESULTS AND DISCUSSION

### Order of reaction with respect to [D-ribose]:

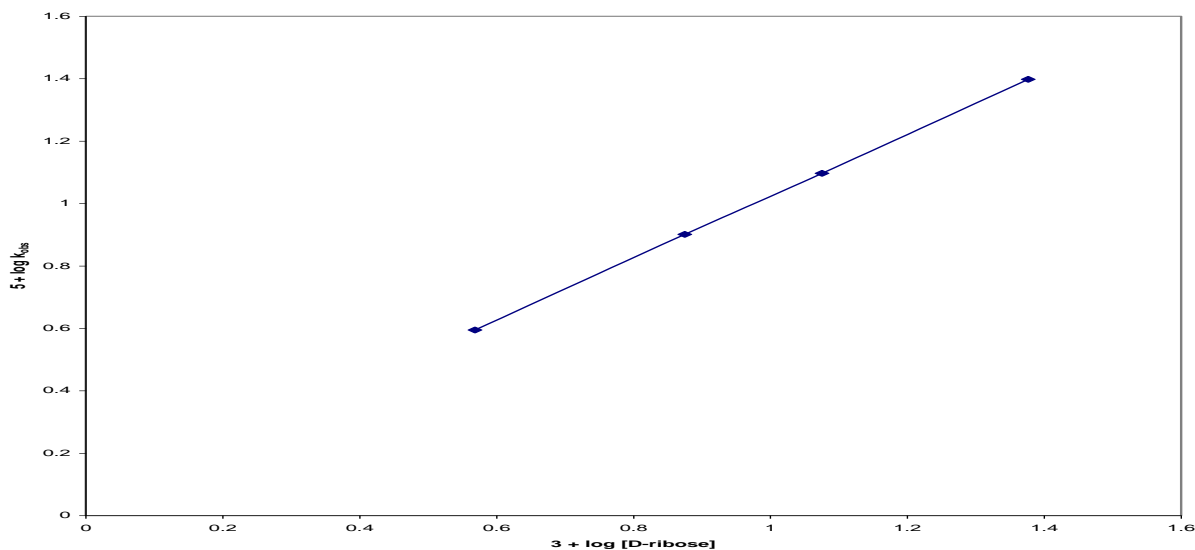


Figure 1. Plot of  $\log k_{\text{obs}}$  vs  $\log [\text{D-ribose}]$  at 313 K.  $[\text{V}^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ ,  $[\text{Ir}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $I = 0.534 \text{ mol dm}^{-3}$

The reactions were studied at different concentrations of D-ribose varying in the range  $3.125 \times 10^{-3} \text{ mol dm}^{-3}$  to  $25.0 \times 10^{-3} \text{ mol dm}^{-3}$  but at constant  $[\text{V}^{5+}]$ ,  $[\text{H}^+]$ ,  $[\text{Ir}^{3+}]$ , ionic strength and temperature of  $4.0 \times 10^{-3}$

mol dm<sup>-3</sup>, 0.5 mol dm<sup>-3</sup>, 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, 0.534 mol dm<sup>-3</sup> and 313 K respectively. The average pseudo first order rate constant ( $k_{\text{obs}}$ ) was found to be  $(7.5 \pm 0.12) \times 10^{-5} \text{ s}^{-1}$  indicates that the reaction is first order with respect to D-ribose.

$$k_{\text{obs}} = k_s [\text{D-ribose}] \dots(1)$$

The plot of log  $k_{\text{obs}}$  vs log [D-ribose] gives straight line with a slope of unity indicating that the reaction is first order with respect to [D-ribose] (Figure 1.). The values of  $k_s$  thus obtained with the help of equation 1 are  $(11.0 \pm 0.7) \times 10^{-3}$ ,  $(15.4 \pm 0.4) \times 10^{-3}$ ,  $(19.0 \pm 0.7) \times 10^{-3}$  and  $(33.0 \pm 0.6) \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at the temperatures 308, 313, 318 and 323 K respectively.

**Order of reaction with respect to [vanadium(V)]:** The concentration of vanadium(V) was varied from  $2.0 \times 10^{-3}$  to  $12.0 \times 10^{-3} \text{ mol dm}^{-3}$  at constant [D-ribose], [HClO<sub>4</sub>], [Ir<sup>3+</sup>], ionic strength and temperature of  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-1} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , 0.542 mol dm<sup>-3</sup> and 313 K respectively. The average pseudo first order rate constant ( $k_{\text{obs}}$ ) was found to be  $(47.44 \pm 0.41) \times 10^{-4} \text{ s}^{-1}$  indicates that the reaction is first order with respect to vanadium (V).

$$\frac{-d[V^{5+}]}{dt} = k[V^{5+}]$$

$$\frac{-d \ln [V^{5+}]}{dt} = k_{\text{obs}} \dots(2)$$

**Effect of ionic strength:** The effect of the concentration of sodium perchlorate was studied to establish the nature of intermediate species in the rate determining step. It was observed that the rate constant is independent of the ionic strength of the medium (Table 1), indicating that at least one of the reacting species in the rate determining step was molecular in nature [27].

**Table 1.** Effect of ionic strength on the rate of reaction and values of thermodynamic parameters.

[D-ribose] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $[V^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $[\text{Ir}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , Temp. = 40 <sup>0</sup> [H <sup>+</sup> ] = $5.0 \times 10^{-1}$ .				
[NaClO <sub>4</sub> ]/mol dm <sup>-3</sup>	2.00	4.00	6.00	8.00
I/mol dm <sup>-3</sup>	0.554	0.574	0.594	0.614
$k_{\text{obs}} \times 10^5/\text{s}^{-1}$	$9.74 \pm 0.32$	$10.12 \pm 0.13$	$9.89 \pm 0.54$	$9.97 \pm 0.62$
Thermodynamic parameters	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1} \text{ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
	$55.35 \pm 0.27$	$58.71 \pm 0.41$	$-135.78 \pm 0.37$	$97.85 \pm 0.31$

**Effect of [Ir<sup>3+</sup>]:** The reaction was studied at different concentrations of [Ir<sup>3+</sup>] within the range  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> to  $20.0 \times 10^{-3} \text{ mol dm}^{-3}$  (Table 2). It has been observed that the rate of reaction increases with increase in [Ir<sup>3+</sup>] showing catalytic effect on [Ir<sup>3+</sup>] on the rate of reaction. The catalytic constant  $k_c$  was determined by the equation are reported in the (Table 2) are fairly constant confirming its catalytic action.

$$k_c = \frac{k_{\text{catalysed}} - k_{\text{uncatalysed}}}{[\text{Catalyst}]} \dots(3)$$

It has been observed from the experimental facts that the dependence of rate on [Ir<sup>3+</sup>] and [D-ribose] can be expressed as

$$k_{\text{obs}} = \frac{m[\text{Ir}^{3+}][\text{D-ribose}]}{n+p[\text{Ir}^{3+}]} \dots(4)$$

$$\frac{1}{k_{\text{obs}}} = \frac{n}{m[\text{D-ribose}][\text{Ir}^{3+}]} + \frac{p}{m[\text{D-ribose}]} \dots(5)$$

Where m, n and p are expressed in terms of different rate constants.

**Table 2.** : Effect of  $[\text{Ir}^{3+}]$  on reaction rate

$[\text{D-ribose}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ , Temp =  $40^\circ \text{C}$  and  $I = 0.624 \text{ mol dm}^{-3}$

$[\text{Ir}^{3+}] \times 10^3 / \text{mol dm}^{-3}$	0	5.0	10.0	15.0	20.0
$k_{\text{obs}} \times 10^4 / \text{s}^{-1}$	$0.59 \pm 0.15$	$1.16 \pm 0.03$	$1.74 \pm 0.03$	$2.35 \pm 0.04$	$2.91 \pm 0.06$
$k_c$	.....	11.40	11.50	11.70	11.60

**Effect of  $[\text{H}^+]$  on reaction rate:** Hydrogen ion concentration was varied from  $7.0 \times 10^{-1} \text{ mol dm}^{-3}$  to  $25.0 \times 10^{-1} \text{ mol dm}^{-3}$  at constant  $[\text{D-ribose}]$ ,  $[\text{V}^{5+}]$ ,  $[\text{Ir}^{3+}]$ , ionic strength and temperature of  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $2.534 \text{ mol dm}^{-3}$  and  $313 \text{ K}$  respectively, the rate of reaction was found to increase with increasing perchloric acid concentration. The order with respect to perchloric acid concentration was determined from the plot of  $\log k_{\text{obs}}$  versus  $\log [\text{H}^+]$  (Figure 2) was found to be less than unity (0.436). The plot of  $\log k_{\text{obs}}$  versus  $-\text{H}_0$  (Hammett acidity function) [28] are linear with slope equal to 0.234 in the acid range  $7.5 \times 10^{-1}$  to  $25.0 \times 10^{-1} \text{ mol dm}^{-3}$  (Figure 3).

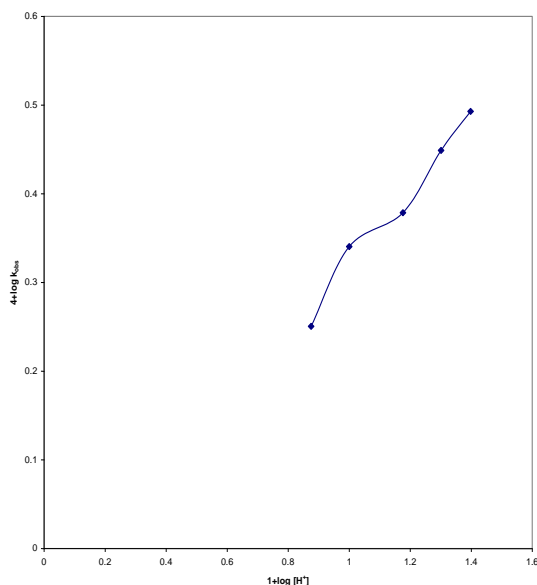


Figure 2. Plot of  $\log k_{\text{obs}}$  vs  $\log [\text{H}^+]$  at  $313 \text{ K}$ .  $[\text{D-ribose}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Ir}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $I = 2.534 \text{ mol dm}^{-3}$

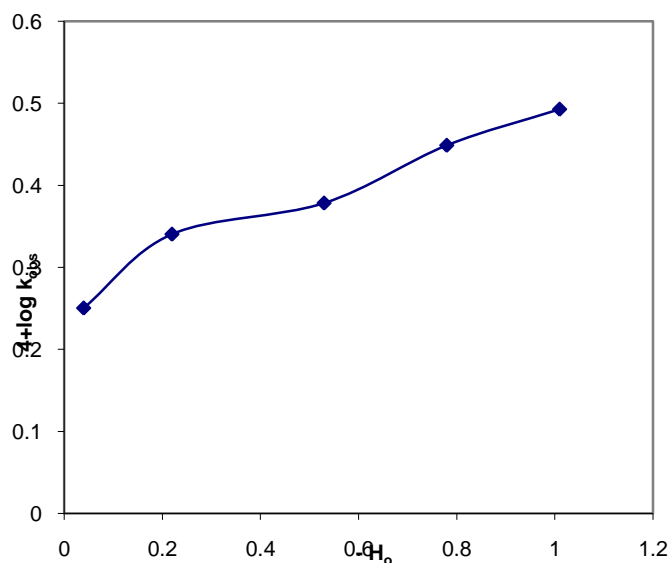
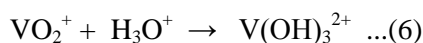


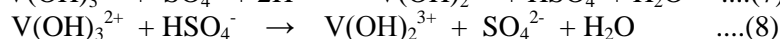
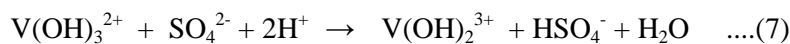
Figure 3. Plot of  $\log k_{\text{obs}}$  vs  $-\text{H}_0$  at  $313 \text{ K}$ .  $[\text{D-ribose}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{V}^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Ir}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 2.534 \text{ mol dm}^{-3}$

In strongly acidic medium vanadium(V) exists [14] only in the form of  $\text{VO}_2^+$ , whereas in the pH range 2 to 6 vanadium(V) exists as  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ,  $\text{HV}_{10}\text{O}_{28}^{5-}$ ,  $\text{V}_{10}\text{O}_{28}^{6-}$ ,  $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$  and  $\text{H}_4\text{V}_{10}\text{O}_{28}^{2-}$ . In higher acid concentration,  $\text{VO}_2^+$  ion is converted into  $\text{V}(\text{OH})_3^{2+}$  as given below



Since the order with respect to  $[\text{H}^+]$  was less than unity i.e. 0.436, the protonated species  $\text{V}(\text{OH})_3^{2+}$  is assumed to be active species.

**Effect of  $[\text{SO}_4^{2-}]$  and  $[\text{HSO}_4^-]$  on reaction rate:** sodium sulphate and sodium bisulphate when added under constant ionic strength showed the decrease in rate (Table 3). The inhibitory action of  $[\text{SO}_4^{2-}]$  and  $[\text{HSO}_4^-]$  on the rate of reaction is due to the fact that the active species of vanadium (V),  $\text{V}(\text{OH})_3^{2+}$  is removed according to the following equilibria:



**Table 3. :** Effect of  $[\text{Na}_2\text{SO}_4]$  and  $[\text{NaHSO}_4]$  on reaction rate

$[\text{D-ribose}] = 2.0 \times 10^{-2}$ ,  $[\text{V}^v] = 4.0 \times 10^{-3}$ ,  $[\text{HClO}_4] = 5.0 \times 10^{-1}$ ,  $[\text{Ir}^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , Temp.  $40^\circ$

	$I / \text{mol dm}^{-3} = 0.594$				
$[\text{Na}_2\text{SO}_4] \times 10^3 / \text{mol dm}^{-3}$	0	5.0	10.0	15.0	20.0
$[\text{NaClO}_4] \times 10^3 / \text{mol dm}^{-3}$	60.0	45.0	30.0	15.0	0
$k_{\text{obs}} \times 10^5 / \text{s}^{-1}$	$24.06 \pm 0.59$	$22.39 \pm 0.58$	$20.03 \pm 0.91$	$17.98 \pm 0.78$	$15.2 \pm 0.59$
	$I / \text{mol dm}^{-3} = 0.554$				
$[\text{NaHSO}_4] \times 10^3 / \text{mol dm}^{-3}$	0	5.0	10.0	15.0	20.0
$[\text{NaClO}_4] \times 10^3 / \text{mol dm}^{-3}$	20.0	15.0	10.0	5.0	0
$k_{\text{obs}} \times 10^5 / \text{s}^{-1}$	$15.2 \pm 0.61$	$14.01 \pm 0.67$	$12.3 \pm 0.72$	$11.61 \pm 0.39$	$9.21 \pm 0.56$

**Effect of temperature on reaction rate:** The reactions were studied at four different temperatures, 308, 313, 318 and 323 K and the observed values of pseudo first order rate constant,  $k_{\text{obs}}$  were used to calculate the activation parameters. The rate was found to increase with increasing temperature. From the Arrhenius plot,  $\log k$  versus  $1/T$ , the energy of activation ( $E_a$ ) was calculated. From the Eyring's plot,  $\log(k/T)$  versus  $1/T$  the value of  $\Delta H^\ddagger$  was calculated (Figure 4) and from which the remaining activation parameters were calculated (Table 1). The negative value of  $\Delta S^\ddagger$  shows the formation of more ordered activated complex and the transition state is highly solvated [27]. The high energy of activation indicates that the reaction is slow at rate determining step.

**Polymerisation test:** Acrylonitrile was added to the partially oxidised reaction mixture. No gel formation was observed even on addition of large excess of methanol. This suggests the absence of free radical intermediates in the reaction mixture.

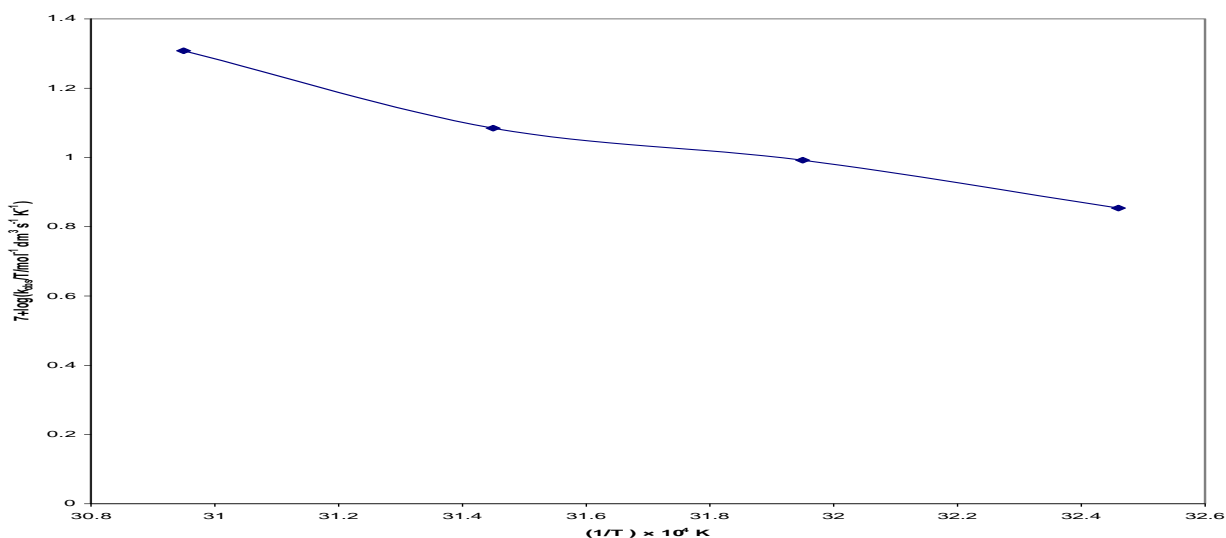
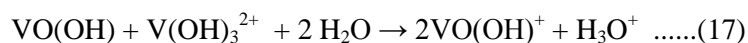
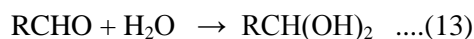
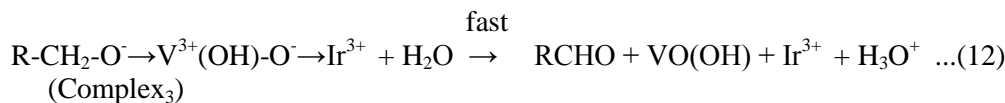
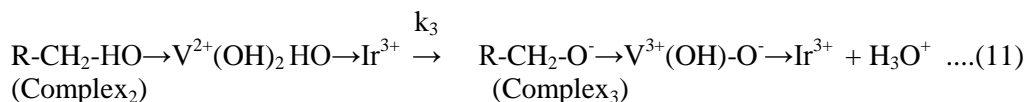
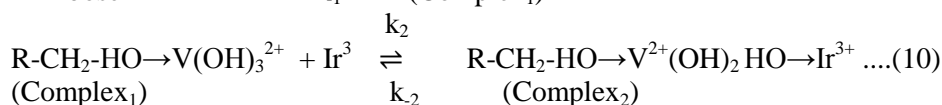
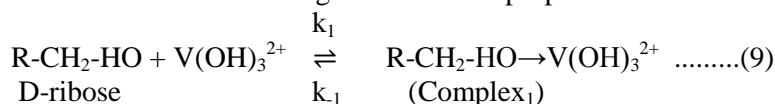


Figure 4. Plot of  $\log k_{obs}/T$  vs  $1/T$ .  $[D\text{-ribose}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[H^+] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ ,  $[V^{5+}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Ir^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.534 \text{ mol dm}^{-3}$

Mechanism: The following mechanism is proposed on the basis of the above kinetic evidences:



D-ribose has been oxidised by vanadium(V) via unstable intermediate complexes followed by the fission of c-c bond to form reaction product. The most reactive species [29-31] of vanadium (V),  $V(\text{OH})_3^{2+}$  combines with OH of D-ribose to form Complex<sub>1</sub>.  $Ir^{3+}$  combines with Complex<sub>1</sub> to form Complex<sub>2</sub>.

Complex<sub>2</sub> forms Complex<sub>3</sub> by the liberation of H<sub>3</sub>O<sup>+</sup>, which leads to the formation of aldehyde, VO(OH) and regeneration of Ir<sup>3+</sup>. The hydrated form of aldehyde ultimately combines with V(OH)<sub>3</sub><sup>2+</sup> to form reaction product. There was no evidence in favour of the formation of proposed Complexes, but it cannot annul the proposed mechanism, due to the very low small steady-state concentrations of the proposed Complexes. In acid medium D-galactose has been oxidised by vanadium (V) via Complex formation [32]. The rate law from the above mechanism could be written as

$$\frac{-d[V^{5+}]}{dt} = \frac{k_1 k_2 k_3 [S][V^{5+}][Ir^{3+}]}{k_{-1} k_{-2} + k_{-1} k_3 + k_2 k_3 [Ir^{3+}]} \quad \dots\dots(18)$$

Where S stands for D-ribose. The above rate law explains the first order dependence of rate on each D-ribose and [V<sup>5+</sup>] and fractional order dependence on [Ir<sup>3+</sup>]. The equation (18) could be written as

$$\frac{-d \ln [V^{5+}]}{dt} = k_{obs} = \frac{k_1 k_2 k_3 [S][Ir^{3+}]}{k_{-1} k_{-2} + k_{-1} k_3 + k_2 k_3 [Ir^{3+}]} \quad \dots\dots(19)$$

$$k_{obs} = \frac{k_1 k_2 k_3 [S][Ir^{3+}]}{k_{-1}(k_{-2} + k_3) + k_2 k_3 [Ir^{3+}]} \quad \dots\dots(20)$$

$$k_{obs} = \frac{k_1 k_2 k_3 [S][Ir^{3+}]}{k_{-1} k^* + k_2 k_3 [Ir^{3+}]} \quad \dots\dots(21)$$

Where  $k^* = k_{-2} + k_3$

$$k_{obs} = \frac{m[S][Ir^{3+}]}{n+p[Ir^{3+}]} \quad \dots\dots(22)$$

Where  $m = k_1 k_2 k_3$ ,  $n = k_{-1} k^*$  and  $p = k_2 k_3$

By taking reciprocal of equation (22)

$$\frac{1}{k_{obs}} = \frac{1}{\frac{m[S][Ir^{3+}]}{n+p[Ir^{3+}]}} = \frac{n+p[Ir^{3+}]}{m[S][Ir^{3+}]} = \frac{n}{m[S]} + \frac{p}{m[S]} \quad \dots\dots(23)$$

Where m, n and p are constants and expressed in terms of different rate constants.

From the slope, intercept on 1/k<sub>obs</sub> axis and extrapolated intercept on 1/[Ir<sup>3+</sup>] axis, the values of n/m[S], p/m[S] and -1/n were calculated. A plot of 1/k<sub>obs</sub> versus 1/[D-ribose] at constant [V<sup>5+</sup>] was linear with small intercept (1.248) on Y axis, offering kinetic support for Complex formation.

## APPLICATIONS

The purpose of this study is to determine the kinetic parameters with respect to each reactants of the reactions, as well as to present a suitable reaction mechanism and can be used for the oxidation of many organic and inorganic compounds and provide a condition for the estimation of these compounds.

## CONCLUSIONS

The negative value of entropy of oxidation for the oxidation of D-ribose supports the formation of activated complex. The positively charged V(OH)<sub>3</sub><sup>2+</sup> reacts with D-ribose to form Complex<sub>1</sub> in the slow and rate determining step requires higher energy of activation (E<sub>a</sub>). A plot of 1/k<sub>obs</sub> versus 1/[D-ribose] at constant [V<sup>5+</sup>] was linear with small intercept (1.248) on 1/k<sub>obs</sub> axis offering kinetic support for Complex formation.

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