

Kinetics and mechanism of Ir (III) catalysed oxidation of D-Mannose by acidic solutions of potassium permanganate

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Abstract: The oxidation of D- Mannose with permanganate ion (MnO_4^-) as oxidant was observed in acidic medium by visible spectrophotometric method in the temperature range (300 – 320) K. The reaction exhibit pseudo first order kinetics with respect to change in concentration of D- Mannose, MnO_4^- and H^+ followed by the change in absorbance of oxidant at 546 nm. Negligible effect of ionic strength (μ) on the rate of oxidation has also be noted which supports the presence of at least one neutral species in the rate determining step. The various activation parameters have been calculated. A suitable mechanism consistent with experimental finding has been proposed.

Key Words: D-Mannose, Permanganate ion, first order, Iridium chloride and potassium nitrate

Date of Submission: 01-11-2018

Date of acceptance: 15-11-2018

I. Introduction:

Sugars are a biologically important substance whose microbiological and physiological activities depend largely on their redox behavior [3-5]. The literature investigates many information about the oxidation of sugars by varying of oxidant [3-7] in both acidic and alkaline medium. Such as N-bromosuccinamide and potassium iodate in acidic and alkaline medium using transition metal ions, such as Os(VIII) [7], Pd (II) [8,9], Ru (VIII) [12], ruthenate ion [15], Mn(VII) [12-17], Hg (II) [19] and Ir (III) [12-16]. They are an important sources of energy required for the various metabolic activities of the living organisms; the energy being released as a result of their oxidation. The oxidation of different sugars have been carried out by using transition metal ions. In this case to different reaction conditions such as the effect of pH, ionic strength is very negligible. Potassium permanganate ($KMnO_4$) is major versatile which has been used to oxidize variety of compounds like sugars [16-21], nicotine [13], acetanilide, malachite green [22] etc. In this paper considering the biological importance of carbohydrates and rare information on Ir (III) as catalyst, this research has been investigated. In this research effort have been made to investigate the kinetics of oxidation of D- Mannose by potassium permanganate and effect of Ir(III) upon the reaction rate in sulphuric acid medium leading to the development of reaction mechanism [2-5].

II. Materials And Methods:

The chemical reagents used in this study were obtained from SigmaAldrich, Spectrochem, Merk, Alfa aesar. They were of analytical grade and used without further purification. Stock solution of D- mannose, potassium permanganate in DM water. The reaction was studied on thermostat ($\pm 1^{\circ}C$). The rate of reaction was followed by recording the optical density of $KMnO_4$ as a function of time on visible spectrophotometry. The rate constants were calculated from the slope of $\log(\text{concentration})$ vs time plots. The ionic strength was maintained throughout the experiment at 0.4 mole-dm^{-3} by adding KNO_3 solution.

III. Kinetic Measurements:

The oxidation of D-mannose by potassium permanganate was carried out in acidic medium. The rate of reaction was measured using S 104 D (Cambridge UK) No. 1260. The rate of reaction was followed by measuring the decrease in absorbance at 546 nm to conclude the effect of D-mannose, potassium permanganate, hydrogen sulphate, potassium nitrate concentration and temperature on the rate of oxidation. The reaction

between oxidant and mannose is completed when colour of the solution turned from purple to brown. The kinetic studies were carried out under pseudo-first-order condition with the concentration of the substrate i.e. D-mannose, in large excess compared to that of potassium permanganate.

IV. Product Analysis:

From spot test Chromotropic acid (1,8-dihydronaphthalene-3,6-disulfonic acid) was added to various reaction mixtures of sugar and oxidant then a violet pink colour is formed which conformed the formation of formic acid in the reactions [14] .

V. Stoichiometry Of The Reaction:

An excess amount of permanganate solution as added to the sugar solution and allowed to react for several hours at room temperature. Estimation of residual $[MnO_4]$ showed that 1 mol of sugars i. e. mannose consumed 2 moles of $[MnO_4]$ [1-5] .

VI. Result And Discussion:

The reactions were studied spectrophotometrically at 546 nm using aquamate spectrophotometer with a thermo-spacer cell compartment. The rate data of reaction was obtained in the form of pseudo first order rate constant (K_{obs}) under varying kinetics conditions [fig 1 & table 1]. The order of reaction with respect to D-mannose [table 1 & table 2], oxidation and H^+ has been found identical. The effect of ionic strength product by KNO_3 does not alter the rate constant. This independence of rate of ionic strength leads to the conclusion that at least one of the reacting species is a neutral molecule. The plot of $\log K_{obs}$ vs $\sqrt{\mu}$ as a straight line showed [fig 2] that rate of reaction was independent on ionic strength of the medium.

The oxidation reaction of D-mannose with potassium permanganate has been studied at various initial concentrations (1, 2, 3, 4 and 5) $\times 10^{-4}$ mol dm^{-3} which kept the substrate as well as sulphuric acid concentration temperature constant at 2×10^{-4} mole/ dm^3 of D-mannose, 1×10^{-1} mole/ dm^3 at 313K respectively. That is supported by earlier work [6-10]. The pseudo first order rate constant is independent of the initial concentration of permanganate ion, indicating that reaction is first order with respect to oxidant. The oxidation of D-mannose was studied at various initial concentrations of D-mannose (2×10^{-4} mole/ dm^3) by keeping [oxidant], $[H^+]$, [salt] and temperature constant. The values of pseudo first order rate constant was increased as the [substrate] increased [fig 1 & 3]. It was observed that the plot of $1/K_{obs}$ vs $1/[con]$ has been found to be linear with positive intercept on Y axis and evidence of a complex formation between reducing sugars and permanganate ion ($C_6H_{12}O_6 \dots MnO_4$) [21-27] [fig 2]. The following probable reaction may observed in the oxidation of D-mannose in acidic medium by permanganate ion.

The reaction has been investigated on different hydrogen ion concentration varied by the addition of sulphuric acid at constant ionic strength (μ), oxidant and substrate concentration. The values of K_{obs} against $[H^+]$ are linear passing through the origin indicating that the order with respect to H^+ ion is unity [fig 3]. The rate increases with increase in $[H^+]$ indicating that only one proton is involved in the reaction.

The rate of oxidation of sugar increases with increase in temperature and yielded the values of activation parameters (table-1). The value of activation parameters reflects that at least one of the reacting species in rate determining step involve a neutral molecule [fig 1]. The Arrhenius parameters were calculated as follows. The enthalpy of activation (ΔH^*) was calculated from the activation energy using the equation at temperature of 313K

The entropy of activation (ΔS^*) in each reaction was evaluated in table 1

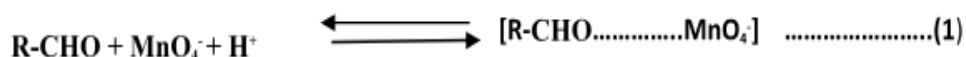
In presence of different concentrations (1.0×10^{-4} - 5.0×10^{-4} mol dm^{-3}) of catalyst the reaction was enhanced by using 2.0×10^{-5} mol dm^{-3} $KMnO_4$, 2.0×10^{-4} mol dm^{-3} D-mannose, 2.0×10^{-2} mol dm^{-3} H_2SO_4 , 0.4 mol dm^{-3} KNO_3 . But pseudo first order rate constants were independent of its changing concentrations (table-1, fig-1)

Reaction mechanism:

On the basis of the results the following mechanism is proposed for the above reaction.

$$-d[\text{MnO}_4^-]/dt = K[\text{R-CHO}][\text{MnO}_4^-]$$

Where R-CHO represents the concentrations of D-mannose and MnO_4^- is of oxidant.



$$d[\text{Complex}]/dt = K_1[\text{R-CHO}][\text{O}] - [k_2 - k_3][\text{Complex}] \cdots \cdots (i)$$

At steady state $d[\text{Complex}]/dt = 0 \cdots \cdots (ii)$

From equation (i) and equation (ii) concentration of complex comes out to be

$$[\text{Complex}] = K_1[\text{R-CHO}][\text{O}] / k_2 + k_3 \cdots \cdots (iii)$$

At steady state rate of disappearance of MnO_4^- may be:

$$d[\text{MnO}_4^-]/dt = K_3[\text{Complex}] \cdots \cdots (iv)$$

$$-d[\text{MnO}_4^-]/dt = K_1 k_3 [\text{R-CHO}][\text{O}] / k_2 + k_3 \cdots \cdots (v)$$

Or,

Total $[\text{MnO}_4^-]$ can be considered as

$$[\text{MnO}_4^-] = [\text{O}] + [\text{Complex}] \cdots \cdots (vi)$$

Now putting the value of complex

$$[\text{MnO}_4^-]_T = [\text{O}] + k_3[\text{R-CHO}][\text{O}] / k_2 + k_3 \cdots \cdots (vii)$$

From equation (vii) we can write

$$[\text{MnO}_4^-] = \frac{(k_1 + k_3)[\text{MnO}_4^-]_T \cdots \cdots (viii)}{(k_2 + k_3) + k_3[\text{R-CHO}]}$$

The final rate can be derived from equation (v) to (viii)

$$-d[\text{MnO}_4^-]/dt = \frac{k_1 k_3 [\text{R-CHO}] (k_2 + k_3) [\text{MnO}_4^-]_{\text{T}}}{\{k_3 + k_2 + k_1 [\text{R-CHO}]\} (k_2 + k_3)} \dots\dots\dots(\text{ix})$$

$$-d[\text{MnO}_4^-]/dt = \frac{k_1 k_3 [\text{R-CHO}] [\text{MnO}_4^-]_{\text{T}}}{k_3 + k_2 + k_1 [\text{R-CHO}]} \dots\dots\dots(\text{x})$$

In the present study $(k_2 + k_3) > k_1 [\text{R-CHO}]$

So, the rate equation reduced to

$$d[\text{MnO}_4^-]/dt = \frac{k_1 k_3 [\text{R-CHO}] [\text{MnO}_4^-]_{\text{T}}}{k_2 + k_3} \dots\dots\dots(\text{xi})$$

$$d[\text{MnO}_4^-]/dt = K [\text{R-CHO}] [\text{MnO}_4^-]_{\text{T}} \dots\dots\dots(\text{xii})$$

Where $k = k_1 k_3 / k_2 + k_3$

The above equation indicates first order kinetics with respect to sugar and permanganate ion concentration.

VII. Conclusion:

When we used Ir(III) chloride as a homogeneous catalyst then the entropy of oxidation of D- mannose was show as -161.90 J/mol/K.. The negative value of entropy of activation observed the interaction between the species, leading to the formation of an activation complex [24].

Acknowledgements:

The authors are thankful to Dr.Sabita Sengar Vice chancellor J.R.U for providing necessary research facilities and also for her kind permission to publish the paper.

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Figure and Table captions:

Fig 1. The linear plot of $\log k$ vs $1/T(K^{-1})$ for D-Mannose.

Fig 2. The linear plot of $1/K$ vs $1/[conc.]$ for D-Mannose.

Fig 3. The linear plot of effect of concentration of H_2SO_4 on rate of oxidation of D-Mannose.

Table 1. values of activation parameters.

Table 2 Variation of rate constant (KS^{-1}) with $KMnO_4$, D-Mannose and H_2SO_4 concentration.

Table 1

VALUES OF ACTIVATION PARAMETERS

Temp. 313 K, $[KNO_3] = 0.4 \text{ mol dm}^{-3}$, $[H^+] = 0.2 \text{ mol dm}^{-3}$.

Substrate = $2.0 \times 10^{-4} \text{ mol dm}^{-3}$

Substrate	$\sqrt{\mu}$ (mol dm^{-3})	E_a (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol)	ΔG^\ddagger (KJ/mol)
D-Mannose	0.4	6.73	5.94	-161.90	56.61

Table 2

Variation of rate constant (KS^{-1}) with $KMnO_4$, D-Mannose and H_2SO_4 concentration

$10^{-5}[KmnO_4]$ (mol/ dm^3)	10^{-4} [D-Mannose] (mol/ dm^3)	$10^{-2}[H_2SO_4]$ (mol/ dm^3)	$10^{-4} K (S^{-1})$
1	4	2	0.94
2	3	2	0.95
3	4	2	1.60
4	1	2	1.45
5	2	3	1.55
2	3	1	1.61
2	4	2	1.73
2	5	3	1.84
4	4	4	1.96
6	4	5	1.98
2	5	2	1.01
2	5	3	1.01
2	3	2	1.02
2	3	2	0.93

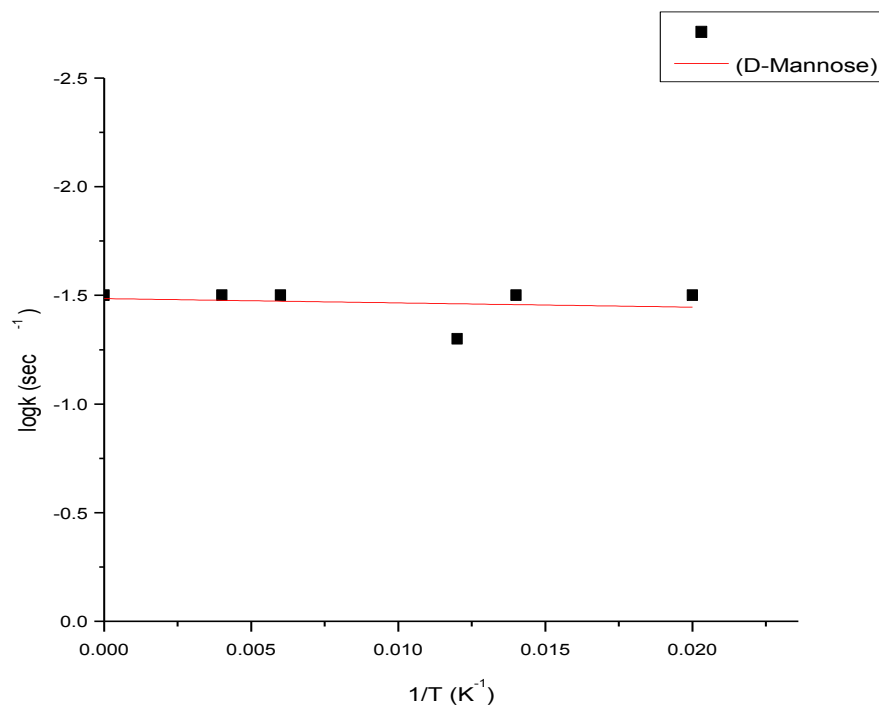


Fig 1

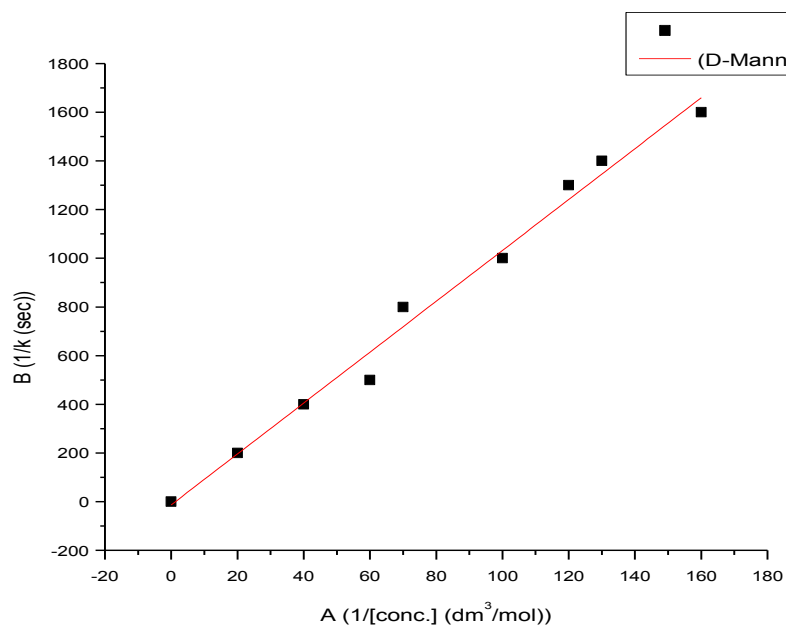


Fig 2

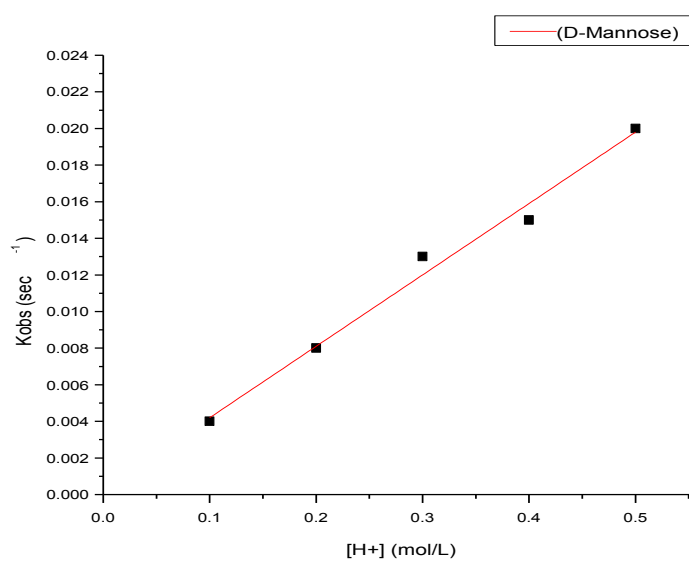


Fig 3