

## Hg (II) Catalysed Oxidation of D-Arabinose and D-Mannose by Acidic Solution of Potassium Permanganate: Kinetics and Mechanism

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### ABSTRACT

The kinetics of Hg (II) catalyzed oxidation of D-Arabinose (Ara) and D-Mannose (Man) by potassium permanganate in acidic medium have been studied spectrophotometrically in the temperature range 30-50°C. The reactions exhibit first order kinetics with respect to [Man] and [MnO<sub>4</sub><sup>-</sup>] while second order with [Ara]. The reaction rates were found to be unaffected by the change in [H<sup>+</sup>]. It has been observed that Hg (II) catalyzed the reaction but as the [Hg(II)] increases, reaction rate becomes independent. Negligible effect of ionic strength (μ) on the rate of oxidation has also been noted which supports the presence of at least one neutral specie in the rate determining step. The rate of oxidation was influenced by the change in temperature. Various activation parameters have been calculated. Formic acid and erythronic acid were identified as main oxidation product in case of arabinose while for mannose formic acid and arabinonic acid were identified. A mechanism consistent with the above findings has also been proposed.

**Keywords:** Permanganate ion, D-Mannose, D-Arabinose, H<sub>2</sub>SO<sub>4</sub>, Catalyst

### 1. INTRODUCTION

The biological and economic importances of the carbohydrates and especially the monosaccharides and disaccharides have been largely responsible for the interest in the study of their bio- and physiochemical properties and reactivities<sup>1</sup>. The literature offers numerous information about the oxidation of sugars by a variety of oxidants<sup>2-5</sup> in both acidic and alkaline media. The reports are also available on catalyzed oxidation of reducing sugars using the transition metals such as, Ru(III), Rd(III), Mn(II), Fe (III), and Pb (II)/ Hg(II)<sup>6-10</sup> as catalysts.

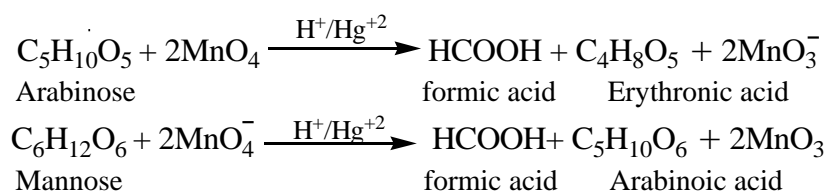
Potassium permanganate (KMnO<sub>4</sub>) is one of the most versatile oxidant that has been used to oxidize variety of compounds like sugars<sup>1,11,12</sup>, Nicotine<sup>13</sup>, acetanilide<sup>14</sup>, malachite green<sup>15</sup> etc. Considering the biological importance of carbohydrate and rare information on Hg (II) as catalyst, this research has been designed. The aim of this work is to investigate the kinetics of oxidation of D-arabinose and D-mannose by potassium permanganate and the effect of Hg (II) upon the reaction rate in sulphuric acid medium leading to the development of reaction mechanism.

### 2. EXPERIMENTAL

The stock solutions for kinetics investigation were prepared in conductivity water. D-Mannose, D-Arabinose, potassium permanganate, sulphuric acid and potassium nitrate used were of AR quality (Merck and BDH). The reaction was studied on thermostat (±1). The rate of reaction was followed by recording the optical density of KMnO<sub>4</sub> as a function of time on visible spectrophotometer (WBA UK.). The rate constants were calculated from the slope of log [concentration] versus time plots. The ionic strength was maintained throughout the experiments at 0.01 mol dm<sup>-3</sup> by adding KNO<sub>3</sub> solution.

### 3. STOICHIOMETRY

Varying [MnO<sub>4</sub><sup>-</sup>] and [Sugar] ratios were equilibrated at room temperature for 12 hrs with conditions [MnO<sub>4</sub><sup>-</sup>] >> [Sugar]. Estimation of residual [MnO<sub>4</sub><sup>-</sup>] in different sets showed that 1 mol of each sugar i.e. Ara and Man consumed 2moles of MnO<sub>4</sub><sup>-</sup>. Following stoichiometric equations could be established.



The products of oxidation like formic, arabinonic and erythronic acid were identified by TLC and by conventional spot test methods<sup>10</sup>.

### 3. RESULT AND DISCUSSION

Kinetics study of oxidation of D-Mannose D-arabinose with  $\text{KMnO}_4$  has been carried out spectrophotometrically in acidic medium at constant ionic strength maintained by  $\text{KNO}_3$ . The reaction was followed by change in optical density of  $\text{KMnO}_4$  in reaction mixture at  $\lambda_{\text{max}}$  545nm. The rate constants are calculated from the slope of the plot of  $\ln A_0 - A_\infty / A_0 - A_\infty$  Vs time. The rate data was obtained in the form of pseudo-first order rate constant ( $k_{\text{obs}}$ ) under varying kinetics conditions.

**Table-1:** Observed values of pseudo-first order rate constants in the oxidation of Arabinose by Permanganate ion

$[\text{KMnO}_4] \times 10^{-4} \text{ mol/dm}^3$	$[\text{Arabinose}] \times 10^{-3} \text{ mol/dm}^3$	$[\text{H}_2\text{SO}_4] \times 10^{-1} \text{ mol/dm}^3$	$k \times 10^{-3} \text{ s}^{-1}$
1	1	5	1.1
1.5	1	5	1.1
2	1	5	1.2
2.5	1	5	1.3
3	1	5	1.4
1	1	5	0.06
1	1.5	5	1.5
1	2	5	2.9
1	2.5	5	3.9
1	3	5	5.3
1	1	5	1.1
1	1	6	1.0
1	1	7	1.2
1	1	8	1.2
1	1	9	1.0

$[\text{HgCl}_2] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $[\text{KNO}_3] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

**Table-2:** Observed values of pseudo-first order rate constants in the oxidation of Mannose by Permanganate ion

$[\text{KMnO}_4] \times 10^{-4} \text{ mol/dm}^3$	$[\text{Mannose}] \times 10^{-3} \text{ mol/dm}^3$	$[\text{H}_2\text{SO}_4] \times 10^{-1} \text{ mol/dm}^3$	$k \times 10^{-3} \text{ s}^{-1}$
1	1	5	0.09
2	1	5	1.0
3	1	5	1.5
4	1	5	2.2
5	1	5	2.6
1	1	5	1.3
1	2	5	1.5
1	3	5	1.6
1	4	5	1.8
1	5	5	2.0
1	1	1	1.1
1	1	2	1.5
1	1	3	1.6
1	1	4	1.7
1	1	5	1.8

$[\text{HgCl}_2] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $[\text{KNO}_3] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

**Table-3:** Effect of Catalyst in the oxidation of Arabinose and Mannose.

$[\text{HgCl}_2] \times 10^{-3} \text{ mol/dm}^3$	$k \times 10^{-3} \cdot \text{s}^{-1}$ Arabinose	$k \times 10^{-3} \cdot \text{s}^{-1}$ Mannose
1	1.1	0.09
2	1.5	1.1
3	1.7	1.1
4	1.8	1.4
5	2.0	1.4

$[\text{KMnO}_4] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{Mannose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Arabinose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$

**Table-4:** Effect of salt in the oxidation of Arabinose and Mannose

$[\text{KNO}_3] \times 10^{-3}$ $\text{mol/dm}^3$	$k \times 10^{-3} \cdot \text{s}^{-1}$ Arabinose	$k \times 10^{-3} \cdot \text{s}^{-1}$ Mannose
1	1.1	3.3
2	1.2	3.2
3	1.2	3.2
4	1.1	3.2
5	1.2	3.2

$[\text{KMnO}_4] = 1 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{Mannose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{Arabinose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$

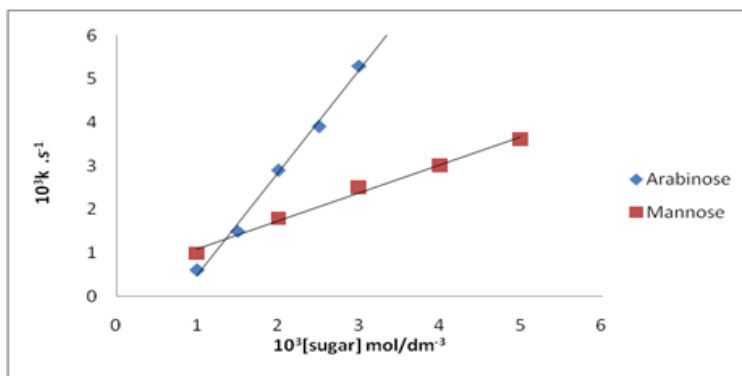
**Table-5:** Effect of temperature on the rate constant and values of Activation Parameters

Parameters	Temperature (K)	Arabinose	Mannose
$k (10^{-3} \text{ s}^{-1})$	303	1.1	2.6
$k (10^{-3} \text{ s}^{-1})$	308	1.2	2.3
$k (10^{-3} \text{ s}^{-1})$	313	1.3	4.5
$k (10^{-3} \text{ s}^{-1})$	318	1.4	6.0
$k (10^{-3} \text{ s}^{-1})$	323	1.5	6.0
$E_a(\text{kJ/mol})$	303	12.75	42.9
$\Delta H^\ddagger(\text{kJ/mol})$	303	9.96	49.13
$\Delta S^\ddagger(\text{J/mol})$	303	-268	-162
$\Delta G^\ddagger(\text{kJ/mol})$	303	81.21	49.13

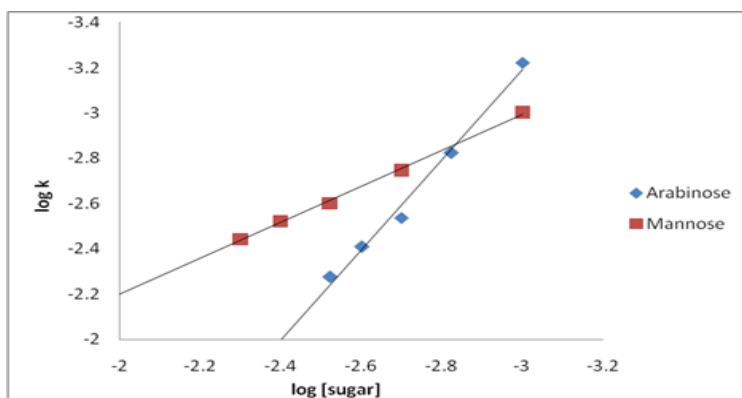
$[\text{KMnO}_4] = 1 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{Mannose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{Arabinose}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$   $[\text{HgCl}_2] = 1 \times 10^{-3} \text{ mol dm}^{-3}$   $[\text{KNO}_3] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

### 3.1 Effect of Variation of Substrate Concentration

The oxidation of arabinose and mannose were studied at various initial concentrations of arabinose ( $1 \times 10^{-3}$ - $3 \times 10^{-3} \text{ mol/dm}^3$ ) and mannose ( $1 \times 10^{-3}$ - $5 \times 10^{-3} \text{ mol/dm}^3$ ) by keeping [oxidant],  $[\text{H}^+]$ , [salt] and temperature constant. The values of pseudo first order rate constant was increased as the [substrate] increased (Tab. 01&02). It was observed that the rate constant increases very rapidly for arabinose as compare to that of mannose i.e. exhibiting slower kinetics by mannose as observed earlier<sup>16</sup>. This is also evidenced by the plot of  $k_{\text{obs}}$  against [substrate] (Fig.01). The order of reaction n, evaluated from the plot of  $\log k$  vs  $\log$  [substrate] found to be 1.99 and 0.792 for the oxidation of arabinose and mannose respectively (Fig.02).



**Fig-1:** Plot of [substrate] against k



**Fig-2:** Plot of  $\log$ [substrate] against  $\log k$

### 3.2 Effect of Variation of Oxidant Concentration

The effect of varying  $[\text{MnO}_4^-]$  ( $1 \times 10^{-4}$  -  $2.5 \times 10^{-4}$  mol/dm<sup>3</sup> for arabinose and  $1 \times 10^{-4}$  -  $5 \times 10^{-4}$  mol/dm<sup>3</sup> for mannose) was investigated by keeping other parameters constant. It was observed that rate of oxidation was increased as the  $[\text{MnO}_4^-]$  increases i.e. oxidation rate is directly proportional to  $[\text{MnO}_4^-]^{1,11,12}$  (Tab. 01&02). A plot of  $k_{\text{obs}}$  against  $[\text{MnO}_4^-]$  was linear (Fig.03) and the value of  $n$  was 0.692 and 1.054 with arabinose and mannose respectively (Fig.04).

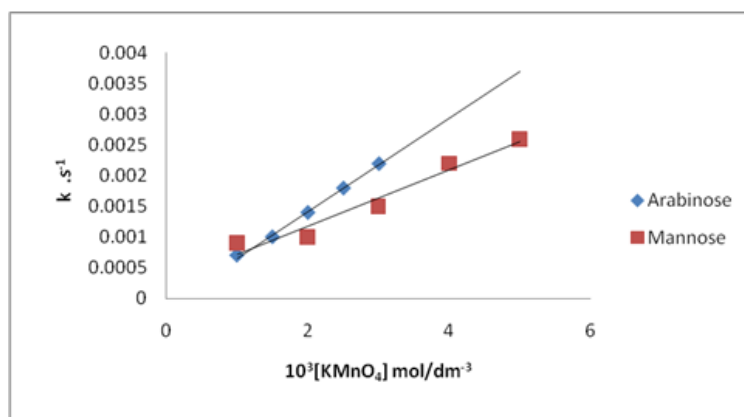


Fig-3: Plot of  $[\text{MnO}_4^-]$  against  $k$

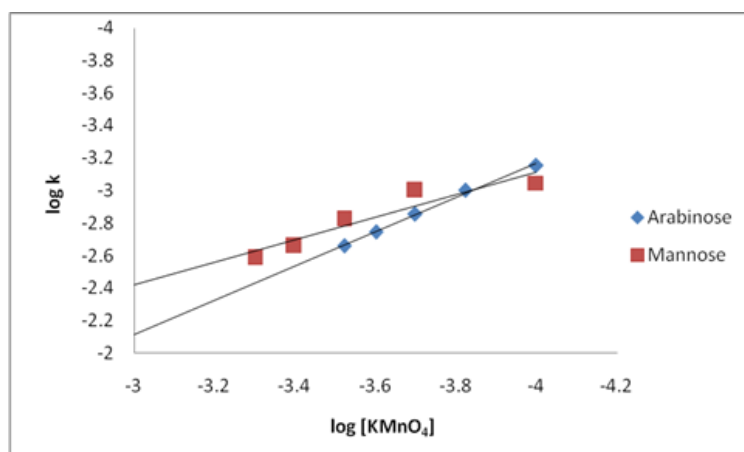


Fig-4: Plot of  $\log [\text{MnO}_4^-]$  against  $\log k$

### 3.3 Effect of Variation of $[\text{H}^+]$ Concentration

The effect of varying  $[\text{H}^+]$  ( $0.5$ - $0.9$  mol/dm<sup>3</sup>  $\text{H}_2\text{SO}_4$  for arabinose and  $0.1$ - $0.5$  mol/dm<sup>3</sup>  $\text{H}_2\text{SO}_4$  for mannose) was investigated by keeping other parameters constant. All the sets of experiment were performed at constant ionic strength maintained by the addition of  $1 \times 10^{-3}$  mol/dm<sup>3</sup>  $\text{KNO}_3$ . An increase in the concentration of  $\text{H}_2\text{SO}_4$  accompany an insignificant change in the values of rate constants (Tab. 01&02). This is also evidenced by Fig.05 & 06 that the reactions are acid independent.

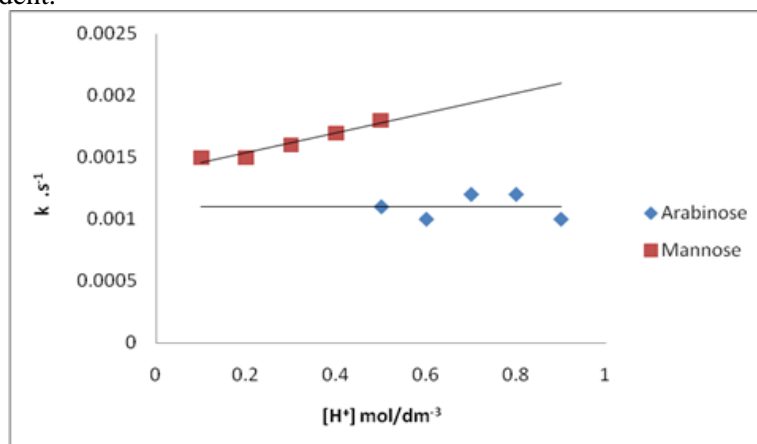


Fig-5: Plot of  $[\text{H}^+]$  against  $k$

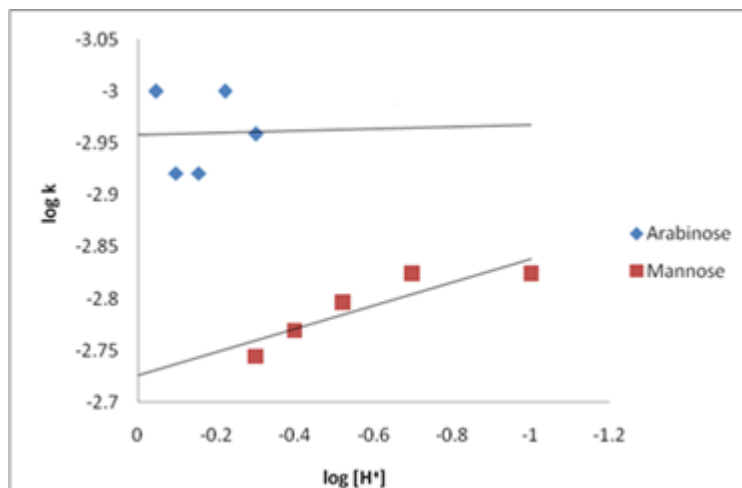


Fig-6: Plot of  $\log [H^+]$  against  $\log k$

### 3.4 Effect of Variation of $[HgCl_2]$ Concentration

To determine the influence of catalyst  $HgCl_2$ , reactions were investigated at different concentrations ( $1 \times 10^{-5}$  to  $5 \times 10^{-3}$  mol/dm<sup>3</sup>) by maintaining  $1 \times 10^{-4}$  mol dm<sup>-3</sup>  $KMnO_4$ ,  $1 \times 10^{-3}$  mol dm<sup>-3</sup> Mannose,  $1 \times 10^{-3}$  mol dm<sup>-3</sup> Arabinose,  $0.5$  mol dm<sup>-3</sup>  $H_2SO_4$  and  $1 \times 10^{-3}$  mol dm<sup>-3</sup>  $KNO_3$ . It was noted that reaction was enhanced by adding  $HgCl_2$  as compared to the earlier work<sup>16</sup> but pseudo first order rate constants were independent of its changing concentrations (Tab.03, Fig. 07 & 08).

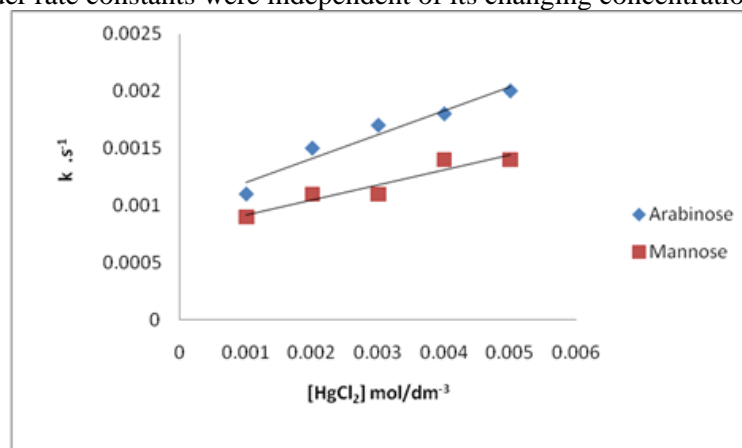


Fig-7: Plot of  $[HgCl_2]$  against  $k$

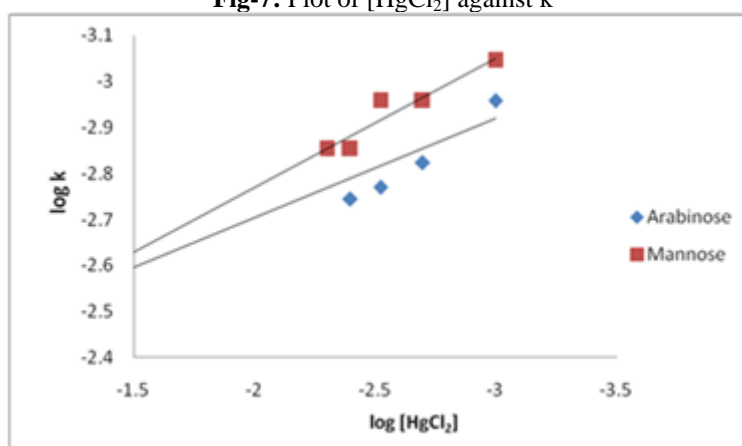


Fig-8: Plot of  $\log [HgCl_2]$  against  $\log k$

### 3.5 Effect of Ionic Strength

The effect of changing ionic strength on the reaction rate was studied by the addition of  $KNO_3$  ( $1 \times 10^{-3}$  to  $5 \times 10^{-3}$  mol dm<sup>-3</sup>) by keeping  $[KMnO_4]$ , [sugars], [acid] and temperature constant. An insignificant change was observed on the values of rate constant (Tab.04) suggesting at least one neutral molecule in the rate determining step. A plot of  $\log k$  vs.  $\sqrt{\mu}$  was also linear with zero slope (Fig.09).

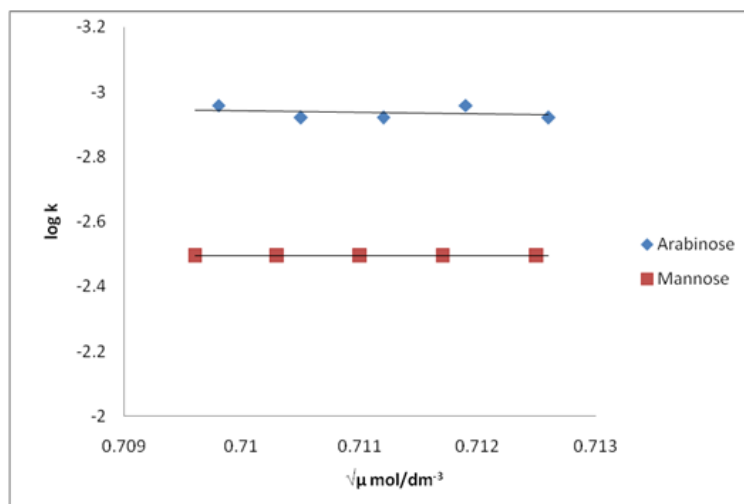


Fig-9: Plot of  $\log k$  against  $\sqrt{\mu}$

### 3.6 Effect of Temperature

The reaction of oxidation of both sugars was studied at different temperatures (30, 35, 40, 45 and 50 °C) to compute various activation parameters like  $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$ . The values of rate constant and activation parameters are reported in Table.05. A linear Arrhenius plot of  $\log k$  versus  $1/T$  (Fig.10) was used to calculate energy of activation,  $E_a$  which is 12.75 KJ/mol and 42.9 KJ/mol for Ara and Man respectively. The greater value of  $E_a$  for Man indicates higher energy barriers due to which it reacts slowly as compare to Ara. This is also confirmed by the values of  $\Delta H^\ddagger$ , 9.96 KJ/mol for Ara and 42.13 KJ/mol for Man evaluated from the plot of  $\ln(k/T)$  against  $1/T$  (Fig.11). The high negative values of  $\Delta S^\ddagger$  suggest the formation of highly solvated activated complex with the reduction of degrees of freedom of molecules.

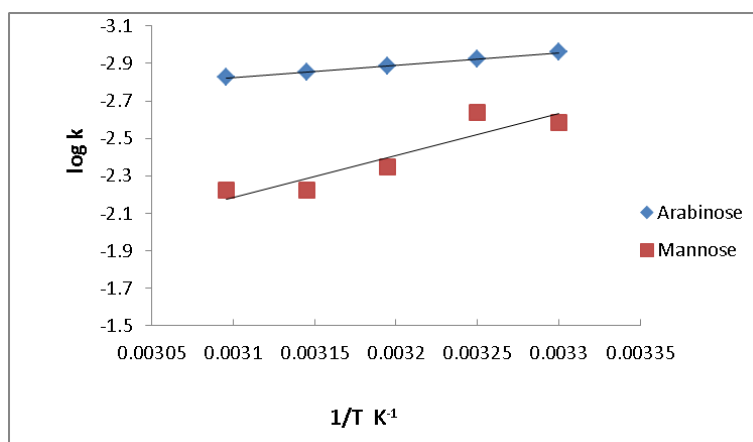


Fig-10: Plot of  $\log k$  against  $1/T$

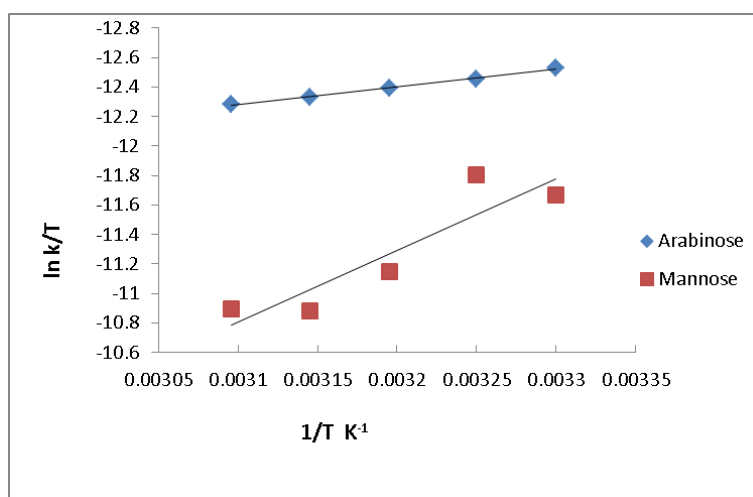
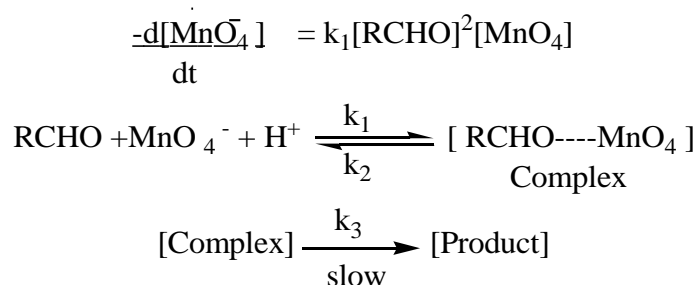


Fig-11: Plot of  $\ln(k/T)$  against  $1/T$

#### 4. REACTION MECHANISM

On the basis of the results the following mechanism is proposed for the reaction<sup>9</sup> of arabinose:



where  $k_1$  and  $k_2$  represent the rate constant in the forward and reverse direction and  $k_3$  is the rate constant of the formation of product. Rate of formation of complex will be given as:

$$\frac{d[\text{Complex}]}{dt} = k_1[\text{RCHO}]^2[\text{MnO}_4^-] - [k_2 + k_3][\text{Complex}] \quad 1$$

At steady state,

$$\frac{d[\text{complex}]}{dt} = 0 \quad 2$$

From eqn. 1 and 2 concentration of complex comes out to be:

$$\frac{d[\text{Complex}]}{dt} = \frac{k_1[\text{RCHO}]^2[\text{MnO}_4^-]}{k_2 + k_3} \quad 3$$

At steady state rate of disappearance of  $\text{MnO}_4^-$  may be:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k_3[\text{Complex}] \quad 4$$

or

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}]^2 [\text{MnO}_4^-]}{(k_1 + k_2)} \quad 5$$

Now the total  $[\text{MnO}_4^-]$  may be considered as:

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-] + [\text{Complex}] \quad 6$$

By putting the value of complex:

$$= [\text{MnO}_4^-] + \frac{k_1[\text{RCHO}]^2[\text{MnO}_4^-]}{k_2 + k_3} \quad 7$$

from eqn. 7 the value of  $[\text{MnO}_4^-]$  comes out:

$$= \frac{(k_2 + k_3)[\text{MnO}_4^-]_T}{(k_2 + k_3) + k_1[\text{RCHO}]^2} \quad 8$$

The final rate law from 5 to 8:

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}]^2 (k_2 + k_3) [\text{MnO}_4^-]_T}{\{(k_2 + k_3) + k_1[\text{RCHO}]^2\} (k_2 + k_3)} \quad 9$$

$$= \frac{k_1 k_3 [\text{RCHO}]^2 [\text{MnO}_4^-]_T}{(k_2 + k_3) + k_1[\text{RCHO}]^2} \quad 10$$

In present experimental conditions,

$$(k_2 + k_3) > k_1[\text{RCHO}]^2$$

Hence above equation reduces to:

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}]^2 [\text{MnO}_4^-]_T}{k_2 + k_3} \quad 11$$

or

$$\frac{-d[\text{MnO}_4^-]}{dt} = k [\text{RCHO}]^2 [\text{MnO}_4^-]_T \quad 12$$

Where,  
 $k = k_1 k_3 / k_2 + k_3$

The above equation indicates second and first order kinetics with respect to arabinose and permanganate ion concentration respectively.

For mannose the rate expression becomes:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k [\text{RCHO}] [\text{MnO}_4^-]_T$$

Therefore, the reaction of mannose follows first order kinetics with respect to mannose and permanganate ion concentration respectively.

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