

# Kinetics and Mechanism of Mn (II) Catalyzed Oxidation of D-Arabinose and D-Xylose by Chromium (VI) Ions in Perchloric Acid Medium.

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## ABSTRACT

The present paper describes the kinetics and mechanism of oxidation of D-arabinose and D-xylose by acidic solution of Chromium (VI) in the presence of Mn (II). First-order dependence of the reaction rate was observed on sugars, HClO<sub>4</sub> at low concentrations and a zero-order observed for sugars at a higher concentration. First-order kinetics with respect to Mn (II) throughout its variation was observed in the oxidation of both sugars. The Cl<sup>-</sup> and ionic strength effect was found to be negligible. Arrhenius activation energy and other thermodynamic activation parameters have been evaluated and lend further support to the proposed mechanism. Formic acid and erythronic acid were reported as the product of oxidation for both sugars.

(Keywords: kinetics, sugars, chromium oxidation, arabinose, xylose, manganese chloride catalysis, perchloric acid)

## INTRODUCTION

Carbohydrates have been reported to be a biologically important substance whose microbiological and physiological activities depend largely on their redox behavior [1]. Various kinetic studies regarding catalyzed oxidations of reducing sugars by various oxidants, such as N-bromosuccinimide and potassium iodate in acidic or alkaline medium using transition metal ions, such as Os(VIII) [2], Pd(II) [3,4], Ru(VIII) [5], ruthenate ion [6], Mn(VII) [15] and Ir(III) [7], as homogeneous catalysts are also available in the literature. Sen Gupta et al. [8] have described in their paper that mechanisms for the oxidation of some aldoses by Cr (VI), V (V), Ir (IV), Au (III) and periodic acid has been investigated in acidic media. In view of the

biological importance of reducing sugars and also the fact that limited information is available on Mn (II)-catalyzed oxidation reactions [9], the present study is therefore undertaken.

In this paper, efforts have been made to determine the kinetic orders with respect to each reactant of the reactions and to propose a suitable reaction path for the oxidation of reducing sugars under investigation. Graphical support for the formation of an activated complex between reactive species of Mn (II) chloride, Cr (VI) and the sugars has been given on the basis of spectrophotometric evidence and also on the basis of observed entropy of activation.

## EXPERIMENTAL

All chemicals were commercially available and used directly as received from the manufacturer. Cr (VI) (Analar) was prepared by dissolving known amount in double distilled water and its concentration was checked iodometrically. Solution of MnCl<sub>2</sub> (Uchem limited) was prepared by dissolving the sample in known strength of dilute hydrochloric acid (0.0001M). The standard solution of arabinose and xylose (A.R. grade) were freshly prepared with doubly distilled water.

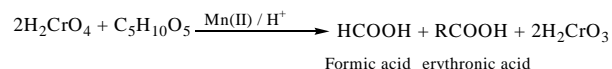
The standard solution of HClO<sub>4</sub> (E. Merck) was used to maintain the required acidity. KCl (Analar) was prepared by dissolving its required amount in double distilled water to fix the Cl<sup>-</sup> ion concentration and the ionic strength was maintained constant by adding NaClO<sub>4</sub> (Analar) solution of known ionic strength. Appropriate quantities of the solutions of Cr (VI), HClO<sub>4</sub>, MnCl<sub>2</sub>, KCl and NaClO<sub>4</sub> were placed in separate glass vessels and kept for sometime in a thermo stated water bath after reaching the assumed temperature the calculated amount of each

reaction mixture were then added together into a particular glass vessel followed by the requisite amount of double-distilled water and then mixed together. The reaction mixture was then placed in a thermo stated water bath maintained at constant temperature of 40 °C ( $\pm 0.5$  °C) and the reaction was initiated by adding the requisite amount of oxidant solution, placed separately in the same bath. The course of the reaction was followed by estimating the decrease in the in the absorbance of Chromium (VI) ion from time to time at a wavelength of 350nm, by using a UNISPEC SM7504UV spectrophotometer.

### STOICHIOMETRY AND PRODUCT ANALYSIS

Reaction mixtures, in which [Cr (VI)] was in large excess of [reducing sugar], were kept in the presence of KCl, NaClO<sub>4</sub>, MnCl<sub>2</sub> and HClO<sub>4</sub> at room temperature for 72 hours. The excess Cr (VI) left in the solution after the reaction was determined iodometrically as described in the literature[17].

Estimation of the un-reacted Cr (VI) showed that 1 mole of each sugar consumes 2 moles of Cr (VI) for oxidation to take place on the assumption that all the sugars are consumed for the oxidation reactions to take place. Formic acid was ascertained as one of the products of oxidation of arabinose and xylose using a spot test [10].



where, R= C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>

### RESULTS AND DISCUSSIONS

The pseudo-first-order rate constants ( $k_{\text{obs}} \text{ s}^{-1}$ ) were determined from the linear part of the plots of log (absorbance) versus time. Kinetic oxidations of D-arabinose and D-xylose by Cr (VI) were investigated in the presence of acidic solution of manganese (II) chloride at different concentrations of the reactants.

A progressive increase in the  $k_{\text{obs}}$  was observed for both sugars which shows that the reaction is first-order as shown in Table 1 at a lower concentration of sugars, which tends to zero order at their higher concentrations. In order to study the effect of [sugar] on the rate of reaction, the reactions have been studied with ten-fold

variation in [sugar] keeping concentrations of all other reactants constant at, 40°C.

**Table 1:** Effect of Variation of [Sugars] of the Medium on Pseudo First-Order Rate Constant  $k_{\text{obs}}$  in the Oxidation of Arabinose and Xylose at 40°C.

[Sugar] $\times 10^{-1} \text{M}$	$k_{\text{obs}} \times 10^{-4} \text{ s}^{-1}$	
	D-arabinose	D-xylose
0.4	1.08	1.20
0.8	1.61	1.63
1.0	1.76	1.79
1.2	2.03	1.98
1.4	2.34	2.31
1.6	2.51	2.44
1.8	2.69	2.51
2.0	2.75	2.59
2.4	2.80	2.65
2.8	2.93	2.70

Reaction conditions:  $[\text{H}^+] = 1.5 \times 10^{-1} \text{M}$ ;  $[\text{Cr (VI)}] = 1.0 \times 10^{-3} \text{M}$ ,  $[\text{MnCl}_2] = 6.0 \times 10^{-4} \text{M}$ ;  $[\text{KCl}] = 5.0 \times 10^{-4} \text{M}$ ;  $[\text{NaClO}_4] = 1.0 \times 10^{-1} \text{M}$

Table 2 shows the effect of varying Mn(II) keeping all other parameters constant, a pseudo-first order rate constants were observed for Mn(II). This indicates that the rate of oxidation of the sugars is catalyst dependent (9).

The rate of oxidation of the sugar increased with increase in acid concentration (Table 3). The Zucker-Hummet plots of the data were linear (Figure 1) indicating that the catalyzed oxidation reaction were acid dependent [20,21]. The effect of varying the KCl was found to be negligible which indicates that the addition of Cl<sup>-</sup> does not influence the oxidation rate of the sugars [16]. The rate of oxidation was reported to be independent of sodium perchlorate from the table above.

The reactions have also been studied at four different temperatures, (i.e., 40, 50, 60, and 70°C) for both the catalyzed and the un-catalyzed medium, observed values of pseudo-first-order rate constant  $k_{\text{obs}}$  were utilized to calculate the activation parameters of the various sugars including their entropy of activation in Table 4a and 4b.

**Table 2:** Effect of Variation of [Mn (II)] on the Rate of Oxidation of D-arabinose and D-xylose at 40 °C.

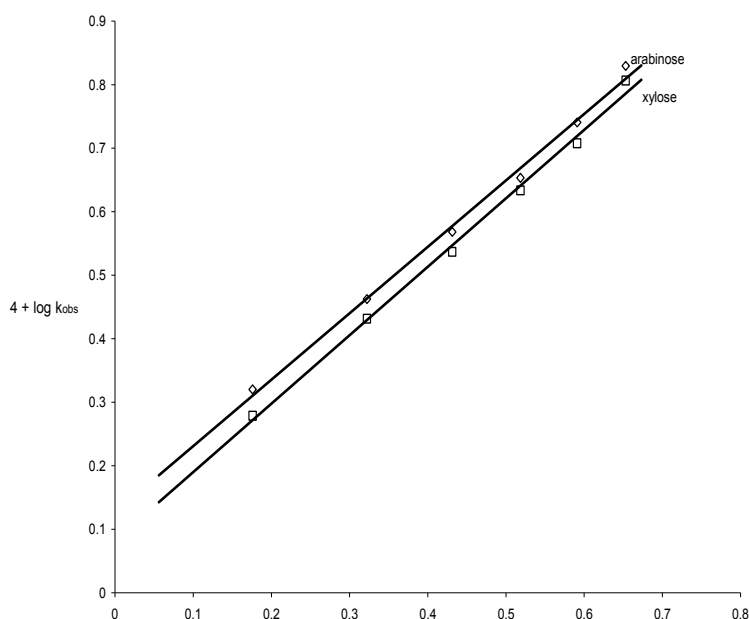
[Cr(VI)]×10 <sup>3</sup> M	[Sugar]×10 <sup>2</sup> M	[MnCl <sub>2</sub> ] ×10 <sup>4</sup> M	k <sub>obs</sub> ×10 <sup>4</sup> s <sup>-1</sup>	
			D-arabinose	D-xylose
1.0	1.0	1.0	0.49	0.40
1.0	1.0	3.0	1.41	1.26
1.0	1.0	5.0	2.55	2.05
1.0	1.0	7.0	3.50	2.56
1.0	1.0	9.0	4.77	3.53
1.0	1.0	11.0	5.51	4.32

Solution conditions: [KCl] = 5.00×10<sup>-4</sup> M, [HClO<sub>4</sub>] = 0.15M, [NaClO<sub>4</sub>] = 0.1M

**Table 3:** Effect of Variation of [HClO<sub>4</sub>] & [KCl] on Rate of Oxidation of D-arabinose & D-xylose at 40 °C.

[HClO <sub>4</sub> ]	[NaClO <sub>4</sub> ] M	[KCl] ×10 <sup>4</sup> M	k <sub>obs</sub> ×10 <sup>4</sup> s <sup>-1</sup>	
			D-arabinose	D-xylose
0.15	0.10	5.0	2.11	1.90
0.21	0.10	5.0	2.90	2.80
0.27	0.10	5.0	3.70	3.44
0.33	0.10	5.0	4.50	4.30
0.39	0.10	5.0	5.50	5.10
0.45	0.10	5.0	6.75	6.40
0.15	0.10	1.0	0.76	0.40
0.15	0.10	2.0	1.3	0.42
0.15	0.10	3.0	0.8	0.40
0.15	0.10	4.0	0.8	0.45
0.15	0.10	5.0	1.0	0.50

Solution conditions: [Sugar] = 1.00×10<sup>-2</sup> M, [Cr (VI)] = 1×10<sup>-3</sup>M, [MnCl<sub>2</sub>] = 6×10<sup>-4</sup> M



Solution conditions: [Sugar] = 1.0×10<sup>-2</sup> M, [Cr (VI)] = 1×10<sup>-3</sup>M, [MnCl<sub>2</sub>] = 6×10<sup>-4</sup>M, [NaClO<sub>4</sub>] = 1.0×10<sup>-1</sup> M, [KCl] = 5×10<sup>-4</sup>M

**Figure 1:** Zucker-Hummet Plots for the Oxidation of Various Sugars.

**Table 4:** Energy of Activation and Other Activation Parameters Observed for the Oxidation of D-Arabinose and D-Xylose at 40 °C.

(a) For the Un-catalyzed Medium:

SUGARS	$E_{act}$ KJmol <sup>-1</sup>	$\Delta H^\ddagger$ KJmol <sup>-1</sup>	$\Delta S^\ddagger$ Jmol <sup>-1</sup>	$\Delta G^\ddagger$ kJmol <sup>-1</sup>	$k_s(s^{-1}) \times 10^{-4}$	$A$ (mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup> )
Xylose	118.58	115.98	83.20	89.94	0.143	$1.43 \times 10^{17}$
Arabinose	116.62	114.02	80.71	88.76	0.210	$1.06 \times 10^{17}$

(b) The Catalyzed Medium:

SUGARS	$E_{act}$ kJmol <sup>-1</sup>	$\Delta H^\ddagger$ kJmol <sup>-1</sup>	$\Delta S^\ddagger$ Jmol <sup>-1</sup>	$\Delta G^\ddagger$ kJmol <sup>-1</sup>	$k_s(s^{-1}) \times 10^{-4}$	$A$ (mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup> )
Xylose	52.00	49.39	-112.20	87.11	1.63	$8.9 \times 10^5$
Arabinose	50.89	48.29	-113.86	83.93	1.61	$7.3 \times 10^5$

Average linear regression coefficients,  $r \geq 0.9$ , were observed for all activation parameters.

On the basis of observed first to zero-order kinetics with respect to the various sugars, zero-order kinetics in reducing sugar concentration, first-order dependence on Mn (II) chloride and positive effect of  $[H^+]$  on the rate of reaction, the following experimental rate law in the form of the eq. (i) below can be given for the oxidation of both arabinose and xylose as:

$$- \frac{d \text{Cr (VI)}}{dt} = \frac{k[\text{Mn(II)}] [S] [H^+] [\text{Cr(VI)}_T]}{a + b [S]} \quad \text{(i)}$$

where a and b are constants and have different values for different organic substrates.

The second- order rate constant ( $k_2$ ) for the oxidation of the sugars at different temperatures from 40°C to 70°C were determined. The plots of  $\log k_2$  against  $1/T$  were linear for both the catalyzed and un-catalyzed oxidation. The Arrhenius activation energies  $E_a$  for the un-catalyzed oxidation of Xylose and Arabinose were 118.58 and 116.62kJmol<sup>-1</sup>, respectively, while the catalyzed oxidation Arrhenius activation energies were 52.00 and 50.89 kJmol<sup>-1</sup> for arabinose and xylose respectively where the values of the un-catalyzed  $E_a$  is greater than the  $E_a$  of the catalyzed reaction, this suggest that catalysis takes place[22].

The negative entropies of activation for the catalyzed reaction  $\Delta S^\ddagger$  indicates that the reactions proceed through hybrid transfer between the sugar molecules and Cr (VI) in Mn (II) [18], This trends is also a characteristic of oxidation of

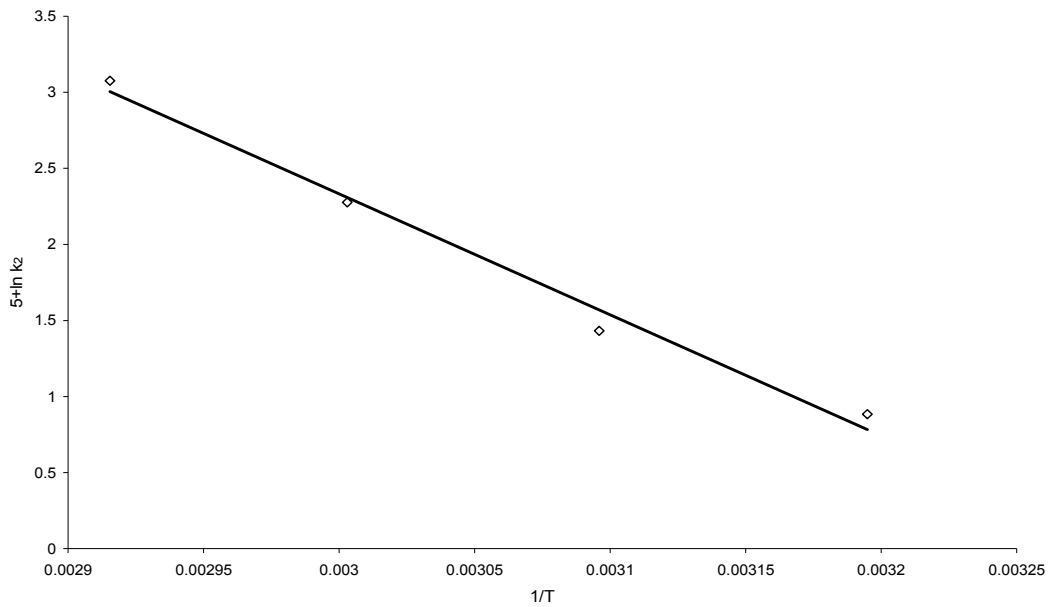
alcohols and aldehydes in Cr(VI), which is also supported by Mohammed Ilyas, et al. [9]. Figures 2 and 3 gives the Arrhenius plot for the catalyzed oxidation of the sugars.

#### **Spectrophotometric Evidence for the Formation of Complexes in the Reactions Under Investigation:**

In order to prove the formation of a complex between the Sugars, Cr (VI) and MnCl<sub>2</sub> a spectral graph used. When comparison is made between the spectrum recorded for the solution of Cr(VI) and H<sup>+</sup> and spectra recorded for the solutions of Cr(VI) and H<sup>+</sup> with two different concentrations of sugar, it was found that with the addition of sugar solution there is an increase in absorbance from 1.082 to 1.243 and 1.281 with a shift in  $\lambda_{max}$  towards longer wavelength of about 370nm (Figure 4) [16]. This increase in absorbance with the increase in sugar and Cr(VI) concentrations clearly indicates that there is a formation of complex species[Mn (II)--S--Cr (VI)].

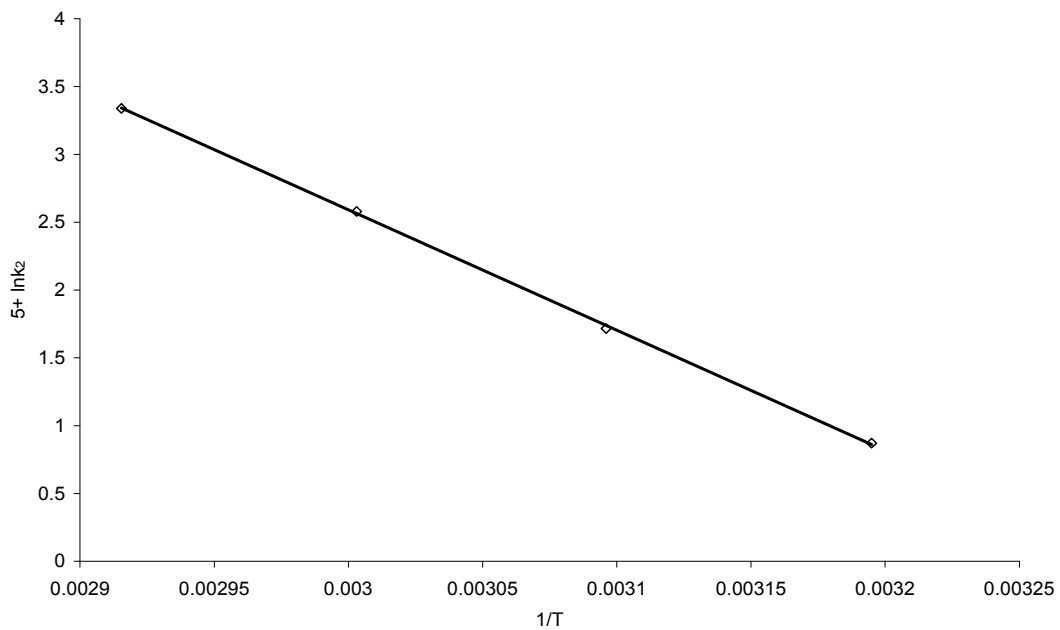
#### **Test for Free Radicals:**

To test the presence of free radicals in the reaction, 20% acryl amide solution was added to reaction mixtures containing the substrate and the Chromium VI solution and was placed in an inert atmosphere for 24 hours. On further addition of methanol, it was found that there is no precipitate in the reaction mixture. This clearly shows that there is no formation of free radicals in the redox reactions under investigation (23).



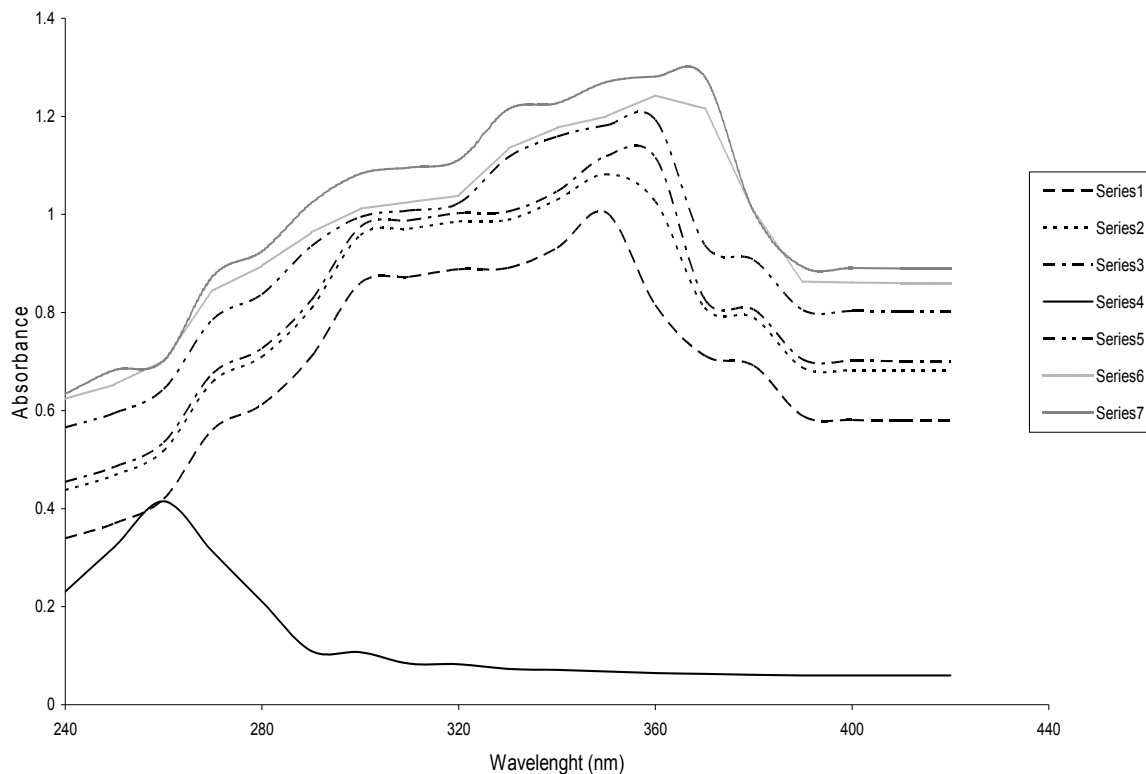
Solution condition: [Sugar] =  $1 \times 10^{-2}M$ , [Oxidant] =  $1 \times 10^{-3}M$ , [NaClO<sub>4</sub>] = 0.1M [KCl] =  $5 \times 10^{-4} \text{ mol dm}^{-3}$ ; [HClO<sub>4</sub>] = 0.15M.

**Figure 2:** Arrhenius Plot for the Catalyzed Oxidation of Xylose.



Solution condition: [Sugar] =  $1 \times 10^{-2}M$ , [Oxidant] =  $1 \times 10^{-3}M$ , [NaClO<sub>4</sub>] = 0.1M [KCl] =  $5 \times 10^{-4} \text{ mol dm}^{-3}$ ; [HClO<sub>4</sub>] = 0.15M.

**Figure 3:** Arrhenius Plot for the Catalyzed Oxidation of Arabinose.



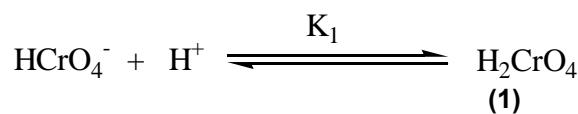
- (1)  $[Cr(VI)] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;
- (2)  $[Cr(VI)] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $[H^+] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;
- (3)  $[Cr(VI)] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $[H^+] = 20.00 \times 10^{-2} \text{ mol dm}^{-3}$ ;
- (4)  $[Sugar] = 1 \times 10^{-2} \text{ mol dm}^{-3}$
- (5)  $[Cr(VI)] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$  and  $[Sugar] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$
- (6)  $[Mn(II)] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$  and  $[Cr(VI)] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Sugar] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ ;
- (7)  $[Mn(II)] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$  and  $[Cr(VI)] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[Sugar] = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

**Figure 4:** Evidence for the Formation of Complexes in the Catalyzed Oxidation Reaction.

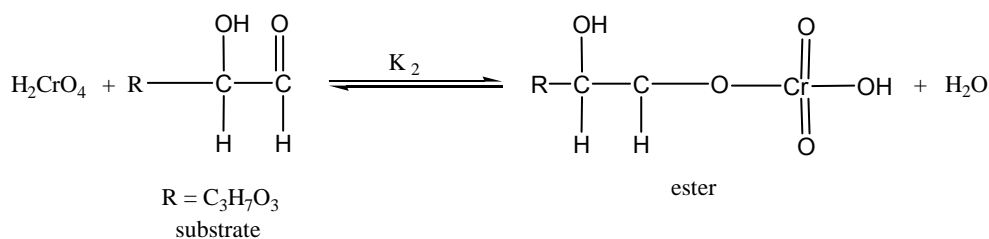
### Reaction Scheme:

Reaction scheme based on the kinetic results observed and the spectrophotometric evidence for the formation of intermediate complex is proposed as follows:

The formation of a protonated chromic acid molecule  $H_2CrO_4$  is believed to occur according to the equation below [19].

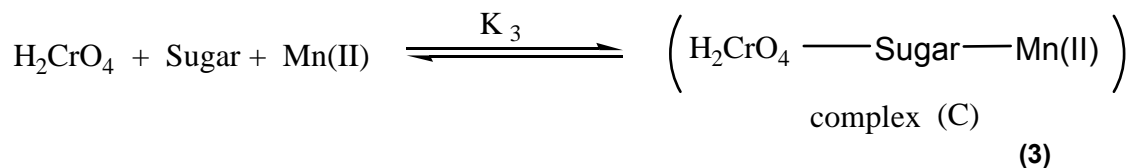


The direct oxidation of Mn(II) by chromium(VI) is thermodynamically unfavorable [14], the protonated chromic acid reacts with the substrate to form a chromate ester [9].

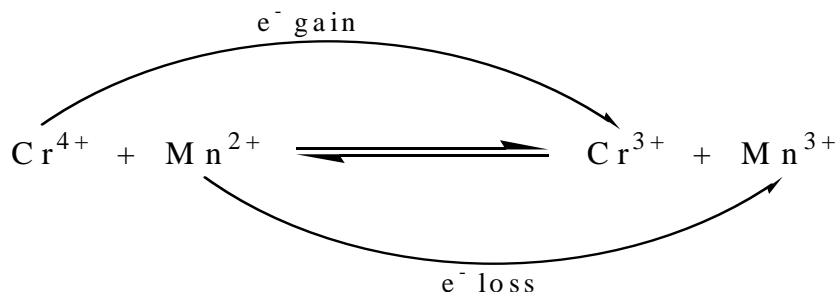


(2)

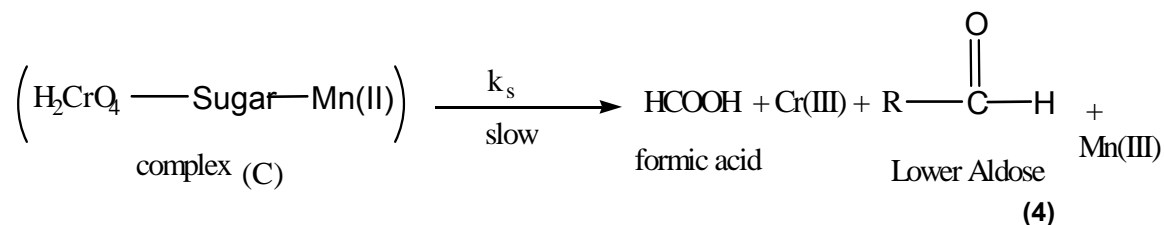
For catalysis, in presence of Mn (II), the reaction will proceed through the formation of a tri-molecular complex [11, 12] according to the equation below:



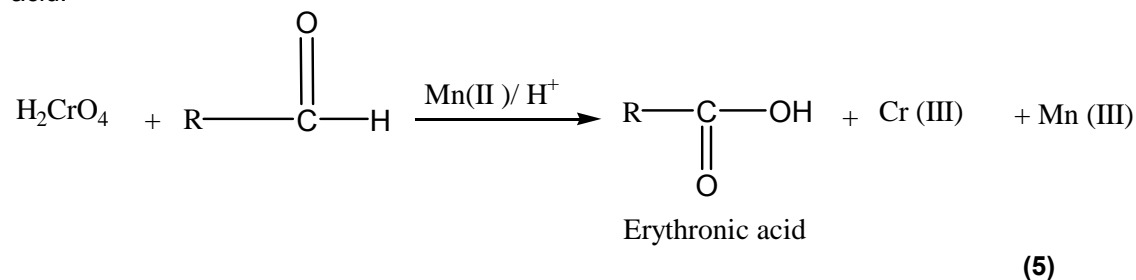
The positive catalytic effect of Mn (II) is due to a one-step three-electron reduction of chromium (VI) in the rate determining step, which is in conformity the reduction of Cr (VI) to Cr (III).



One of the electrons transferred is donated by manganese (II) atom which transforms Cr(IV) to Cr(III) shown above (a pale brown color observed initially was noticed to have changed to a dark brown coloration confirming manganese III) and the other two electrons by the aldose sugars which is in accordance with Mohammed Ilyas,2007 [9]. The negative entropies of activation  $\Delta S^\ddagger$  indicates that the reactions precede through hybrid transfer between the sugar molecules and Cr (VI) in Mn (II) [18].



The lower aldose undergoes further oxidation with the protonated chromic acid to yield the Erythronic acid.



A common reaction scheme proposed above for the oxidation of arabinose and xylose finds support from the same order of frequency factor (A) and also by almost same values of free energy of activation  $\Delta G^\ddagger$  observed for both the redox systems [16]. From the proposed

mechanism above the rate of the reaction in terms of decrease in the Cr (VI) can be written as;

$$-\frac{d \text{Cr(VI)}}{dt} = 2 k_s [C] \quad (6.1)$$

Where '2' indicates that 1 mole of arabinose and xylose is oxidized by 2 moles of Cr (VI). The above equation 6.1 can also be written as shown in equation 6.2 from the mechanism above;

$$-\frac{d \text{Cr (VI)}}{dt} = 2 k_s K_3 [\text{Mn(II)}] [S] [H_2CrO_4] \quad (6.2)$$

where  $K_1 [H^+] [HCrO_4^-] = [H_2CrO_4]$   
Equation 6.2 then becomes;

$$-\frac{d \text{Cr (VI)}}{dt} = 2 k_s K_3 K_1 [\text{Mn(II)}] [S] [HCrO_4^-] [H^+]$$

According to the proposed mechanism, the total concentration of Cr (VI), i.e.  $[\text{Cr (VI)}]_T$  at any moment in the reaction can be expressed as:

$$\begin{aligned} \text{Cr(VI)}_T &= \text{Cr(VI)} + C_1 \\ \text{Cr (VI)}_T &= \text{Cr (VI)} + K_2 [\text{Cr(VI)}] [S] \\ \text{Cr(VI)}_T &= \text{Cr(VI)} [1 + K_2 [S]] \\ \text{Cr(VI)} &= \frac{\text{Cr (VI)}_T}{1 + K_2 [S]} \end{aligned} \quad (7.0)$$

where  $\text{Cr(VI)} = HCrO_4^-$   
Substituting Eq.7.0 into Eq.6.2 gives:

$$-\frac{d \text{Cr (VI)}}{dt} = \frac{2 k_s K_3 K_1 [\text{Mn(II)}] [S] [\text{Cr(VI)}]_T [H^+]}{1 + K_2 [S]} \quad (8.0)$$

This can also be expressed as;

$$k_{\text{obs}} = \frac{-\frac{d \text{Cr (VI)}}{dt}}{[\text{Cr(VI)}]_T} = \frac{2 k_s K_3 K_1 [\text{Mn(II)}] [S] [H^+]}{1 + K_2 [S]} \quad (9.0)$$

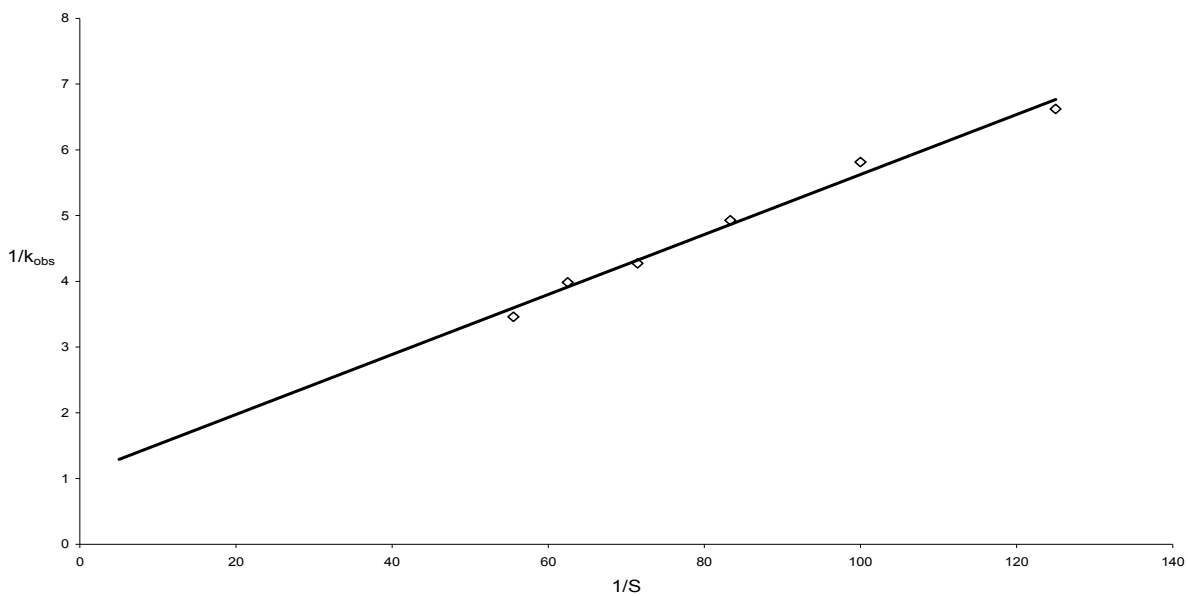
$$\frac{1}{k_{\text{obs}}} = \frac{1}{2 k_s K_3 K_1 [\text{Mn(II)}] [S] [H^+]} + \frac{K_2}{2 k_s K_3 K_1 [\text{Mn(II)}] [H^+]} \quad (10.0)$$

From the plot  $1/k_{\text{obs}}$  against  $1/[S]$  is made from which the constants  $1/k_s K_3 K_1$  and  $K_2/k_s K_3 K_1$  are determined from the slope and intercept respectively.

According to the equation above; when plots were made between  $1/k_{\text{obs}}$  and  $1/[S]$  a positive intercept would be observed which confirms the validity of

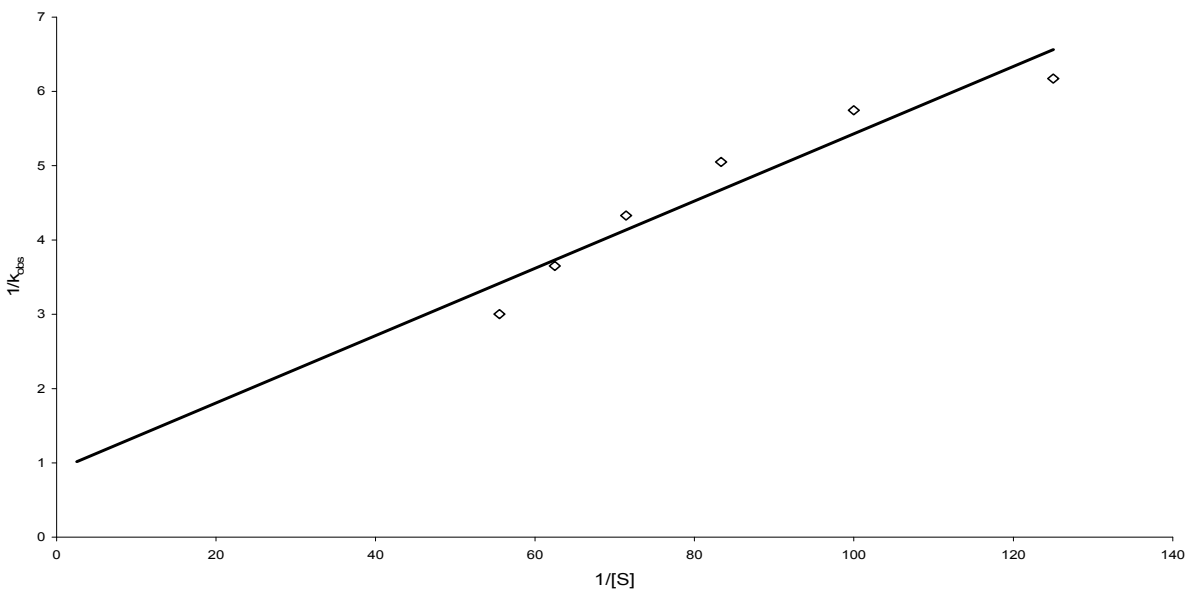
the mechanism and also the rate law (Figure 5 and 6).

The values of  $k_s K_1 K_3$  and  $K_2$  for Xylose and Arabinose can also be calculated from the double reciprocal plots as shown in the graphs below:



Solution condition:  $[Cr(VI)] = 0.001M$ ,  $[MnCl_2] = 0.0006M$ ,  $[KCl] = 5.00 \times 10^{-4} M$ ,  $[HClO_4] = 0.15M$ ,  $[NaClO_4] = 0.1M$

**Figure 5:** Plot of  $1/k_{obs}$  against  $1/[arabinose]$ .



Solution conditions:  $[Cr(VI)] = 0.001M$ ,  $[MnCl_2] = 0.0006M$ ,  $[KCl] = 5.00 \times 10^{-4} M$ ,  $[HClO_4] = 0.15M$ ,  $[NaClO_4] = 0.1M$

**Figure 6:** Plot of  $1/k_{obs}$  against  $1/[xylose]$ .

The values of  $k_s K_1 K_3$  for xylose and arabinose to be  $14.66 \text{ s}^{-1}$  and  $13.02 \text{ s}^{-1}$  respectively and the value of  $K_2$  as  $2.06 \text{ mol.dm}^{-3} \text{ s}$  and  $1.63 \text{ mol}^3 \text{ s}^{-1}$ , respectively.

## CONCLUSION

In the present study of oxidation of arabinose and xylose using Mn (II) chloride as a homogeneous catalyst, the entropy of activation was found as  $-113.86 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $-112.20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively. The observed negative entropy of activation clearly supports the interaction between the species, leading to the formation of an activated complex [16].

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