Kinetics and Mechanism of Ir (III) Catalysed Oxidation of D-Arabinose and D- Xylose by Acidic Solutions of Potassium per Manganate

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Abstract: *The kinetics of oxidation of D-arabinose and D-xylose by KMnO4 in acidic medium has been studied in the temperature range $30\text{-}40^0C$ in presence of Ir (III) catalyst. The reaction observed first oder kinetics on sugar which were independent on increasing of concentration of Ir (III) and ionic strength effect was found to be negligible. Arrhenius activation perameters have been calculated. Oxidative products were formic acid and erythronic acid.*

Keywords: *kinetics, sugars, Potassium permanganate, sulphuric acid, D-arabinose, D-xylose, Iridium chloride, Potassiumnitrate.*

I. Introduction

Carbohydrates are a biologically important substance whose microbiologicall and physiological activities depend largely on their redox behavior [1,2]. The literature investigates many information about the oxidation of sugars by varing of oxidant[3-6] 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) [10], ruthenate ion [11], Mn(VII) [12,14], Hg (II) [15] and Ir (III) [13].

Potassium permanganate ($KmnO_4$) is major versatile which has been used to oxidize variety of compounds like sugars [16-18], nicotine [19], acetanilide, malachite green [20] 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- arabinose and D- xylose by potassium permanganate and effect of Ir(III) upon the reaction rate in sulphuric acid medium leadinh to the development of reaction mechanism [3-6].

II. Materials

All chemicals were commercially available and used directly as received from manufacturer. The stock solutions were prepared for kinetics investigation in conductivity water of D- arabinose (spectrochem), D-xylose (spectrochem), Potassium permanganate (sigma aldrich), sulphuric acid (merck) and potassium nitrate (spectrochem)

III. Spectral measurement

The absorption spectra of different concentration of Potassium permanganate were recorded in the visible region between 300-600 nm. The values of Λ_{max} is 554 nm.

IV. Kinetics measurement

We studied efffect of substrate and oxidant concentration, PH added salt and temperature on the rate of oxidation of D-arabinose and D-xylose. The oxidation reaction using $KmnO_4$ as oxidant were done in H2SO4 medium in the range of 1-3.

The rate of reaction was measure using an aquamate UV visible spectrophotometer with serial no. 223118 equipped with a thermostated cell compartment and and interfaced with a computer. The rate of disappearance of KmnO4 was monitored at 554 nm.

The collect experimental data, appropriate quantities of solution of substrate and KNO_3 were measured into a glass vessel in a thermostated water bath. The reaction commenced by adding equisite volume of the oxidant solution placed separately in the same bath. The reaction was measured by withdrawing at reqlular intervals of time, an aliquot of the mixture and quickly transfering it into a sample cell and measuring the absorbance with the spectrophotometer at a predetermined Λ_{max}. The kinetics data was collected under a pseudo first order reaction condition with the concentration of substrate in large excess, compared to that of oxidant. The pseudo first order rate constant (Kobs) were calculated from the plot of log A (absorbance) against time.

V. Result and discussions

The kinetics of oxidations of D-arabinose and D-xylose by Ir (III) were investigated in the presence of acidic solution of $KmnO_4$ at different concentrationsof the reactants at constant ionic strength maintained by KNO_3. The reaction was followed by change in optical desity of $KmnO_4$ in reaction mixture at λ_{max} is 554 nm. The rate constants are calculated from the slope of the plot of log A_0-A_∞ vs time. The rate data was obtained in the form of pseudo first order rate constant (K_{obs}) under varing kinetics condition [7-10].

i. Effect of variation of oxidant concentration

The oxidation reaction of sugar with potassium permanganate has been studied at various initial concentrations (1, 2, 3, 4 and 5) $\times 10^{-5}$ mol dm^{-3} which kept the substrate as well as sulphuric acid concentration temperature constant at 2×10^{-4} mole/dm^3 of D-arabinose and D-xylose 2×10^{-4}mole/dm^3, 2×10^{-4}mole/dm^3 at 313 K respectively. That is supported by earlier work [9,18,20]. 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.

ii. Effect of variation of substrate concentration

The oxidation of D-arabinose and D-xylose were studied at various initial concentrations of D-arabinose (2×10^{-4} mole/dm^3) and D-xylose (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. It was obserbed that the plot of 1/K 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 ($C_6H_{12}O_6$.....MnO_4)[21-24]. The following probable reaction may observed in the oxidation of D-arabinose and D-xylose 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. The rate increases with increase in [H^+] indicating that only oneproton is involved in the reaction.

iii. Effect of variation of [$IrCl_3$] concentration

In presence of different concentratons (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} KMnO4, 2.0×10^{-4} mol dm^{-3} D-arabinose, 2.0×10^{-4} mol dm^{-3} xylose, , 2.0×10^{-2} mol dm^{-3} H_2SO_4, , 2.0×10^{-4} mol dm^{-3} KNO_3. But pseudo first order rate constants were independent of its changing concentrations (table-3 , fig-4)

The rate of oxidation of sugar increases with increase in temperature and calculated the values of activation parameters(table-4). The value of activation parameters shows that at least one of the reacting species in rate determining step involve a neutral molecule. The Arrehenius parameters were calculated from this way. The enthalpy of activation(ΔH^*)was calculated from the activation energy using the equation $K= A*e^{-Ea/RT}$ at temperature of 313K
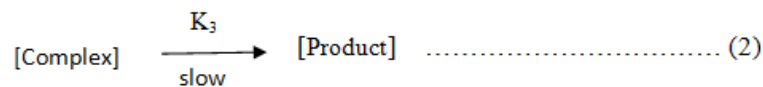
The entropy of activation (ΔS^*) in each reaction was the calculated as follows;

VI. Reaction mechanism

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

$$-d\,[MnO_4^-]/dt \quad = K[R\text{-}CHO][MnO_4^-]$$

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

$$R\text{-}CHO + MnO_4^- + H^+ \quad \rightleftharpoons \quad [R\text{-}CHO\ldots\ldots\ldots MnO_4^-] \quad \ldots\ldots\ldots\ldots (1)$$

$$[Complex] \quad \xrightarrow[\text{slow}]{K_3} \quad [Product] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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

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

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

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

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

$$d[MnO_4^-]/dt \quad = \quad K_3[Complex] \quad \ldots\ldots\ldots\ldots\ldots(iv)$$

$$\text{Or,} \quad -d[MnO_4^-]/dt \quad = \quad K_1 k_3[R\text{-}CHO]\,[O]\,/k_2 + k_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots(v)$$

Total $[MnO_4^-]$ can be considered as

$$[MnO_4^-]_T \quad = \quad [O] + [Complex] \quad \ldots\ldots\ldots\ldots (vi)$$

Now putting the value of complex

$$[MnO_4^-]_T \quad = \quad [O] \quad + \quad k_3[R\text{-}CHO]\,[O]\,/k_2 + k_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (vii)$$

From equation (vii) we can write

$$(k_1 + k_3)[MnO4^-]_T \quad \ldots..(viii)$$

$$(k_2 + k_3) + k_3[R\text{-}CHO]$$

$$[MnO_4^-] = \underline{\hspace{3cm}}$$

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

$$-d[MnO_4^-]/dt = \frac{k_1k_3[R\text{-}CHO]\,(k_2+k_3)\,[MnO_4^-]_T}{\{k_3+k_2+k_1\,[R\text{-}CHO]\}(k_2+k_3)} \quad \ldots\ldots\ldots\ldots\ldots(ix)$$

$$-d[MnO_4^-]/dt = \frac{k_1k_3[R\text{-}CHO]\,[MnO_4^-]_T}{k_3+k_2+k_1\,[R\text{-}CHO]} \quad \ldots\ldots\ldots\ldots(x)$$

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

So, the rate equation reduced to

$$d[MnO_4^-]/dt = \frac{k_1k_3[R\text{-}CHO]\,[MnO_4^-]_T}{k_2+k_3} \quad \ldots\ldots\ldots\ldots\ldots(xi)$$

$$d[MnO_4^-]/dt = K[R\text{-}CHO][MnO_4^-]_T \quad \ldots\ldots\ldots\ldots(xii)$$

Where $k = k_1k_3/k_2+k_3$

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

VII. Conclusion

In presence of Ir(III) chloride as a homogeneous catalyst the entropy of oxidation of D-arabinose and D-xylose was show as -179 J/mol/K and -178 J/mol/K respectively. The negative value of entropy of activation observed the interaction between the species, leading to the formation of an activation complex [12].

Acknowledgements

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Figure and table captions

Fig1. The linear plot of $\ln(A_0-A_\infty)/(A_t-A_\infty)$ vs time on rate of oxidation of D-xylose and D-arabinose.

Fig2. The linear plot for oxidation of D-xylose and D-arabinose at different $\mu^{1/2}$

Fig3. The linear plot of effect of concentration of oxidant KMnO4 on rate of oxidation of D-xylose and D-arabinose.

Fig4. The linear plot of concentration of substrate(10^{-4} mol dm^{-3}) vs K (10^{-4} S^{-1}) for effect of variation of substrate concentration.

Fig5. The linear plot of 1/K vs 1/[conc.] for D-xylose and D-arabinose.

Fig6. The linear plot of Kobs vs [H+] shows the effect of H+ on oxidation of D-xylose and D-arabinose.

Table1. Variation of rate constant (KS^{-1}) with KMnO$_4$, D-Arabinose and H$_2$SO$_4$ concentration.

Table2. Variation of rate constant (KS^{-1}) with KMnO$_4$, D-Xylose and H$_2$SO$_4$ concentration.

Table3. Effect of catalyst in the oxidation of D-arabinose and D-xylose.
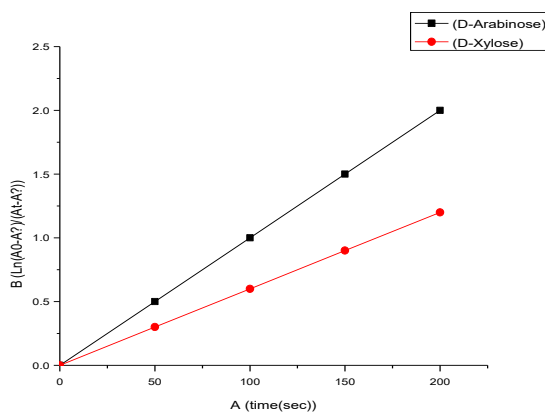
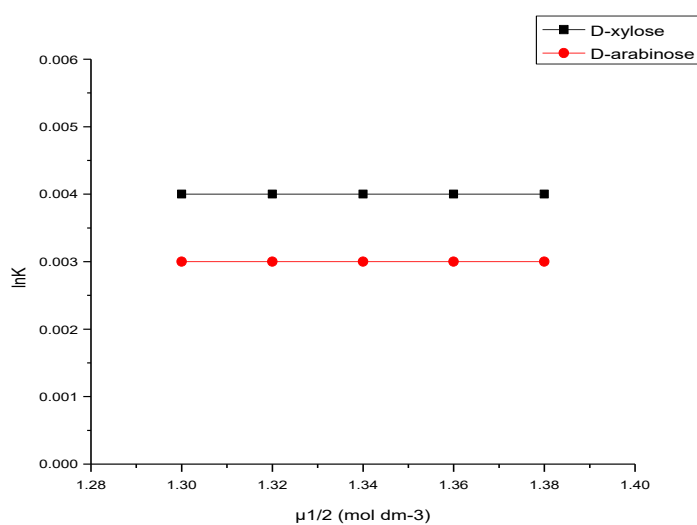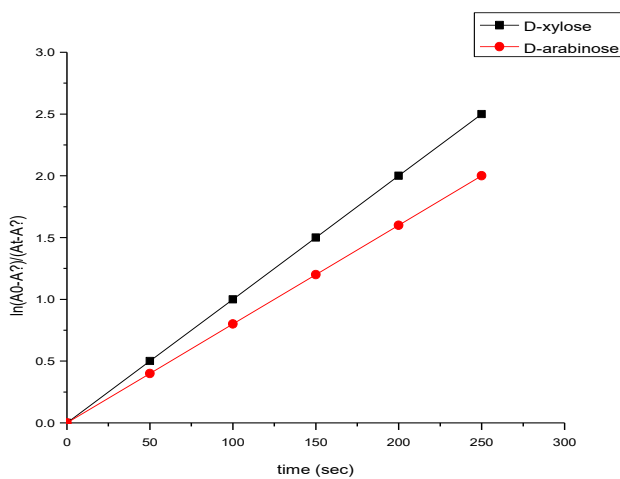Table4. values of activation parameters.
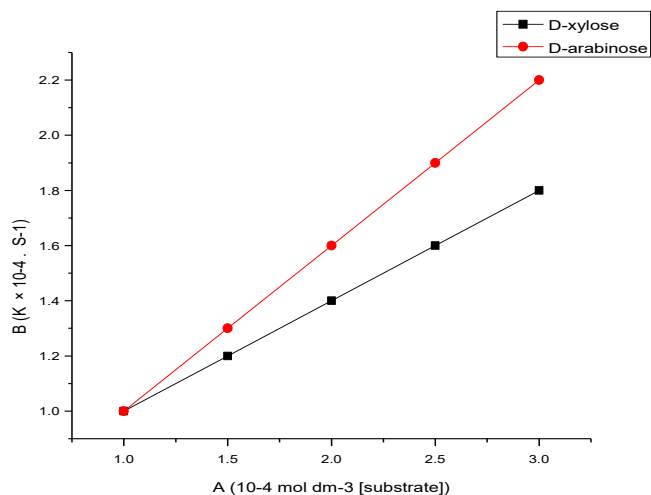
Fig1

Fig2

Fig3

Fig4
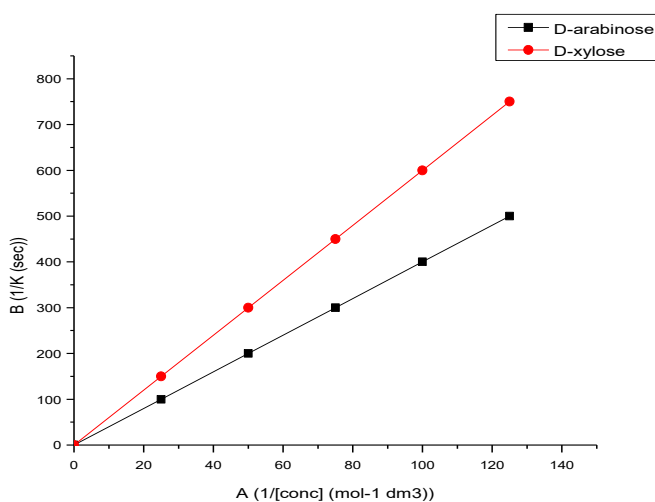
Fig5
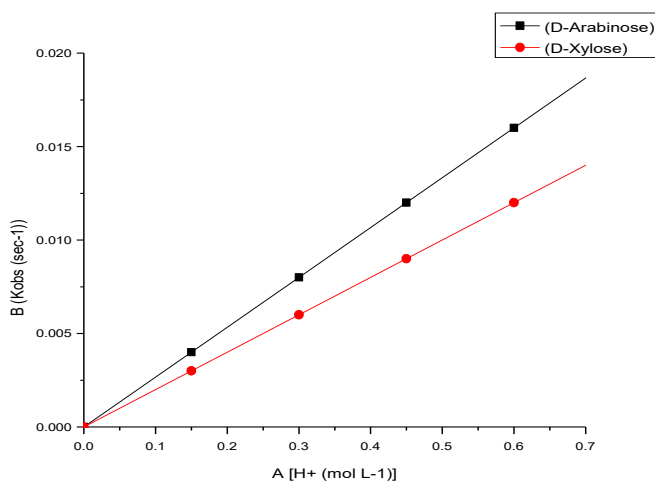
Fig6

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

10^{-5}[KmnO$_4$] (mol/ dm^3)	10^{-4} [D-Arabinose] (mol/ dm^3)	10^{-2}[H2SO4] (mol/ dm^3)	10^{-4} K (S^{-1})
1	4	1	1.44
2	4	2	1.58
3	3	3	1.67
4	1	4	1.61
5	2	5	1.46
2	3	2	1.44
2	4	2	1.46
2	1	2	1.20
5	2	3	1.30
6	3	2	1.40
2	4	4	1.50
3	3	2	1.60
2	3	5	1.20
2	3	2	1.40

Table 2
Variation of rate constant (KS^{-1}) with KMnO$_4$, D-Xylose and H$_2$SO$_4$ concentration

10^{-5}[KMnO$_4$] (mol/ dm^3)	10^{-4} [D-xylose] (mol/ dm^3)	10^{-2}[H2SO4] (mol/ dm^3)	10^{-4} K (S^{-1})
1	4	2	0.93
2	3	2	0.95
3	4	2	1.62
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

Table 3
Effect of catalyst in the oxidation of D-arabinose and D-xylose

[IrCl$_3$] $\times 10^{-4}$ mol-dm^{-3}	K $\times 10^{-4}$. S^{-1} arabinose	K $\times 10^{-4}$. S^{-1} xylose
1	1.58	1.61
2	1.61	1.62
3	1.57	1.62
4	1.58	1.60
5	1.60	1.63

Table- 4
VALUES OF ACTIVATION PARAMETERS
Temp. 313 K,[KNO$_3$] = 0.4 mol dm^{-3}, [H$^+$] = 2.0×10^{-2} mol dm^{-3}.
Substrate = 2.0×10^{-4} mol dm^{-3} D-arabinose, and 2.0×10^{-4} mol dm^{-3} D-xylose.

Substrate	$\sqrt{\mu}$ (mol dm^{-3})	Ea (KJ/mol)	ΔH* (KJ/mol)	ΔS* (J/mol)	ΔG$^{\neq}$ (KJ/mol)
D-Arabinose	0.4	20.96	55.69	-179.54	87.29
D-xylose	0.4	21.02	56.10	-178.23	86.52