Kinetics and mechanism of oxidation of L-sorbose and sucrose with potassium permanganate in acedic medium by spectrophotometry

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Abstract: *The oxidation of L- sorbose and sucrose with permanganate ion ($KMnO_4$) as oxidant was observed in acidic medium by visible spectrophotometric method in the temperature range (300 – 320) K. The reaction exihibit first oder kinetics with respect to change in concentration of L- sorbose, sucrose, 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 activstion parameters have been calculated. A suitable mechanism consistent with experimental finding has been proposed.*

Key Words: *L- Sorbose, Sucrose, Permanganate ion, first order, Indium chloride and potassium nitrate.*

I.   Introduction

Carbohydrate are a major source of energy which is compare with fuel by many investigater [10-18]. The biological and economic of the carbohydrates and mainly the mono and di-saccharide was highly dipendable for the study of their bio and physiochemical properties and reactivities [1-7]. Kinetics study of oxidation of reducing sugars L-sorbose and sucrose [3-9] by N-bromoacetamide in presence of Indium(III) chloride as a homogenous catalyst in H_2SO_4 acidic medium follows first order kinetics both with respect to sugar in different ionic strength and temperature.

The recent researcher discuss with the spectrophotometry study of kinetics and oxidation of L-sorbose and sucrose [2-3] by potassium permanganate in acidic medium and reaction will study at different concentration of substrate oxidation, ionic strength, H^+ ion and temperature. This paper describes the kinetics and mechanism of oxidation of L-sorbose and sucrose with potassium permanganate in acidic medium by spectrophotometry[4-6].

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 L-sorbose, sucrose, potassium permanganate in DM water. The reaction was studied on thermostat($\pm 1^0C$). The rate of reaction was followed by recording the optical density of KMno4 as a function of time on visible spectrophotometry. The rate constantswere calculated from the slop of log(concentration) vs time plots. The ionic strength was maintained throughout the experiment at 0.4 mole-dm^{-3} by adding KNO_3 solution.

III.   Result And Discussion:

The reactions were studied spectrophotometrically at 546nm 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(Kobs) under varying kinetics conditions[fig 1 & table 1]. The order of reaction with respect to L-sorbose and sucrose[table1 & table 2], oxidation and H^+ has been found identical. The effect of ionic strength product by KNO3 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 logKvs √μ as a straight line showed[fig 2] that rate of reaction was independent on ionic strength of the medium.

The oxidation reaction of sugar 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 L-sorbose and sucrose 4×10^{-4}mole/dm^3, 1×10^{-1}mole/dm^3 at 313K 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. The rate of reaction with sucrose was slower as compare with L-sorbose. By addition of catalyst(InCl3). It may be due to the hydrolysis of sucrose it to simpler units of monosaccharide.

The oxidation of L- sorbose and sucrose were studied at various initial concentrations of sorbose(2×10^{-4} mole/dm^3) and sucrose(4×10^{-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 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][fig 4]. The following probable reaction may observed in the oxidation of L-sorbose and sucrose 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 5]. 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-3). The value of activation parameters reflects that at least one of the reacting species in rate determining step involve a neutral molecule[fig 6]. The Arrehenius parameters were calculated as follows. The enthalpy of activation(ΔH^*)was calculated from the activation energy using the equationat temperature of 313K

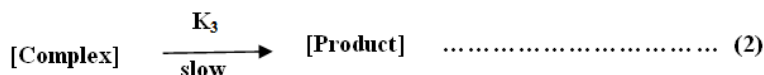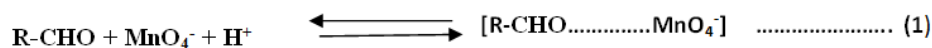The entropy of activation (ΔS^*) in each reaction was evaluated in table 3

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} L-sorbose, 4.0×10^{-4} mol dm^{-3} sucrose, 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-4 , fig-4)

IV. Reaction Mechanism:

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

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

Where R-CHO represents the concentrations of L-Sorbose and MnO$_4^-$ is of oxidant.

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

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

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

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

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

$$[Complex] = K_1[R\text{-}CHO]\,[O]\,/k_2 + k_3$$

At steady state rate of disappearance of MnO_4^- may be: .... **(iii)**

$$d[MnO_4^-]/dt = K_3[Complex] \quad .... \text{ (iv)}$$

Or, $\quad -d\,[MnO_4^-]/dt = K_1k_3[R\text{-}CHO]\,[O]\,/k_2 + k_3 \quad .... \text{ (v)}$

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

$$[MnO_4^-] = [O] + [Complex] \quad .... \text{ (vi)}$$

Now putting the value of complex

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

From equation (vii) we can write

$$[MnO_4^-] = \frac{(k_1+k_3)[MnO4^-]_T \,...................(viii)}{(k_2+k_3) + k_3[R\text{-}CHO]}$$

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

$$-d\,[MnO_4^-]/dt = \frac{k_1k_3[R\text{-}CHO]\,(k_2+k_3)\,[MnO_4^-]_T}{\{k_3+k_2+k_1\,[R\text{-}CHO]\}(k_2+k_3)_3} \quad ....\text{(ix)}$$

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

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

So, the rate equation reduced to

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

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

Where $k = k_1k_3/k_2+k_3$

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

V.   Conclusion

When we used In(III) chloride as a homogeneous catalyst then the entropy of oxidation of L-sorbose and sucrose was show as -167 J/mol/K and -192 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 [24].

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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 L-sorbose and sucrose.

Fig2. The linear plot for oxidation of L-sorbose and sucrose at different $\mu^{1/2}$

Fig3. The linear plot of effect of concentration of oxidant KMnO4 on rate of oxidation of L-sorbose and sucrose.

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 L-sorbose and sucrose.

Fig6. The linear plot of logk vs $1/T(K^{-1})$ for L-sorbose and sucrose.

Table1. Variation of rate constant (KS^{-1}) with $KMnO_4$, L-sorbose and H_2SO_4 concentration.

Table2. Variation of rate constant (KS^{-1}) with $KMnO_4$, sucrose and H_2SO_4 concentration.

Table3. values of activation parameters.

Table4. Effect of catalyst in the oxidation of L-sorbose and sucrose.

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

10^{-5}[KmnO$_4$] (mol/ dm^3)	10^{-4} [L-Sorbose] (mol/ dm^3)	10^{-2}[H2SO4] (mol/ dm^3)	10^{-4} K (S^{-1})	[KNO$_3$] (mol/ dm^3)
2	3	2	1.85	0.4
3	3	3	1.86	0.4
4	3	4	1.77	0.4
5	2	5	1.83	0.4
6	3	6	1.40	0.4
2	4	2	1.45	0.4
2	5	2	1.42	0.4
2	6	2	1.20	0.4
6	4	2	1.40	0.4
6	6	2	1.50	0.3
2	3	4	1.60	0.5
4	3	2	1.70	0.4
2	3	6	1.40	0.4
2	3	2	1.30	0.4

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

10^{-5}[KmnO$_4$] (mol/ dm^3)	10^{-4} [Sucrose] (mol/ dm^3)	10^{-2}[H2SO4] (mol/ dm^3)	10^{-4} K (S^{-1})	[KNO$_3$] (mol/ dm^3)
2	5	2	0.96	0.4
3	5	2	0.99	0.4
4	5	2	0.99	0.4
5	2	2	1.10	0.4
6	3	3	1.20	0.5
2	4	2	1.02	0.4
2	5	3	1.03	0.4
2	6	4	0.99	0.4
4	4	5	0.96	0.4
6	6	6	0.98	0.5
2	6	2	1.01	0.3
2	6	3	1.02	0.4
2	3	2	1.04	0.4
2	3	2	0.98	0.4

TABLE- 3
VALUES OF ACTIVATION PARAMETERS
Temp. 313 K,[KNO$_3$] = 0.4 mol dm^{-3}, [H$^+$] = 0.2 mol dm^{-3}.
Substrate = 2.0 × 10^{-4}mol dm^{-3} L- sorbose, and4.0 × 10^{-4} sucrose.

substrate	√μ (mol dm^{-3})	Ea (KJ/mol)	ΔH* (KJ/mol)	ΔS* (J/mol)	ΔG≠ (KJ/mol)
L- Sorbose	0.4	51.20	28.14	-167	80.42
sucrose	0.4	23.45	10.29	-192	70.39

Table 4

Effect of catalyst in the oxidation of L-sorbose and sucrose

[InCl$_3$] × 10^{-4} mol-dm^{-3}	K × 10^{-4} . S^{-1} sucrose	K × 10^{-4} . S^{-1} L- sorbose
1	1.23	1.65
2	1.25	1.62
3	1.27	1.66
4	1.30	1.68
5	1.21	1.63
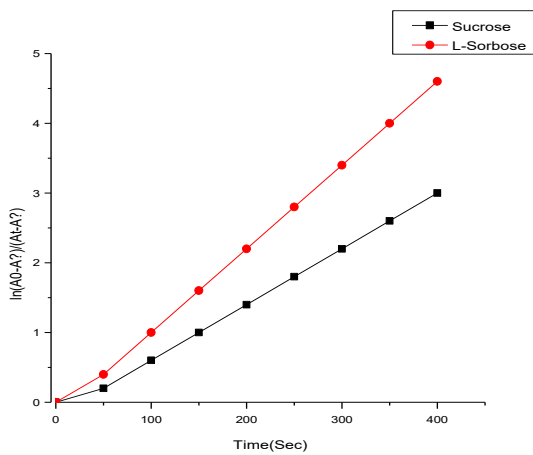
Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6