

Kinetics and Mechanism of Sugar Oxidation by KMnO_4 in NaOH Medium.

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ABSTRACT

The kinetics of potassium permanganate oxidation of sugars have been studied in sodium hydroxide solution. The reaction shows first-order dependence on [Glucose] and $[\text{OH}^-]$ and the oxidation process is independent of $[\text{MnO}_4^-]$ for all the reducing sugars. The reaction is unaffected by ionic strength of the solution, Michaelis-Menten kinetics show the presence of an intermediate complex.

Activation parameters have been evaluated and a tentative reaction mechanism has been proposed. A single rate expression

$$\frac{-d[\text{MnO}_4^-]}{dt} = k[S][\text{OH}^-] \text{ is given.}$$

(Keywords: potassium permanganate, ferrous ammonium sulfate, glucose, fructose, xylose, sodium hydroxide)

INTRODUCTION

Kinetics and mechanism of sugar oxidation in both acidic and alkaline media have been delved into extensively. In fact, several oxidants have been employed, which include diperiodatoargentate(III)¹, chromic acid², and Vanadium(V)³. In this study the data obtained was compared with those of simpler mono- and polyhydric alcohols and a three step mechanism involving-H bond fusion yielding glucosones as main products was suggested. Other oxidants includes, osmium tetroxide⁴, Cu(II) ⁵, periodate⁶, Iridate(IV), Tetrachloroaurate(III)⁷, Thallium(III)⁸, mixture of chromic and perchloric acids⁹, and Mn(III) ¹⁰.

Oxidation of sugars by KMnO_4 have also received some attention¹¹. However, this research will help

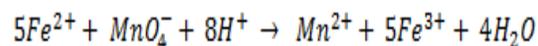
serve as an appraisal to previous investigations by focusing on the reaction in NaOH medium which hitherto has not been reported.

MATERIALS AND METHODS

Stock solutions of sugars, sodium hydroxide, and potassium nitrate, KMnO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (BDH (AR) grade) were prepared freshly with double-distilled water.

Standardization of Potassium Permanganate

Stock solution of potassium permanganate was standardized in acidified ferrous ammonium sulfate.



Spectral Measurement

The maximum absorption of the oxidant, KMnO_4 was reported to be 525nm. All kinetic studies were undertaken at this fixed wavelength.

Kinetic Measurement

The rate of oxidation as a function of oxidant, substrate, ionic strength, and temperature were studied using a uv-1800 Shimadzu spectrophotometer with a thermostated cell compartment and interfaced with a computer. Appropriate quantities of the solution of alcohol, potassium nitrate, and sodium hydroxide were measured into the cuvette. Consequently, the reaction was kick started by adding requisite volume of the oxidant solution (all stock solutions were kept in the water bath for 30 minutes before the kinetic runs).

The kinetic data were obtained via pseudo- first order condition with the concentration of the substrate in large excess compared with the oxidant concentration. The pseudo- first order rate constant (k_{obs}) were calculated from the plot of $\ln A$ versus time.

Product Analysis

Thin layer chromatography was used to identify the oxidation products by using silica gel G with 1-butanol-acetic acid-water as mobile phase. The result indicated the presence of gluconic acid ($R_f = 0.38$) for glucose.

Polymerization Test

10% acrylamide was added to the reaction mixture. Gel formation was not observed, indicating absence of free radicals.

RESULTS AND DISCUSSION

Effect of Oxidant

The reaction was studied at various [oxidant], but at constant [sugar], [NaOH], [KNO₃], and temperature. The fairly constant values of k_{obs} with [oxidant] was observed (Table I). This indicates the independency of the reaction rate with the concentration of the oxidant.

Effect of Sugar Concentration

The reaction was investigated at various [sugar], but at constant [oxidation], [NaOH], [KNO₃] and temperature. k_{obs} increases with increase in [sugar] (Table 2), and a plot of $\ln k_{obs}$ versus $\ln[sugar]$ gave a slope of 1, indicating a first order dependence with respect to [sugar]. Double-reciprocal plot of $1/k_{obs}$ versus $1/[sugar]$ gave an intercept, showing the presence of an intermediate complex(Figure 1). The second order rate constants were $2.21M^{-1}S^{-1}$ (glucose), $2.28 M^{-1}S^{-1}$ (fructose) and $2.89M^{-1}S^{-1}$ (xylose).

Table 1: Pseudo-First Order Rate Constant versus [KMnO₄].

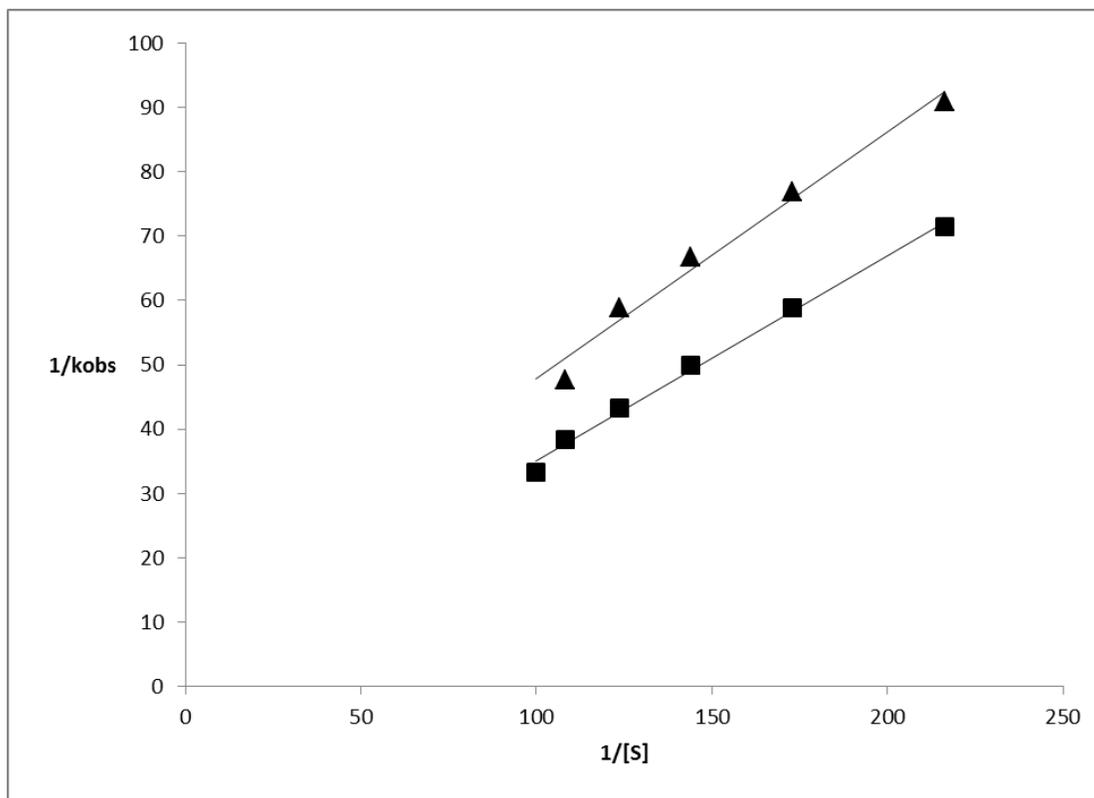
10 ⁴ [KMnO ₄]/M	10 ³ k _{obs} /s ⁻¹		
	Glucose	Fructose	Xylose
0.96	7.01	8.11	11.15
1.16	6.96	7.96	11.11
1.35	6.85	8.09	10.89
1.54	6.97	7.87	11.13
1.73	6.94	8.06	11.07

[sugar] 2.31 x 10⁻³M [NaOH] 1.16 X 10⁻³M [KNO₃] 0.347M T=298K

Table 2: [Sugar] Dependence.

10 ³ [sugar]/M	10 ² k _{obs} /s ⁻¹		
	Glucose	Fructose	Xylose
4.62	0.90	1.10	1.40
5.78	1.30	1.30	1.70
6.94	1.50	1.50	2.00
8.09	1.80	1.70	2.31
9.25	2.00	2.10	2.60
10	2.20	2.40	3.01

[KMnO₄] 1.73 X 10⁻⁴M [NaOH] 1.16 X 10⁻³M [KNO₃] 0.347M T=298K



(■ Xylose ▲ Fructose)

Figure 1: Plot of $1/k_{\text{obs}}$ versus $1/[S]$

Effect of Hydroxyl Ion Concentration

Hydroxyl ion dependence on the rate of oxidation was monitored by varying $[\text{OH}^-]$, while [oxidant], [sugar], $[\text{KNO}_3]$, and temperature remained constant. k_{obs} increased with increase in $[\text{OH}^-]$ (Table 3), and the slope of the plot of $\ln k_{\text{obs}}$ versus $\ln[\text{OH}^-]$ gave 1 for all the sugars, showing a first order dependence on $[\text{OH}^-]$.

Effect of Ionic Strength

The effect of ionic strength on the rate of oxidation was studied at constant [oxidant], [sugar], $[\text{OH}^-]$, and temperature. While ionic strengths were varied for all the kinetic runs. k_{obs} was invariant with the ionic strength of the solution and a plot of $\ln k_{\text{obs}}$ versus $I^{1/2}$ gave a straight line with slope zero, suggesting that a non-ionic specie is involved in the rate limiting step (Figure 2).

Effect of Temperature

The effect of temperature was investigated at various temperature and maintaining all initial concentrations of the reactants constant. k_{obs} increased with increase in temperature. The Arrhenius energy of activation was evaluated from the plot of $\ln k_{\text{obs}}$ vs $1/T$. Table 4 shows the values of E_a and all the activation parameters were obtained by using the below relationship¹²:

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$E_a = \Delta H^\ddagger + RT$$

$$\Delta G^\ddagger = 2.303RT \left(\log \frac{RT}{Nh} - \log k \right)$$

$$\Delta S^\ddagger = 2.303R \log A - \log \frac{e^{RT}}{Nh}$$

Table 3: [OH⁻] Dependence.

104[OH ⁻]/M	10 ³ k _{obs} /s ⁻¹		
	Glucose	Fructose	Xylose
3.85	4.01	4.50	6.15
7.71	5.22	6.00	8.28
11.60	6.92	8.06	11.05
15.40	8.15	11.32	13.27

[KMnO₄] 1.73 X 10⁻⁴M [sugar] 2.31 x 10⁻³M [KNO₃] 0.347M T=298K

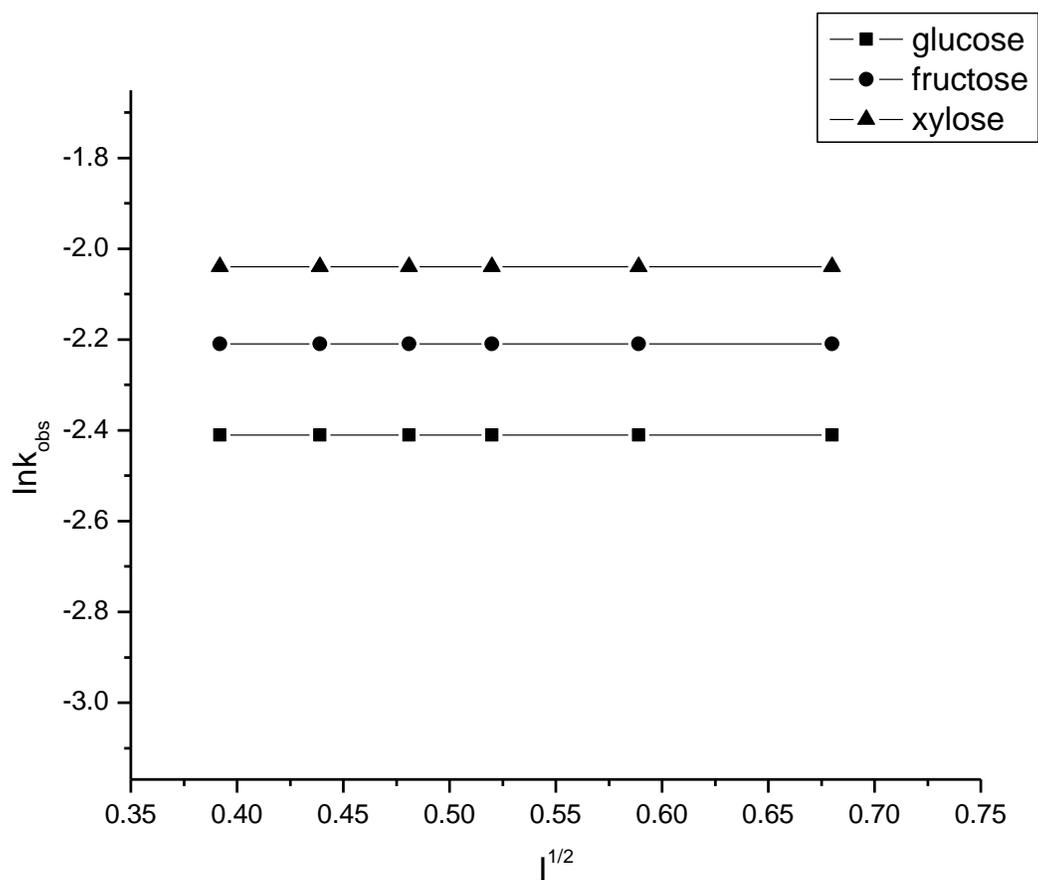


Figure 3: Plot of ln k_{obs} versus I^{1/2}

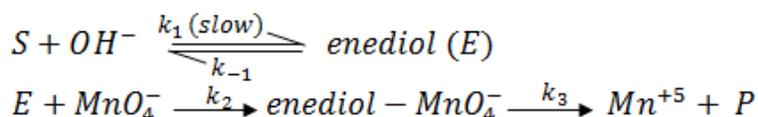
Table 4: Activation Parameters.

Sugar	E _a (kJmol ⁻¹)	ΔH [#] (kJmol ⁻¹)	ΔS [#] (KJK ⁻¹ mol ⁻¹)	ΔG [#] (kJmol ⁻¹)
Glucose	20.39	17.73	-0.167	31.09
Fructose	19.20	16.70	-0.165	31.01
Xylose	15.62	15.83	-0.174	30.42

Mechanism and Rate Law

The presence of enediol was manifested as a result of the decolorization of 2,6-dichlorophenolindophenol by the reaction solution. Furthermore, Michaelis-Menton plot of $1/k_{\text{obs}}$ versus $1/[\text{sugar}]$ revealed the presence of an intermediate complex.

The major reaction product have been identified to be acid. Similar ΔG^\ddagger indicate same mechanism for all the sugars investigated and $-\Delta S^\ddagger$ is indicative of the fact that the entropy decreased upon achieving the transition state, which often reveal an association mechanism. Furthermore, $-\Delta S^\ddagger$ show that the reaction occurred between ions of similar charges.



The above data showed that the rate law is:

$$\frac{-d[MnO_4^-]}{dt} = k_1[S][OH^-] \quad (1)$$

$$\frac{d[E]}{dt} = k_1[S][OH^-] - k_{-1}[E] - k_2[E][MnO_4^-] \quad (2)$$

Applying steady state approximation:

$$0 = k_1[S][OH^-] - k_{-1}[E] - k_2[E][MnO_4^-]$$

$$k_{-1}[E] + k_2[E][MnO_4^-] = k_1[S][OH^-]$$

$$[E] = \frac{k_1[S][OH^-]}{k_{-1} + k_2[MnO_4^-]} \quad (3)$$

$$\frac{-d[MnO_4^-]}{dt} = k_2[E][MnO_4^-] \quad (4)$$

From Equations 3 and 4:

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_2 k_1 [S][OH^-][MnO_4^-]}{k_{-1} + k_2[MnO_4^-]} \quad (5)$$

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_1[S][OH^-][MnO_4^-]}{\frac{k_{-1}}{k_2} + [MnO_4^-]} \quad (6)$$

Step 2 is very fast (k_2 is far greater than k_{-1}). Therefore $\frac{k_{-1}}{k_2}$ is negligible. Thus

Equation 6 becomes:

$$\frac{-d[MnO_4^-]}{dt} = k_1[S][OH^-]$$

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