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Kinetics and mechanism of oxidation of sugar and sugar alcohols by KMnO$_4$

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The kinetics of carbonate sugars and sugar alcohols by potassium permanganate in oxidation hydrogen / NaOH buffer have been investigated spectrophotometrically under pseudo-first order conditions and over a wide range of experimental conditions. Each reaction is first order with respect to the substrate and oxidant. The kinetic data for the oxidation by alkaline KMnO$_4$ solution reveal that pseudo-first order rate constants increased as the pH, Ionics strenghts, temperature as well as the KMnO$_4$ concentration increased. The rate constant also increases with increase in sugar concentration with the exception of sorbitol which its rate constant decreased with increase in sugar concentration. The mechanisms were found to proceed through the formation of enediol intermediate complex. The order of reactivities of sugar and sugar alcohols was sucrose > maltose > sorbitol > glucose> mannitol >fructose. The Arrhenius activation energy and other dynamic activation parameter are reported.

Keywords: KMnO$_4$ (Potassium permanganate), pseudo-first order (K$_{obs}$), activation, oxidation, reactivities, mechanism.

INTRODUCTION

Carbohydrate are a major sources of energy for living organisms and the understanding of the oxidation of sugars is therefore of immence importance. (Pigman and Horton, 1972). The oxidation of sugars especially the mono and D-Sacharides have been the subject of extensive research and several reviews already exist on it (Evans, 1929; Pigman and Horton, 1980). Sugar oxidation occurs under different conditions of pH temperature and ionic strength giving product that depend on the reactions used (Gupta et al., 1983). The kinetics and mechanism of oxidation of monosacharides and disaccharides have been studied in both acidic and alkaline media, employing different transition metal ions, inorganic acids, complex ions and hydrogen peroxide as oxidants. The results showed that the mechanism may depend on the nature of the substrates, in some cases it involves the formation of intermediate complex, free radical or transition states (Gupta and Basu, 1979).

Earlier the oxidation of sugars and sugar alcohols with various oxidant and catalysed by acids have been reported (Gupta and Basu, 1979; Norman, 1987; Gupta et al., 1981).

Most of the studies carried out in perchloric acid media reported that the reaction was acid catalysed. (Shukla and Kesaryari, 1984; Moore, 1972). Compared to studies on the oxidation of sugars, the oxidation of sugar acohols has received little attention. This paper describes the kinetics and mechanism of oxidation of sugars and sugar alcohols. We want to compare the reactivities of both sugars and sugar alcohols, their rates of oxidation and to establish the reaction pathways for the oxidation reaction.

MATERIALS AND METHODS

Chemical reagents

The chemical reagents used in this study were obtained from Aldrich chemical company. They were of analytical grade and used without further purification. Stock solutions of D-glucose, D-fructose, D-maltose, D-sucrose, D-mannitol, D-sorbitol, potassium perman-ganate in distilled water. Fresh solution of buffer was also pre-

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Table 1. Variation OF rate constant with KMnO$_4$ concentration AT = 35°C, pH = 11.0, [KNO$_3$] = 0.2 M, [Sugar] = 0.005 M.

[KMnO$_4$] X 10^{-4}M	GLUCOSE k_{obs}X 10^3, s^{-1}	FRUCTOSE k_{obs}X 10^3, s^{-1}	SUCROSE k_{obs}X 10^3, s^{-1}	MALTOSE k_{obs}X 10^3, s^{-1}	MANNITOL k_{obs}X 10^3, s^{-1}	SORBITOL k_{obs}X 10^3, s^{-1}
2	-	11.70	1.20	2.20	9.00	2.43
3	17.20	13.80	3.00	2.50	-	2.85
4	22.70	16.20	3.50	2.60	15.00	2.94
5	-	18.00	3.60	2.83	16.00	-
6	23.70	18.20	3.70	-	17.00	3.05
7	-	18.50	3.80	-	18.00	3.15
8	-	19.00	3.90	3.00	20.00	3.83

pared when needed from its component in distilled water.

Spectral measurement

The absorption spectra of different concentration of KMnO$_4$ were recorded in the visible region between 300 - 600 nm. The values of λmax is 546 nm.

Kinetic measurement

We studied the effect of substrate and oxidant concentration, pH added salt and temperature on the rate of oxidation of fructose, sucrose, maltose, glucose, mannitol and sorbitol. The oxidation reactions using KMnO$_4$ as oxidant were done in NaHCO$_3$/NaOH alkaline buffer in the range of 9.6 - 11.0.

The rate of reaction was measure using an aquamate uv visble spectrophotometer with serial no 112817 equipped with a thermo-stated cell compartment and interfaced with a computer. The rate of disappearance of KMnO$_4$ was monitored at 546 nm.

To collect experimental data, appropriate quantities of solution of substrate and potassium nitrate were measured into a glass vessel in a thermostated water bath. The reaction commenced by adding requisite volume of the oxidant solution placed separately in the same bath. The reaction was measured by withdrawing at regular 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 λmax. The kinetic 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 constants (k_{obs}) were calculated from the plot of log A (Absorbance) against time, (Baipal, 1996; Gupta and Nasu, 1979; Odebunmi et al., 1999).

RESULTS AND DISCUSSION

Pseudo-order conditions were maintained throughout the experiments with the first concentration of the sugars always in excess of the concentration of the oxidant.

Effect of oxidant concentration

The reaction were studied at various initial oxidant con-centration (oxidant)$_o$, but at constant initial concentration of the sugars, (sugars)$_o$, constant pH ionic strength, and temperature. The first-order rate constants (k_{obs}) at various initial concentrations of KMnO$_4$ have been evaluated from the slopes of the plot of logarithm of absorbance versus time. The result presented in Table 1 shows that the first-order rate constants exhibit a steady increase with increase in the concentration of KMnO$_4$ solution reaction. The is totally dependent on KMnO$_4$ concentration.

Effect of substrate concentration on rate of oxidation

The reactions were studied spectrophotometrically at 546 nm using aquamate spectrophotometer with a thermo-spacer cell compartment. The pseudo first-order rate constants were determined at different initial concen-trations of the sugars while maintaining constant the other variables, that is, the concentration of the KMnO4 solution; pH, ionic strength and temperature (Table 2A). The values of k_{obs} for the KMnO$_4$ oxidation of sugar were calculated from the slopes of the plots of log absorbance against time.

The second order rate constants k_2 was obtained from the slope of the linear plot (Figure 1) of pseudo-first order rate constant, k_{obs} against substrate concentration. The values are presented as Table 2b. The reaction rate increased with an increase in substrate concentration. A marginal decrease in reaction rate was observed in the case of sorbitol as a substrate. From the values of the second-order rate constant (k_2), the relative reactivity of the sugars and sugar alcohols are sorbitol > maltose > glucose > fructose > sucrose> mannitol.
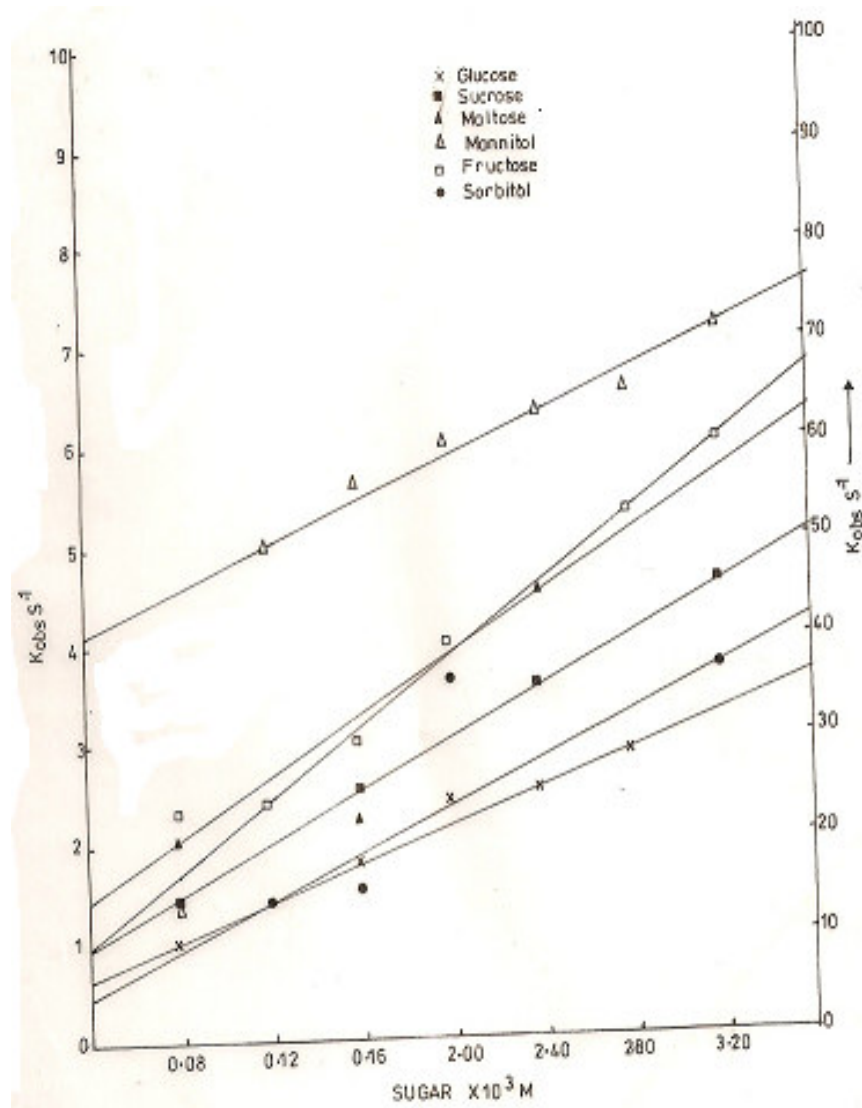
Sorbitol is the most reactive sugars followed by maltose. This shows that disaccharides are more reactive than monosaccharides and for the sugar alcohols; sor-bitol is more reactive than mannitol. The order is sorbitol greater than mannitol.

Effect of variation of pH

The effect of pH on the rate of oxidation of the sugars

Table 2A. Variation of rate constant with the substrate concentration at TEMP = 35°C, PH =11.0, [KNO$_3$] = 0.2 M, [KMnO$_4$] = 0.005 M.

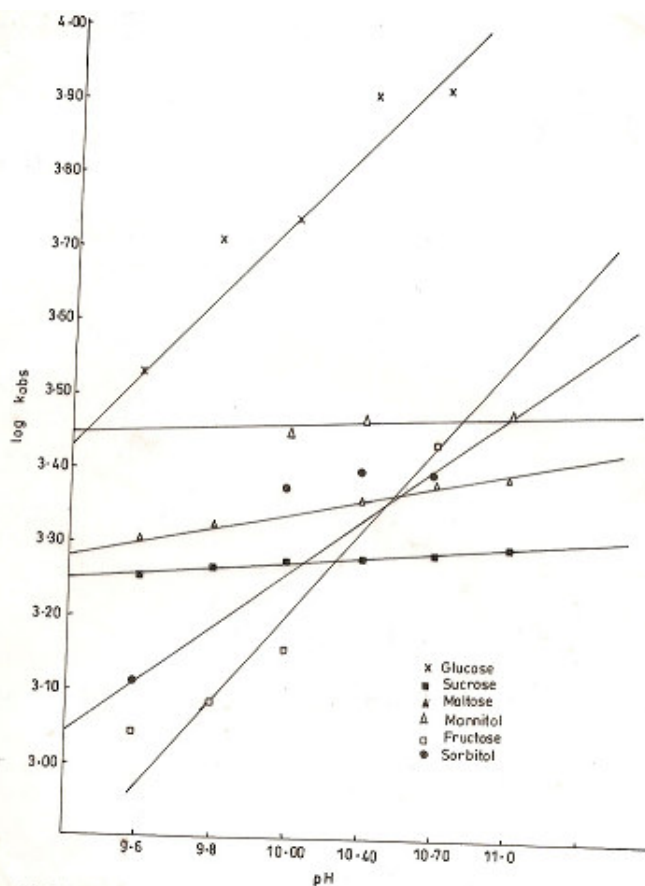| [SUGAR]	GLUCOSE k_{obs} (s^{-1})	FRUCTOSE k_{obs} (s^{-1})	SUCROSE k_{obs} (s^{-1})	MALTOSE k_{obs} (s^{-1})	MANNITOL k_{obs} (s^{-1})	SORBITOL k_{obs} (s^{-1})
0.08	0.009	0.0025	0.0013	0.0080	0.0011	0.0127
0.12	0.014	0.0052	0.0038	0.0090	-	0.0126
0.16	-	0.0055	-	0.0075	0.0018	0.0125
2.00	0.062	0.0056	0.0052	-	0.0020	0.0107
2.40	0.0.65	0.0058	0.0061	0.0088	0.0021	0.0106
2.80	0.070	-	0.092	0.0097	0.0022	-
3.20	-	0.0063	0.094	0.0098	0.0024	-

Figure 1. k$_{obs}$ versus sugar: For sugar oxidation by KMnO$_4$.

and sugar alcohols was studied at 35°C in the pH range 9.60 to 11.00, constant ionic strength of 0.2M, constant concentrations of KMnO$_4$ and substrates (0.05) M. The results obtained show that the rate of oxidation increased significantly with increase in the pH of the reaction medium. The plots of logk$_{obs}$ against pH were linear (Figure 2) for all the reactions. These show that the reactions were based-catalyzed.

Table 2B. Second - Order rate constants for oxidation of sugar by $KMnO_4$ at T = 35°C.

Sugar	k_2 dm^3 mol^{-1} s^{-1}
Glucose	4.32×10^{-4}
Fructose	3.31×10^{-4}
Sucrose	1.38×10^{-3}
Maltose	5.76×10^{-4}
Mannitol	3.68×10^{-4}
Sorbitol	5.48×10^{-4}

x Glucose
■ Sucrose
▲ Maltose
Δ Mornitol
□ Fructose
● Sorbitol

Figure 2. log kobs versus pH for sugar oxidation by KMnO4 at 60°C.

Effect of salt concentration

The effect of variation of the concentration of KNO_3 on the rate of oxidation of the sugars by $KMnO_4$ was studied at constant concentration of $KMnO_4$ (2.5×10^{-3}), Sugar (5.0×10^{-3}), pH (11.0) and temperature (35°C). The concentration of KNO_3 varied between 0.10 and 0.40 M. The results presented in Table 3 shows that the oxidation rate was found to increase with increase in ionic strength.

This same trend was observed by Gupta and Nasu (1980), Odebunmi and Co-workers (1999), Gupta and CO workers (1983) and Olavi-et al (1985). When log k_{obs} was plotted against $\sqrt{I}$ it was observed that the product

ZAZB is +Ve. This shows that the rate constant increases with increase in ionic strength for both sugars and sugar alcohols. This suggests that the reactions occur between ions of similar charge (Figure 3).

Effect of temperature

The oxidation of the sugars was carried out at different temperatures from 30°C to 60°C while maintaining constant the concentrations of $KMnO_4$ (0.005 M) substrates (0.1 M), KNO_3 (0.2 M) and pH (11.00). The first order rate constant increases with increase in temperature as the data in Table 4 show. The Arrehenius parameters (that is, Ea and A) were calculated from the logarithmic plot of the second order rate constant as a function of the reciprocal of the temperature in Kelvin. The values of the Arrenhenius activation energy, Ea for the oxidation of glucose, fructose, sucrose, sorbitol, mannitol and maltose obtained from the slope of the linear plots are 80.77, 60.00, 42.86, 60.00 60.78 and 46.59 kJ mol^{-1} respectively, showing that fructose and sorbitol have equal activation energy.

The other thermodynamic activation parameters were calculated as follows. The enthalpy of activation ($\Delta H^{\#}$) was calculated from the activation energy using the equation: $\Delta H^{\#}$ = Ea - RT, at Temperature of 313K.

The entropy of activation ($\Delta S^{\#}$) in each reaction was then evaluated as follows:

$$k_r = \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{\frac{\Delta H^{\neq}}{-RT}}$$

$$A = \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}}$$

(where K = Boltzman constant)

$$\log_e A = \log_e \frac{kT}{h} + \frac{\Delta S^{\#}}{R}$$

$$\Delta S^{\#} = 2.303 \, R \left(\log_{10} A - \log_{10} \frac{kT}{h}\right)$$

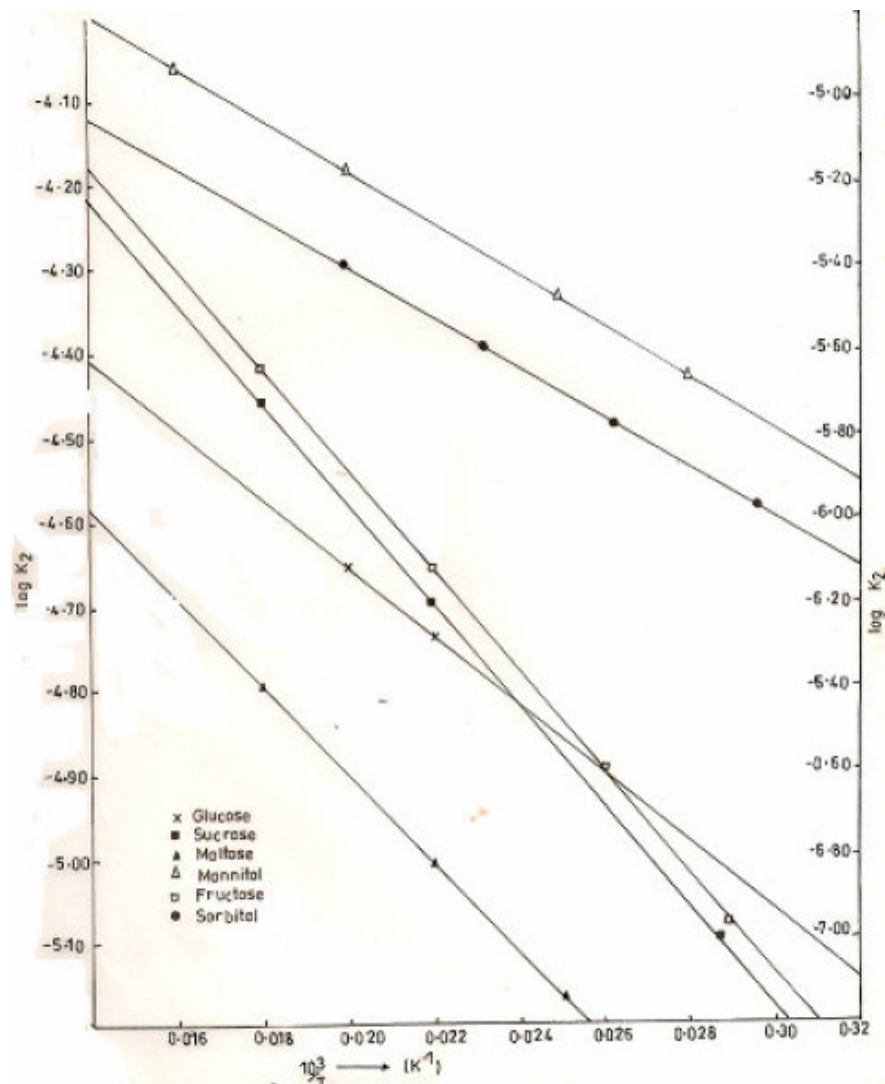All the calculations were done at T = 313K, hence $\Delta S^{\#}$ = 2.303R (Log_{10} - 12-81).

The value of $\Delta G^{\#}$ have been calculated at 313 K from the relation $\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#}$. The values of the activation parameter are recorded in Table 4. The negative value of entropies of activation ($\Delta S^{\#}$) indicate that the reaction occur between ions of similar charge (Shukla and Kesariyam, 1984).

Reaction mechanism and rate laws

In the oxidation of substrates with potassium permanga-

Table 3. Variation of rate constants with the KNO$_3$ concentration; T = 35°C, pH = 11.0, [KMnO$_4$] = 2.5 X 10^{-3} M, [Sugar] = 5.0 X 10^{-3} M

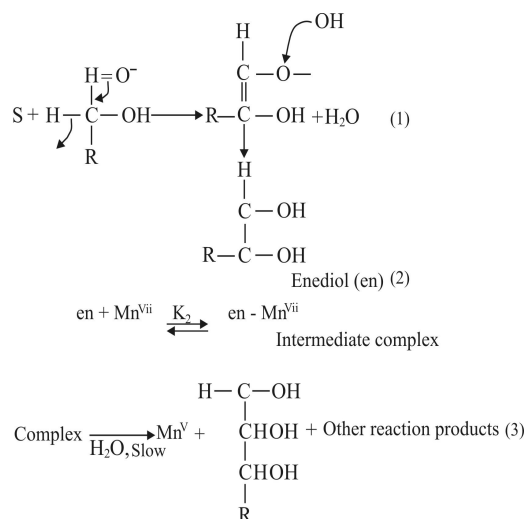| (KNO$_3$) M	GLUCOSE k_{obs}X 10^2 S^{-1}	(FRUCTOSE k_{obs}X 10^2 S^{-1}	SUCROSE k_{obs}X 10^2 S^{-1}	MALTOSE k_{obs}X 10^2 ,S^{-1}	MANNITOL k_{obs}X 10^2 S^{-1}	SORBITOL k_{obs}X 10^2 S^{-1}
0.10	40.56	12.85	1,20	2.38	2.00	2.10
0.15	59.26	15.20	1.40	2.40	2.30	2.18
0.20	89.50	23.30	1.60	2.42	-	-
0.25	95.30	30.70	1.80	2.77	3.00	2.20
0.30	-	36.10	1.90	2.95	4.00	2.40
0.40	98.20	40.10	2.00	-	11.00	2.90

Figure 3. log k$_{obs}$

ganate an enediol formation resulted and there is forma-tion of a 1.1 intermediate complex. The oxidation of the sugars takes place by the interaction between the Mn (VII) and the sugars resulting in electron transfer between them to give an enediolintermediate complex which disproportionates in a slow step to give a free radical.

The free radical then reacts with another molecule of Mn (VII) in a fast step to give products (Figure 4). Therefore the general rate law for the reaction is

$$V = \frac{ks\ k_1\ k_2\ [S]\ [OH^-]\ [Mn^{vii}]_T}{1 + k_1\ k_2\ [S]\ [OH^-]} = K_{obs}\ [oxidant]$$

Table 4. Arrhenius and thermodynamic activation parameters for the oxidation of the sugars by alkaline KM KMnO₄ at 313K.

Substrate	Ea kJmol⁻¹	A dm³mol⁻¹s⁻¹	$\Delta H^{\#}$ kJmol⁻¹	$\Delta S^{\#}$ kJmol⁻¹	$\Delta G^{\#}$ kJ mol⁻¹
Glucose	80.77	2.59×10^{7}	77.47	-103.33	109.80
Fructose	60.00	1.90×10^{5}	56.70	- 144.20	101.83
Sucrose	42.86	3.01×10^{2}	39.56	- 197.82	101.48
Sorbitol	60.00	1.90×10^{5}	56.70	- 144.20	101.83
Mannitol	60.78	1.51×10^{5}	57.48	- 146.11	103.21
Maltose	46.59	2.79×10^{4}	43.29	- 160.15	93.42

Figure 4. steps showing the oxidation of sugar.

From which $k_{obs} = \dfrac{ks\, k_1\, [S]\, [OH]}{1 + k_1\, k_2\, [S]\, [OH]}$

The above mechanisms and rate laws and variations of them have earlier been proposed for the transition metal ion of some sugar and sugar alcohols (Gupta and Basu, 1979; Gupta et al., 1979; Fadnis, 1986; Bajpal et al., 1996).

Relative reactivities of the sugars

The average values of the second order rate constants for the oxidation of the reducing sugars by alkaline KMnO₄ follow the order sorbitol > maltose > glucose > fructose > sucrose > Mannitol. From this result sorbitol is the most reactive while mannitol is the least reactive. It can be said that disaccharides are more reactive than monosaccharides.

For the sugar alcohols, sorbitol is more reactive than mannitol, the order is sorbitol > mannitol. While Aldo-hexoses are more reactive than ketohexoses, that is glucose > fructose. More kinetic and extra kinetic data are needed to be able to offer satisfactory explanation for these observations.

Conclusion

At the end of this research work, it was found that the reaction rates were enhanced by increase in tempe-rature, pH, ionic strength and substrate concentration. Oxidation with KMnO₄ was found to be faster compared to V₂O5 and other oxidant that has been used before. Therefore, KMnO₄ is a more powerful oxidizing agent in sugar conversion.

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