



KINETICS OF OXIDATION OF SOME REDUCING SUGARS BYMn (VII)AND Cr (VI) IN THE PRESENCE OF TRANSITION METAL IONS A COMPARATIVE STUDY

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ABSTRACT

The present paper describes the rate of oxidation of galactose, mannose, And FRUCTOSE& maltose IN ACIDICSOLUTION OF KMNO₄. The rate of reaction was monitored spectrophotometrically under a wide range of experimental conditions. The effect OF CO (II), CR (III) Fe (III) as homogenous catalysts was also studied. The reaction were also monitored at different temperatures. Activation parameters were evaluated. Pseudo first order rate constant increased with increasing in temperature, concentration of sugar and oxidant. The rate of oxidation also increased with increase in ionic and acidic strength of the reaction medium and depends on the concentration of Fe (III)and Cr (III) ions but not on concentration Co(II) ion. The lower value of EA RECORDED with Fe (III) or Cr (III) ions in the mixture suggests a positive rate enhancement withCr (III) ion > Fe (III) ion, the higher value of Ea with Co (II) suggest inhibition. On sugar reactivities, the result shows, galactose > mannose > fructose > maltose.

KEY words: Kinetics, oxidation glucose, GALACTOSE, FRUCTOSE, maltose
potassium permanganate, Homogenous catalyst

INTRODUCTION

Oxidation of sugar s yield products which are of great importance such AS GLUCONIC acidsor other important pharmaceutical intermediates like D-ribonicacid and D-glucuronic acid).(1,2,3.)Kinetics of oxidation of sugars has thus been subject of extensive research in recent years. A vast amount of literature is available on the kinetics of oxidation of simple sugar with various oxidants(4,5)in different media such as alkaline(mostly), acidic and micellar were embarked upon. (6,7,8,9,10,11,12,13) Reaction mechanism proposed in some reports involved formation of intermediate complexes(13,14),other reports was based on formation of free radicals (2,14) Although much works are yet to be done on catalytic oxidation, especially, using homogenous transition metal catalyst, with much data on on kinetics and mechanism of the oxidation reaction,it is difficult to correlate these data because of the wide variation in reaction conditions used and also because of divergent and diversity in the various works. (8)

This present work carried out kinetics of oxidation of different hexose sugars by potassium permanganate(VII) in the presence of different transition metal ions as homogenous catalyst.. Influence of various experimental conditionsrs were studied.

Experimental: Chemical Reagents

All the stock solutions for this kinetic work were prepared FROM DISTILLED water. D- mannose, D-fructose D-galactose and D-maltose used were of E Merck. Potassium permanganate and potassium dichromate of BDH were employedas the oxidants. Sulphuric acid (E-merck), and potassium nitrate (sigma aldrich) were used to maintain the required acidity and ionic strength respectively. Other chemical reagents used were sodium carbonate potassium hydrogen phthalate, and transition metalions of iron, cobalt and chromium were also utilised.

Kinetic Measurements

The kinetic measurements were made at 545nm and 350 for KMnO₄ and K₂Cr₂O₇respectively by monitoring the absorbance changes on a Beckman coulter Du 730 spectrophotometer The studies were carried out under pseudo first order conditions with the concentration of the substrate in large excess compared to that of the oxidant.(17) To measure the reaction rates, different flasks containing appropriate quantity (volume and concentration of each solution to constitute the reaction mixture under the kinetic condition) were arranged in a thermostated water bath to attain a constant temperature before directly added together in a particular glass vessel. The



reaction was initiated by introducing the oxidant solution into the mixture. The progress of the reaction was followed by taken absorbance measurement. as a function of time (14,19)

The experimental data were analysed based on Beer-lambert law. The absorbance A of a dilute solution is proportional to its concentration, c and path length, l . ($a = \epsilon cl$) where ϵ is molar absorptivity constant

Rates of reaction were determined from the table records of absorbance versus time. A plots of $\ln A_0/\ln A_t$ against the respective time was used to determine the value of rate constant k , obtained from the slope of the equation

RESULTS AND DISCUSSION

The Effect of Reactant Concentration

The effect of varying sugar concentration on the rate of KMnO_4 oxidation was carried without including any transition metal ion in the reaction mixture. The observed rate constants k_{obs} for each sugar were determined from the plots of $\ln A_0/A_t$ against t gives a straight line whose slope gives the value of observed rate constants k_{obs} (pseudo-first order rate constants). The result presented in table 1.1a and b shows that the rate increased with increase in sugar concentration for both KMnO_4 and K_2CrO_7

oxidation with lower k_{obs} in K_2CrO_7 oxidation respectively. The second order rate constants k_2 obtained from the slope of the plot of log of pseudo-first order rate constant k_{obs} against substrate concentration (figure 1 KMnO_4 oxidation) were linear for each sugar, suggesting that the reactions were pseudo first order with respect to the sugar concentrations.

The values KMnO_4 oxidation are thus 1.305, 0.812 and 0.866 and 2.334 $\text{m}^{-1}\text{s}^{-1}$, for fructose, maltose galactose, and mannose respectively, the relative reactivity of the sugar under study is thus galactose mannose > fructose > maltose. THE RESULTS also show that the structure of reducing sugars is relevant to the rate of its oxidation. (4)

The k_{obs} measurement was repeated but at different initial concentrations of the oxidants and at constant initial concentration of the sugar. The results in table 1.2 show the pseudo-first order rate constants exhibit a steady increase with increase in the oxidant concentration, suggesting pseudo-first order dependence of reaction rate on KMnO_4 concentration. (5,8).

TABLE 1.1a variation of substrate concentration on KMnO_4

[UBSTRATE] $\times 10^{-2}\text{M}$	MANNOSE $K_{\text{OBS}} \times 10^3$ s^{-1}	MALTOSE $K_{\text{OBS}} \times 10^3$ s^{-1}	GALACTOSE $K_{\text{OBS}} \times 10^{-5}\text{s}^{-1}$	FRUCTOSE $K_{\text{OBS}} \times 10^3$ s^{-1}
1.0	3.3	0.6	2.5	1.3
2.0	4.3	1.8	5.5	2.6
3.0	6.9	2.6	9.7	3.6
4.0	9.8	3.4	11.1	5.5
5.0	11.7	3.9	13.9	6.2

TABLE 1.1b variation of substrate concentration on oxidation K_2CrO_7 oxidation

CONC $\times 10^3$ M	FRUCTOSE $K_{\text{OBS}} \times 10^3$	GALACTOSE- $K_{\text{OBS}} \times 10^{-3}$	MALTOSE- $K_{\text{OBS}} \times 10^{-3}$	MANNOSE- $K_{\text{OBS}} \times 10^3$
1	0.39	1.67	0.65	1.2
2	0.68	2.44	1.5	3.5
3	1.33	4.82	2.57	4.8
4	1.56	5.88	3.2	6.7
5	1.77	6.25	3.45	7.1



TABLE 1.2 EFFECT OF OXIDANT CONCENTRATION
ON KMnO_4 OXIDATION

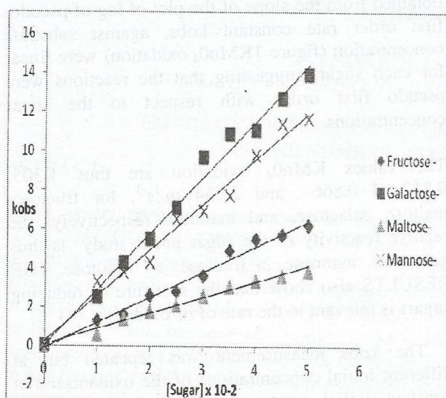


Fig. 1.3b Plot of k_{obs} against sugar concentrations for KMnO_4 Sugar oxidation

The Effect of ionic and acidic strength of the medium

The results presented in table 1.3 shows that the oxidation rate was found to increased with increase in KNO_3 concentration. Increase in rate constant with ICREA (4). This suggests that the reactions occur between ions of similar charges (18).

Also the results in table 1.4 show that the rate of oxidation increased with increase in acidic strength of the reaction medium The plots OF THE same trend was observed by Shankar and Bihari (21). These results suggest that the hydrogen ion may be involved in the rate determining step of the oxidation reaction. It also shows that the reactions were acid DEPENDENT (20).

TABLE 1.3 Effect the variation of salt concentration

[KNO_3] $\times 10^{-1}$ M	MANNOSE $K_{\text{OBS}} \times 10^{-3}$ S^{-1}	MALTOSE $K_{\text{OBS}} \times 10^{-3}$ S^{-1}	GALACTOSE $K_{\text{OBS}} \times 10^{-3}$ S^{-1}	FRUCTOSE $K_{\text{OBS}} \times 10^{-3}$ S^{-1}
1.0	3.5	0.9	2.4	1.6
2.0	3.9	1.7	3.1	1.9
3.0	4.4	2.3	3.7	2.2
4.0	4.9	3.0	4.5	2.2
5.0	5.7	3.4	5.8	2.5



Table 1.4 effect of the H ion concentration

[H ₂ SO ₄] X 10 ⁻¹ M	MANNOSE K _{OBS} X10 ⁻⁵ S ⁻¹	MALTOSE K _{OBS} X10 ⁻⁵ S ⁻¹	GALACTOSE K _{OBS} X10 ⁻⁵ S ⁻¹	FRUCTOSE K _{OBS} X10 ⁻⁵ S ⁻¹
1.0	4.8	1.7	5.1	2.4
2.0	5.9	1.9	5.8	2.6
3.0	6.4	2.1	6.6	4.3
4.0	7.2	2.3	7.5	4.6
5.0	7.9	2.4	8.4	5.1

The Effect OF PRESENCE OF METAL

The experiment on the effect of variation of reactant concentration was repeated, with the reaction carried out with the separate inclusion of constant concentration of these metal ion (Fe(III), Cr(III) and Co(II) ions in the reacting mixture. The data in table 1.5 show k_{obs} for the case of KMnO₄ fructose oxidation. The result compare with absence of metal ion show that k_{obs} for each initial concentration of sugar are greater in the case of Fe(III), and Cr(III) ions, while lower in case of Co(II) ion. The values of the second order rate constant k₂ presented in table 1.6 show the reactivity rate of sugars observed shows galactose > mannose > fructose > maltose, positive enhancement of Fe(III) and Cr(III) (with Cr(III) > Fe(III)), and negative enhancement of Co(II) ion.

Table 1.5 Presence of the metal ion on the effect of sugar concentration

CONCENTRATION OF SUGAR	FRUCTOSE - NO METAL ION	FRUCTOSE + FE(III) ION	FRUCTOSE + CR(III) ION	FRUCTOSE + CO(II) ION
X 10 ⁻² M	KOBS X 10 ⁻³	KOBS X 10 ⁻³	KOBS X 10 ⁻³	KOBS X 10 ⁻³
1	1.3	1.4	2.1	0.94
2	2.6	3.8	4.5	2.5
3	3.6	5.7	5.7	2.8
4	5.5	8.2	8.2	4.5
5	6.2	8.6	9.9	4.6

Table 1.6 Second Order Rate Constants IN the presence of each metal ion

SUGAR	SECOND ORDER RATE CONSTANTS FOR REACTION K ₂ X 10 ⁻¹ DM ³ MOL ⁻¹			
	NO METAL ION	+FE (III) ION	+CR (III) ION	+CO (II) ION
FRUCTOSE	1.305	1.880	2.07	1.01
MALTOSE	0.812	0.945	1.17	0.80
GALACTOSE	2.866	3.978	4.38	1.70
MANNOSE	2.334	3.163	3.70	1.37



Table1.7: Activation energy for the KMnO_4 oxidation for Reaction of Sugar by KMnO_4 AT 313 K
of SUGARS

SUGAR	EA (KJ MOL^{-1})	EA (KJ MOL^{-1}) +FE (III) ION	EA (KJ MOL^{-1}) + CR (III) ION	EA (KJ MOL^{-1}) + CO (II) ION
FRUCTOSE	70.10	38.50	31.51	74.06
MALTOSE	61.42	54.40	41.10	67.40
GALACTOSE	34.74	26.58	20.80	38.94
MANNOSE	42.78	27.05	20.11	46.70

effect of temperature on oxidation of sugars by KMnO_4

Dependence of rate constant for oxidation of sugars by KMnO_4 on temperature is determined at different temperatures (40-70) °c. This was carried

out both in the presence and absence metal ion, pseudo-first order rate constant increased with increase in temperature. The plot of $\log k_2$ against $1/T$ was linear (fig 2 and 3 for maltose oxidation in the absence and presence of Fe(III) ion). The values of activation energy (E_a) were calculated from the slopes and presented in table17 The values of E_a obtained in the metal ion presence of Fe (III) and Cr (III) ions are lower than, while E_a in the case of Co(II) is higher than E_a in the absence of metal ion This suggest provision alternative reaction pathway, an indication of positive enhancement and inhibition respectively in the rate sugar oxidation respectively (8,16)

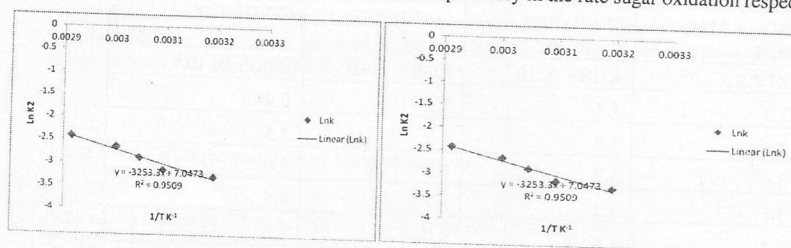


FIG.2 A PLOT OF LN K AGAINST 1/T OF
 KMnO_4 OXIDATION

FIG.3 A PLOT OF LN K AGAINST 1/T OF KMnO_4 OXIDATION

OF MANNOSE IN THE ABSENCE OF METAL ION OF MANNOSE IN THE PRESENCE OF FE (III) ION

CONCLUSION

During the course this work, it was found that the configuration of sugars has some bearing on the rate of their oxidation. The reaction rates were enhanced by increase in both reactants concentration and temperature, acidic and ionic strength of the medium is. The reaction rates is first order kinetic with respect to oxidant and sugar. The reaction is also depends on the concentration of Fe (III) and Cr (III)

ions but not on Co(II) ion. The lower value of E_a with Fe (III) or Cr (III) ions in the mixture suggests positive rate enhancement, while the higher value of E_a with Co (II) suggest inhibition. Extra kinetic experiment would further establish the observation



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