

CATALYTIC CONUNDRUM: ALKALINE MEDIUM MN(VII) OXIDATION INSIGHTS WITH D-SORBITOL AND D-DULCITOL – UNMASKING SUBSTRATE INHIBITION

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Abstract

Sugar alcohols, also known as polyols, serve as valuable sugar substitutes due to their similar sensory properties to sugars, but with reduced calorie content and fewer negative health effects. Unlike traditional sugars, sugar alcohols are not completely absorbed into the bloodstream, making them a healthier alternative for managing blood sugar levels and protecting against tooth decay. This study focuses on the oxidation kinetics and mechanisms of two specific sugar alcohols, D-sorbitol and D-dulcitol, by alkaline KMnO_4 , shedding light on their reactivity and potential applications.

Keywords: Sugar alcohols, Oxidation kinetics, Alkaline KMnO_4 , D-sorbitol, D-dulcitol

Introduction

Sugar alcohols are polyols which are good substitute for sugars. They are neither an alcohol nor sugars as the name suggests(1). However, they possess similar properties as sugars in terms of appearance and sweetness(2-5). Sugar alcohols have lower calories and fewer negative health effects compared to the regular sugars(6). In fact, studies have shown that sugar alcohols can lead to health improvement because unlike sugars, sugar alcohols are not completely absorbed into the blood stream from the intestine, therefore have little effect on blood sugar and it also protect against tooth decay because bacteria that live in the mouth do not feed on sugar alcohols(7-11). The relative sweetness of sugar alcohols to regular sugars are sorbitol and mannitol 60%, maltitol 75%, Erythritol 70% and lactitol 35%. This implies that they taste considerably less sweet than regular sugars and have minty or cool taste(12). The kinetics of sugar alcohols by KMnO_4 in hydrogen/ NaOH buffer was reported(13). Ruthenium(III) catalysed oxidation of sugar alcohols by dichloroisocyanuric in acetic acid-perchloric medium(14), catalytic oxidation of sugar alcohols to lactic acid(15), oxidation of D-sorbitol and D-mannitol by potassium periodate in Alkaline medium(16) and oxidation of sugar alcohols by nitrous oxide(17) have been reported in the literature. Furthermore, few or scanty research have been reported on the oxidation of sugar alcohols compared to sugars and substrate inhibition due to stable complex formation between D-sorbitol and D-mannitol with periodate have been reported(16). Therefore, this paper describes the kinetics and mechanism of oxidation of D-sorbitol and D-dulcitol by Alkaline KMnO_4 .

Experimental

All the reagents utilized were of analytical grade. Requisite quantities of all the reactants were thermo stated at 298K to attain equilibrium. Appropriate quantities of sugar alcohols, NaOH and KNO_3 were

measured into the cuvette and the reaction was initiated by adding requisite volume of KMnO_4 solution. The kinetics of the reaction was followed by monitoring decrease in absorbance of $[\text{KMnO}_4]$ with time at λ_{max} 525nm using uv-1800 Shimadzu spectrophotometer. Consequently, first order rate constant(k_1) were obtained from a plot of $\ln A$ versus time.

Results and Discussion

The kinetic study was carried out under pseudo-first order conditions with the concentration of sugar alcohols in excess of that of KMnO_4 . Increase in pseudo-first order rate constant(k_1) with increase in $[\text{KMnO}_4]$ was observed(Fig.1).

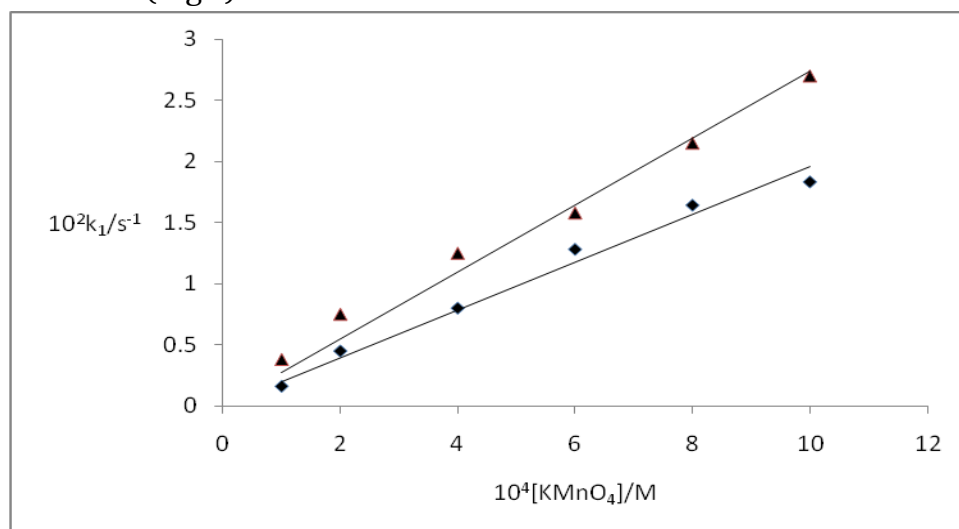
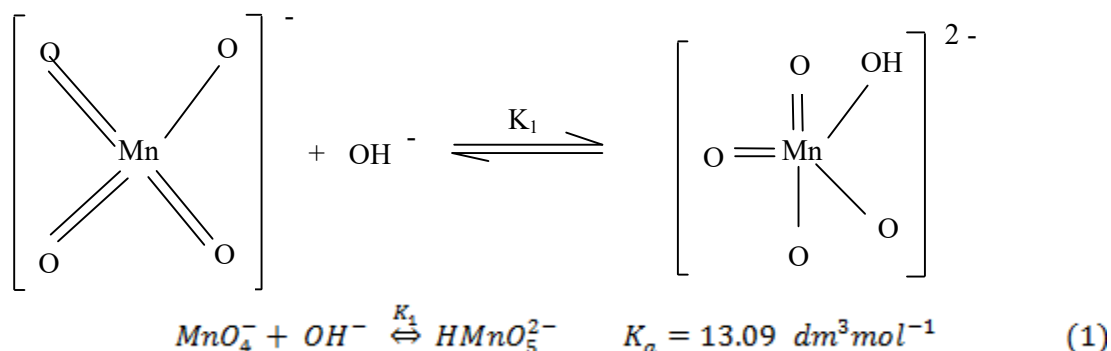


Fig1: Plot pseudo first order rate constant(k_1) versus $[\text{KMnO}_4]$ (▲ D -sorbitol ■ D -dulcitol) [Sugar alcohol] $3 \times 10^{-2} \text{M}$ $[\text{OH}^-]$ $3 \times 10^{-3} \text{M}$ μ 0.05M T 298K

The reaction orders obtained from the slope of $\log k_1$ versus $\log [\text{variant}]$, maintaining all other concentrations constant revealed first order each to $[\text{KMnO}_4]$, $[\text{OH}^-]$. The rate constants decreased with an increase in sugar alcohol concentration. However, the rate constant increases with increase in alkaline concentration and temperature and no appreciable change in rate constant with ionic strength was observed. The stoichiometry of the reaction showed 1 mole of sugar alcohol consuming 1 mole of KMnO_4 . The dissociative equilibria of permanganate ion in alkaline medium and the corresponding equilibrium constant is shown below (18)



Oxidation of Sorbitol and Dulcitol by KMnO_4

Decrease in observed rate constant with increase in sugar alcohol concentration was observed for the two substrates (Table 1).

Table 1: Effect of [Sugar alcohol]

$10^2[\text{Sugar alcohol}]/\text{M}$		$10^2 k_{\text{obs}}/\text{s}^{-1}$	
		D-dulcitol	D-sorbitol
0.80		3.00	3.21
1.00		2.89	3.01
2.00	2.58	2.56	3.00
1.98	2.15	5.00	1.11
1.56			
7.00		0.23	0.67

$[\text{KMnO}_4] 8 \times 10^{-4} \text{M}$ $[\text{OH}^-] 3 \times 10^{-3} \text{M}$ $\mu 0.05 \text{M}$ $T 298 \text{K}$

Kinetic data clearly shows that in alkaline medium, rate of oxidation are much higher in sorbitol than dulcitol (16). The result could be linked to the geometries of the sugar alcohols. Sorbitol is an epimer of glucose while dulcitol is an epimer of galactose. The two sugar alcohols have C5 and C6 with cis -OH group. The structural difference in their geometries is on C3. Hence, due to the cis-geometries of 5,6 hydroxyls in the sugar alcohols. HMnO_5^{2-} is able to complex with the sugar alcohol via the -OH group on C5 and C6. Consequently, the breakdown of the complex leads to C-C fussion to give aldehydes and later carboxylic acids. Decrease in rate constants with increase in [sugar Alcohol] suggests stable complex formation between sugar alcohol and the oxidant.

Effect of Temperature

Rate constant (k_1) increased with an increase in temperature. Activation parameters were obtained from Arrhenius and Eyring's equations and tabulated (Table 2). Positive values of free energy of activation (ΔG^\ddagger) and enthalpy of activation (ΔH^\ddagger) suggests highly solvated transition state and same value of ΔG^\ddagger for the two sugar alcohols indicates same mechanism. Furthermore, negative entropy of activation (ΔS^\ddagger) suggests the formation of an activated complex with reduction in the degree of freedom of molecules, leading to a slow decomposition of the rigid activated complex and that the reaction was via associative mechanism (14,19,20). The values of ΔH^\ddagger and ΔS^\ddagger suggest electron transfer process (21).

Table 2: Activation parameters

Sugar alcohol	ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
D-sorbitol	13.44	0.23	81.98
D-dulcitol	6.46	0.25	80.96

$[\text{KMnO}_4] 8 \times 10^{-4} \text{M}$ $[\text{Sugar alcohol}] 3 \times 10^{-2} \text{M}$ $[\text{OH}^-] 3 \times 10^{-3} \text{M}$ $\mu 0.05 \text{M}$ $298 \text{K} \leq T \leq 328 \text{K}$

Effect of Ionic Strength

No appreciable change in rate constants with ionic strength was observed for the two substrates. This suggests presence of a neutral molecule in the rate determining step.

Effect of Alkalinity

Oxidation reaction increases with increase in sodium hydroxide concentration for both substrates (Fig. 2), showing faster reaction in sorbitol than dulcitol.

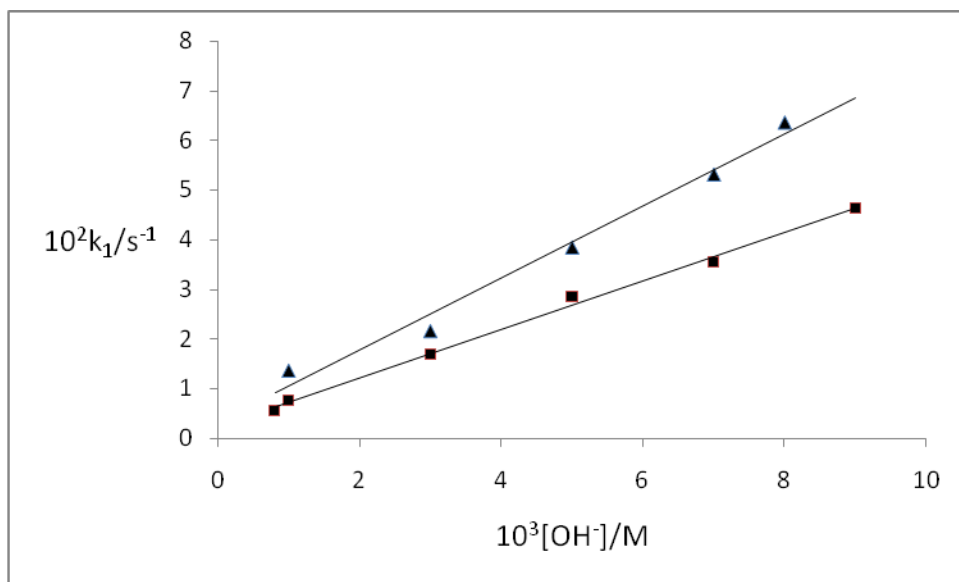


Fig2: Plot of pseudo first order rate constant(k_1) versus $[\text{OH}^-]$ (▲ D-sorbitol ■ D-dulcitol)
 $[\text{KMnO}_4] 8 \times 10^{-4} \text{M}$ [Sugar alcohol] $3 \times 10^{-2} \text{M}$ $\mu 0.05 \text{M}$ $T 298 \text{K}$

Polymerization

Oxidation of sugar alcohols by KMnO_4 in nitrogen atmosphere did not induce polymerization of acrylamide scavenger. This indicates absence of free radicals in the course of the reaction.

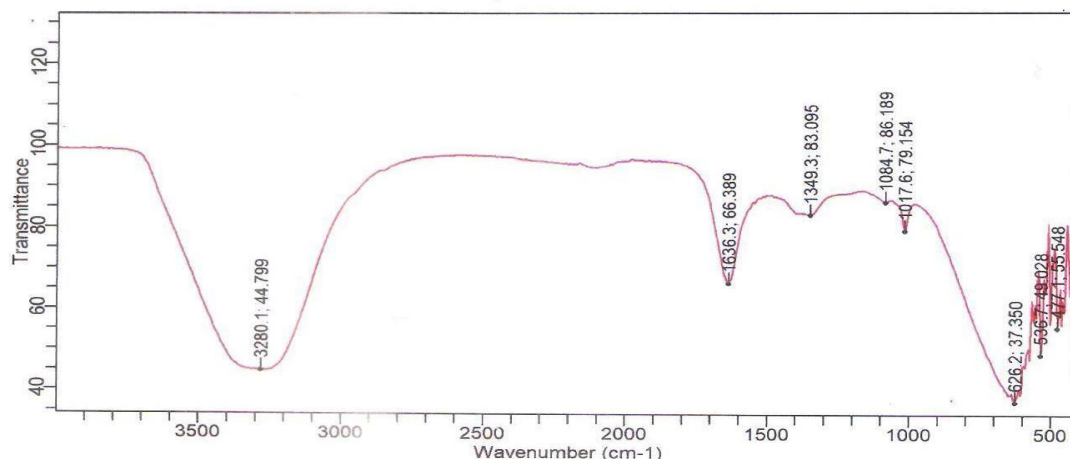


Fig. 3: FTIR Spectrum of the Product

Product Analysis

FTIR analysis of the product showed a very broad band –OH stretching of carboxylic acid at 3400-2400 cm^{-1} and a medium intensity due to C-O stretching attributed to carboxylic acid at 1320-1210 cm^{-1} . Furthermore, the spectrum showed a C=O stretching of carboxylic acid at 1725-1700 cm^{-1} (Fig.3).

Rate Law

$$\begin{aligned} \text{HMnO}_5^{2-} + S &\xrightleftharpoons{K_2} \text{Complex} \xrightarrow{k_3} \text{Products} \\ [\text{MnO}_4^-]_T &= [\text{HMnO}_5^{2-}] + \text{Complex} \\ &= K_1[\text{MnO}_4^-][\text{OH}^-] + k_3K_2K_1[\text{MnO}_4^-][\text{OH}^-][S] \\ [\text{MnO}_4^-] &= \frac{[\text{MnO}_4^-]_T}{K_1[\text{OH}^-] + k_3K_2K_1[\text{OH}^-][S]} \\ \text{Rate} &= k_3[\text{Complex}] \\ &= k_3K_2[\text{HMnO}_5^{2-}][S] \\ &= \frac{k_3K_2K_1[\text{MnO}_4^-][\text{OH}^-][S]}{K_1[\text{OH}^-] + k_3K_2K_1[\text{OH}^-][S]} \end{aligned}$$

Conclusion

Decrease in rate of reaction with increase in sugar alcohol concentration can be attributed to the formation of stable manganese-sugar alcohol complex which resists oxidation. The inert complex contains a higher proportion of sugar alcohol molecules because the 1:1 complex formed take part in the oxidation reaction. In alkaline medium, the active specie of KMnO_4 is HMnO_5^{2-} and from the positive effect of OH^- on the reaction, it implies that the sugar alcohol complexes with HMnO_5^{2-} . Higher rates in sorbitol compared to dulcitol can be attributed to the scission of substrate and stability of complex formed. Moreover, same values of Gibb's free energy of activation for both substrates revealed same mechanism.

Acknowledgement

The authors wish to thank the management of Osun State University, Osogbo for their financial support and the technical staff at the Central Science Laboratory of Obafemi Awolowo University, Ile-Ife for the use of their state of the art facilities.

Reference

- Godswill A.C(2017). Sugar Alcohols: Chemistry, production, Health concerns and Nutritional importance of Mannitol, Sorbitol, Xylitol and Erythritol. Int. J. Adv. Res/Sci Tec & Enrg. Vol 3 Issue 2, 31-66.
- Tiefenbacher K.F(2017). The technology of wafers and waffles: Operational Aspect, Elsevier, 165.
- Makinen K.K(2016). Gastrointestinal Disturbances Associated with the consumption of sugar Alcohols with special consideration of xylitol. Int. J. Dent. 5967907.
- Meister K.A, Doyle M.E(2009). Obesity and Food technology. Am. Cncl on Science, Health, 14.

- O'Donnell K and Kearsley M(2012). Sweeteners and sugars Alternatives in Food Technology. John Wiley & Sons, 322-324.
- Wolever T.M.S, Pickarz A, Hollands M, Younker H(2002). Sugar Alcohols and Diabetics. A Review Canadian Journal of Diabetics. 26(4), 356-362.
- Bradshaw D.J, Marsh P.D(1994). Effect of Sugar Alcohols on the composition and metabolism of a mixed culture of oral Bacteria grown in a chemostat, Caries Research 28(4), 251-256.
- Honkala S, Runnel R, Saag M, Olak J, Nommela R, Russak S, Makinen P.L, Wahlberg T, Falony G, Makinen K, Honkela(2014). Effect of erythritol and xylitol on dental caries prevention in children, Caries Res. 48(5), 482-490.
- Milchovich S, Dunn-Long B(2011). Diabetes Mellitus: A practical Handbook, 10th Edition, Bull publishing company, 79.
- Ford-Martin P, Blumer I(2004). The Everything Diabetics Book, 1st Edition Everything Books, 124.
- Cammenga H.K, Figura L.O and Zielasko B(1996). Thermal behavior of some sugar alcohols, Journal of Thermal Analysis, 47(2), 427-434.
- Schiwech H, Bar A, Vogel R, Schwarz E, Kunz M, Dusautois C, Clement A, Lefranc C, Lussem B, Moser M, Pters S(2012). Sugar alcohols, Ullmann's Encyclopedia of Industrial Chemistry, Weinheim, Wiley-VCH
- Okoro H.K and Odebunmi E(2009). Kinetics and mechanism of oxidation of sugar and sugar alcohols by KMnO₄, International Journal of Physical Sciences, 4(9) 471-476.
- Kumar Y.L, Nadh R.V and Radhakrishnamurti P.S(2016). The kinetics of ruthenium(III) catalysed oxidation of sugar alcohols by dichloroisocyanuric acid in aqueous acetic acid-perchloric medium. Russian Journal of Physical Chemistry A. vol. 90, issue 2, 300-307.
- Manes M.G, Campos J, Shaminghausen L.S, Lin E and Crabtree R.H(2015). Selective catalytic oxidation of sugar alcohols to lactic acid, Green chemistry, issue 1
- Kumar Y.L, Nadh R.V and Radhakrishnamurti P.S(2014). Substrate inhibition: Oxidation of D-Sorbitol and D- Mannitol by potassium periodate in Alkaline Medium. Russian Journal of Physical Chemistry A, vol. 88, No 5, 780-784.
- Carlos B.P.J and Karel K(2017). Catalytic oxidation of sugar alcohols using nitrous oxide. 21st International conference on circuits, systems, communications and computers, vol. 125, MATEC Web of conference 125.
- Fawy A, ElGuesmi N, Ali H.M and Abdallah M(2018). Oxidation of Tryptophan by permanganate ion in Acid, Neutral and Alkali Media. A comparative Kinetic and Mechanistic Study, J. Mater. Environ. Sci., vol. 9, issue 6, 1645-1655.

- Rangappa K.S, Anitha N, Madegouda N.M(2001). Mechanistic investigations of the oxidation of substituted phenyl alcohols by manganese(III) sulfate catalysed by ruthenium(II) in acid solution. *Synth React Inorg Met Org Chem* 31: 1499-1518.
- Bugarcic Z.D, Nandibewoor S.T, Hamza M.S.A, Heimemann F, Van Eldik R(2006). Kinetics and mechanism of the reactions of Pd(II) complexes with azoles and diazine. Crystal structure of [Pd(bpma)(H₂O)(ClO₄)₂.2H₂O. *Dalton Trans*, 2984-2990.
- Farokhi S.A, Nandibewoor S.T(2004). The kinetics and mechanism of oxidative Decarboxylation of Benzoic Acid by Acid Permanganate(stop flow technique)- An Autocatalytic Study, *Can J Chem*, 82: 1372-1380.