

Substrate Inhibition: Oxidation of D-Sorbitol and D-Dulcitol by Mn(VII) in Alkaline Medium

Dayo Felix Latona¹ & Adegoke Emmanuel Akinola²

Abstract

The oxidation of D-sorbitol and D-dulcitol by potassium permanganate in alkaline medium showed substrate inhibition for both substrates due to the formation of 1:1 manganese-sugar alcohol complex which resists oxidation. Consequently, the reaction was inverse first order with respect to sugar alcohol for both substrates, first order each with respect to $[KMnO_4]$, $[OH^-]$ and independent of ionic strength for both substrates investigated. Activation parameters were obtained and a plausible mechanism was proposed from kinetic and spectroscopic studies.

Keywords: Complex, D-dulcitol, D-sorbitol, ionic strength, $KMnO_4$, Rate law.

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 $[KMnO_4]$ 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.

¹ Department of Pure and Applied Chemistry, Osun State University, PMB 4494 Osogbo, Nigeria. e-mail: dayo.latona@uniosun.edu.ng

² Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria

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).

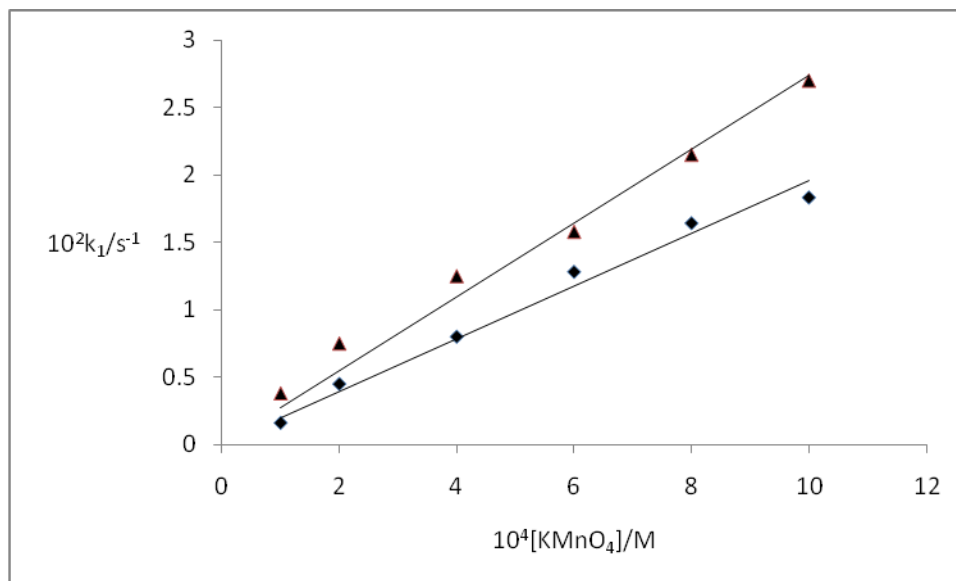
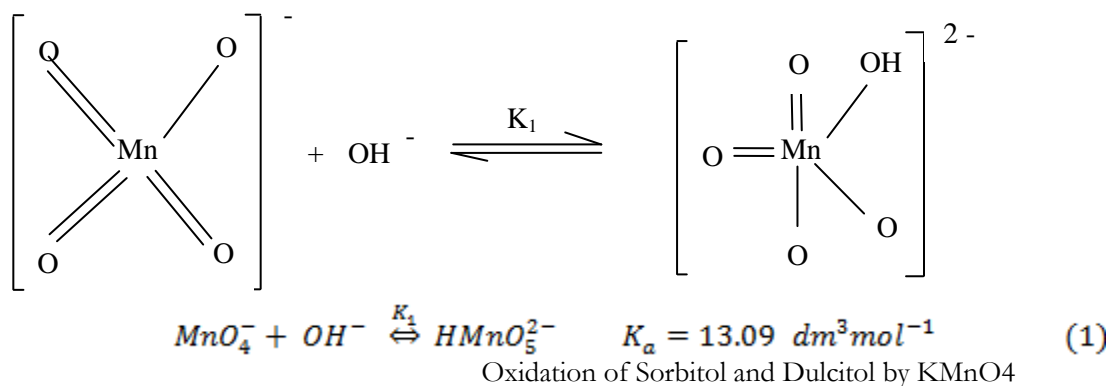


Fig1: Plot pseudo first order rate constant (k_1) versus $[\text{KMnO}_4]$ (▲ D-sorbitol ■ D-dulcitol) [Sugar alcohol] $3 \times 10^{-2} \text{M}$ $[\text{OH}^-]$ $3 \times 10^{-3} \text{M}$ μ 0.05M T 298K

The reaction orders obtained from the slope of $\log k_1$ versus \log [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)



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 [Sugar alcohol]/M	10 ² k _{obs} /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

[KMnO₄] 8x 10⁻⁴M [OH⁻] 3x10⁻³M μ 0.05M T 298K

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. HMnO₅²⁻ 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(k₁) 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[#]) and enthalpy of activation(ΔH[#]) suggests highly solvated transition state and same value of ΔG[#] for the two sugar alcohols indicates same mechanism. Furthermore, negative entropy of activation(ΔS[#]) 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[#] and ΔS[#] suggest electron transfer process(21)

Table 2: Activation parameters

Sugar alcohol	ΔH [#] (kJ mol ⁻¹)	-ΔS [#] (kJ mol ⁻¹ K ⁻¹)	ΔG [#] (kJ mol ⁻¹)
D-sorbitol	13.44	0.23	81.98
D-dulcitol	6.46	0.25	80.96

[KMnO₄] 8x 10⁻⁴M [Sugar alcohol] 3x10⁻²M [OH⁻] 3x10⁻³M μ 0.05M 298K≤T≤328K

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.

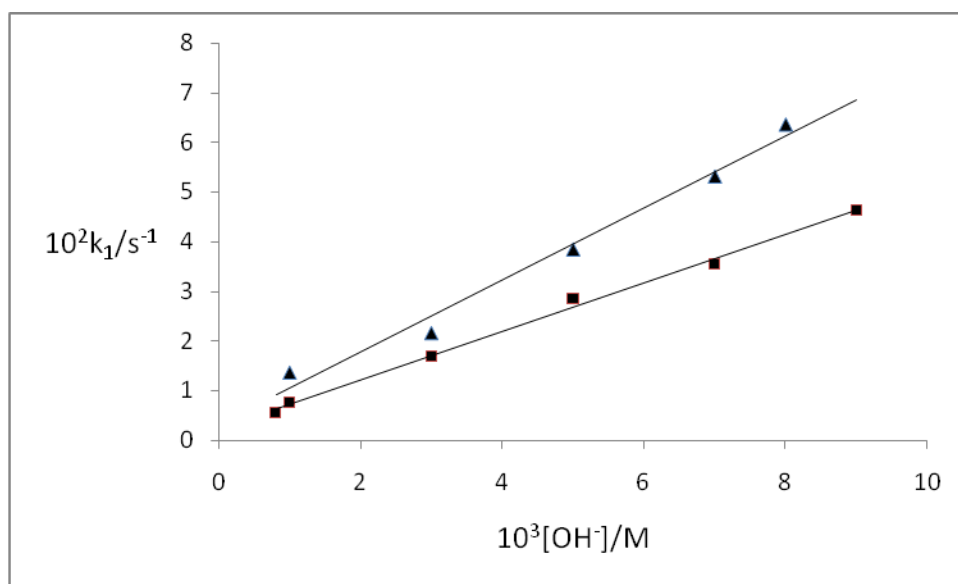


Fig2: Plot of pseudo first order rate constant(k_1) versus $[\text{OH}^-]$ (▲-sorbitol ■-dulcitol)
 $[\text{KMnO}_4]$ $8 \times 10^{-4}\text{M}$ [Sugar alcohol] $3 \times 10^{-2}\text{M}$ μ 0.05M T 298K

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.

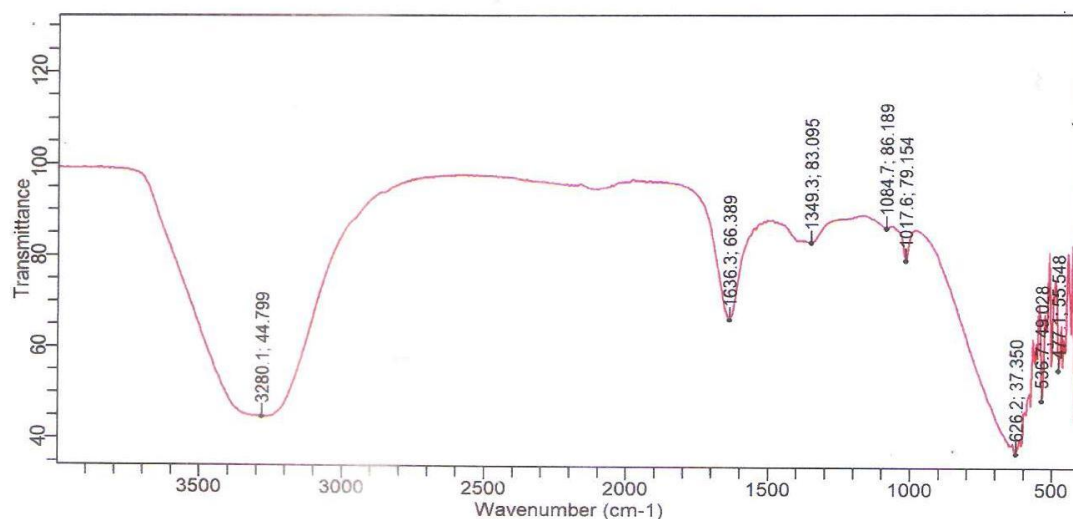
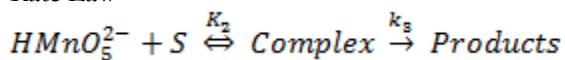


Fig. 3: FTIR Spectrum of the Product

Product Analysis

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

Rate Law



$$\begin{aligned}
 [MnO_4^-]_T &= [HMnO_5^{2-}] + \text{Complex} \\
 &= K_1[MnO_4^-][OH^-] + k_3K_2K_1[MnO_4^-][OH^-][S] \\
 [MnO_4^-] &= \frac{[MnO_4^-]_T}{K_1[OH^-] + k_3K_2K_1[OH^-][S]} \\
 \text{Rate} &= k_3[\text{Complex}] \\
 &= k_3K_2[HMnO_5^{2-}][S] \\
 &= \frac{k_3K_2K_1[MnO_4^-][OH^-][S]}{K_1[OH^-] + k_3K_2K_1[OH^-][S]} \\
 &= \frac{k_3K_2K_1[MnO_4^-]_T[OH^-][S]}{K_1[OH^-] + k_3K_2K_1[OH^-][S]}
 \end{aligned}$$

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.

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