

Full Length Research Paper

Kinetics and mechanism of oxidation of sugar and sugar alcohols by vanadium pentoxide

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The kinetics of oxidation of sugars and sugar alcohols by vanadium pentoxide (V_2O_5) in acidic medium have been investigated spectrophotometrically under pseudo-first order conditions and over a wide range of experimental conditions. Each reaction was first order with respect to the substrate and oxidant. The kinetic data for the oxidation by V_2O_5 solution showed that increase in temperature and sugar concentration increased the rate of the reactions. It was also observed that with increase in pH and KNO_3 concentration, the reaction rate decreased with increase in V_2O_5 concentration with the exception of fructose which showed significant increase in reaction rates. The mechanism of these reactions involved the formation of a 1:1 intermediate complex. The order of reactivities of the sugars was Maltose > Fructose > Sucrose > Glucose > Sorbitol > Mannitol.

Key words: Oxidation, sugar and sugar alcohols, kinetics, vanadium pentoxide, activation parameter, intermediate complex, substrate, oxidants, mechanism.

INTRODUCTION

A carbohydrate is an organic compound with the general formula $C_m(H_2O)_n$ that consist only of carbon, hydrogen and oxygen, the last two in the ratio 2:1 atom ratio. Carbohydrates can be viewed as hydrates of carbon, hence their name (Flitsch and Uliju, 2003). They can be classified as monosaccharides, disaccharides, oligosaccharides and polysaccharides. Thus monosaccharides and disaccharides are referred to as "sugar". Polysaccharides serve for the storage of energy (that is, starch and glycogen) and structural components (that is cellulose in plants and chitin in anthropods, while the monosaccharide is the simplest carbohydrates in that they cannot be hydrolized to smaller carbohydrates (Maton et al., 1993).

Carbohydrates perform numerous roles in living things and they are sources of energy for vital metabolism processes. They are also constituents of cellular substances such as nucleic acids and are enzyme co-factors and

structural components of cell walls and cell membranes. Carbohydrates, simple or compound, are one of the major food components. Present in the wide range of them are usually refined foods such as white sugar, white bread or cola. (Donald and George, 1977).

In a recent study, based on the effects on risk of heart diseases and obesity, the Institute of Medicine recommends that American and Canadian adults get between 45-65% of dietary energy from carbohydrates. The Food and Agricultural Organization and World Health Organization (WHO) jointly recommend that nutritional dietary guidelines set a goal of 55-75% of total energy from carbohydrates, but only 10% is directly from sugars (Food and Nutrition Board, 2002-2005; WHO, 2003). However, the biological and economic importance of the carbohydrates and especially the mono and disaccharides has been largely responsible for the interest in the study of their biological and physicochemical properties and reactivities (Moody and Richard, 1981; Neyhart et al., 1995; Odebunmi and Marufu, 1999; Odebunmi et al., 1999; Sen Gupta et al., 1981; Okoro and Odebunmi, 2008; Okoro and Odebunmi, 2009).

Studies have been made on the structural elucidation,

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Table 1. Variation of rate constant with OXIDANT V_2O_5 concentration at 35°C pH = 11.00, $KNO_3 = 0.2M$; [Sugar] = 0.05 M.

[V_2O_5] $\times 10^{-4} M$	[Glucose] $k_{obs} \times 10^2, s^{-1}$	[Fructose] $k_{obs} \times 10^2, s^{-1}$	[Sucrose] $k_{obs} \times 10^2, s^{-1}$	[Maltose] k_{obs} $\times 10^2, s^{-1}$	[Mannitol] k_{obs} $\times 10^2, s^{-1}$	[Sorbitol] $k_{obs} \times 10^2, s^{-1}$
2	14.30	n.a	8.30	n.a	5.90	2.40
3	8.10	10.70	2.75	2.10	n.a	1.60
4	4.80	13.20	2.50	1.50	3.10	1.40
5.	3.00	n.a	2.20	1.40	2.00	n.a
6	2.30	33.30	1.70	1.40	1.40	n.a
7.	2.00	35.60	1.50	1.30	1.30	1.40
8	1.60	n.a	n.a	1.30	n.a	n.a

K_{obs} = First order rate constant; S^{-1} = Time in s; n.a = No data available.

chemical degradation and oxidation reactions, among others (Odeunmi et al., 1999; Rudrum and Shaw 1965). Many transition metals, inorganic acids, complex ions as well as hydrogen peroxide and enzymes have been employed in a variety of oxidation studies in both acidic and alkaline media (Fadnis, 1986; Gupta et al., 1981; Sen Gupta et al., 1985). Although a large amount of data already exist on the kinetics and mechanisms of the oxidation reactions (Fadnis and Shrivastava, 1983a; 1983b; Olavi et al., 1985; Poulsen and Garner, 1962; Sen Gupta and Nath Basu, 1979; 1981a; 1981b; 1986). Correlation of data is difficult because of wide variations in reaction conditions used.

The aim of the present study was the investigation of the kinetics of oxidation of sugar and sugar alcohols by V_2O_5 within the same buffer systems. Analyzing the relative oxidizing power or oxidizing power abilities of oxidants as well as the determination of the reaction path.

MATERIALS AND METHODS

Chemical reagents

The chemical reagents used in this study were obtained from Sigma Aldrich Chemical Company. They were used without further purification. Stock solutions of D-glucose, D-Fructose, D-Maltose, D-Sucrose, D-Mannitol, D-Sorbitol, Vanadium pentoxide were prepared in distilled water. Fresh solutions of buffer were also prepared when needed from the components in distilled water.

Spectral measurements

The absorption spectra of different concentrations of V_2O_5 were recorded in the visible region between 415 and 500 nm. The value of λ_{max} of 450 nm was obtained in agreement with literature (Stroh and West, 1982). The values of absorbance were recorded at different concentration ranges between 1×10^{-4} and $9 \times 10^{-4} M$. A linear graph was obtained from the plots of absorbance against concentration. The molar absorptivity was calculated from the slope to be $8.33 \times 10^{-3} M^{-1} cm^{-1}$.

Kinetics measurement

The effect of substrate and oxidant concentration, pH, added salt

concentration and temperature on the rate of oxidation by V_2O_5 on Fructose, Sucrose, Maltose, Glucose, Mannitol and Sorbitol was studied. The rate of reaction was measured using an aquamate UV-Visible spectrophotometer equipped with a thermostated cell compartment and interfaced with a computer. The consumption rate of V_2O_5 was monitored at 450 nm. The reactions were initiated by mixing the requisite amount of the oxidant with the substrate solution. The kinetic studies were carried out under pseudo-first order conditions with the concentration of the substrate in a large excess of that of the oxidant. The pseudo-first order rate constant (k_{obs}) was calculated from the plot of $\log A$ (absorbance) against time as presented by Stroh and West (1982).

RESULTS AND DISCUSSION

Effect of variation in reactant concentration

The first-order rate constants (k_{obs}) at various initial concentrations of V_2O_5 have been evaluated from the slopes of the plot of logarithm of absorbance versus time. The results presented in Table 1 show that the first-order rate constant decreases as the concentration of V_2O_5 increases. Only fructose shows significant increase in rate with increase in concentration.

From the literature, these results follow the same trend with as that of Olavi et al. (1985) who reported the kinetics of the oxidation of D-fructose with vanadium (V) in perchloric acid media. The reaction was found to be first-order with respect to the fructose concentration but the values of the rate constant increases slightly with increase in vanadium (V) concentration.

The presented result has shown significant decrease in rate constant as the oxidant concentration increased except that of fructose. These results show that each oxidation reaction was first order with respect to oxidant and sugar concentrations. The average second-order rate constants were computed to be 0.681, 0.696, 0.699, 0.812, 0.986 and $1.076 M^{-1} s^{-1}$ for the oxidation of mannitol, sorbitol, glucose, sucrose, fructose and maltose respectively.

Therefore the oxidation rates follow the order: maltose > fructose > sucrose > glucose > sorbitol > mannitol. This finding is in agreement with the literature (Odeunmi and

Table 2a. Variation of rate constant with substrate concentration at 35°C [KNO₃] = 0.2M, [Oxidant] = 5X10⁻²M.

[Sugar] M	[Glucose] k _{obs} × 10 ⁻³ , s ⁻¹	[Fructose] k _{obs} × 10 ⁻³ , s ⁻¹	[Sucrose] k _{obs} × 10 ⁻³ , s ⁻¹	[Sorbitol] k _{obs} × 10 ⁻³ , s ⁻¹	[Mannitol] k _{obs} × 10 ⁻³ , s ⁻¹	[Maltose] k _{obs} × 10 ⁻³ , s ⁻¹
0.08	1.00	2.30	1.00	n.a	14.00	2.00
0.12	n.a	2.40	1.40	1.40	50.00	n.a
0.16	1.80	3.00	n.a	1.50	56.00	2.22
2.00	2.40	4.00	3.40	3.60	60.00	2.40
2.40	2.50	n.a	3.50	3.60	63.00	4.50
2.80	6.40	n.a	n.a	n.a	65.00	n.a
3.20	6.60	6.00	n.a	3.70	n.a	n.a

K_{obs}=First order rate constant; S⁻¹= Time in s; n.a= No data available.

Table 2b. Second-order rate constants for oxidation at 35°C.

Sugar	k ₂ , dm ³ mol s ⁻¹
Glucose	0.699
Fructose	0.986
Maltose	1.076
Sucrose	0.812
Mannitol	0.681
Sorbitol	0.696

k₂= Second order rate constant.

Owalude, 2005; Sen Gupta et al., 1985). This is an improvement on the published data which showed only a slight increase. These results generally show that the reaction rate depends on oxidant concentration.

Pseudo-first order rate constants were determined at different initial concentrations of the sugars while maintaining constant, the pH, ionic strength and temperature. The results in Table 2a show that the rate of oxidation increased as the concentration of the sugar is increased. The second order rate constant K₂ was obtained from the slope of the linear plot of pseudo-first-order rate constant, k_{obs} against substrate concentration. The values are presented in Table 2b. From the value of the second order rate constant (K₂), the relative reactivity of the sugars and sugar alcohols are: maltose > fructose > sucrose > glucose > sorbitol > mannitol.

From these results, it can be inferred that Maltose is the most reactive sugar due to its greater reactivity. While the two sugar alcohols are the least reactive.

Effect of variation of pH

The effect of pH on the rate of oxidation of the sugars was studied at 35°C in the pH range of 9.6 to 11.00 and at constant ionic strength of 0.2 M, constant concentration of V₂O₅ (0.005 M) and substrate (0.005 M). Only maltose showed an increase in rate constant with an

increase in pH.

This is the same trend observed by Owalude (2004), who studied the kinetics and mechanism of oxidation of sugars by KMnO₄ and found that the reaction rate was enhanced by an increase in pH of the reaction medium. The plots of log k_{obs} against pH were linear for all reactions and this shows that the reactions were base catalyzed (Figure 1).

Effect of salt concentration

The effect of variation of concentration of KNO₃ on the rate of oxidation of the sugars by V₂O₅ was studied at constant concentration of V₂O₅ (2.5x10⁻³ M), sugar (5.0x10⁻³ M), pH (11.00) and temperature (35°C). The concentration of KNO₃ was varied between 0.10 and 0.40 M. The oxidation rate decreases as the concentration of the KNO₃ solution increased as presented in Table 3. These results show that k_{obs} depends on KNO₃ concentration.

A survey of the literature shows a wide dependence of sugar oxidation in relation to salt concentration. Some reports show an enhancement of reaction rate by added salt (Olavi et al., 1985; Sen Gupta et al., 1986) others show inhibition of rate by addition of salt (Fadnis and Shrivastava, 1983a).

The result presented in this work are within this range, agreeing largely with those of Owalude (2004); Sen. Gupta et al. (1985) and Shukla and Kesarwani (1984a; 1984b) and disagreed with what we reported earlier for oxidation of glucose, mannose and their corresponding alcohols by the same oxidants (Odeunmi and Marufu, 1999; Odeunmi et al., 1999).

A plot of log k_{obs} against √I gave a straight line which shows a decrease in rate constant with increase in ionic strength. This observation also shows that the reaction occurred between ions of different charges. It was also observed that sucrose gives a straight line which shows dependence on KNO₃. The charge on the molecules is zero meaning that the two reacting species are at the transition state (Frost and Pearson, 1970).

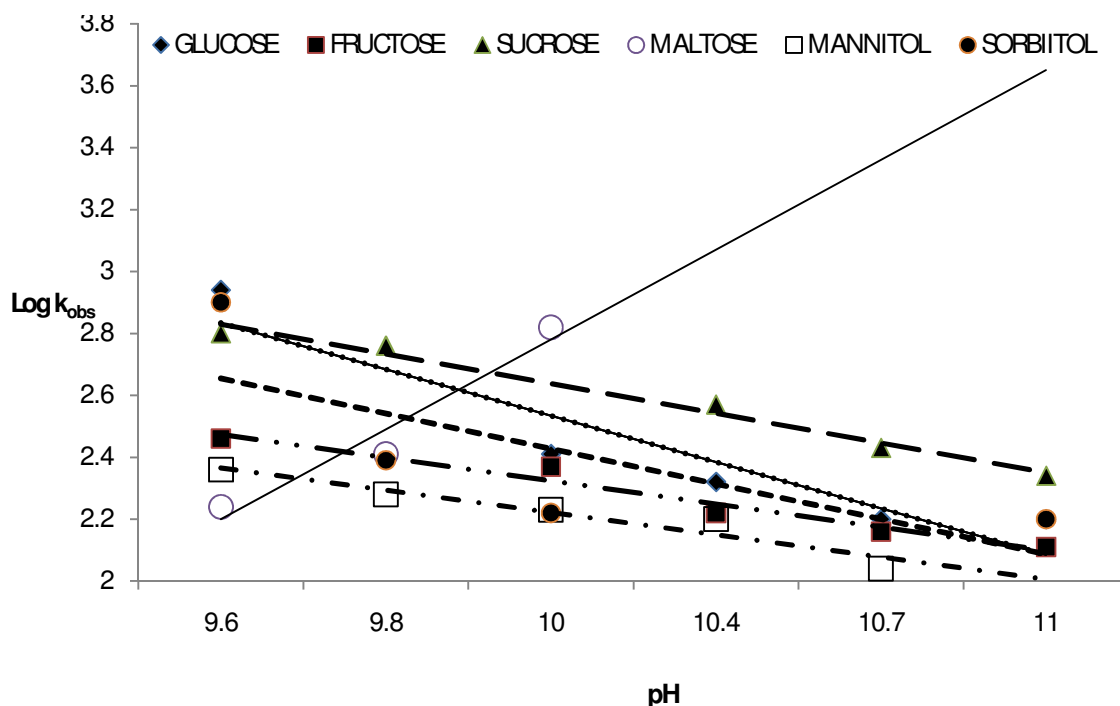


Figure 1. Log k_{obs} versus pH for V_2O_5 oxidation.

Table 3. Variation of rate constant with concentration at 35°C pH = 11.00, $[V_2O_5] = 2.5 \times 10^{-3}M$ [sugar] = $5.0 \times 10^{-3}M$.

[KNO ₃] M	[Glucose] $k_{obs} \times 10^1, s^{-1}$	[Fructose] k_{obs} $\times 10^1, s^{-1}$	[Sucrose] $K_{OBS} \times 10^1, S^{-1}$	[Maltose] K_{OBS} $\times 10^1, S^{-1}$	[Mannitol] $k_{obs} \times$ $10^1, s^{-1}$	[Sorbitol] $k_{obs} \times 10^1, s^{-1}$
0.10	6.70	3.16	2.50	2.44	1.80	1.20
0.15	2.10	3.15	2.30	1.75	n.a	0.48
0.20	n.a	1.67	2.20	1.40	1.60	0.30
0.25	0.55	1.22	1.80	1.38	0.50	0.26
0.30	0.21	n.a	1.70	1.38	n.a	0.18
0.40	0.20	1.11	1.60	n.a	0.40	n.a

k_{obs} =First order rate constant; S^{-1} = Time in s; n.a= No data available; M= Molar concentration of HNO_3 .

Table 4. Arrhenius and thermodynamic activation parameter for the oxidation of the sugars by V_2O_5 at 313K.

Substrate	E_a $KJmol^{-1}$	A $mol^{-1} s^{-1}$	ΔH^\ddagger $dm^3 kJ mol^{-1}$	ΔS^\ddagger $kJmol^{-1}$	$\Delta G^\ddagger \times 10^3$ $kJmol^{-1}$
Glucose	1571.43	4.51×10^{23}	1567.90	207.63	-63.42
Sucrose	1545.45	5.27×10^{23}	1542.00	208.93	-63.85
Fructose	474.58	2.79×10^5	471.13	-141.01	00.52
Maltose	175.00	2.77×10^5	171.05	-141.07	00.22
Mannitol	1611.11	7.16×10^{24}	1607.66	230.63	-70.58
Sorbitol	2956.32	4.10×10^{44}	2953.07	608.93	-187.64

E_a = Arrhenius activation energy; ΔS^\ddagger = Entropy of activation; ΔG^\ddagger = Gibb's free energy of activation; A = Pre- exponential factor; ΔH^\ddagger = Enthalpy of activation.

Effect of variation of temperature

The oxidation of the sugars was carried out at different

temperatures while maintaining constant the concentration of V_2O_5 (0.005 M), substrates (0.1 M), pH (11.00), and KNO_3 (0.2 M). The pseudo-first-order rate constant

increased with increase in temperature. The Arrhenius parameters (that is, E_a 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 other thermodynamic activation parameters were calculated following the literature procedures (Mortimer and Taylor, 2002). The enthalpy of activation (ΔH^\ddagger) were calculated from the activation energy using the equation $\Delta H^\ddagger = E_a - RT$ at a temperature of 313°K. The entropy activation (ΔS^\ddagger) in each reaction was then evaluated as follows:

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

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

(Where k = Boltzman constant)

$$\log_e A = \log_e \frac{KT}{h} + \frac{\Delta S^\ddagger}{R}$$

$$\Delta S^\ddagger = 2.303R(\log_{10} A - \log_{10} \frac{KT}{h})$$

All the calculations were done at $T = 313^\circ\text{K}$, Hence equation becomes

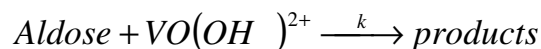
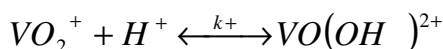
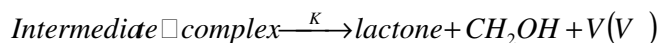
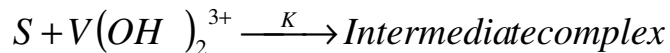
$$\Delta S^\ddagger = 2.303R(\log_{10} A - \log_{10} 12.81)$$

$$\Delta G = \Delta H^\ddagger - T\Delta S$$

The values of ΔG^\ddagger have been calculated at 313°K from the relation. The oxidation of all sugars and sugar alcohols was found to follow the normal Arrhenius equation for temperature dependence of reaction rate. The values of the activation parameters are presented in Table 4. The Arrhenius activation energies (E_a) were calculated from the slopes of the plots. The data in above Table show that the Arrhenius activation energy for oxidation of sorbitol, mannitol, maltose, fructose, sucrose, glucose by V_2O_5 decreased in the order sorbitol > mannitol > glucose > sucrose > fructose > maltose, respectively.

From these results, it can be inferred that values of E_a for the sugar alcohols that is, sorbitol and mannitol are greater than those of disaccharide and the monosaccharide sugars, the (E_a) for the aldohexose (glucose) is greater than the ketohexose sugar (fructose). Therefore the Arrhenius activation energy (E_a) for the monosaccharide follow the order glucose > fructose. The negative values of entropies of activation (ΔS^\ddagger) for fructose and maltose indicate that the reaction occurs

between ions of similar charge. This observation is in agreement with Olavi et al. (1985). The positive value of entropy of activation for mannitol, sorbitol, glucose, and sucrose shows that the reaction occurs between ions of opposite charges (Shukla and Kesarwani, 1984a).



$$\frac{-d[V(V)]}{dt} = \frac{k[\text{aldose}][VO(OH)^{2+}]}{kK[\text{Aldose}][V(V)]H^+}$$

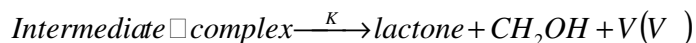
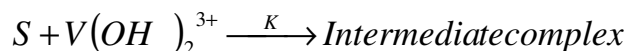
$$[V(V)] = [VO_2^+] + [VO(OH)^{2+}]$$

$$[VO(OH)^{2+}] = V(V) \frac{K[H^+]}{1+K[H^+]}$$

$$k_{obs} = \frac{d[V(V)]}{dt} \times \frac{1}{[V(V)]} = kK \frac{\text{Aldose}[H^+]}{1+K[H^+]}$$

Reaction mechanism and rate law

The double reciprocal plots of the pseudo-first order rate constants against the substrate concentration were linear (Figure 2) indicating that the reaction between each substrate and oxidant takes place through a 1:1 intermediate complex (Fadnis 1986; Sen. Gupta and Chatterjee 1984). The complex decomposes slowly to give the lactone of the C5-acid, a free radical (CH_2OH) and $V(IV)$ by rupture of the C-C bond. The free radical reacts further with vanadium (V) to give formaldehyde and vanadium (IV) according to the scheme below.



The formation of 1.1 intermediate complexes was

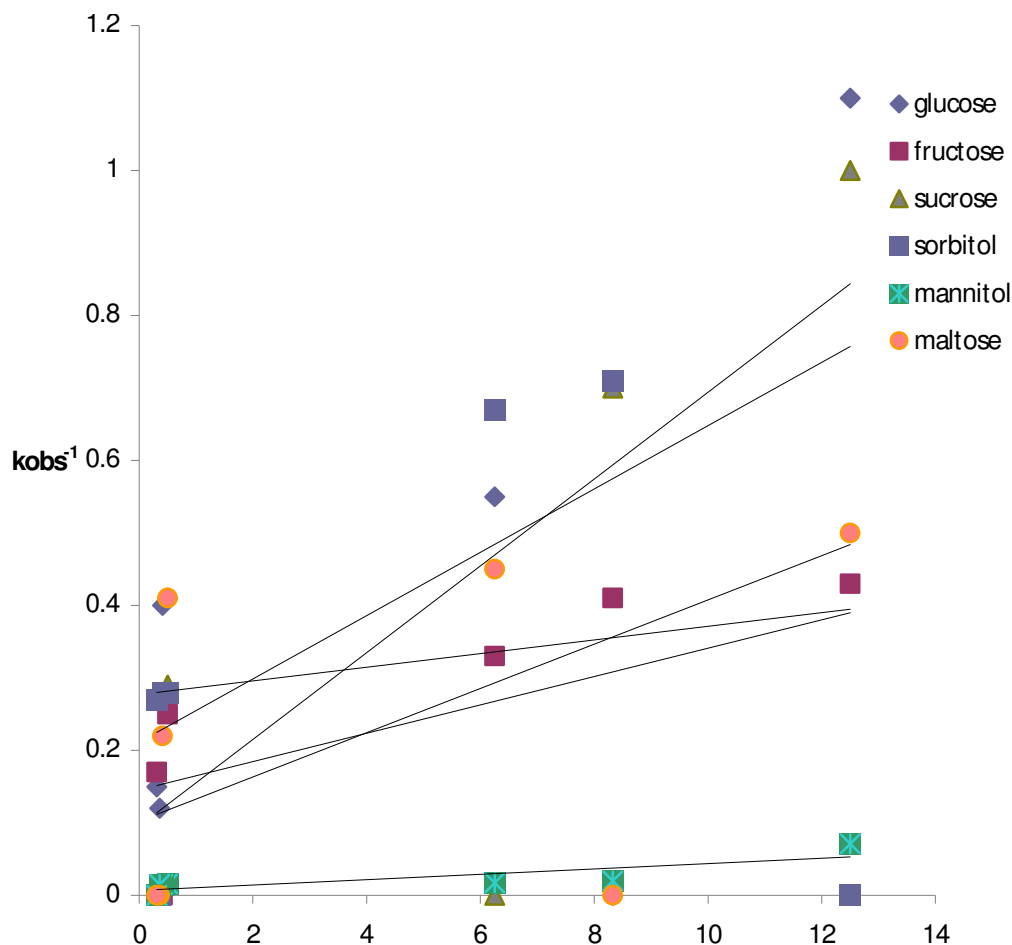
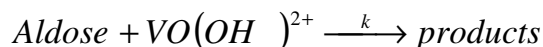
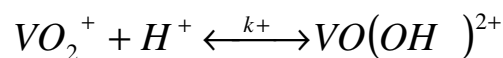


Figure 2. Double reciprocal plot: $1/k_{obs}$ against $1/[Substrate]$ for sugar Oxidation with V_2O_5 .

corroborated by the mixture of ketohexoses V (V) at 450 nm. The observed hydrogen ion dependence on rate constant suggests that these oxidations are affected by the monoprotonated V(V) species, $VO(OH)^{2+}$ [or its hydrated form $V(OH^{2+})_3$ which remains in equilibrium with the non-protonated species VO_2^+ (or its hydrated form, $V(OH)_4^+$].

The reactions are believed to occur according to the steps below:



The corresponding rate would be

$$\frac{-d[V(V)]}{dt} = \frac{k[aldose][VO(OH)^{2+}]}{kK[Aldose][V(V)]H^+}$$

$$\text{Hence total } [V(V)] = [VO_2^+] + [VO(OH)^{2+}]$$

$$[VO(OH)^{2+}] = V(V) \frac{K[H^+]}{1+K[H^+]}$$

$$k_{obs} = \frac{d[V(V)]}{dt} \times \frac{1}{[V(V)]} = kK \frac{Aldose[H^+]}{1+K[H^+]}$$

The rate expression is in keeping with the observed orders with respect to each reactant. Moreover the linear plots of $\log k_{obs}$ against ionic strength supports the view that the reaction takes place between a neutral molecule and ions

Relative reactivities of the sugars

The average values of the second-order rate constants for the oxidation of the reducing sugar by V_2O_5 are 1.076, 0.986, 0.812, 0.699, 0.696 and 0.681 $M^{-1}s^{-1}$ for maltose, fructose, sucrose, glucose, sorbitol and mannitol, respectively. The order of the reactivity is maltose > fructose > sucrose > glucose > sorbitol > mannitol. From these results, it can be inferred that maltose is the most

reactive sugar, while the two sugar alcohols are the least reactive sugars. For the monosaccharide's, ketohexoses are more reactive than aldohexoses. The order is fructose > glucose. It can be inferred from the observation that the order of reactivity of all the sugars is disaccharide > monosaccharide > sugar alcohols.

Conclusion

During the course of this work, it was found that the reaction rates were enhanced by increase in temperature, pH, ionic strength and substrate concentration with V_2O_5 as oxidant. In addition simple and complex sugars are more reactive than sugar alcohols. The mechanism of reaction involved formation of 1:1 intermediate complex confirming that the reaction rate is dependent on rate constant. However, Oxidation with V_2O_5 has received very little attention over the past years compared with the other oxidant such as $KMnO_4$. Therefore, extent of oxidation with the use of V_2O_5 should be revisited in due course.

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