



Kinetics and mechanism of oxidation of D-xylose and L-arabinose by chromium(VI) ions in perchloric acid medium

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ABSTRACT

The kinetics of oxidation of D-Xylose and L-Arabinose by Cr(VI) ions in perchloric acid medium have been investigated spectrophotometrically under pseudo-first-order conditions. The reactions exhibit first-order rate dependence each on the substrate and oxidant. The order with respect to $[H^+]$ is unity while no effect on the reaction rate is found with respect to the ionic strength. The Arrhenius (E_a) and thermodynamic activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) are evaluated and the reaction mechanism is interpreted in terms of formation of a 1:1 intermediate complex between a protonated chromic acid molecule and a neutral sugar molecule in sharp contrast to the results of our earlier studies on the C₆ and C₁₂ sugars.

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INTRODUCTION

Kinetics of the oxidation of carbohydrates has been given prominent attention in the past (Pigman, 1957; Krishna and Rao, 1995). This has been attributed to the fact that microbiological and physiological activities of carbohydrates is dependent on their redox behaviour (Khan et al., 2004). The study of mechanism of oxidation of sugars by different oxidizing agents is therefore of immense importance. Oxidation reactions have also been carried out in relation to structural elucidation, chemical degradation and mechanisms of action of oxidants (Odebunmi et al., 1999; Pandeewaran et al., 2004; Shukla et al., 2004; Khan et al., 2006). These oxidation reactions have been carried out both in alkaline as well as in acidic media using such oxidants as metallic ions, inorganic acids, organometallic complexes and enzymes. Despite a large amount of data available, correlation of data is difficult due to variation in the reaction conditions employed in these reactions (Sen Gupta and Charterjee, 1984).

In continuation of our previous studies (Odebunmi et al., 1999; Odebunmi and Owalude, 2005), D-xylose and L-arabinose are selected to find out if the same mechanism is operative as in case of C₆ and C₁₂ sugars (Odebunmi and Owalude, 2005). This paper therefore describes the kinetics of oxidation of D-Xylose and L-Arabinose by Cr(VI) ions in perchloric acid medium at different ionic strength and temperature, and proposes a mechanism consistent with observed rate data.

MATERIALS AND METHODS

Chemical reagents

All the reagents were obtained from Aldrich chemicals and were used as received. Stock solutions of the sugars and Cr(VI) were prepared using deionised doubly distilled water.

Spectra measurement

Absorption spectrum of solutions of different concentrations of Cr(VI) was scanned from 300 nm in the UV region to 600 nm in the visible region. The kinetic data

were collected at 371 nm, the wavelength corresponding to maximum absorbance.

Kinetic measurements

The kinetic studies were carried out under pseudo-first-order conditions with the concentration of the sugars in large excess. All reactant solutions were placed in a thermostated water bath for one hour to attain the desired temperature of 40 °C. Appropriate quantities of the reagent solutions were mixed in a 250 cm³ conical flask already placed in the thermostated bath. The reaction was monitored with Aquamate V4.60 UV-visible spectrophotometer by measuring the decrease in absorbance at 371 nm, the reaction was completed when Cr(VI)-sugar solution turned from yellow to green. The rate constants calculated were averages of two measurements. The results are generally reproducible within $\pm 2\%$. (Upadhyay and Kambo, 2000).

Test for free radicals

A series of reaction mixtures containing the Chromium(VI) solution and each of the substrates was carried out under the exact kinetic conditions with the addition of 20% (w/v) acrylamide. The reaction mixture was allowed to stand for 24 hours, no gel formation was noticed. Control experiments from which either Cr(VI) or aldose were excluded also produced no gel formation. These indicated that no free radicals were formed during these reactions (Sen Gupta and Basu, 1979a).

Statistical analyses

Statistical significance was determined using Duncan Multiple Range Test and values were considered statistically significant at $P < 0.05$ (Bewick et al., 2004).

RESULTS AND DISCUSSION

Effect of variation of reactants concentration

The pseudo-first-order rate constants (k_{obs}) were determined (as the slope of a logarithmic plot of absorbance as a function of time) at different initial concentrations of the oxidant, but at constant initial concentration of the sugars, constant pH, ionic strength, and temperature. The values of the k_{obs} presented in table 1 indicate that the rate of the reaction

was independent of the concentration of chromium(VI) for the two sugars, suggesting a first-order dependence of the reaction rate on Chromium(VI). (Sen Gupta and Basu, 1979a). In another set of experiments, the pseudo-first-order rate constants were measured at different initial sugar concentrations, but at constant initial concentration of Cr(VI), pH, ionic strength and temperature, the results in table 2 show that k_{obs} increased as the concentration of the sugars increased. The plots of k_{obs} against $[\text{sugar}]_0$ (Figure 1) were linear with a non zero intercept on the y-axis. The linearity of the plots up to 70% conversion confirms the first-order dependence of rate of reaction on $[\text{sugar}]$, (Lohdip et al., 1995). From the values of the second-order rate constants obtained, the relative reactivity of the sugars is Arabinose > Xylose.

Effect of variation of pH

The effects of variation of acidity at ionic strength of 0.2M, maintained constant by the addition of NaClO₄, constant initial concentrations of Cr(VI) and sugar at temperature of 40 °C on the pseudo-first order rate constants was measured. The rate of oxidation of the sugars increased with increasing acid concentration. The plot of $\log k_{\text{obs}}$ against $\log [\text{HClO}_4]$ was linear (Figure 2), indicating that these reactions are acid-catalysed (Zucker and Hammet, 1939; Richard, 1970). The values of the slopes of the plots of $\log k_{\text{obs}}$ against $\log [\text{H}^+]$ are approximately 1 in each case; therefore the order with respect to $[\text{H}^+]$ for both sugars is unity.

Effect of ionic strength

The effect of different initial concentration of solutions of sodium perchlorate on the pseudo-first-order rate constants was investigated at constant concentration of sugar, Cr(VI), perchloric acid and temperature at 40 °C. The reactions were found to be independent of the ionic strength (Table 3), indicating involvement of a neutral reactant molecule in the rate determining step (Bajpai et al., 1996).

Effect of variation of temperature

The oxidation reactions were carried out at different temperatures, but at constant concentrations of the sugars, HClO₄, ionic

Table 1: Variation of rate constant with chromium(VI) concentration at 40 °C, [SUGAR] = 1 x 10⁻² M, [HClO₄] = 2.4M, [NaClO₄] = 1 x 10⁻²M.

[Cr(VI)] x 10 ⁻⁴ M	Xylose		Arabinose	
	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹
1.00	1.40±0.48	0.0014±0.29	3.88±0.38	0.0039±0.31
2.00	1.43±0.26	0.0014±0.35	2.25±0.28	0.0023±0.28
3.00	1.78±0.45	0.0015±0.45	5.17±0.89	0.0052±0.24
4.00	2.00±0.36	0.0017±0.16	4.94±0.61	0.0049±0.53
5.00	-	-	6.50±0.52	0.0065±0.48
6.00	1.53±0.52	0.0017±0.39	5.61±0.38	0.0056±0.43
7.00	1.67±0.62	0.0017±0.38	-	-

Values are mean of at least 2 determinations ± SD

Table 2: Variation of rate constants with sugar concentration at 40 °C, [Cr(VI)] = 5x10⁻⁴M, [HClO₄] = 2.4M, [NaClO₄] = 0.2M.

[Sugar]x 10 ⁻² M	Xylose		Arabinose	
	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹
1.00	1.67±0.20	0.0017±0.51	-	-
1.20	1.80±0.19	0.0015±0.32	4.20±0.36	0.0035±0.39
1.40	-	-	4.67±0.32	0.0033±0.46
1.60	3.22±0.25	0.0020±0.28	6.00±0.48	0.0038±0.26
1.80	3.40±0.36	0.0019±0.36	6.40±0.52	0.0036±0.39
2.00	3.83±0.48	0.0019±0.27	7.93±0.38	0.0040±0.41
2.20	4.22±0.39	0.0019±0.65	10.67±0.40	0.0049±0.52

Values are mean of at least 2 determinations ± SD

Table 3: Variation of rate constants with Sodium perchlorate concentration at T= 40 °C, [Cr(VI)] = 5 x 10⁻⁴ M, [HClO₄] = 2.4M, [Sugar] = 1 x 10⁻²M.

[NaClO ₄] M	Xylose		Arabinose	
	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	k _{obs} x 10 ⁵ s ⁻¹	k ₂ M ⁻¹ s ⁻¹
0.05	1.00±0.51	0.0010±0.39	3.42±0.62	0.0034±0.63
0.08	1.13±0.52	0.0011±0.56	4.00±0.31	0.0040±0.52
0.125	1.61±0.36	0.0016±0.61	4.71±0.29	0.0047±0.39
0.15	1.23±0.29	0.0017±0.62	4.45±0.38	0.0048±0.63
0.16	1.89±0.61	0.0019±0.54	4.81±0.65	0.0048±0.62
0.20	2.00±0.63	0.0020±0.48	4.16±0.81	0.0049±0.51
0.25	2.14±0.35	0.0021±0.63	-	-

Values are mean of at least 2 determinations ± SD

strength and chromium(VI). The plot of log k₂ as a function of temperature is linear for the two sugars (Figure 3) and the Arrhenius activation energies (E_a) were determined from the slopes of the plots as presented in Table 4. The data showed that the Arrhenius activation energies for the oxidation of Xylose and Arabinose decreased in the order Arabinose > Xylose. The values of the thermodynamic

activation parameters (ΔS[‡], ΔH[‡], and ΔG[‡]) (Table 4) were estimated following the literature procedure (Singh et al., 1991). The enthalpy of activation exhibited the same trend as was observed for the Arrhenius activation energy. The large negative values of entropy of activation for the two sugars indicate a rigid activated complex in the transition state (Khan and Abid, 2003).

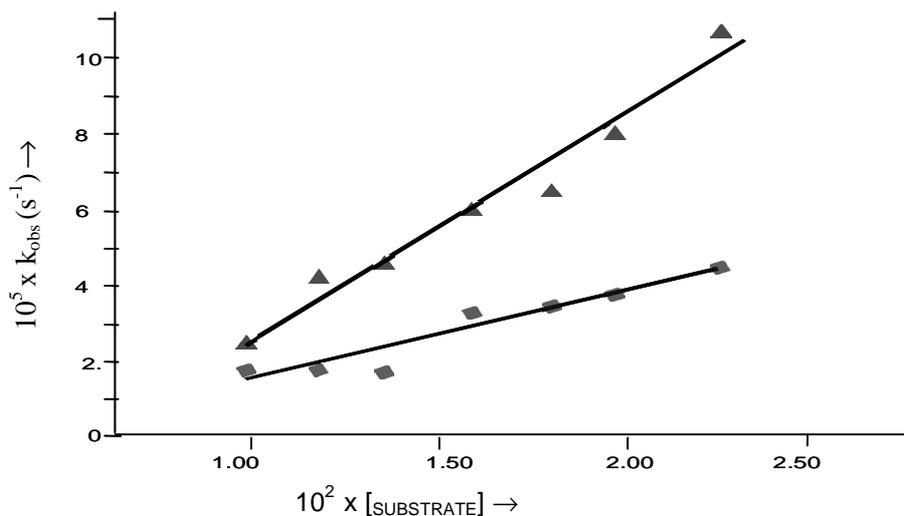


Figure 1: Plots of k_{obs} against the sugar concentration at 40 °C, $[\text{HClO}_4] = 2.4\text{M}$, $[\text{NaClO}_4] = 0.2\text{M}$, $[\text{Cr(VI)}] = 5 \times 10^{-4}\text{M}$ for oxidation of D-xylose and L-arabinose. \blacksquare - D-xylose, \blacktriangle - L-arabinose.

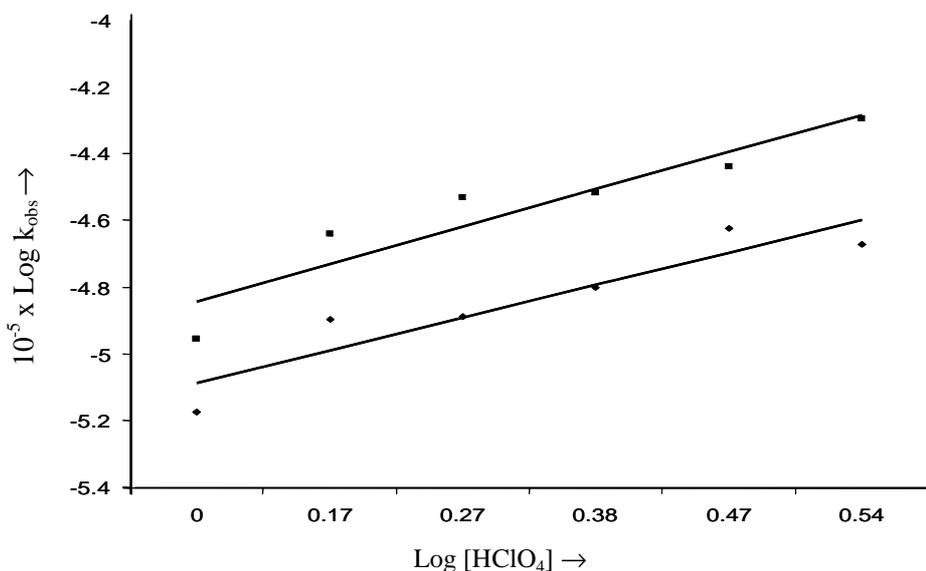


Figure 2: Zucker-Hammet plot for oxidation of D-xylose and L-arabinose. \blacksquare - D-xylose, \blacklozenge - L-arabinose.

Reaction mechanism and rate laws

Similar values of the free energy change (ΔG^\ddagger) obtained from this work is suggestive of a common mechanism for the oxidation of both aldopentoses (Bajpai et al., 1996). The double reciprocal plots of the pseudo-first-order rate constants against the sugar concentrations were linear (Figure 4),

this provides ample evidence for the formation of a 1:1 intermediate complex between the oxidant and the sugars at the transition state (Singh et al., 1970; Odebunmi et al, 1999). The linear plots of $1/k_{\text{obs}}$ against $1/[\text{S}]$ in Figure 4 is also an indication that the rate of the oxidation of these sugars is related to the substrate concentration by the relation

Table 4: Activation parameters, complex formation and rate constant for disproportionation for the oxidation of sugars by chromium(VI) in perchloric acid medium at 313k.

Sugars	E_a kJmol ⁻¹	ΔH^\ddagger kJmol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	ΔG^\ddagger kJmol ⁻¹	K_1 M ⁻¹	$k_s \times 10^{-4}$ s ⁻¹
Xylose	49.70±0.5	47.10±0.25	- 83.39±0.5	73.20±0.5	10.54	17.00
Arabinose	51.81±0.5	49.21±0.3	- 82.64±0.6	75.08±0.25	15.14	36.00

Average linear regression coefficients, $r \geq 0.9$, were observed for all the activation parameters.

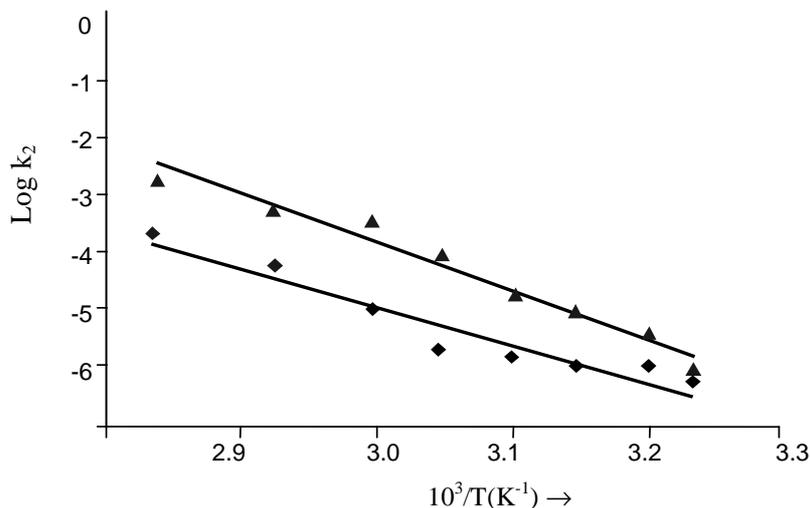


Figure 3: Arrhenius plot for oxidation of D-xylose and L-arabinose.
 ◆ - D-xylose, ▲ - L-arabinose.

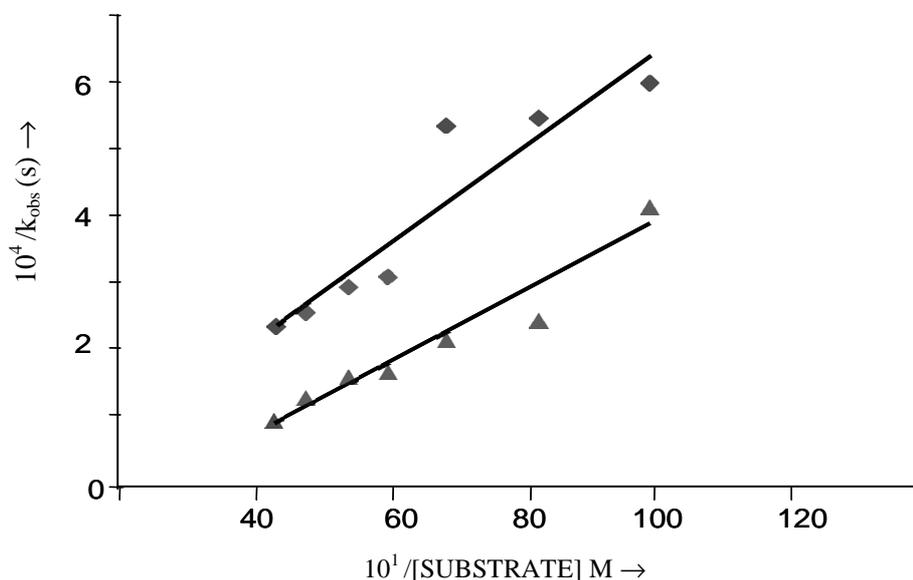
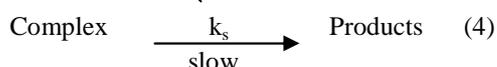


Figure 4: Double reciprocal plot $1/k_{obs}$ against $1/[SUBSTRATE]$ for oxidation of D-xylose and L-arabinose at 40 °C.
 ◆-D-xylose, ▲-L-arabinose.

$$\frac{1}{k_{obs}} = a \left(\frac{1}{[S]} \right) + b \dots\dots\dots(1)$$

where *a* and *b* are the slope and intercept of the linear plot respectively (Dalal and Ram, 2001). It has been confirmed that the reactive specie of Chromium(VI) in acidic solution is H⁺CrO₃ (Martinez et al., 1975). Based on our kinetic data and the literature evidence, the following reaction mechanism is proposed:



The protonated chromic acid which is the reactive specie reacts with a neutral sugar molecule to form the intermediate complex which then dissociates in a slow step to yield the products. In the mechanism of oxidation of C₆ and C₁₂ sugars, the reaction at the transition state was reported to occur between a protonated sugar molecule and protonated chromic acid molecule (Odebunmi and Owalude, 2005), a different trend is noticed with the C₅ sugars under the present study. The rate of the reactions in all cases were independent on the ionic strength of the medium, indicating that a neutral molecule is involved at the transition state in sharp contrast to the C₆ and C₁₂ sugars. This difference in mode of action of these two classes of sugars could therefore be explained in terms of their structural differences.

The aldopentoses and aldohexoses have been reported to exist only in furanoid and pyranoid forms with the latter being more stable (Gupta and Basu, 1979b). The stable pyranoid form exists mainly in chair conformations and these conformations provide the least strain and minimum Van der Waals' repulsions (Neckers and Doyle, 1977). According to Pearson's hard and soft acid-base theory (Frost and Pearson, 1970), these sugars are hard bases therefore a rapid and reversible transfer of H⁺ to the ring oxygen atom of the sugars is expected to occur in

strong acidic medium as represented by the equation below (Gupta and Basu, 1979a).



Aldopentoses with fewer than 6 carbons experience a kind of strain because the ring structure forces the carbon bonds into angles that are less than the normal 109.5° angle, which represents the lowest energy configuration for the sp³ hybridized carbon atoms (Wade, 1999). This angle strain causes a higher potential energy and less stability. The C₅ sugars under the present study because of their five member ring structure could only exist in the less stable furanoid form, therefore the ring strain and greater Van der Waals' repulsions effects would make the protonation of their ring oxygen very difficult. So the reaction at the transition state of the C₅ sugars will preferentially occur between the neutral sugar molecule and the protonated Cr(VI) ions. This also explains why these reactions of the C₅ sugars did not go through a free radical mechanism as in the case of the C₆ and C₁₂ sugars (Odebunmi and Owalude, 2005). Equation 5 is thus applicable to C₆ and C₁₂ sugars only because of their six member ring structure.

The rate law derived from the above mechanism is

$$\frac{-d [Cr(VI)]}{dt} = \frac{k_s K_1 K_2 [H^+][S][H_2CrO_4]_T}{1 + K_1 K_2 [H^+][S]} \quad (6)$$

From which

$$k_{obs} = \frac{k_s K_1 K_2 [H^+][S]}{1 + K_1 K_2 [H^+][S]} \quad (7)$$

Therefore

$$\frac{1}{k_{obs}} = \frac{1}{k_s K_1 K_2 [H^+][S]} + \frac{1}{k_s} \quad (8)$$

From equation (7) above, it is evident that at sufficiently low substrate concentrations, the inequality 1 >> K₁K₂[S][H⁺] is valid and equation (7) reduces to:

$$k_{\text{obs}} = k_s K_1 K_2 [H^+][S] \quad (9)$$

Rate law (9) explains all the experimental results i.e. the first-order dependence of the reaction rate with respect to each, substrate, the oxidant as well as the H^+ . Equation (8) is also consistent with the plots in Figure 4.

Conclusion

From the observed kinetic data and the polymerisation test, the following conclusions can be drawn:

- The rate of the oxidation of D-xylose and L-arabinose did not depend on the ionic strength of the medium of the reaction, indicating that a neutral molecule is involved at the transition state.
- This reaction did not go through a free radical mechanism as in the case of the C_6 and C_{12} sugars.
- The observed negative value of entropy of activation for both D-xylose and L-arabinose supports the formation of a rigid activated complex as proposed in step II of the mechanism.
- The reaction mechanism involves formation of an intermediate complex between a protonated chromium(VI) ions and a neutral sugar molecule which dissociates in a slow step to give the products.

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