

N-chlorophthalimide Oxidation of L-Arabinose and D-Xylose in Aqueous Acetic Acid Medium

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Abstract: *The mechanistic study on oxidation of L-arabinose and D-xylose by N-chlorophthalimide in aqueous acetic acid medium has been investigated in 20% aqueous acetic acid medium at 333 K. Reversible formation of reactive intermediates has been observed. The reaction showed first-order dependence in NCP and independent in the ionic strength of the medium with aldose, kinetic evidence support two step reaction mechanism involving a fast pre-equilibrium step followed by a rate determining disproportionation step. Negative value of activation of entropy indicated an ordered transition state for the reaction. The influence of the pentose structure such as steric effect and lengthening of chains on the overall reaction rate were discussed.*

Key words: *L-arabinose, D-xylose, N-chlorophthalimide. oxidation, kinetics.*

1. INTRODUCTION

Long-long ago the word sugar has been derived from the Sanskrit epic which means sweet sand and isolated as a sucrose from the juice of sugar cane. Previously it was thought that hydrated carbons are called carbohydrates. The carbohydrates term applied to a group of organic compounds monomeric, oligomeric and polymeric in nature. It is of prime importance specially enriched in stereochemistry, with practical and theoretical point of view. It plays key roles in master molecule DNA, on this very basis carbohydrates are usually classified according to their degree of polymerisation as mono-saccharides, di-saccharides, oligo-saccharides etc. It's complex reaction mechanism tremendously difficult in understanding the process of photosynthesis. The aldoses undergoing investigation possesses (5-carbon, sugar) regarded as pentose easily oxidised to yields aldonic acids via C-C bond cleavage under sufficiently drastic conditions. The detailed information on the rates and mechanism of the reaction are very important for synthetic and analytical work.

Sugars are naturally occurring compounds largely distributed in plants, fruits etc. They are of chemical and pharmacological interest, provide us food, clothing, and fulfils modern needs of the human being.

It is interesting and fascinating to investigate the mechanistic pathway of redox reaction which was little probed as the mechanism varied greatly with the nature of oxidant and reducing agent employed. Carbohydrates are biologically important poly-functional compounds whose oxidation are important in their metabolism. Carbohydrate shows variety of interesting physio-chemical properties which are becoming increasingly appreciated by organic chemists.^[1]

Pentose are oxidised extensively by different oxidising agents (NBSA^[2], NBP^[3], QCC^[4] etc.) and in all these reactions, available aldehydic group is attacked by the oxidant earlier acclaimed by few eminent authors.

N-chlorophthalimide is halo oxidant easily synthesized in the laboratory Its psycho-activity is limited and needs to be elaborated. The widespread utilization of NCP for the efficient oxidation of alcohols.^[5,6] testifies for this trend. In this paper, we present kinetic data which may shed some light on the mechanistic aspects of the reactions left unavailable for the oxidation of L-arabinose and D-xylose by NCP.

2. EXPERIMENTAL

All the reagents and solvent used in the study were of analytical grade (A.G.). The aqueous solution of L-arabinose (A.R., B.D.H.) and D-xylose (B.D.H.) was prepared in double distilled water. The solution of N-chlorophthalimide (A.G.) was prepared in 80% acetic acid as mentioned in literature. The purity of the NCP has been checked by iodometric method according to standard procedures. The solution of NCP was stored in a black coated flask to save it from photochemical deterioration. Acetic acid (B.D.H.) and acrylonitrile (SD fine) were employed for the study of solvent polarity and detection of free radicals in reaction mixture.

Kinetic measurements

The entire kinetic measurements were performed under pseudo first-order condition [pentose] \gg [NCP] in thermostat maintained at reaction temperature. The flask containing known quantity of NCP in aqueous acetic acid solvent and another flask containing substrate (L-arabinose or D-xylose) and known amount of other additives were clamped in a thermostatic bath for 30 minutes before the commencement of the kinetic runs. The reaction was started by mixing required amount of NCP to the other contents of the reaction vessel. The whole reaction mixture was mixed thoroughly and was followed by measuring the values of unreacted [NCP] in the reaction mixture iodometrically.^[7] The parameters (a_0) and ($a-x$) represent the values at 0 time (the time of initiating the reaction) and at given instant of time (during the progress of reaction) respectively. The rate constant were computed by feeding the kinetic data in integration and graphical method. The replicate kinetic values for the reaction were found within $\pm 3\%$ error.

3. RESULTS AND DISCUSSION

In stoichiometry determination of the NCP-pentose reactions, [NCP] was taken 10-15 times in slightly excess over [pentose] in aqueous acetic acid medium and reaction was allowed to proceed till the reaction for 36 hours is completed. The [NCP] was recorded periodically. The determination of unconsumed NCP was found that 1 mole of NCP was needed to oxidised 1 mole of pentose. The following stoichiometric reaction can be depicted as :



where R = C₄H₉O₄ for L-arabinose and D-xylose (Pentose) respectively.

Arabinoic acid and xylonic acid were corresponding products of the reactions, identified by TLC^[8] and conventional spot test method. ^[9,10]

Addition of olefinic monomer (acrylonitrile) to the reaction mixture did not afford vinyl polymer even under elevated temperatures and inert atmosphere. This observation revealed that free radical intermediates not formed during the oxidation.

The rate of oxidation of aldoses was investigated at 333 K by varying five-times concentrations of NCP, at fixed reaction conditions. The rate of NCP is found proportional to the first power of the concentration of NCP.

The aldoses reaction were conducted kinetically and have a fractional-order dependence (Table 1) in substrates which helped them to substantiate the formation of NCP-aldose complex. The values of second-order rate constant does not show constancy. The oxidation of aldoses involve rate limiting disproportionation of cyclic complex. The existence of complex formed at the top of the barrier of the transition state is further confirmed by graphic plots of $\frac{1}{k_{obs}}$ against $\frac{1}{[aldose]}$, which yields non-zero intercept on the rate axis. (Fig.1).

Table 1: Dependence of rate on concentration of aldose

$10^3 \times [NCP]$ (mol dm⁻³) = 3.33 (1, 2) ; $[H^+]$ (mol dm⁻³) = 0.25 (1), 0.333 (2) ;

CH₃COOH-H₂O %, (v/v) = 20 (1, 2) ; Temperature K = 333 (1, 2)

10^2 [aldose] (mol dm ⁻³)	10^4 k (s ⁻¹)	
	L-arabinose (1)	D-xylose (2)
0.80	1.79	1.31
1.00	2.26	1.65
1.25	2.81	1.97
1.66	3.49	2.46
2.00	4.06	2.93
2.50	4.61	3.53
3.33	4.86	4.06

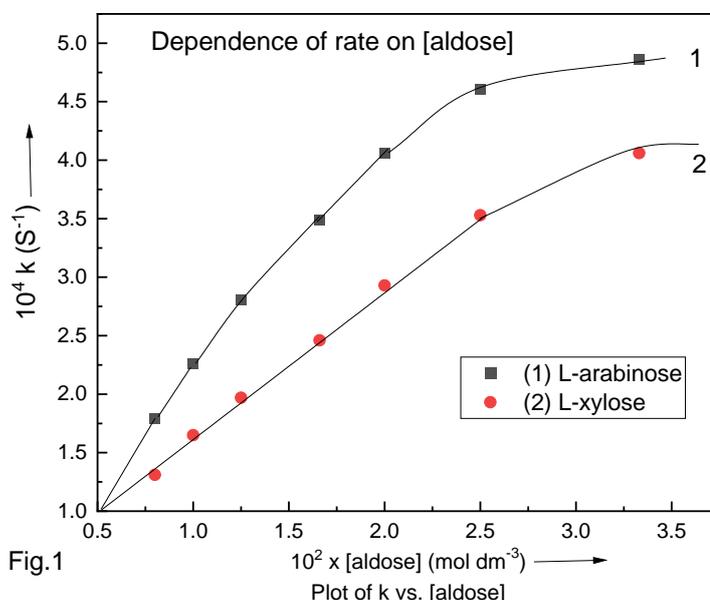


Fig.1

$10^3 \times [NCP]$ (mol dm⁻³) = 3.33 (1, 2) ; $[H^+]$ (mol dm⁻³) = 0.25 (1), 0.333 (2) ;
CH₃COOH-H₂O % (v/v) = 20 (1, 2) ; Temp. K = 333 (1, 2)

The rate was sensitized at varying $[H^+]$ and $[Cu^{++}]$ by maintaining other participating moiety constant. The study leads that although reaction is acid catalysed but observes acid dependent and acid independent paths of $[H^+]$ followed BUNNET-OLSEN plot yielding non zero intercept with fractional-order slope values.

The oxidation was studied in aqueous acetic acid medium. Considering that no-reaction occurs with the solvent chosen. The study reveals that the oxidation of each aldose increases steadily by increase in percentage composition of solvents (Table 2). The graphic plot of $\log k$ versus $\frac{1}{D}$ yielded positive slopes leading that neutral species takes part in the rate determining process (Fig. 2).

Table 2: Dependence on rate of Solvent polarity

$10^3 \times [NCP] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)} ; 10^2 \times [\text{aldose}] \text{ (mol dm}^{-3}\text{)} = 1.66 \text{ (1), 2.00 (2)} ;$

$[H^+] \text{ (mol dm}^{-3}\text{)} = 0.25 \text{ (1), 0.333 (2)} ; \text{ Temperature K} = 333 \text{ (1, 2)}$

CH ₃ COOH % (v/v)	$10^3 \times \frac{1}{D}$	$10^4 k \text{ (s}^{-1}\text{)}$	
		L-arabinose	D-xylose
10	15.50	3.05	2.47
20	17.17	3.49	2.93
30	19.15	3.88	3.58
40	21.98	5.20	4.86

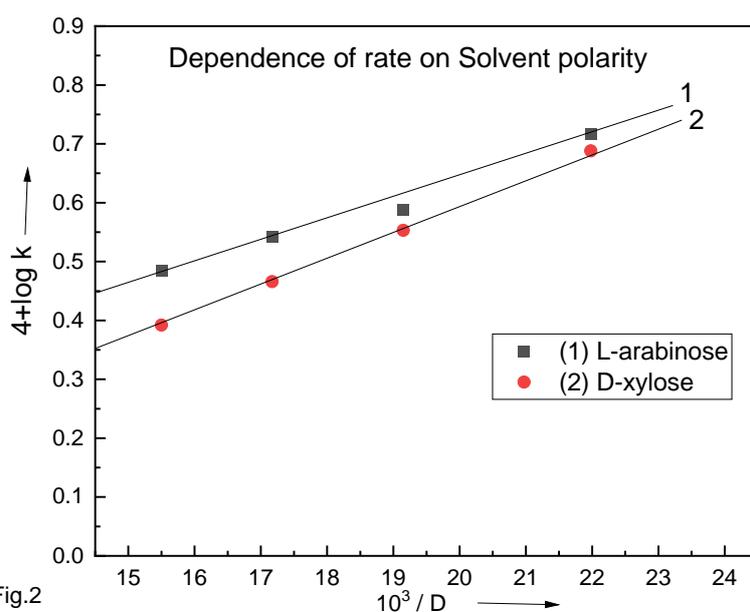


Fig.2

Amis plot of $\log k$ against $1/D$

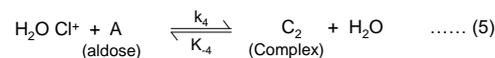
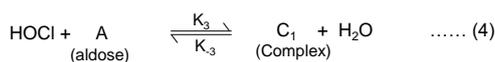
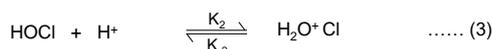
$10^3 \times [NCP] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)} ; 10^2 \times [\text{Aldose}] \text{ (mol dm}^{-3}\text{)} = 1.66 \text{ (1), 2.00 (2)} ;$

$[H^+] \text{ (mol dm}^{-3}\text{)} = 0.25 \text{ (1), 0.333 (2)} ; \text{ Temp. K} = 333 \text{ (1, 2)}$

The oxidation reaction of aldoses shows inertness towards the added varying concentration of primary salt and ionic strength of the medium whereas phthalimide and Mn^{+2} ion were found to indicate slightly retarding trend in the reaction kinetics.

Reaction mechanism

Considering H_2O^+Cl active species of oxidant NCP and involvement of aldehydic form of substrate, the proposed mechanism may be formulated as:



Rate law

Taking into account the various steps involved in the foregoing mechanism and employing steady state conditions, the final rate law for two controlling steps involved in the protonated equilibrium may be deduced as :

$$k_{obs} = \frac{k_1 k_3 k_5 [A][H_2O]}{(k_{-3} + k_5) k_{-1} [Ph.] + k_3 k_5 [A]} + \frac{k_2 k_4 k_6 [A][H^+]}{k_{-2} k_{-4} + k_{-2} k_{-6} + k_4 k_6 [A]}$$

Transforming above equation to in inverse form and graphic plots of k^{-1} versus substrate^{-1} give rise non-zero intercept on ordinate axis supports the formation of complex and rate dependency on acidity of the reaction.

The sequence of general trends of rate constant is :



The foregoing order of reactivity pertaining to the rate constant controlled by the steric polar nature of complex and values of entropy of activation. There is a loss in partition function (transitional energy^[11]) when activated complex is formed at the contour of the transition state.

Cantor *et al.*^[12] correlated percentage composition / concentration of aldehyde form with structure of aldose. The above order of reactivity is supported by oxidation by Tl(III)^[13] based on above facts of aldehyde form. Another reason is D-xylose (pentose) has lowest aldehydic percentage and L-arabinose has the highest, that is, why the rate of oxidation of L-arabinose is slower than that of D-xylose.

The order of reactivity co-relates the chain length with the rate of reaction i.e. lengthening in chains, the reaction rate decreases. The entropy of activation for the two reactions have been found to be negative (Table 3). This is due to compactness of transition state as compare to ground state, causing a restriction on the transitional and rotational freedom, thus reducing the entropy of the system. Thus leading towards high polar transition state.^[14,15]

Table 3: Activation Parameters for the reaction between some aldoses and N-chlorophthalimide

Aldose	Ea (kJ mol ⁻¹)	A (s ⁻¹)	ΔH [#] (kJ mol ⁻¹)	ΔG [#] (kJ mol ⁻¹)	-ΔS [#] (JK ⁻¹ mol ⁻¹)
L-arabinose	38.52	3.84 × 10 ²	32.59	92.17	180.25
D-xylose	42.27	12.64 × 10 ²	38.90	93.20	164.29

The activation energy also played vital role in deciding above order of reactivity which is highest for the slowest reaction indicating that reaction is enthalpy controlled. The Gibbs's free energy (ΔG[#]) for the two reactions are almost lie in the same vicinity, for the slightly different structures of pentose suggesting, that similar mechanism is prevailing for each aldose.

Conclusions

The most striking feature of the kinetics and mechanism of NCP mediated oxidation of aldoses such as L-arabinose and D-xylose is that H₂O⁺Cl reactive species attacks to aldehydic group of the aldose stoichiometrically (1:1) to form polar activated complex at the transition state restricting translational energy. The activated complex decomposes in the rate determining step to form aldonic acids. The overall process revealed first-order dependence on [NCP] and [H⁺]. The present study showed acceleration in all the acids over a wide concentration range. These effects were analysed by Olson-theory of acidity functions accordingly. The lengthening of chains, percentage composition of aldehydic group and activation parameters are solely responsible for the above order of activity and mechanism.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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