

Oxidation of Some Aldoses by N-Chlorophthalimide in Aqueous Acetic Acid Medium - A Kinetic Study

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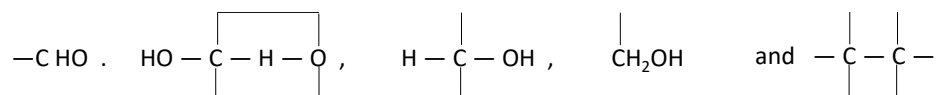
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Abstract: D-glucose and D-ribose oxidation by N-chlorophthalimide has been examined in aqueous acetic acid medium. The main product of the oxidation is the corresponding aldonic acid. The reaction is first-order in [NCP]. Michaelis-Menten type kinetics have been observed with respect to the aldoses and independent in the ionic strength of the solution. The temperature dependence of kinetics i.e. negative entropy of activation revealed the presence of symmetrical transition state in the rate determining disproportionation step. The acid dependent and independent paths of $[H^+]$ was explained. A suitable mechanism in consistence with the kinetic results has been proposed.

Keywords: D-ribose, D-glucose, N-chlorophthalimide. oxidation, kinetics.

1. INTRODUCTION

The origin of carbohydrate can be traced back to civilization during antiquity and is well documented in Egyptian literature. Carbohydrates are bio-logically important poly-junctional compounds quite literally provide us with the basic necessities of life-food, clothing, shelter, paper textile, pharmaceutical etc. Most of the carbohydrates possesses five-or six-carbon chain in their structures because they are derived from pentoses (5-carbon sugars) and hexoses (6-carbon sugars). They are differentiated by their stereochemistry. The aldehydes are hemiacetal group which is the most easily oxidized with common grouping :



The primary alcoholic group may be converted into aldehyde and $-COOH$ group, whereas secondary alcohol group at 2 and 5 position of hexose may be transformed to keto group. Most oxidants bring about C-C fission under sufficiently drastic conditions. A perusal of literature indicates that kinetics of oxidation of sugars[1-6] have been studied extensively using different oxidizing agents in various medium.

NCP is a N-halo oxidant which is very effective and economically cheap oxidant successfully exploited as an input technology employed as an oxidant for the catalysed and uncatalyzed reactions.^[7-10] However such studies with aldoses appeared to be scanty. In this text of the work we want to present the kinetics and mechanism of D-glucose and D-ribose using NCP in aqueous acetic acid medium with regards to behaviour of reactive species of oxidant and influences of various additives on the reaction rate which are interpreted by the theories of acidity functions.

2. EXPERIMENTAL

All the chemicals employed in the investigations are of analytical grade. The NCP (A.G.) was used as received and its purity has been checked by standard procedures. The D-glucose and D-ribose both belongs to A.R., B.D.H.,^[10] (loc. cit.) their freshly prepared solutions in double distilled water were used. All other necessary solutions pertaining to the kinetic studies were prepared properly and standardized where ever necessary.

Kinetic measurements

The oxidation reaction was studied under pseudo first-order condition $[\text{aldose}] \gg [\text{NCP}]$. The thermostat was adjusted to derived reaction temperature. Reaction was initiated by the rapid addition of known amounts of aldose to reaction mixture containing the required amount of NCP. In the reaction vessel after stirring, the progress of the NCP-aldose reaction was monitored by iodometric^[11] determination of unconsumed [NCP] in known aliquots of the reaction mixture at different time intervals. The rate constant of the reactions in each kinetic run was determined by integration and graphical methods. The kinetic data is reproducible with precision of 3% error.

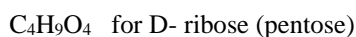
3. RESULTS AND DISCUSSION

The stoichiometry was accomplished in duplicate by analysing the reaction mixture under experimental conditions in which the concentration of aldoses was 10-15 times more than concentrations of oxidant. Consequently the stoichiometry was found to be 1 mole of NCP per mole of each aldose.

The stoichiometric reaction can be formulated by equation:



where R = C₅H₁₁O₅ for D-glucose (hexose) and



The corresponding products of the formation of the reactions were aldonic acids, in each case was identified properly by employing physical, chemical, spot test and chromatographic (TLC) methods.

The oxidation of aldoses by NCP in nitrogen atmosphere did not induce polymerization of acryl amide.

The effect of five-fold [NCP] was studied on each aldose at fixed pre-set conditions. The unit slope calculated from the linearity of parallel plots (a-x) versus time ascertained first-order of the reaction with respect to [NCP].

The oxidation reaction followed Michaelis-Menten kinetics (Table 1). The double reciprocal plots of $\frac{1}{k_{\text{obs}}}$ versus $\frac{1}{[\text{aldose}]}$ are found linear with an intercept on the rate ordinate (Fig.1) showing the complex formation between oxidant species and aldose in pre-equilibrium step.

Table 1: Dependence of rate on concentration of aldose

$10^3 \times [\text{NCP}]$ (mol dm⁻³) = 2.50(2), 3.33 (1) ; $[\text{H}^+]$ (mol dm⁻³) = 0.20 (2), 0.40 (1) ;

CH₃COOH-H₂O %, (v/v) = 50 (1), 60 (2) ; Temperature K = 333 (1, 2)

10 ² [aldose] (mol dm ⁻³)	10 ⁴ k (s ⁻¹)	
	D-glucose (1)	D-ribose (2)
0.50	-	1.34
1.00	1.23	2.75
1.25	1.63	3.34
1.50	-	3.89
1.66	1.99	-
2.00	2.42	5.06
2.50	2.73	5.78
3.33	2.99	6.46

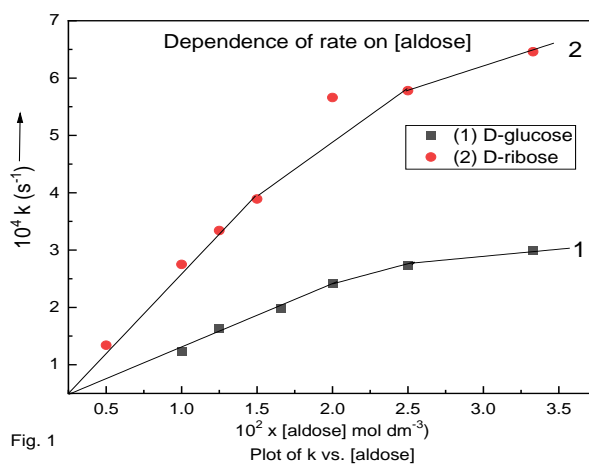


Fig. 1

Plot of k vs. [aldose]
 $10^3 \times [\text{NCP}]$ (mol dm⁻³) = 2.50 (2), 3.33 (1) ; $[\text{H}^+]$ (mol dm⁻³) = 0.20 (2), 0.40 (1) ;
 CH₃COH-H₂O %, (v/v) = 50 (1), 60 (2) ; Temp. K = 333 (1, 2).

The reaction is catalysed by H⁺ ions. The two rate controlling steps-acid dependent and acid independent paths are involved in the protonated equilibrium (Table 2) has the following form of

$$k_{\text{obs}} = a + b [\text{H}^+] \dots (2)$$

Table 2: Dependence of rate on acidity

$10^3 \times [\text{NCP}]$ (mol dm⁻³) = 2.50 (2), 2.22 (1); $10^2 \times [\text{aldose}]$ (mol dm⁻³) = 1.50 (2), 2.0 (1);
 $\text{CH}_3\text{COOH-H}_2\text{O}$ %, (v/v) = 50 (1), 60 (2); Temperature K = 333 (1, 2)

[H ⁺] (mol dm ⁻³)	10 ⁴ k (s ⁻¹)	
	D-glucose (1)	D-ribose (2)
0.08	-	2.11
0.10	0.86	2.42
0.15	-	3.14
0.20	1.30	3.89
0.25	1.40	4.42
0.333	2.07	5.93
0.40	2.42	-
0.50	2.93	-

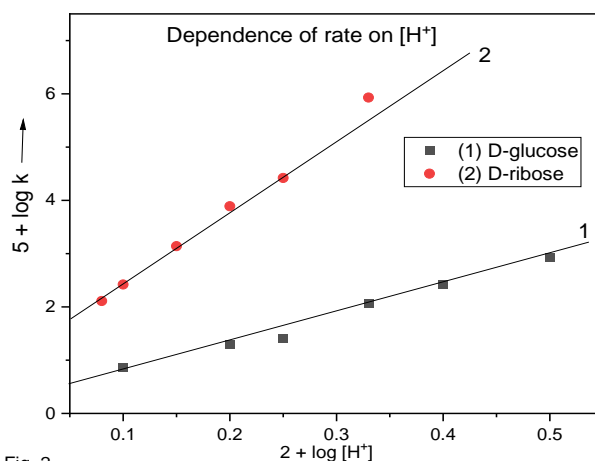


Fig. 2

Plot of log k vs. log [H⁺]
 $10^2 \times [\text{Aldose}]$ (mol dm⁻³) = 1.50 (2), 2.0 (1); $10^3 \times [\text{NCP}]$ (mol dm⁻³) = 2.50 (2), 3.33 (1);
 $\text{CH}_3\text{COOH-H}_2\text{O}$ %, (v/v) = 50 (1), 60 (2); Temp. K = 333 (1, 2)

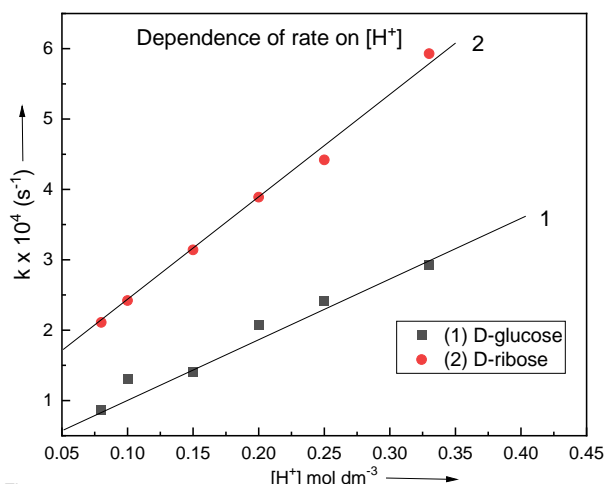


Fig. 3

Graphical plot of k vs. [H⁺]
 $10^2 \times [\text{Aldose}]$ (mol dm⁻³) = 1.50 (2), 2.0 (1); $10^3 \times [\text{NCP}]$ (mol dm⁻³) = 2.50 (2), 3.33 (1);
 $\text{CH}_3\text{COOH-H}_2\text{O}$ % (v/v) = 50 (1), 60 (2); Temp. K = 333 (1, 2)

The graphic plots of log k versus log [H⁺] (Fig.2) and k versus [H⁺] (Fig. 3) yielded linear with non-zero intercepts with slope values less than one.

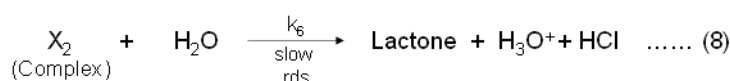
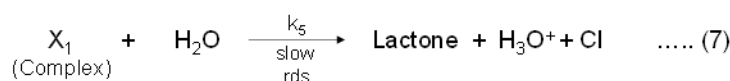
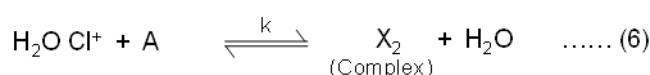
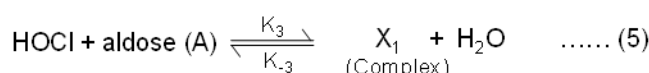
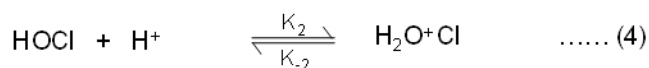
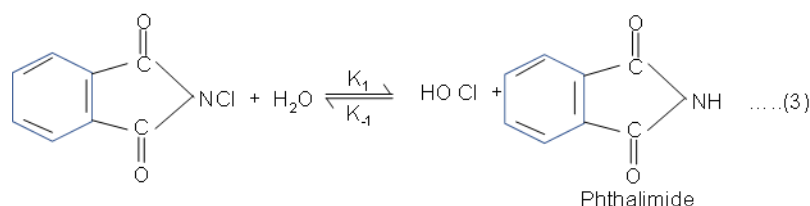
The oxidation was studied in aqueous acetic acid medium. The choice of solvent was limited and there was no reaction with the solvent chosen. It was found that k_{obs} increases gradually with decrease in dielectric constant of the medium. Amis plot of log k versus $\frac{1}{D}$ was also followed by the kinetics indicating that neutral species involved in the rate determining step.

The ionic strength of the medium (μ) and primary salt has no effect on the rate. The successive addition of [Phthalimide], a reductant product of oxidant NCP retarded the rate of oxidation indicates that phthalimide does not participate as reactive species in the

reaction mechanism. The rate of reaction was catalysed by added transition metal catalyst Cu^{+2} ions whereas presence of Mn^{2+} ions found to retard the rate.

Reaction mechanism

Mechanistically reaction mechanism based on kinetic results, $\text{H}_2\text{O}^+\text{Cl}$ active species of oxidant and involvement of both aldehydic and pyranose form of substrate, may be synchronised as :



Taking into account the various steps involved in the mechanism and execution of study state approximation. The acid dependent rate law is finally enumerated as :

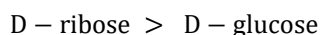
$$k_{\text{obs}} = \frac{k_2 k_4 k_6 [\text{aldose}][\text{H}^+]}{k_{-2} k_{-4} + k_{-2} k_6 + k_4 k_6 [\text{aldose}]} \quad \dots\dots (10)$$

and rate law for acid dependent and acid independent paths combinedly formulated by the equation (11)

$$k_{\text{obs}} = \frac{k_1 k_3 k_5 [\text{aldose}][\text{H}_2\text{O}]}{(k_{-3} + k_5) k_{-1} [\text{Phth}] + k_3 k_5 [\text{aldose}]} + \frac{k_2 k_4 k_6 [\text{aldose}][\text{H}^+]}{k_{-2} k_{-4} + k_{-2} k_6 + k_4 k_6 [\text{aldose}]} \quad \dots\dots (11)$$

Equation (11) for the proposed forgoing mechanism fully supports the results of our kinetics observations. It explains the order with respect to $[\text{H}^+]$ is one and Michaelis-Menten type kinetics.

In the present investigation, the general trends of order based on rate measurements were observed as:



Most of the thermodynamic factors could not be co-related qualitatively because of the irregular trend. This could probably indicate commutative effect of reveal parameters like polar-nature, steric, hydrophobic, hydrophilic interactions which control the reaction rate. However, observed large negative increase of entropy of activation probably suggest a systematic arrangement of atoms in the transition state to solvation. Polar nature of the activated complex is due to loss of transitional energy^[12] that takes place. The proposed activity is also supported by the fact that activation energy E_a is highest for the slowest reaction and vice versa^[13] (Table 3).

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

Aldose	E_a (kJ/ mol)	A (s^{-1})	ΔH^\ddagger (kJ/ mol)	ΔG^\ddagger (kJ/ mol)	$-\Delta S^\ddagger$ ($\text{JK}^{-1} \text{mol}^{-1}$)
D-glucose	44.16	20.33×10^2	42.73	93.73	154.29
D-ribose	31.72	3.65×10^3	29.99	91.56	186.27

The Gibb's energy (ΔG^\ddagger) values for the reactions are by and large appeared to be constant indicates that similar type of mechanism is operative in the present reaction. The two aldoses are differing in their configuration and length of chain falls in D-ribose belongs to pentose whereas D-glucose is related to hexose. The study reveals that pentose oxidised at a faster rate as compare to hexose. The order of reactivity co-relates the chain length with the rate of reaction i.e. with lengthening in chains the rate of reaction decreases. Moreover D-glucose has the lowest aldehydic percentage rather than D-ribose which has the highest. Similar views has also been reported by several authors in the oxidation of aldoses by different oxidants such as $\text{K}_2\text{Cr}_2\text{O}_7$ [14] and bromine [15] etc. Overall the reactions are found enthalpy controlled.

Conclusions

Stoichiometrically (1:1) the main reacting species $\text{H}_2\text{O}^+\text{Cl}$ forms the activated complex with the aldehydic aldose in the transition state. The activated complex decomposes in a slow rate determining step to yields corresponding aldonic acids. The reaction mechanism combinedly follow rate dependent and independent paths of $[\text{H}^+]$. The structure and reactivity of rate oxidation was discussed based lengthening of chains and thermodynamic parameters.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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