



## Oxidation Kinetics of Some Aldopentoses with Tetraethylammonium Chlorochromate in Aqueous Acetic Acid Medium Studied Spectrophotometrically

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**Abstract** Aldopentoses are biologically important molecules and their oxidation mechanism are difficult to understand because of multifunctionality in their molecules and the various structural forms in which they exist in solution [1]. The reactivity of newly developed tetraethylammonium chlorochromate (TEACC) as oxidant has been extensively studied and reviewed in many transformations [2]. In view of these facts, oxidation kinetics of some aldopentoses viz. D-ribose and D-xylose with TEACC have been examined spectrophotometrically in aqueous acetic acid (50% v/v) medium in the presence of perchloric acid at constant ionic strength in the 25°C to 40°C range. A rate law that explains all experimental results based on the study of dependence of pseudo-first order rate constant,  $k$ , on [oxidant], [substrate] and [acid] has been derived. A reaction mechanism involving hydride ion transfer via complex formation has been proposed on the basis of product identification and kinetic results.

**Key words:** Oxidation, Kinetics, Mechanism, D-xylose, D-ribose, tetraethylammonium chlorochromate

### Introduction

It is great deal of attraction to determine the mechanism of oxidation of monosaccharides which contain poly functional groups most organic compounds [3-16]. D-ribose produced by our body and it is used as medicine for heart disease, mental function and many other conditions. D-xylose occurs naturally from wood and plant foods. It is used in absorption test to check how our intestines are absorbing a simple sugar called D-xylose. In view of these and because of their special role in medicinal chemistry, kinetic and mechanistic studies on oxidation of these aldopentoses have been a great attention. Tetraethylammonium chlorochromate (TEACC) [17] add to the selected list of new Cr(VI) oxidants introduced newly as oxidizing agent for effective and selective oxidation of organic substrate under mild conditions. A survey of literature, shows that no work has been carried out on the kinetics of oxidation of D-ribose and D-xylose tetraethylammonium chlorochromate (TEACC).

### Experimental

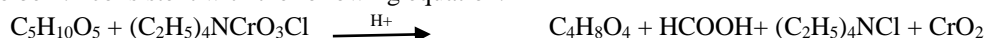
**Materials** - Tetraethylammonium chlorochromate (TEACC) was prepared by anhydrous chromium (VI) oxide dissolved in 6M HCl and stirred at 0°C for 5 min. To it a solution of tetraethylammonium hydroxide (20% in H<sub>2</sub>O) (Lancaster) was added and resulting orange yellow solid was washed and dried under reduced pressure for 2hr; Cr content was determined iodometrically. Solution of D-ribose and D-xylose were always freshly prepared in aqueous



acetic acid 50% (v/v). The ionic strength was maintained constant with the use of concentrated solution of NaClO<sub>4</sub> (C.D.H.). Perchloric acid (C.D.H.) and all other chemical were used as such without further purification.

**Kinetics measurements:** The reaction were performed under pseudo-first order condition by keeping a large excess of [aldopentoses] with respect to [TEACC]. The medium of the reaction was always 1:1 (v/v) acetic acid-water in the presence of perchloric acid. Kinetic measurements were made in Shimadzu UV 160A spectrophotometer at 350 nm. The optical density was measured at various intervals of time. Computation of rate constants was made from the plot of log [TEACC] against time.

**Stoichiometry and product analysis:** The stoichiometry of reaction was performed by conducting the oxidation of aldopentoses under the conditions of a known excess of tetraethylammonium chlorochromate. A mixture of aldopentoses (0.01 mol dm<sup>-3</sup>) and TEACC (0.10 mol dm<sup>-3</sup>) was kept for several hours at 30°C for the reaction to go to completion. The unconsumed oxidant was estimated iodometrically at the end of the reaction. The stoichiometry was found to be 1:1 consistent with the following equation.



For product analysis the reaction mixture containing aldopentoses and tetraethylammonium chlorochromate in the stoichiometric proportion 1:1 was left as to equilibrate at 30°C for 24 h. The reaction mixture was neutralized with NaHCO<sub>3</sub>, extracted with chloroform, washed with water and dried over anhydrous MgSO<sub>4</sub>. The formation of D-erythrose and L-erythrose were confirmed by osazone formation<sup>18</sup> and the presence of formic acid was confirmed by sport test [19].

## Results

The pseudo-first order rate constants were determined at various initial concentrations of reactants. The results obtained are given in Table 1. Plots for different concentrations of tetraethylammonium chlorochromate vs time were linear and the rate constants were independent of initial concentration of tetraethylammonium chlorochromate, showing first order dependence of the rate of [TEACC]. The reaction is first order with respect to [aldopentoses], too. A plot of log *k*<sub>1</sub> against log [aldopentoses] was linear with a slope of unity thereby confirming first order dependence in [aldopentoses].

Rates of oxidation were found to increase with increase in [H<sup>+</sup>] and the slopes of the pots of log *k*<sub>1</sub> vs log [HClO<sub>4</sub>] were approximately unity showing that the reaction is acid catalyzed and follows the first order dependence in [HClO<sub>4</sub>].

Consequently the empirical rate law is described as follows:

$$\frac{d[\text{TEACC}]}{dt} = k_{\text{obs}} [\text{aldopentoses}] [\text{TEACC}] [\text{HClO}_4]$$

**Table 1:** Rate constant for oxidation of aldopentoses by TEACC at 30°C, Solvent: Acetic acid-water (50-50% v/v)

[TEACC] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[D-ribose] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[D-xylose] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] × (mol dm <sup>-3</sup> )	D-ribose <i>k</i> <sub>1</sub> × 10 <sup>4</sup> (s <sup>-1</sup> )	D-xylose <i>k</i> <sub>1</sub> × 10 <sup>4</sup> (s <sup>-1</sup> )	<i>k</i> <sub>2</sub> × 10 <sup>2</sup> (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> ) D-ribose	<i>k</i> <sub>2</sub> × 10 <sup>2</sup> (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> ) D-xylose
0.22	1.66	1.66	0.77	7.74	5.56		
0.44	1.66	1.66	0.77	7.70	5.55		
0.66	1.66	1.66	0.77	7.69	5.58		
0.88	1.66	1.66	0.77	7.70	5.57		
1.11	1.66	1.66	0.77	7.74	5.59		
1.33	1.66	1.66	0.77	7.73	5.58		
1.11	0.33	0.33	0.77	1.55	1.10	4.69	3.33
1.11	0.66	0.66	0.77	3.08	2.22	4.67	3.36
1.11	1.00	1.00	0.77	4.68	3.38	4.68	3.38
1.11	1.33	1.33	0.77	6.19	4.50	4.65	3.38
1.11	1.66	1.66	0.77	7.74	5.59	4.66	3.37
1.11	2.00	2.00	0.77	9.32	6.78	4.66	3.39
1.11	1.66	1.66	0.38	4.40	1.90		



1.11	1.66	1.66	0.58	5.95	3.47
1.11	1.66	1.66	0.77	7.74	5.59
1.11	1.66	1.66	0.96	9.40	6.96
1.11	1.66	1.66	1.16	11.88	9.35
1.11	1.66	1.66	1.35	14.28	11.70

The reaction rate was not influenced by ionic strength when  $\text{NaClO}_4$  was initially added to the reaction mixture over the range  $0.83 \times 10^{-1}$  to  $5.00 \times 10^{-1}$  mol  $\text{dm}^{-3}$ . Similar observation was also reported in the oxidation of acrylic acid by TEACC [20].

When the reaction was initiated by adding acrylonitrile into a solution containing aldopentoses and TEACC, no retardation in the rate was observed. No turbidity due to polymerization of acrylonitrile was observed. Thus, the formation of radical intermediate may be ruled out in the course of the reaction.

*Effect of solvent:* The reaction has been studied under various compositions of acetic acid-water mixture. It has been observed that the reaction rate increase with the increase of  $\text{CH}_3\text{COOH}$  in acetic acid-water mixture (Table 2). A linear plot between  $\log k_1$  and  $1/D$  (inverse of dielectric constant) with a positive slope suggests an interaction between an ion and a dipole [21].

**Table 2:** Dependence of rate on solvent composition

[aldopentoses] =  $1.66 \times 10^{-2}$  mol  $\text{dm}^{-3}$ , [TEACC] =  $1.11 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , [ $\text{HClO}_4$ ] = 0.77 mol  $\text{dm}^{-3}$ , [ $\text{NaClO}_4$ ] =  $1.66 \times 10^{-1}$  mol  $\text{dm}^{-3}$ , temp. = 30°C.

m,	$k_1 \times 10^4$ ( $\text{s}^{-1}$ )		1/D
	D-ribose	D-xylose	
40 : 60	6.90	4.74	0.020
50 : 50	7.74	5.59	0.024
60 : 40	8.40	6.35	0.028
70 : 30	10.10	8.08	0.036
80 : 20	12.65	10.40	0.048

The reaction rates at different temperatures were determined and the values of activation parameters were calculated from the slope of linear plot of  $\log k_1$  vs  $1/T$ . The data are presented in Table 3. An inspection of data shows that these reactions are characterized by high negative value of entropy of activation ( $\Delta S^*$ ). This indicates that solvation effect is predominant in the reaction, which suggests the formation of a charged rigid transition state. Furthermore, the high positive value of energy of activation and enthalpy of activation indicate that the intermediate is highly solvated.

**Table 3:** Temperature dependence and activation parameters of oxidation of [aldopentoses] by [TEACC]

[aldopentoses] =  $1.66 \times 10^{-2}$  mol  $\text{dm}^{-3}$ , [TEACC] =  $1.11 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , [ $\text{HClO}_4$ ] = 0.77 mol  $\text{dm}^{-3}$ , [ $\text{NaClO}_4$ ] =  $1.66 \times 10^{-1}$  mol  $\text{dm}^{-3}$ , temp. = 30°C.

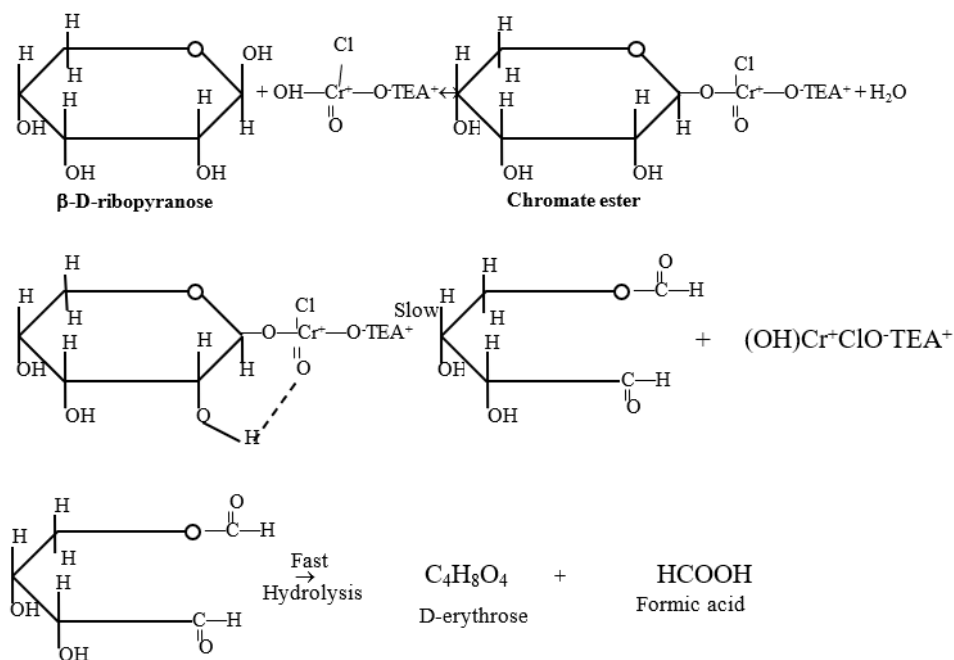
Temperature (K)	298	303	308	313	Ea	$\Delta H^*$	$\Delta G^*$	$-\Delta S^*$
	$k \times 10^4$ ( $\text{Sec}^{-1}$ )	$k \times 10^4$ ( $\text{Sec}^{-1}$ )	$k \times 10^4$ ( $\text{Sec}^{-1}$ )	$k \times 10^4$ ( $\text{Sec}^{-1}$ )				
D-ribose	5.65	7.74	10.51	14.40	48.40	45.88	92.29	153.18
D-xylose	3.90	5.59	7.96	11.24	54.74	52.22	93.16	126.62



## Discussion

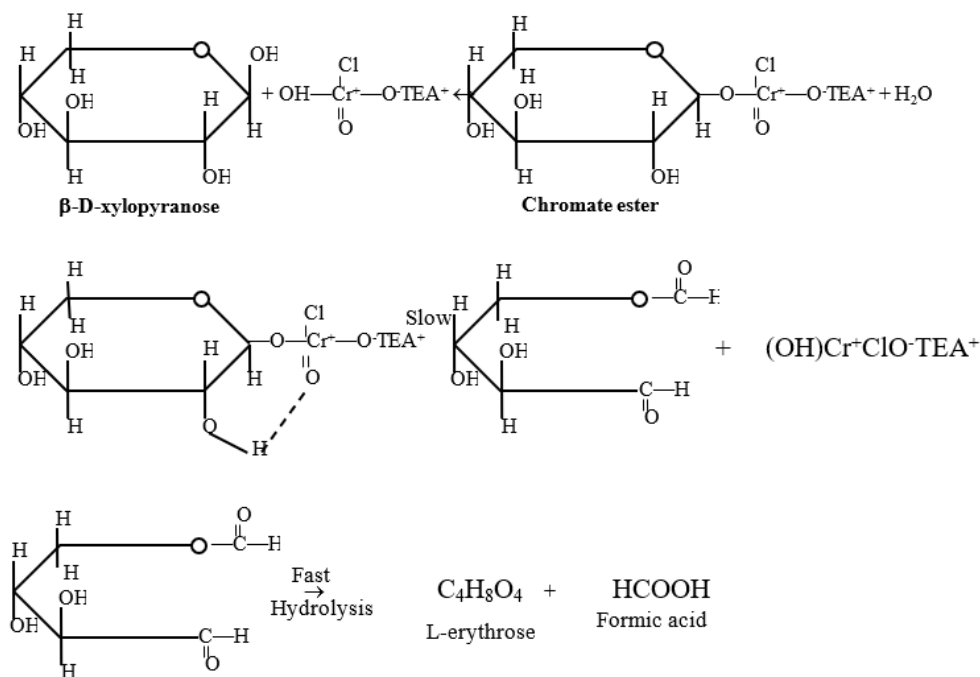
D-ribose exists mainly in  $\beta$ -pyramid form.

The formation of D-erythrose and formic acid leads to a mechanism show in scheme below:



D-xylose exists mainly in  $\beta$ -pyramid form

The formation of L-erythrose and formic acid leads to a mechanism show in scheme below:



Perusal of the UV spectrum of oxidant TEACC without aldopentoses (Fig. 1C), in the presence of D-ribose (Fig. 1A) and D-xylose (Fig. 1B) shows no appreciable deviation in the  $\lambda_{\max}$  values. This indicates that no complex formation take place during the course of both reaction studied.

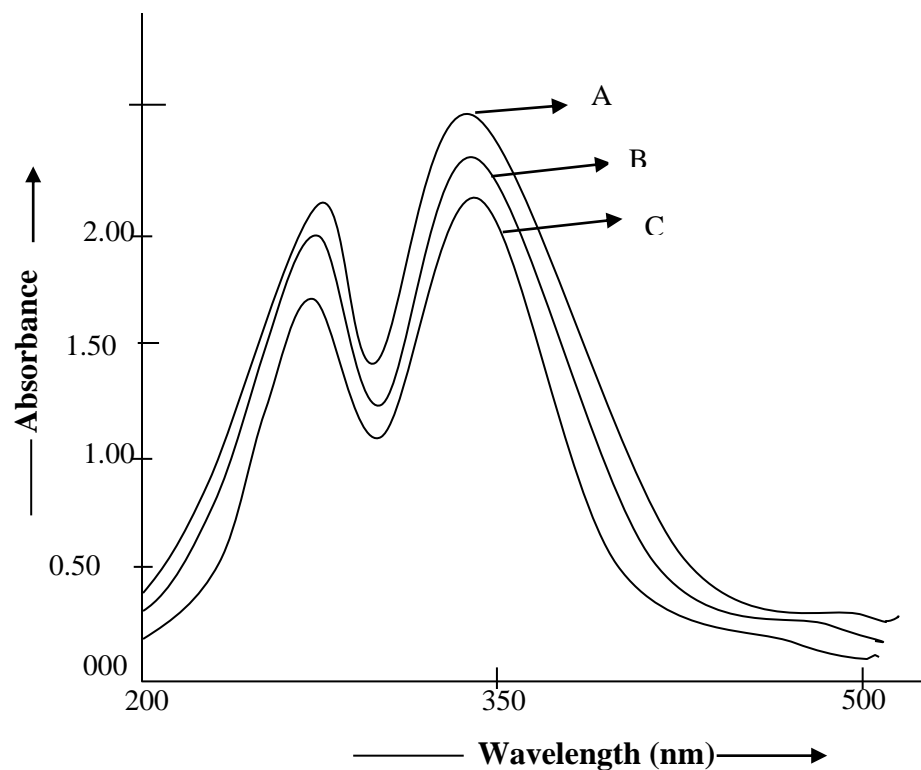


Figure 1: UV spectra of TEACC in aqueous acetic acid (50% v/v) (A) with D-ribose (B) with D-xylose (C) without substrate

**Rate law:** Based on the proposed mechanism the rate law for the TEACC oxidation of sugar (S) may be derived as-



$$\text{Rate} = -\frac{[\text{TEACC}]}{dt} \propto [\text{Ester}]$$

$$\text{Or } -\frac{[\text{TEACC}]}{dt} = k [\text{Ester}] \quad \dots\dots(5)$$

From equation (1), (2) and (5)

$$-\frac{[\text{TEACC}]}{dt} = k K_1 K_2 [\text{S}] [\text{TEACC}] [\text{H}^+]$$

$$-\frac{[\text{TEACC}]}{dt} = k [\text{S}] [\text{TEACC}] [\text{H}^+] \quad \dots\dots (6)$$

This mechanism is similar to earlier observations [22].

### Conclusion

The oxidation of aldopentoses by TEACC in aqueous acetic acid medium proceeds hydride ion transfer via complex formation mechanism involving specific cleavage of C<sub>1</sub>-C<sub>2</sub> bond of the substance to give the products.

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