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## Kinetics and Mechanism of Oxidation of L-Arabinose by Pyridinium Chlorochromate in Aqueous Acetic Acid

Dipti<sup>a</sup>, Ashish Tomar<sup>a\*</sup>,  
Jaiveer Singh<sup>b</sup> and Arun Kumar<sup>a</sup>

<sup>a</sup> Department of Chemistry, Meerut College,  
Meerut-250001 (U.P.) India

<sup>b</sup> Department of Chemistry, Nehru College,  
Chhibramau-209721, Kannauj (U.P.) India

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*We report in the present paper the kinetic and mechanistic study of the oxidation of L-arabinose by pyridinium chlorochromate  $C_5H_5NHCrO_3Cl$ . The reaction has been carried out in aqueous acetic acid 50% (v/v) medium in presence of perchloric acid at constant ionic strength. The reaction has been found to be first order with respect to each of the oxidant and substrate under pseudo-first order conditions. The reaction is catalyzed by acid and follows a first order dependence on  $H^+$  ion concentration. The ionic strength variation has no effect on the reaction rate. The decreases in dielectric constant of the medium increase the rate of reaction. A 1:1 stoichiometry is observed in the oxidation and the reaction rate is not retarded by the addition of radical trapping agent acrylonitrile. Effect of temperature on the rate of oxidation has been studied to show the validity of Arrhenius equation and various activation parameters have been computed. The products are identified to be L-erythrose and formic acid. On the observed facts a hydride ion transfer mechanism is proposed.*

*Keywords: L-arabinose, Kinetics, Mechanism, Pyridinium Chlorochromate.*

### Introduction

The kinetic of oxidation of organic compounds which contain a large number of functional groups is of considerable interest from the mechanistic point of view and have been studied fairly well<sup>1-16</sup>. L-Arabinose is in fact more common in nature and is found in nature as a component of biopolymers such as hemicelluloses and pectin. In view of this, kinetic and mechanistic studies on oxidation of L-arabinose has been given a great deal of attention. Among halochromate of nitrogen containing heterocyclic compounds, pyridinium chlorochromate<sup>17</sup> is a versatile oxidizing agent for the effective

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\* Corresponding author E-mail address: ashishtomar1983@yahoo.co.in

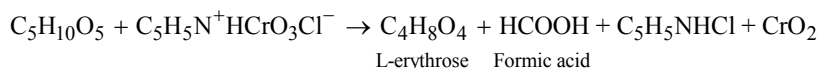
and selective oxidation of organic substrate under mild conditions. A survey of literature, however, revealed that no work has been carried out on the kinetics of oxidation of L-arabinose with pyridinium chlorochromate.

### Experimental

*Materials* – Pyridinium Chlorochromate (PCC) was prepared<sup>17</sup> by anhydrous chromium (VI) oxide dissolved in 6M HCl and stirred at 0 °C for 5 min. Pyridine was carefully added over 10 min. Recooling to 0 °C gave Yellow orange solid, which was collected on a sintered glass funnel and dried under reduced pressure for 2hr; Cr content was determined iodometrically. Solution of L-arabinose was 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 was performed under pseudo-first order condition by keeping a large excess of [L-arabinose] with respect to [PCC]. 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 400 nm. The optical density was measured at various intervals of time. Computation of rate constants was made from the plot of log [PCC] against time.

*Stoichiometry and product analysis*: The stoichiometry of reaction was performed by conducting the oxidation of L-arabinose under the conditions of a known excess of pyridinium chlorochromate. A mixture of L-arabinose (0.01 mol dm<sup>-3</sup>) and PCC (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 L-arabinose and pyridinium 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 L-erythrose was confirmed by osazone formation<sup>18</sup> and the presence of formic acid was confirmed by sport test<sup>19</sup>.

### 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 pyridinium chlorochromate vs time were linear and the rate constants were independent of initial concentration of pyridinium chlorochromate, showing first order dependence of the rate of [PCC]. The reaction is first order with respect to [L-arabinose], too. A plot of log *k*<sub>1</sub> against log [L-arabinose] was linear with a slope of unity thereby confirming first order dependence in [L-arabinose].

Rates of oxidation were found to increase with increase in [H<sup>+</sup>] and the slopes of the plots 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>].

Table 1. Rate constant for oxidation of L-arabinose by PCC at 25 °C, Solvent: Acetic acid-water (50-50 % v/v)

[PCC] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[L-arabinose] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] × (mol dm <sup>-3</sup> )	k <sub>1</sub> × 10 <sup>4</sup> (s <sup>-1</sup> )	k <sub>2</sub> × 10 <sup>2</sup> (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )
0.22	0.80	2.32	3.69	
0.44	0.80	2.32	3.73	
0.66	0.80	2.32	3.73	
0.88	0.80	2.32	3.74	
1.33	0.80	2.32	3.74	
1.55	0.80	2.32	1.55	
1.33	0.33	2.32	3.09	4.70
1.33	0.66	2.32	3.74	4.68
1.33	0.80	2.32	4.70	4.67
1.33	1.00	2.32	6.28	4.70
1.33	1.33	1.74	2.75	4.72
1.33	0.80	2.32	3.74	
1.33	0.80	2.90	4.63	
1.33	0.80	3.48	5.61	
1.33	0.80	4.06	6.55	

Consequently the empirical rate law is described as follows:

$$-\frac{d[\text{PCC}]}{dt} = k_{\text{obs}}[\text{L-arabinose}][\text{PCC}][\text{HClO}_4]$$

The reaction rate was not influenced by ionic strength when NaClO<sub>4</sub> was initially added to the reaction mixture over the range 0.83 × 10<sup>-1</sup> to 5.00 × 10<sup>-1</sup> mol dm<sup>-3</sup>. Similar observation was also reported in the oxidation of diols by PCC<sup>20</sup>.

When the reaction was initiated by adding acrylonitrile into a solution containing L-arabinose and PCC, 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 CH<sub>3</sub>COOH in acetic acid-water mixture (Table 2). A linear plot between log k<sub>1</sub> and 1/D (inverse of dielectric constant) with a positive slope suggests an interaction between an ion and a dipole<sup>21</sup>.

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<sub>1</sub> 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 (ΔS<sup>\*</sup>). 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 2. Dependence of rate on solvent composition. [L-arabinose] =  $0.80 \times 10^{-2} \text{ mol dm}^{-3}$ , [PCC] =  $1.33 \times 10^{-3} \text{ mol dm}^{-3}$ , [HClO<sub>4</sub>] =  $2.32 \text{ mol dm}^{-3}$ , [NaClO<sub>4</sub>] =  $1.66 \times 10^{-1} \text{ mol dm}^{-3}$ , temp. = 25 °C.

CH <sub>3</sub> COOH : H <sub>2</sub> O	$k_1 \times 10^4 \text{ (s}^{-1}\text{)}$	1/D
40 : 60	2.89	0.020
50 : 50	3.74	0.024
60 : 40	4.26	0.028
70 : 30	5.16	0.036
80 : 20	7.46	0.048

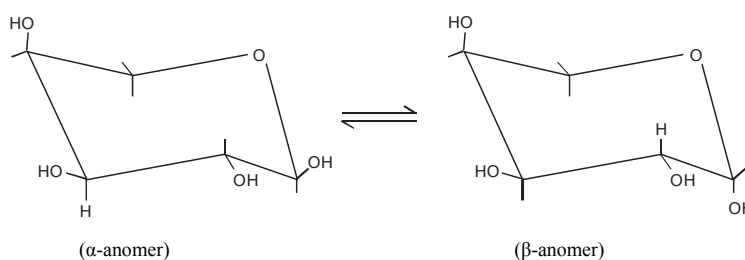
Table 3. Temperature dependence and activation parameters of oxidation of [L-arabinose] by [PCC]

Temperature (K)	$K_1 \times 10^4 \text{ (sec}^{-1}\text{)}$	Temperature Coefficient	E <sub>a</sub> (kJ mol <sup>-1</sup> )	Log <sub>10</sub> A	ΔH* (kJ mol <sup>-1</sup> )	ΔG* (kJ mol <sup>-1</sup> )	-ΔS* (kJ mol <sup>-1</sup> )
293	2.69	-	-	5.73	49.73	91.76	143.44
298	3.74	1.97	50.20	5.71	49.69	92.55	143.82
303	5.31	1.97	51.78	5.72	49.65	93.26	143.93
308	7.37	2.01	54.52	5.71	49.61	94.00	144.13
313	10.65	-	-	5.73	49.57	94.61	143.90

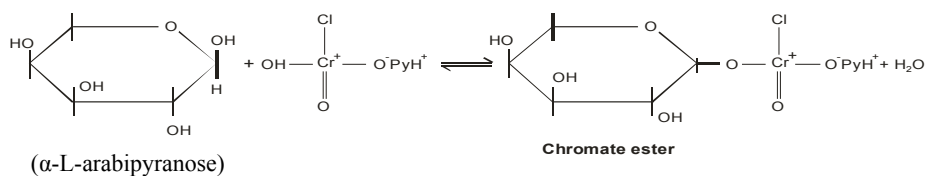
Mean = 52.16 kJ mol<sup>-1</sup>

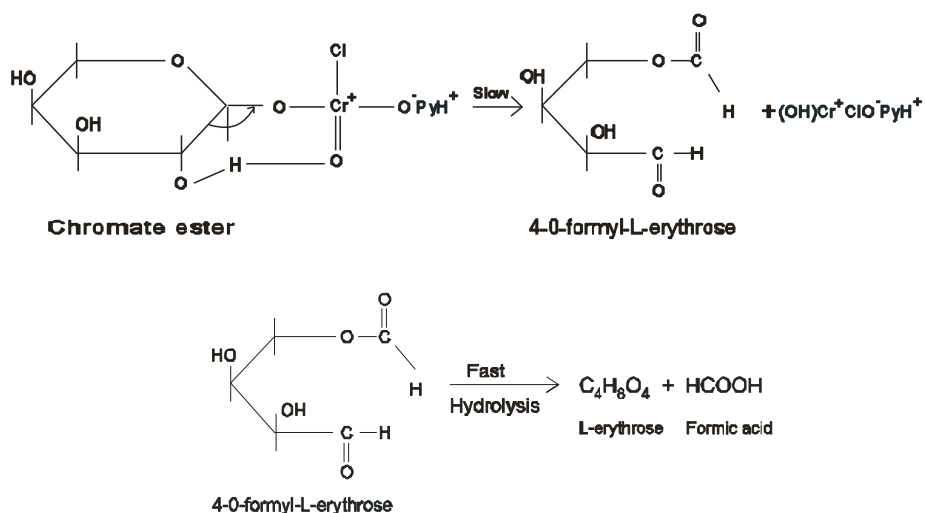
## Discussion

L-arabinose exists mainly in α-pyranid form



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





There is no evidence of complex formation. Perusal of the UV spectrum of oxidant PCC without L-arabinose (Fig. 1A) and in the presence of L-arabinose (Fig. 1B) shows to appreciable deviation in the  $\lambda_{\max}$  values, but the product formations suggest a mechanism involving intermediate complex formation.

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

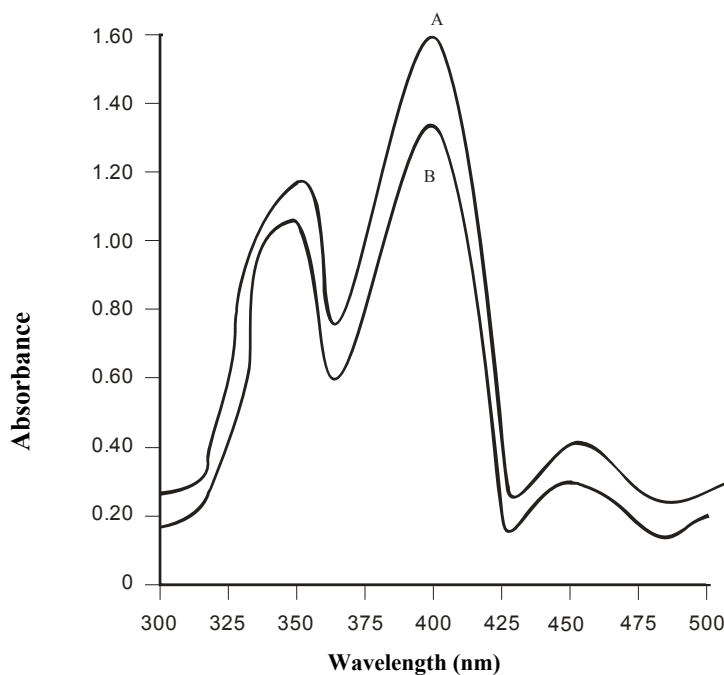


Fig. 1. UV-spectra of PCC in aqueous acetic acid 50 % (v/v) (A) and PCC in aqueous acetic acid 50 % (v/v) with L-arabinose (B)



$$\text{Rate} = -\frac{[\text{PCC}]}{dt} \propto [\text{Ester}] \quad (5)$$

$$\text{Or } -\frac{[\text{PCC}]}{dt} = k [\text{Ester}]$$

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

$$-\frac{[\text{PCC}]}{dt} = k K_1 K_2 [\text{S}] [\text{PCC}] [\text{H}^+] \quad (6)$$

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

This mechanism is similar to earlier observations<sup>22-23</sup>.

### Conclusion

The oxidation of L-arabinose by PCC in aqueous acetic acid medium proceeds via hydride ion transfer 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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## **Кинетика и механизм окисления L-арабинозы хлорхроматом пиридина в водном растворе уксусной кислоты**

**Дипти<sup>а</sup>, А. Томар<sup>а</sup>,  
Д.В. Сингх<sup>б</sup>, А. Кумар<sup>а</sup>**

<sup>а</sup> Мирут Колледж,  
Мирут, Индия

<sup>б</sup> Неру Колледж, Чхибрамау,  
Каннаудж, Индия

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*В статье представлены результаты изучения кинетики и механизма окисления L-арабинозы хлорхроматом пиридина (C<sub>5</sub>H<sub>5</sub>NHCrO<sub>3</sub>Cl) в водном растворе уксусной кислоты 50 % об. в присутствии хлорной кислоты при постоянной ионной силе. Установлено, что реакция имеет первый порядок по каждому из окислителей и псевдопервый порядок по субстрату. Реакция катализируется кислотой, и её скорость зависит от концентрации ионов H<sup>+</sup>. Скорость реакции не зависит от ионной силы раствора и увеличивается с уменьшением диэлектрической проницаемости реакционной среды. При стехиометрии 1:1 наблюдалось окисление и отсутствует торможение реакции при добавлении акрилонитрила в качестве ловушки радикалов. Изучено влияние температуры на скорость окисления и рассчитаны параметры уравнения Арениуса. Продуктами реакции являются L-эритроза и муравьиная кислота. На основании полученных данных предложен механизм реакции.*

*Ключевые слова: L-арабиноза, кинетика, механизм, хлорхромат пиридина.*

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