



Oxidation Kinetics of L-Arabinose with Quinolinium Chlorochromate

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Oxidation kinetics of L-arabinose with quinolinium chlorochromate (QCC) have been investigated spectrophotometrically. Under pseudo-first order condition, the oxidation is first order with respect to both [QCC] and [L-arabinose]. The oxidation rate was promoted by [acid] and remains unaffected by [NaClO₄]. A 1:1 stoichiometry is observed. Activation energy and concerned thermodynamic parameters worked out from reaction rate at different temperatures. Mechanism consistent with the observed data has been proposed.

Keywords: Oxidation, Kinetic, Mechanism, L-Arabinose, Quinolinium chlorochromate, Spectrophotometrically.

INTRODUCTION

Oxidation kinetics employing Cr(VI) centered mild oxidizing agents and organic substrates is a subject of extensive research in recent years [1-3]. Quinolinium chlorochromate (QCC) is such one recently reported useful, Cr(VI) oxidant [4-6]. Oxidation reaction of reducing sugars is important as they are poly-functional compounds and have biological relevance. Earlier [7,8] and recent [9-11] reviews on oxidation kinetics of carbohydrates including reducing sugars with different oxidants are significant. Kinetic studies on L-arabinose oxidation with different oxidants *viz.* Mn(VII) [12], Ce(IV) [13], Ti(III) [14], chloramine-T [15] N-bromosaccharin [16] and N-bromophthalimide [17] has also been reported. L-Arabinose may play a fundamental role in carbohydrate chemistry because it is more common in nature and is a major constituents of glycoproteins, arabinogalactan, polysaccharides, hemicelluloses and pectin. Our interest in the kinetic and mechanistic approach to oxidation of reducing sugars [18] and unsaturated substrates [19] using modified Cr(VI) reagents and also in view of the fact that no information is available on quinolinium chlorochromate (QCC) oxidation of L-arabinose promoted us to investigate the title reaction.

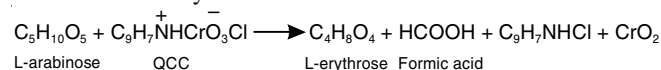
EXPERIMENTAL

Quinolinium chlorochromate was safely prepared by the careful addition of quinoline (Loba-chemie) to a cooled (0 °C) stirred mixture of anhydrous chromium trioxide and 6 M HCl followed by the filtration of yellow orange solid [5]. The solution of L-arabinose (Sigma Aldrich) prepared by dissolving

known quantities of the substrate in water:acetic acid mixture (1:1 v/v). The ionic strength was maintained constant using a concentrated solution of NaClO₄ (B.D.H.). Perchloric acid (E. Merck) and other chemicals (A.R., B.D.H.) were used as obtained.

Kinetic procedure: All kinetic measurements were carried out in 50 % acetic acid-50 % water mixture containing HClO₄ and NaClO₄ under pseudo-first order conditions by using excess of L-arabinose over QCC at constant temperature (± 0.1 K). The reactions were monitored by decrease in [QCC] spectrophotometrically at 440 nm upto 80 % completion of the reaction with the help of systronics 106 spectrophotometer. Neither reactant nor product has any absorption at this wavelength. The optical density was recorded at different time intervals. The pseudo-first order rate constant, k_{obs} , were determined from plot of $\log [QCC]$ versus time.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined by allowing excess of oxidant to react with L-arabinose under kinetic conditions. The decrease of [QCC] was observed until a constant value of optical activity was obtained and unreacted [QCC] was determined. Several determinations indicated that one mole of QCC reacted with one mole of L-arabinose under the condition of kinetic run. The stoichiometry is 1:1.



L-Erythrose and formic acid were detected as the final products in the oxidation of L-arabinose by QCC. L-Erythrose was confirmed by osazone formation [20] and by paper chromatography [21] and formic acid by spot test [22].

RESULTS AND DISCUSSION

Effect of variation of reactants concentration: The pseudo-first-order rate constants (k_{obs}) ascertained at different [QCC], [L-arabinose] and $[\text{HClO}_4]$ are reported in Table-1. The rate constants do not depend on [QCC], confirming first order kinetics in [QCC].

[QCC] $\times 10^3$ (mol dm ⁻³)	[L-arabinose] $\times 10^2$ (mol dm ⁻³)	[HClO ₄] $\times 10^1$ (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)	$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)
1.33	1.66	6.13	6.23	—
2.00	1.66	6.13	6.20	—
2.66	1.66	6.13	6.25	—
3.33	1.66	6.13	6.24	—
4.00	1.66	6.13	6.28	—
3.33	0.66	6.13	2.50	3.78
3.33	1.00	6.13	3.74	3.74
3.33	1.33	6.13	4.98	3.74
3.33	1.66	6.13	6.24	3.76
3.33	2.00	6.13	7.48	3.74
3.33	1.66	3.10	3.12	—
3.33	1.66	6.10	6.24	—
3.33	1.66	7.70	7.82	—
3.33	1.66	9.20	9.36	—
3.33	1.66	10.70	10.92	—

Solvent: Acetic acid-water mixture (50-50 % v/v); $[\text{NaClO}_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$

The rate constant increases with increase in [L-arabinose]. A plot of $\log k_1$ versus $\log [\text{L-arabinose}]$ is linear with unit slope (Fig. 1). This confirms first order kinetics with respect to [L-arabinose].

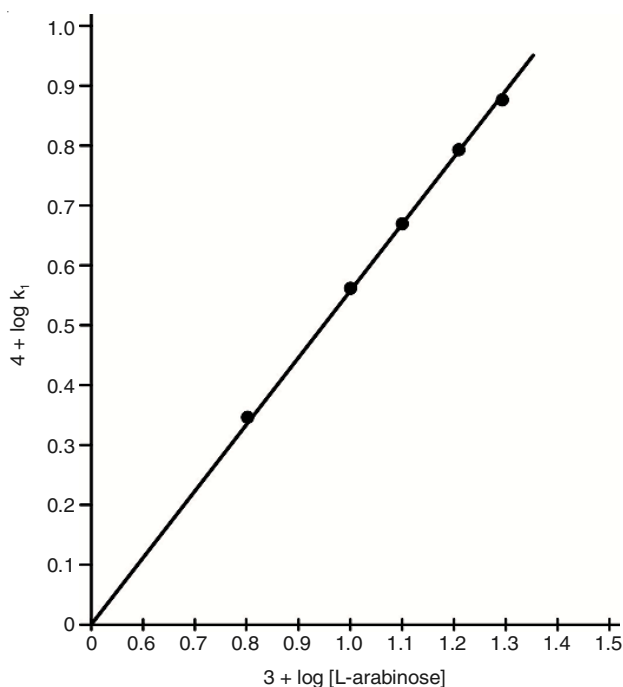


Fig. 1. Plot of $\log k_1$ versus $\log [\text{L-arabinose}]$; $[\text{QCC}] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HClO}_4] = 6.13 \times 10^{-1} \text{ mol dm}^{-3}$; $[\text{NaClO}_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$; Solvent: Acetic acid-Water mixture (50-50 % v/v); Temperature-303 K

The rates of oxidation of L-arabinose increases with increase in $[\text{H}^+]$ and plot of $\log k_1$ against $\log [\text{HClO}_4]$ was linear (Fig. 2). with a slope of unity, indicating-acid acts as a catalyst and follow a first order kinetics on $[\text{HClO}_4]$.

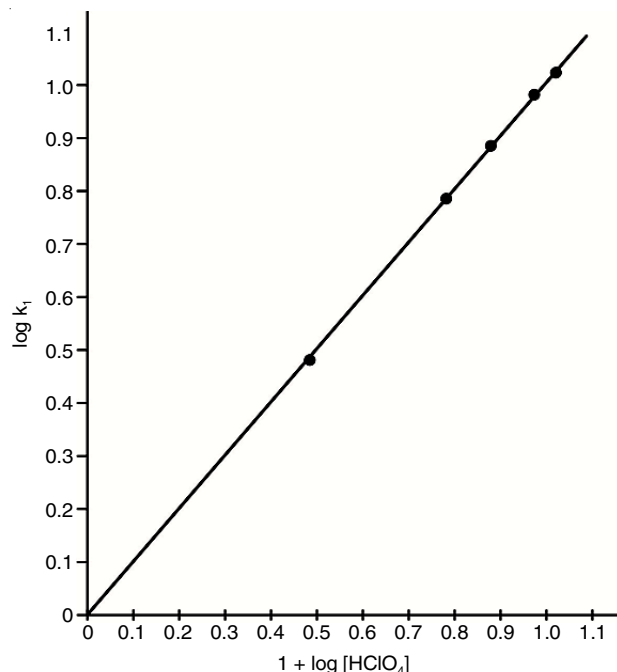


Fig. 2. Plot of $\log k_1$ versus $\log [\text{HClO}_4]$; $[\text{QCC}] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{L-arabinose}] = 1.66 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{NaClO}_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$; Solvent: Acetic acid-water mixture (50-50 % v/v); Temperature - 303 K

The initial addition of NaClO_4 to the reaction mixture varying from 0.66×10^{-1} to $4.00 \times 10^{-1} \text{ mol dm}^{-3}$ did not cause any significant change in reaction rate, showing negligible effect of ionic strength variation. This indicated the participation of a neutral reactant molecule in the reaction sequence [23]. The results of same kind were also obtained in the oxidation of alcohol by QCC [24].

Free radicals formation during the course of reaction was tested by adding acrylonitrile to the reaction mixture containing L-arabinose and QCC under kinetic conditions. No turbidity due to polymerization of acrylonitrile was observed. This rules out free radicals formation during oxidation.

Effect of solvent: The rate of oxidation reaction increases with decrease in dielectric constant (D) of the medium (Table-2). A plot of $\log k_1$ versus $1/D$ is linear with positive slope (Fig. 3), suggesting a reaction between a positive ion and dipole [25]. This confirm involvement of protonated Cr(VI) during the course of oxidation process.

$\text{CH}_3\text{COOH}:\text{H}_2\text{O}$	$k_1 \times 10^4$ (s ⁻¹)	1/D
40:60	4.26	0.020
50:50	4.98	0.024
60:40	5.72	0.028
70:30	7.38	0.036
80:20	10.20	0.048

$[\text{QCC}] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{L-arabinose}] = 1.66 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{NaClO}_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$; $[\text{HClO}_4] = 6.13 \times 10^{-1} \text{ mol dm}^{-3}$; Temperature - 298 K

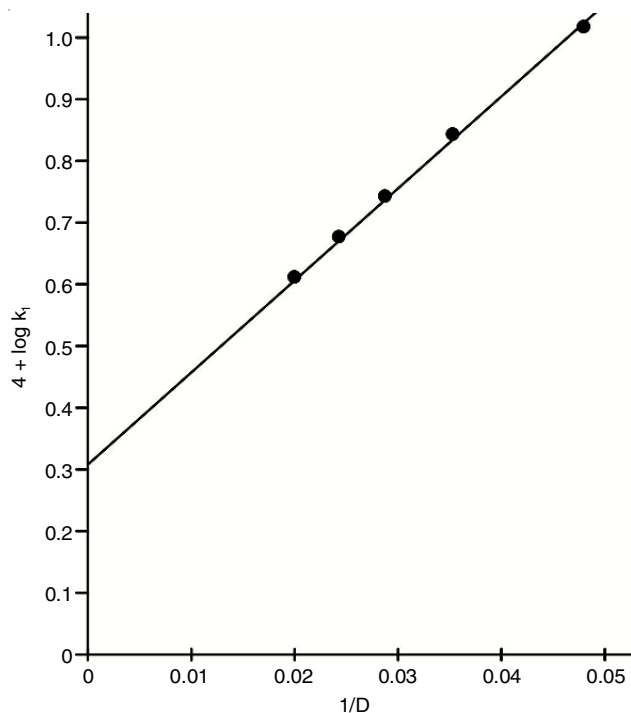


Fig. 3. Plot of $\log k_1$ versus $1/D$; $[QCC] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$; $[L\text{-arabinose}] = 1.66 \times 10^{-2} \text{ mol dm}^{-3}$; $[HClO_4] = 6.13 \times 10^{-1} \text{ mol dm}^{-3}$; $[NaClO_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$; Temperature-298 K

Effect of temperature: The kinetic studies were conducted at several temperature and activation parameters were evaluated following the standard literature procedure (Table-3). The large negative values of entropies of activation indicate bimolecularity of reaction and also more ordered activated complex in the transition state.

TABLE-3
EFFECT OF TEMPERATURE ON REACTION
RATE AND ACTIVATION PARAMETERS

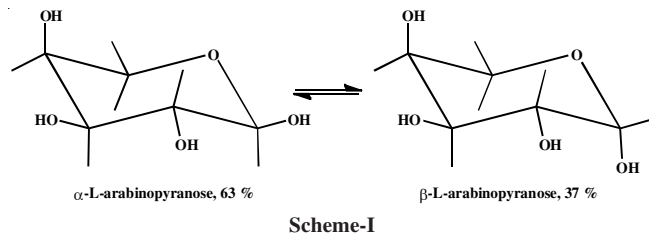
Temp. (°C)	$k_1 \times 10^4$ (s ⁻¹)	E_a (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)
20	3.62	—	37.82	91.00	181.51
25	4.98	40.20	37.78	91.85	181.43
30	6.24	38.80	37.74	92.85	181.88
35	8.28	41.78	37.70	93.70	181.81
40	10.60	—	37.66	94.61	181.96

$[QCC] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$; $[L\text{-arabinose}] = 1.66 \times 10^{-2} \text{ mol dm}^{-3}$; $[NaClO_4] = 1.66 \times 10^{-1} \text{ mol dm}^{-3}$; $[HClO_4] = 6.13 \times 10^{-1} \text{ mol dm}^{-3}$; Solvent: Acetic acid-Water mixture (50-50 % v/v)

Mechanism: L-Arabinose can exist as pyranose, furanose and open chain aldehydic form. L-Arabinose exists in pyranoid form in equilibrium with the furanoid form [26]. The pyranoid forms are more stable than furanoid forms as derives from steric interaction. Literature [27,28] indicates that pyranose form of pentose is involved in the oxidation with metal ion. L-Arabinose exists mainly in a-pyranoid form with equatorial orientation of glycosidic hydroxyl group in equilibrium with anomeric form of it [29] (Scheme-I).

The more reactivity of α -anomer is understandable from the conformational point of view.

An increase in oxidation rate with acidity suggest protonation of QCC species. This interacts with substrate in the



oxidation reaction. Involvement of such form of oxidant is reported in chromic acid oxidation [30] proceeding in acid media [31].

The UV spectra recorded using spectrophotometer type 106 in water acetic acid mixture (50 % v/v) did not show shift in the $\lambda_{\max}$, thereby indicating no existence of intermediate complex formation between oxidant and substrate (Fig. 4).

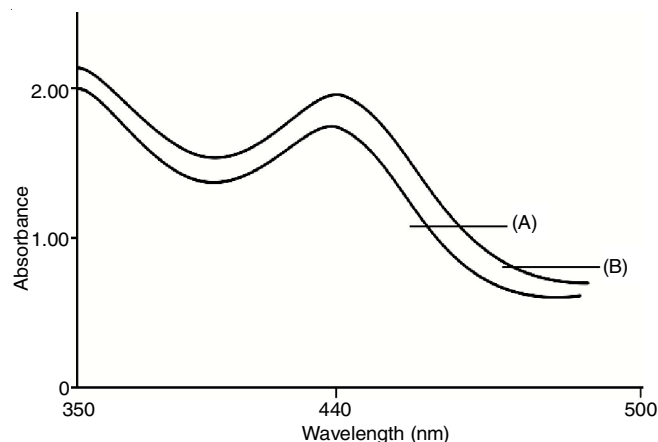
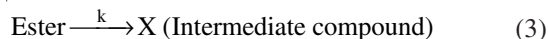
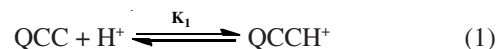


Fig. 4. UV spectra in water acetic acid mixture (50 % v/v) of oxidant QCC without L-arabinose (A) and with L-arabinose (B)

The observed data lead to the conclusion that in the oxidation of L-arabinose, a chromate ester is formed in a rapid pre-equilibrium step as shown in Scheme-II.

This is in accord with our earlier observation, made for reducing sugars [32,33].

Rate law:



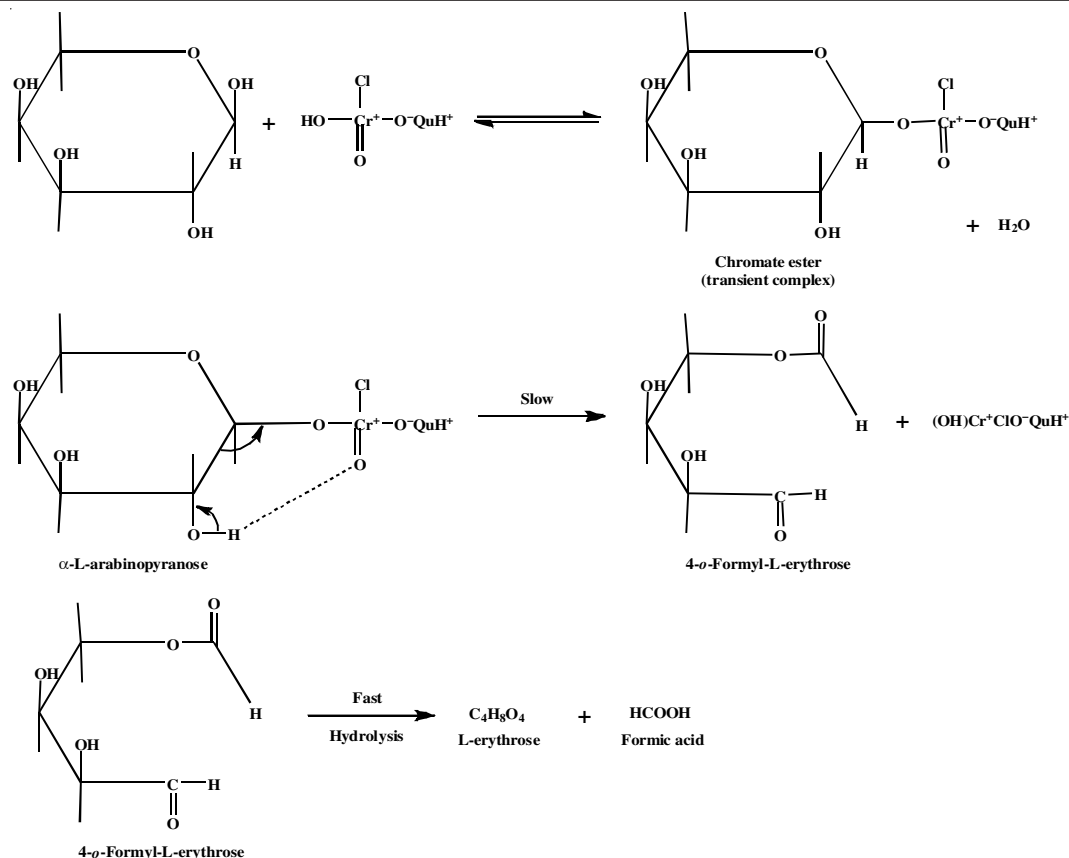
$$\text{Rate} = -\frac{d[QCC]}{dt} \propto [\text{Ester}]$$

$$\text{or} \quad -\frac{d[QCC]}{dt} = k [\text{Ester}] \quad (5)$$

Therefore, from eqns. 1, 2 and 5:

$$-\frac{d[QCC]}{dt} = k k_1 k_2 [S][QCC][H^+]$$

$$-\frac{d}{dt}[QCC] = k[S][QCC][H^+]$$



Scheme-II

Conclusion

Oxidation kinetics of L-arabinose with QCC in water acetic acid mixture (1:1 v/v) occurs through a pathway that involves a specific cleavage of C₁-C₂ bond of substrate to give products.

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