

Oxidation Studies of Some Reducing Sugars with Quinolinium Fluorochromate: A Kinetic and Mechanistic Approach

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Abstract

The kinetics of oxidation of D-fructose and L-sorbose with quinolinium fluorochromate (QFC) in aqueous-acetic acid (50%v/v) medium have been studied. The oxidation reaction is first order in [oxidant] and [substrate] for both the ketosugars. The reaction is acid catalyzed and obeys first order kinetics in [acid] in both the substrates studied. A medium of low dielectric constant promotes the oxidation for both the substrates. Ionic strength variation has no effect on reaction rate and no visible polymerization of acrylonitrile was observed in each substrate. The reaction has 1:1 stoichiometry. Activation and thermodynamic parameters have been evaluated by studying reaction rates at several temperature. An aldehyde and acid have been detected as the oxidation products. A mechanism consistent with kinetic data has been suggested.

Keywords: Oxidation, Kinetics, Mechanism, Ketosugars, Quinolinium Fluorochromate.

Introduction

In carbohydrate chemistry, D-fructose and L-sorbose plays an important role because D-fructose is one of the three dietary monosaccharides and L-sorbose is an intermediate compound in the formation of vitamin-C (ascorbic acid) and also in the formation of rare sugars such as L- tagatose. In view of these and because of their special role in biological process, kinetic and mechanistic studies on oxidation of D-fructose and L-sorbose have been given a great attention.

Review of Literature

Recently a variety of chromium (VI) complexes have been prepared and tested to be effective oxidants¹⁻¹². Quinolinium fluorochromate (QFC)^{13, 14} is one of them. It has been employed for the oxidation study, in view of its ease of preparation, high stability, mildness and selectivity. A literature survey reveals that there have been no oxidation studies of ketohexoses viz. D-fructose and L-sorbose by QFC. Hence the present investigation is undertaken and the kinetic results of oxidation of both substrates with QFC in acetic acid-water (1:1 v/v) solvent are reported in this paper.

Aim of the Study

Oxidation kinetics of biologically important molecules with newly developed quinolinium fluorochromate mild oxidant have been studied.

Experimental

Materials

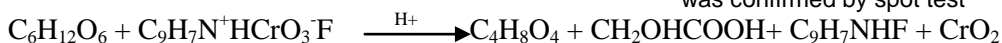
Quinolinium fluorochromate (QFC) was safely prepared by careful addition of Quinoline (Loba-chemic) to a solution of chromium trioxide in 40% HF acid followed by the filtration of yellow orange crystal¹³. The solutions of D-fructose (Lancaster) and L-sorbose (Lancaster) were always freshly prepared. The ionic strength was maintained constant with the use of concentrated solution of NaClO₄ (C.D.H.). Perchloric acid (C.D.H.) and all other chemical were used as such without further purification. Kinetic measurements were made in Shimadzu UV 160 A spectrophotometer at 440 nm. Doubly distilled water was used for all kinetic run.

Kinetic Measurements

All the kinetic measurements were carried out in 50% acetic acid-50% water mixture containing HClO₄ and NaClO₄ under pseudo-first order

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conditions by keeping excess of substrate over quinolinium fluoro-chromate ($\pm 0.1K$). Kinetic measurements were made in Shimadzu UV 160 A spectrophotometer at 440 nm. The pseudo-first order rate constant k_{obs} , were determined from the linear plot of $\log [\text{oxidant}]$ versus time. Replicate runs showed that the rate constant were reproducible to within $\pm 2\%$ error.



Sugar

QFC

Aldehyde

Results and Discussion

In each case, the oxidation followed a first order kinetics both with respect to [substrate] and [oxidant]. The results obtained are given in Table 1. Plots for different concentration of quinolinium

Table 1. Rate constant for Oxidation of D-fructose and L-sorbose by QFC at 25°C

[QFC] $\times 10^3$ (mol dm ⁻³)	[D-fructose] $\times 10^2$ (mol dm ⁻³)	[L-sorbose] $\times 10^2$ (mol dm ⁻³)	[H ⁺] \times (mol dm ⁻³)	D-fructose $k_1 \times 10^4$ (s ⁻¹)	L-sorbose $k_2 \times 10^4$ (s ⁻¹)
0.22	0.80	0.80	2.32	4.62	4.21
0.44	0.80	0.80	2.32	4.60	4.18
0.66	0.80	0.80	2.32	4.63	4.21
0.88	0.80	0.80	2.32	4.60	4.22
1.11	0.80	0.80	2.32	4.62	4.19
1.33	0.80	0.80	2.32	4.60	4.29
1.11	0.33	0.33	2.32	1.90	1.72
1.11	0.66	0.66	2.32	3.76	3.44
1.11	0.80	0.80	2.32	4.62	4.19
1.11	1.00	1.00	2.32	5.78	5.26
1.11	1.33	1.33	2.32	7.68	7.01
1.11	1.66	1.66	2.32	9.55	8.76
1.11	0.80	0.80	1.74	3.51	3.18
1.11	0.80	0.80	2.32	4.62	4.19
1.11	0.80	0.80	2.90	5.80	5.41
1.11	0.80	0.80	3.48	7.11	6.45
1.11	0.80	0.80	4.06	8.30	7.51
1.11	0.80	0.80	4.54	9.20	8.40

Rates of oxidation were found to increase with increase in [H⁺] and the slopes of the plots of $\log k_1$ vs $\log [\text{HClO}_4]$ were approximately unity showing that the reaction is acid catalyzed and follows the first-order dependence in [HClO₄].

Consequently the empirical rate law is described as follows:

$$\frac{d[\text{QFC}]}{dt} = k_{obs} [\text{substrate}][\text{QFC}][\text{HClO}_4]$$

Effect of Ionic Concentration

The reaction rate was not influenced by ionic strength when NaClO₄ was initially added to the reaction mixture over the range 0.83×10^{-1} to 5.00×10^{-1} mol dm⁻³. Similar observations were also reported in the oxidation of L-sorbose by TEACC¹⁷.

Asian Resonance

Stoichiometry and Product Analysis

Stoichiometry of the reaction for both the substrates was found to be 1 : 1 as determined by carrying out several sets of experiments with varying amounts of [QFC] largely in excess over [substrate]. The reaction mixture was kept 24 hr to ensure the completion of the reaction. The unreacted quinolinium fluoro-chromate was estimated iodometrically.

The formation of aldehyde was confirmed by osazone formation¹⁵ and the presence of glycollic acid was confirmed by spot test¹⁶

fluoro-chromate vs time were linear and the rate constants were independent of initial concentration of quinolinium fluoro-chromate, showing first-order dependence of the rate on [QFC]. The reaction is first-order with respect to [D-fructose] and [L-sorbose], too.

Effect of Radical Forming Agent

When the reaction was initiated by adding acrylonitrile into a solution containing ketohexoses and QFC, no retardation in the rate was observed. No turbidity due to polymerization of acrylonitrile was observed, therefore formation of radical intermediate ruled out during 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 CH₃COOH in acetic acid-water mixture (Table 2). Which suggests an interaction between ions formed during reaction and developing dipole moment¹⁸.

Table 2. Dependence of Rate on Solvent Composition

[KetoHexoses] = $0.80 \times 10^{-2} \text{ mol dm}^{-3}$, [QFC] = $1.11 \times 10^{-3} \text{ mol dm}^{-3}$, [HClO₄] = 2.32 mol dm^{-3} , [NaClO₄] = $1.66 \times 10^{-1} \text{ mol dm}^{-3}$, temp. = 25°C.

CH ₃ COOH : H ₂ O	1/D	D-fructose $k_1 \times 10^4 \text{ (s}^{-1}\text{)}$	L-sorbose $k_1 \times 10^4 \text{ (s}^{-1}\text{)}$
40 : 60	0.020	4.01	3.54
50 : 50	0.024	4.62	4.31
60 : 40	0.028	5.22	4.92
70 : 30	0.036	6.50	6.11
80 : 20	0.048	9.05	8.66

The reaction rate at different temperature 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 observation of data (Table 3) shows that the reactions are characterized by a high negative value

of entropy of activation (ΔS^*). 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.

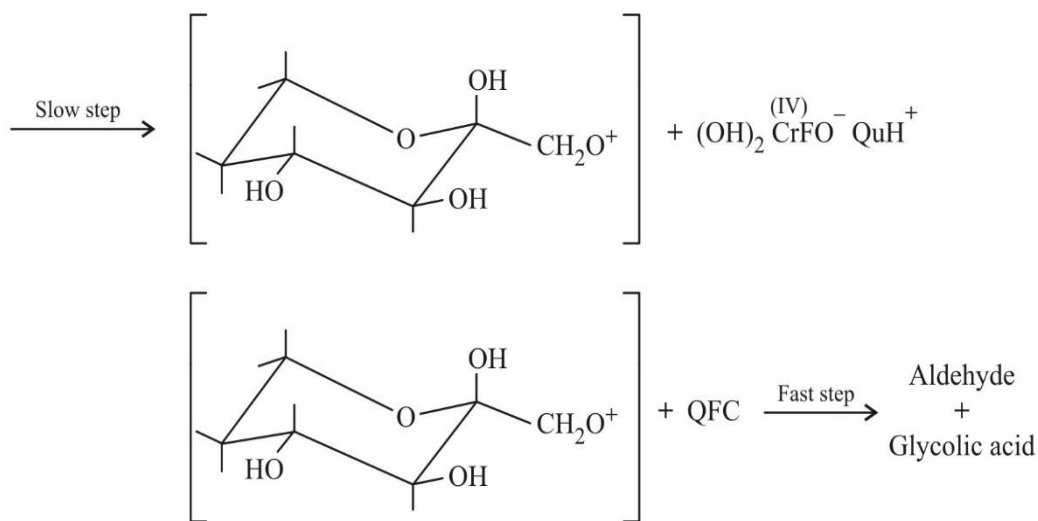
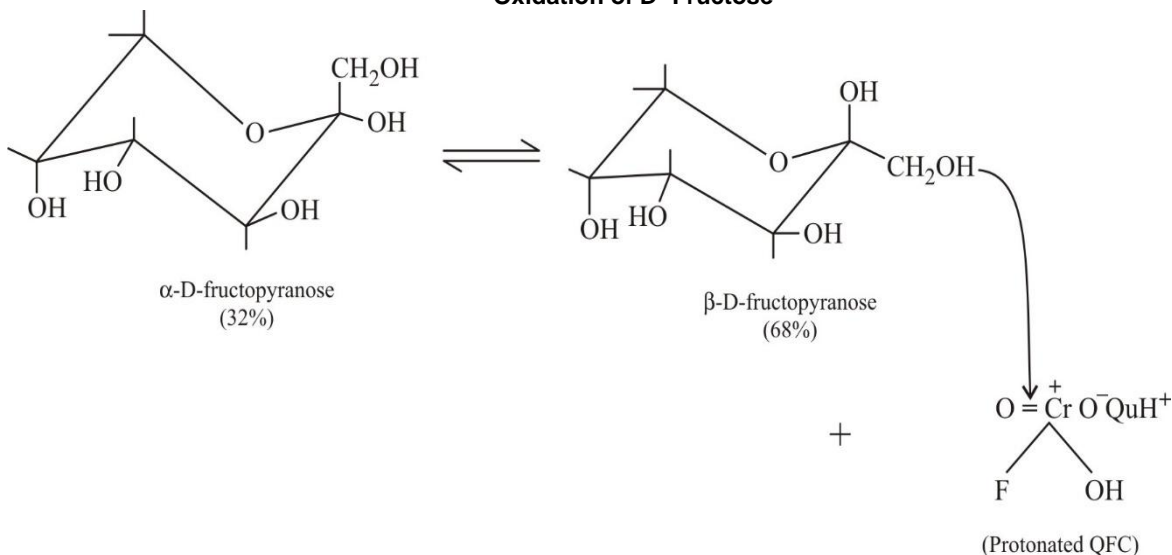
Table 3. Activation Parameters of the comparative study at 25°C.

KetoHexoses	E _a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	$-\Delta S^*$ (kJ mol ⁻¹)
D-fructose	51.74	49.25	92.03	143.57
L-sorbose	53.53	51.05	92.20	138.09

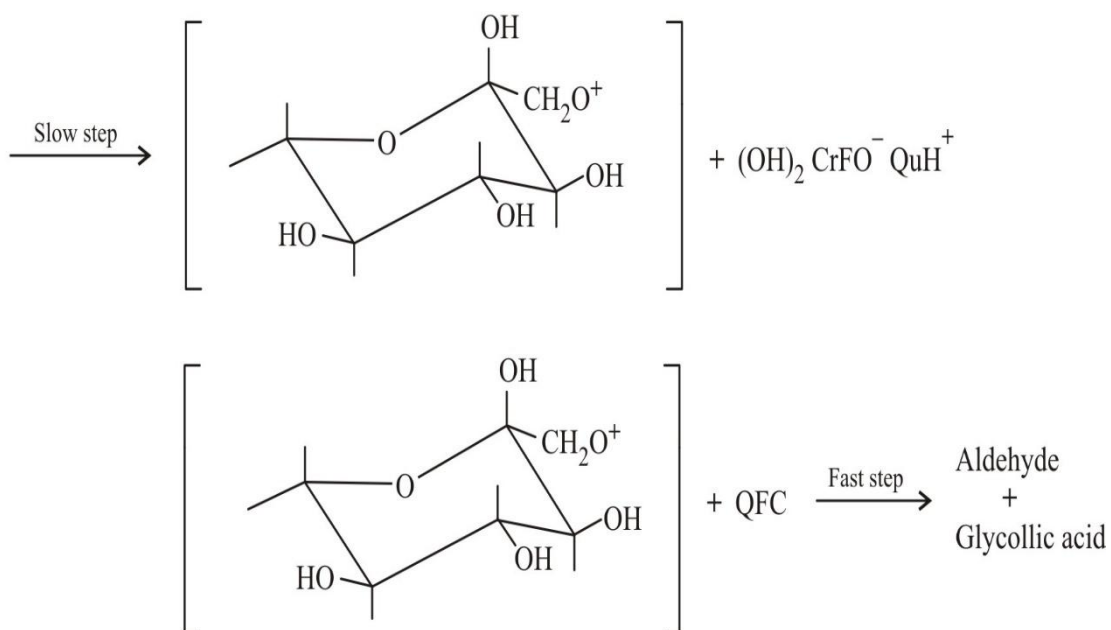
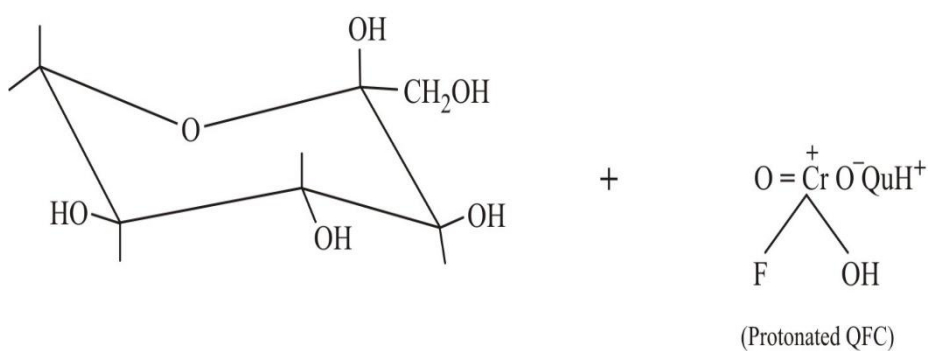
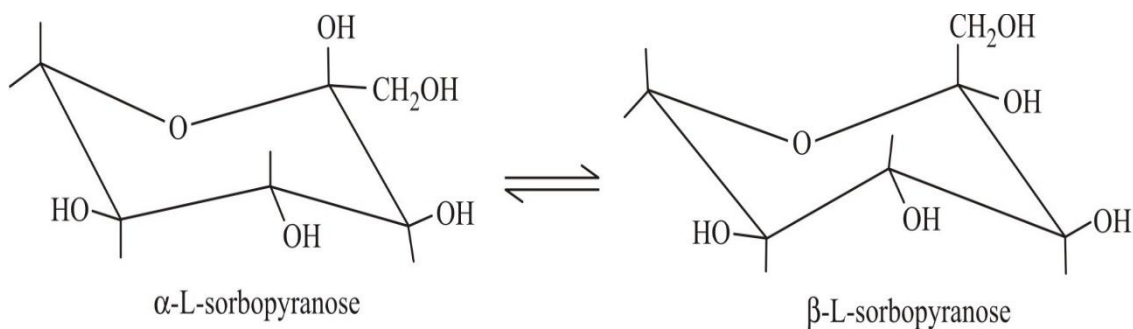
In view of product identification and observed facts. The oxidation of D-Fructose may be assumed to

follow the direct hydride ion transfer of $\square \square \square$ fructopyranose as shown in scheme 1.

Oxidation of D- Fructose



Scheme 1
Oxidation of L- Sorbose



Scheme 2

UV spectra recorded did not show the existence of intermediate complex formation. This indicates the instability of intermediate (Fig.1).

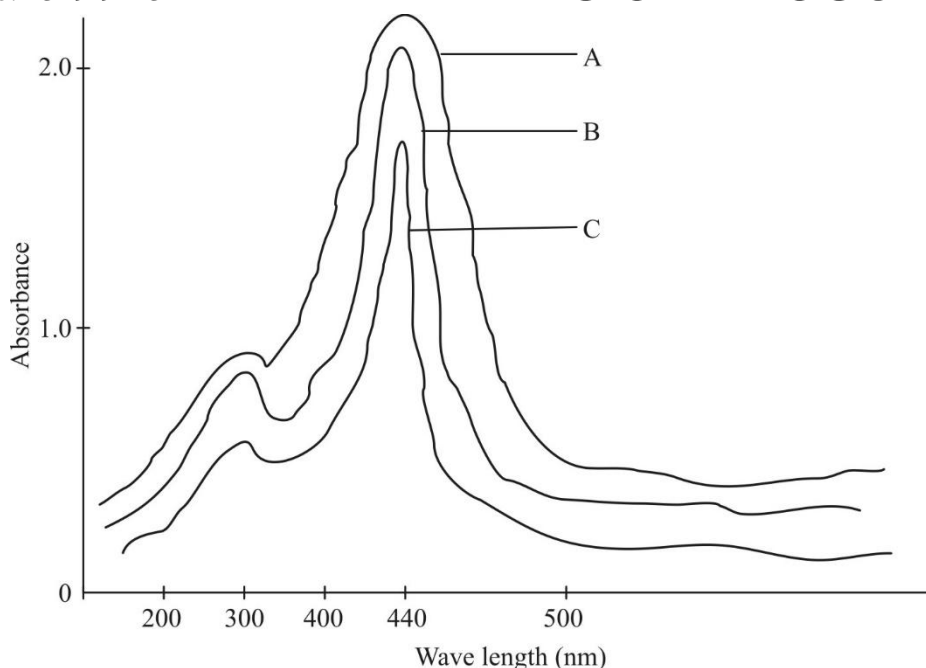
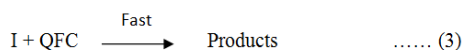
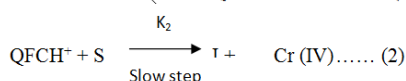
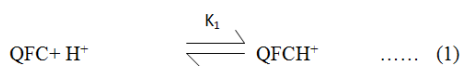


Fig. 1. UV spectra of QFC in aqueous acetic acid (50% v/v) (A) without substrate (B) with D-fructose (C) with L-sorbose

Rate Law

Based on the proposed mechanism the rate law for the QFC oxidation of sugar (S) may be derived as-



$$\text{Rate} = - \frac{d[\text{QFCH}^+]}{dt} \propto [\text{QFCH}^+][\text{S}] = k_1[\text{QFCH}^+][\text{S}]$$

$$\text{Rate} = k_1[\text{QFCH}^+][\text{S}] \quad \dots\dots(4)$$

Applying law of mass action to Eq. (1) we get,

$$K_1 = \frac{[\text{QFCH}^+]}{[\text{QFC}] + [\text{H}^+]}$$

$$[\text{QFCH}^+] = K_1[\text{QFC}][\text{S}] \quad \dots\dots(5)$$

Substituting the value of $[\text{QFCH}^+]$ from Eq. (5) into Eq.(4)

$$\text{Rate} = k_2 K_1 [\text{S}][\text{QFC}][\text{H}^+]$$

$$= k_{\text{obs}} [\text{S}][\text{QFC}][\text{H}^+] \quad \dots\dots(6)$$

Conclusion

The oxidation of ketohexoses by QFC in aqueous acetic acid medium proceeds by hydride

ion transfer mechanism. In the present study, D-fructose is more reactive than L-sorbose. The reason being that L-sorbose exists mainly in α -pyranoid form while D-fructose in β -pyranoid form.

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