

Research Article

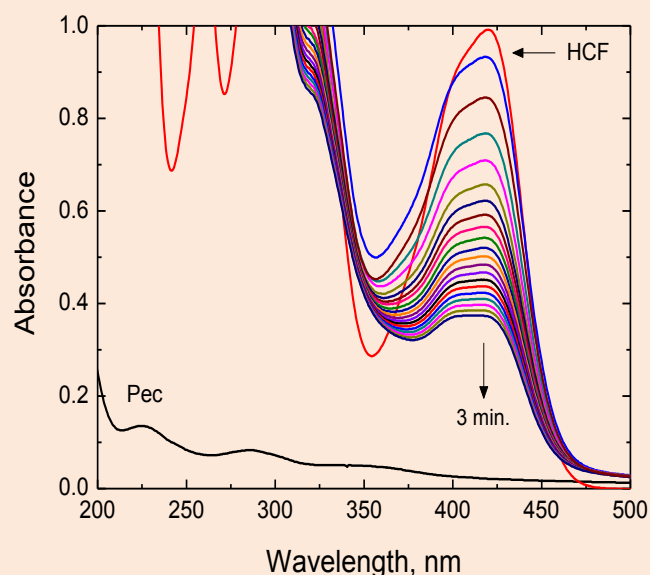
Oxidation of Pectate Biopolymer by Hexacyanoferrate(III) in Aqueous Alkaline Medium. A Kinetic and Mechanistic Study

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Abstract

In aqueous alkaline medium, the kinetics of oxidation of pectate biopolymer (Pec) by hexacyanoferrate(III) (HCF) has been studied spectrophotometrically under the conditions, $[Pec] \gg [HCF]$, at a constant ionic strength of 1.0 mol dm^{-3} and at $25 \text{ }^\circ\text{C}$. The reaction showed first order dependence on $[HCF]$, whereas the reaction orders with respect to both $[Pec]$ and $[OH^-]$ are less than unity. The oxidation rate was found to increase with the increase on the ionic strength and dielectric constant of the reaction medium. Initial addition of reaction product, hexacyanoferrate(II), did not have any significant effect on the oxidation rate. Based on the kinetic results, a plausible mechanism has been proposed which involves the formation of a 1:1 intermediate complex between HCF and the deprotonated pectate species in a pre-equilibrium step. The rate law associated with the oxidation mechanism is derived and the reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to the slow step of the mechanism along with the thermodynamic quantities of the equilibrium constants are also calculated and discussed.

Keywords: Kinetics, mechanism, oxidation, pectate, hexacyanoferrate(III)



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Introduction

Oxidation reactions are very important in nature and are regarded as key transformations in organic synthesis. Also, the study of carbohydrates is one of the most exciting fields of organic chemistry. The biological and economic importance of carbohydrates is responsible for the great interest in the study of their biochemical and physicochemical properties. The oxidation of carbohydrates is an important way in which new compounds and materials with interesting properties can be provided. Among these carbohydrates, naturally occurring pectate polysaccharide is very attractive. Pectate is a copolymer of poly(1,4- α -D-galacturonate) water-soluble substance [1]. Pectate may form physical gels under specific conditions, and their functional groups ($-OH$ and $-COO^-$) also allow different chemical and physical modifications. Bearing in mind their gelling ability, stabilizing properties and high viscosity in aqueous solutions, pectate and its derivatives are widely used in food [2,3], cosmetics and pharmaceutical industries [4]. In addition, oxidized pectates present more reactive groups and a faster degradation when these ones are used in supports for drug controlled delivery and cell transplantation [5,6]. The rate of oxidation of pectate depends on the oxidant nature and pH of the medium [7,8]. A literature survey revealed very limited works are reported about the kinetics and mechanism of oxidation of pectate using oxidants like chromium(VI) in acid medium [7] and potassium permanganate in alkaline medium [8].

Hexacyanoferrate(III) (HCF) is an efficient one-electron oxidant and has been observed to be a substitution inert-transition metal complex [9,10]. Its usefulness may be due to its stability, water solubility and its moderate reduction potential of 0.45 V, leading to its reduction to hexacyanoferrate(II), a stable product [11,12]. Oxidation of organic compounds by HCF in alkaline media has been a subject of much interest [13-20]. However, few studies on the HCF oxidation of polysaccharides [21] and reducing sugars [22-24] are reported.

In the present work, we report the study of the redox reaction of pectate biopolymer with HCF in alkaline medium to provide information on the relative reactivity of pectate toward HCF and to elucidate a plausible oxidation reaction mechanism.

Experimental

Materials

The reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. The sample of sodium pectate used was E. Merck grade. The samples of potassium hexacyanoferrate(III), sodium hydroxide and sodium perchlorate were of BDH grade. Stock solutions of both oxidant and substrate were freshly prepared using doubly distilled water. The concentration of HCF solution was ascertained spectrophotometrically and by iodometric titration [25a]. Hexacyanoferrate(II) solution was prepared by dissolving potassium hexacyanoferrate(II) (S.D fine Chem.) in water and standardizing with cerium(IV) solution [25b].

Kinetic Measurements

The kinetics of the pectate-HCF redox reaction was studied under pseudo-first order conditions using an excess of pectate over HCF. Reactant solutions were thermally equilibrated at 25 °C prior to the kinetic run and NaClO₄ was used to maintain a constant ionic strength. The HCF consumption was followed spectrophotometrically by monitoring the decay in the absorbance of HCF as a function of time at its absorption maximum, $\lambda = 420$ nm, until at least 90% conversion. The other constituents of the reaction mixture did not absorb significantly at this wavelength. The applicability of Beer's law for HCF at 420 nm has been verified giving $\epsilon = 1063 \pm 21 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in a good agreement with the value reported elsewhere [26]. The absorbance measurements were made on a Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. The spectral changes during oxidation of pectate by HCF in alkaline medium are shown in **Figure 1**. The scanned spectra indicate gradual disappearance of HCF(III) band with time as a result of its reduction to HCF(II).

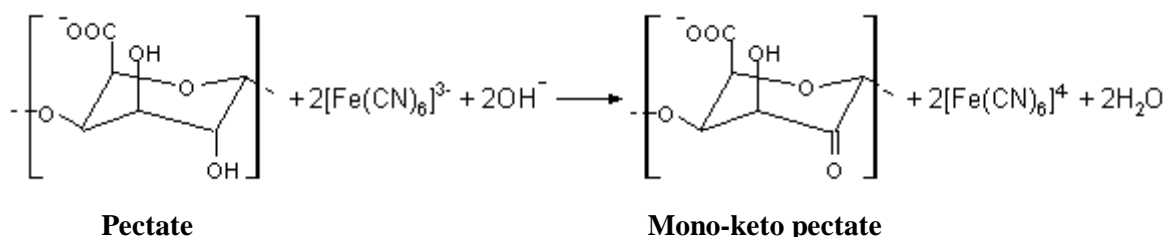
First order plots of $\ln(\text{absorbance})$ versus time were found to be straight lines up to at least 75% of the reaction completion and the pseudo-first order rate constant values (k_{obs}) were calculated as the gradients of such plots. Average values of at least two independent kinetic runs of the rate constant were taken for the analysis. The rate constants were reproducible to within 4%. The order of reaction with respect to the reactants were determined from the slopes of the $\log k_{\text{obs}}$ versus $\log(\text{concentration})$ plots by varying the concentrations of substrate and acid, in turn, while keeping other conditions constant.

Few kinetic runs were carried out after bubbling purified nitrogen and compared with those taken under air, and the results were found to be the same. Thus the dissolved oxygen did not affect the oxidation rate.

Results

Stoichiometry and Product Analysis

The stoichiometry was determined spectrophotometrically which indicates the consumption of two HCF ions for one unit of pectate biopolymer to yield the oxidation products as shown in the following equation,



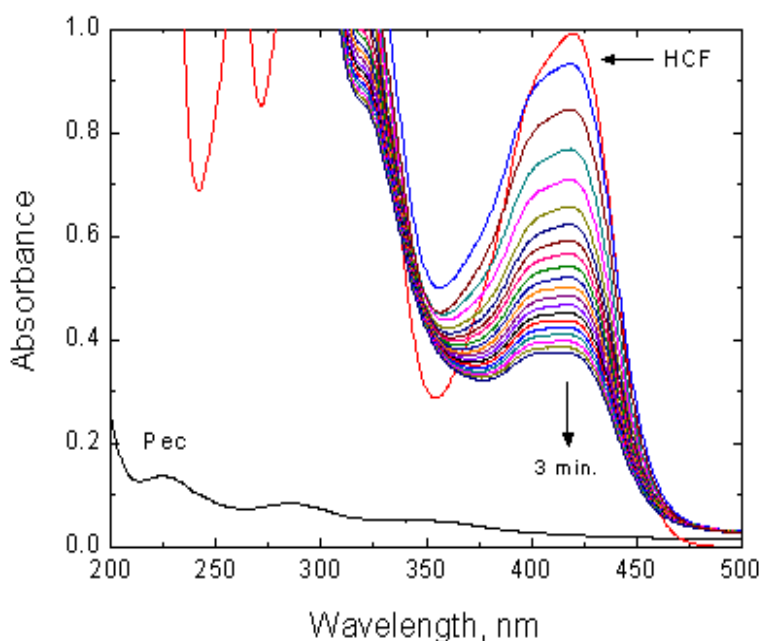


Figure 1 Spectral changes during the oxidation of pectate by HCF in alkaline medium. $[Pec] = 12.0 \times 10^{-2}$, $[HCF] = 7.0 \times 10^{-4}$, $[OH^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$ at 25°C .

The above stoichiometric equation is consistent with the results of product analysis carried out by spectral data and elemental analysis [8,27,28] which showed conversion of one of the two secondary hydroxyl groups to the keto group to yield mono-keto pectate.

Rate Dependence on [HCF]

Hexacyanoferrate(III) oxidant was varied in the range of 3.0×10^{-4} to $12.0 \times 10^{-4} \text{ mol dm}^{-3}$ while other variables such as the concentration of the reductant and sodium perchlorate were kept constant. The pH and temperature were also kept constant. It has been observed that the increase in the oxidant concentration does not alter the oxidation rate of pectate (**Table 1**). This indicates that the oxidation rate was independent of oxidant concentration indicating that the order of reaction with respect to the oxidant was confirmed to be one.

Rate Dependence on [Pec]

The observed rate constant was determined at different initial concentrations of pectate reductant keeping others constant. A plot of the observed rate constant versus $[Pec]$ at constant pH was linear with positive intercept (Figure not shown) confirming the fractional-first order dependence with respect to pectate concentration.

Rate Dependence on $[OH^-]$

The reaction rate was measured at constant $[Pec]$, $[HCF]$, ionic strength and temperature but with various $[OH^-]$ ($0.1 - 0.9 \text{ mol dm}^{-3}$). The rate of reaction was found to increase with increase in $[OH^-]$. Plot of k_{obs} versus $[OH^-]$ was linear with a positive intercept confirming fractional-first order dependence with respect to $[OH^-]$.

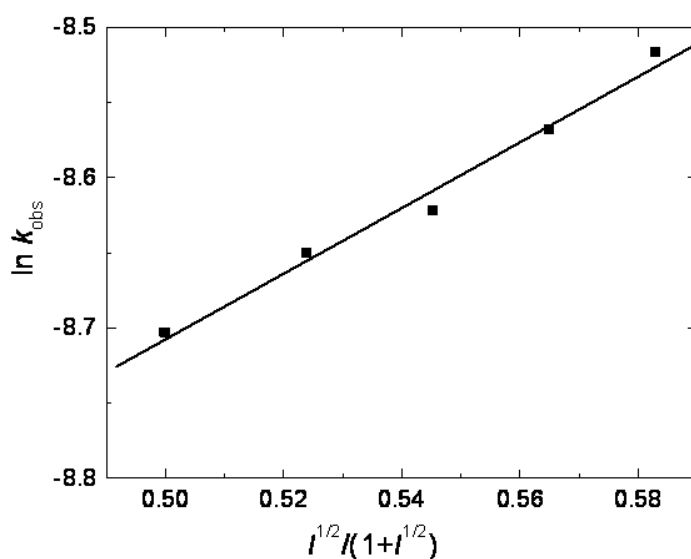
Table 1 Effect of variation of [HCF], [Pec], [OH⁻] and ionic strength, *I*, on the first order rate constant (*k*_{obs}) in the oxidation of pectate by HCF in alkaline medium at 25 °C.

10⁴ [HCF] mol dm ⁻³	10³ [Pec] mol dm ⁻³	[OH⁻] mol dm ⁻³	<i>I</i> mol dm ⁻³	10⁵ <i>k</i>_{obs} s ⁻¹
3.0	12.0	0.5	1.0	15.9
5.0	12.0	0.5	1.0	16.5
7.0	12.0	0.5	1.0	16.6
9.0	12.0	0.5	1.0	17.2
12.0	12.0	0.5	1.0	16.8
7.0	4.0	0.5	1.0	7.1
7.0	8.0	0.5	1.0	13.0
7.0	12.0	0.5	1.0	16.6
7.0	16.0	0.5	1.0	22.1
7.0	20.0	0.5	1.0	26.3
7.0	16.0	0.1	1.0	4.4
7.0	16.0	0.3	1.0	10.5
7.0	16.0	0.5	1.0	16.6
7.0	16.0	0.7	1.0	26.2
7.0	16.0	0.9	1.0	30.3
7.0	16.0	0.5	1.0	16.6
7.0	16.0	0.5	1.2	17.5
7.0	16.0	0.5	1.5	18.1
7.0	16.0	0.5	1.7	18.9
7.0	16.0	0.5	2.0	19.6

Experimental error ± 4%

Rate Dependence on Ionic Strength and Dielectric Constant

The effect of ionic strength on the rate of reaction was studied by varying the NaClO₄ concentration. The results are presented in Table 1. The results showed that the observed first order rate constant was found to increase with increasing ionic strength, and the Debye-Huckel plot, $\ln k_{\text{obs}}$ versus $I^{1/2}/(1+I^{1/2})$, was linear with a positive slope as shown in Figure 2.

**Figure 2** Debye-Huckel plot for the oxidation of pectate by HCF in alkaline medium. [Pec] = 12.0 × 10⁻³, [HCF] = 7.0 × 10⁻⁴ and [OH⁻] = 0.5 mol dm⁻³ at 25 °C.

The effect of dielectric constant (D) was studied by varying the *t*-butyl alcohol–water content (0–40 %) in the reaction mixture with all other conditions being constant. The data revealed that the reaction rate retards with the decrease in dielectric constant of the solvent mixture, i.e. increase the *t*-butyl alcohol content. The plot of $\log k_{\text{obs}}$ versus $1/D$ was linear with a negative slope (**Figure 3**).

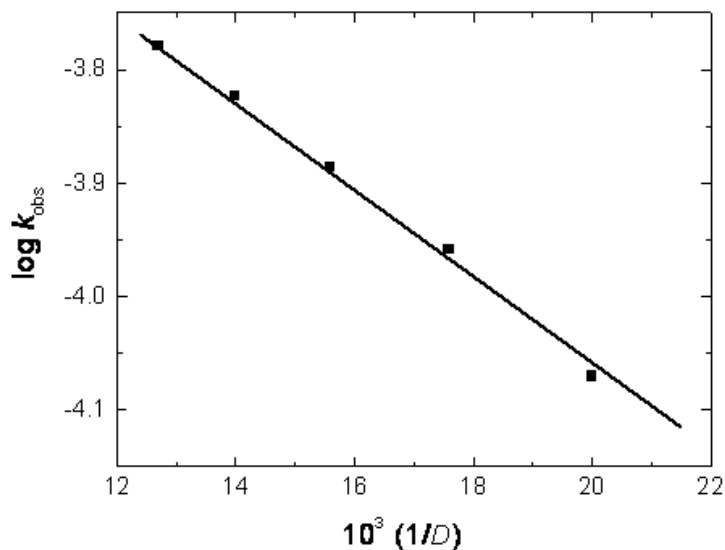


Figure 3 Effect of dielectric constant (D) on the rate of oxidation of pectate by HCF in alkaline medium. [Pec] = 12.0×10^{-3} , [HCF] = 7.0×10^{-4} , [OH⁻] = 0.5 and $I = 1.0 \text{ mol dm}^{-3}$ at 25 °C.

Rate Dependence on Initially Added Product

The effect of added hexacyanoferrate(II) as a reaction product was studied also in the concentration range 3.0×10^{-4} to $12.0 \times 10^{-4} \text{ mol dm}^{-3}$ at fixed concentrations of the oxidant, reductant and alkali. It was found that HCF(II) did not have any significant effect on the rate of reaction.

Rate Dependence on Temperature

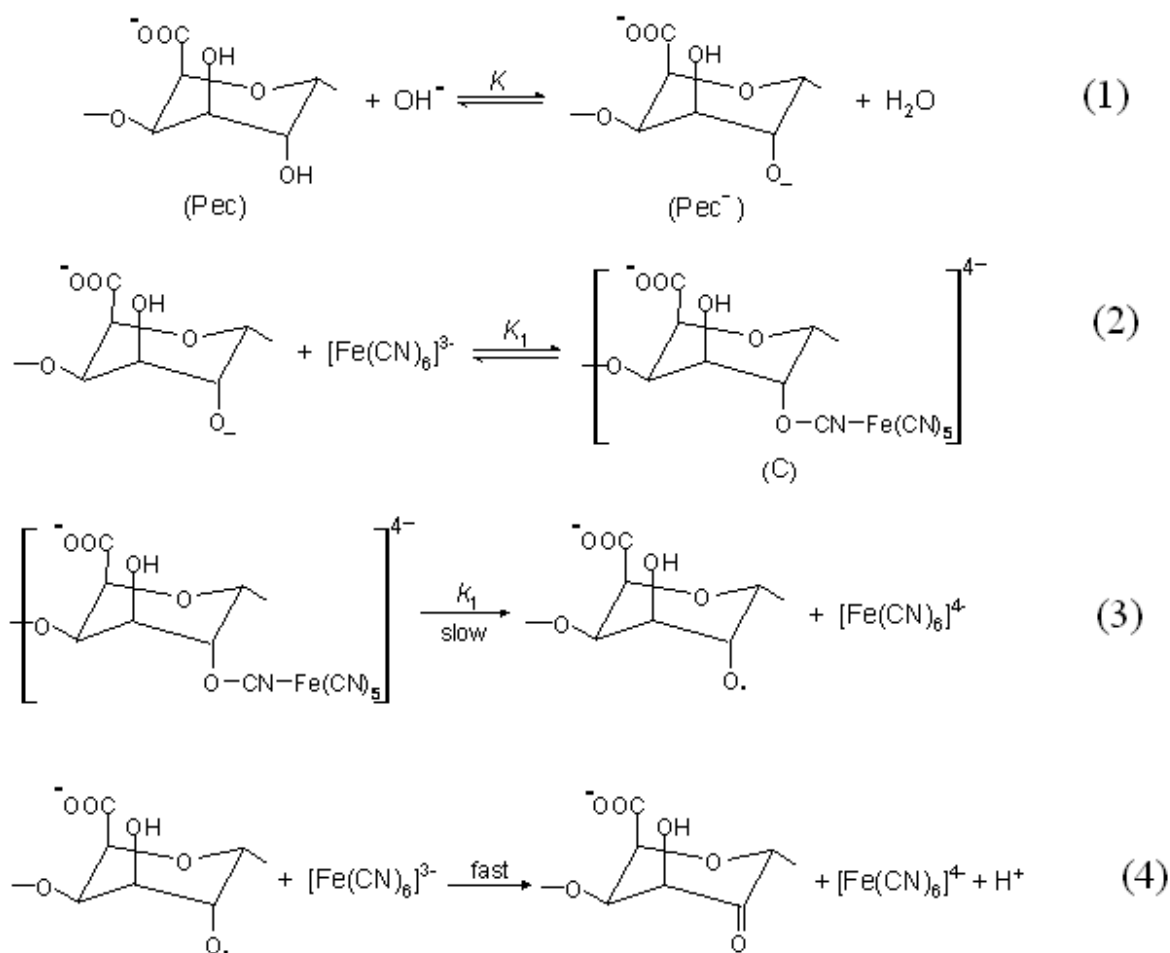
To evaluate the activation and thermodynamic parameters, the reaction rate of was measured at five different temperatures ranging from 20 to 40 °C under varying the concentrations of pectate substrate and alkali. The reaction rate was found to increase with raising temperature. Using Arrhenius and Eyring equations, the activation parameters of the rate constant of the slow step of reaction (k_1) along with thermodynamic parameters associated with the equilibrium constants involved in the reaction mechanism were evaluated and were listed in **Tables 3** and **4**.

Polymerization Test

It is well known that hexacyanoferrate(III) is a generator of free radicals due to its single equivalent change in redox reaction. Hence, the involvement of free radical species in the reaction was assayed by a polymerization test. A known quantity of acrylonitrile monomer was added initially to the reaction mixture in an inert atmosphere, with the result of progressive formation of a white precipitate in the whole reaction mixture indicating presence of free radical during reaction. When the experiment was repeated in the absence of pectate under similar conditions, the test was negative. This indicates that the reaction was routed through free radical path.

Reaction Mechanism

The reaction between pectate and HCF had a stoichiometry of 1:2, i.e., two moles of HCF consumed one mole of pectate. The reaction exhibited first order dependence with respect to [HCF] and less than unit orders with respect to [Pec] and [OH⁻]. The less than unit order in [OH⁻] suggests deprotonation of pectate by the alkali in a pre-equilibrium step to form a more reactive species of the reductant as represented by equilibrium (1) in Scheme 1. The rate was not considerably affected by HCF(II) suggesting that the probability of a fast equilibrium with the product in the rate-determining step was ruled out. Hence, the rate-determining step should be irreversible as is generally the case for one electron oxidants [29] and the oxidation takes place through generation of a free radical as was obtained experimentally. Also, the rate of reaction increased with increasing the ionic strength and dielectric constant of the medium suggesting that the reaction occurs between two similarly charged ions [30,31].



Scheme 1 Mechanism of oxidation of pectate by HCF in alkaline medium

On the other hand, the obtained less than unit order in [Pec] may be as a result of formation of a complex (C) between HCF and deprotonated pectate species in a pre-equilibrium step. Complex formation was proved kinetically by the non-zero intercept of the plot $1/k_{\text{obs}}$ versus $1/[\text{Pec}]$ (**Figure 4**) in favor of possible formation of an intermediate complex between the oxidant and substrate, similar to the well-known Michaelis–Menten [32] mechanism for enzyme–substrate reactions. The formed complex (C) slowly decomposed in the rate-determining step to give rise to the initial oxidation products as a substrate radical (Pec[·]) and HCF(II). The substrate radical reacts with another HCF species in a subsequent fast step to yield the final oxidation products as illustrated by **Scheme 1**.

Again, it has been reported [33-35] that the entropy of activation (ΔS^\ddagger) tends to be more negative for reactions of an inner-sphere nature, whereas the reactions of positive ΔS^\ddagger values proceed via an outer-sphere mechanism. The obtained large negative values of ΔS^\ddagger (**Table 2**) suggests that the more plausible mechanism is one-electron transfer of inner-sphere nature where the transfer of an electron occurring from pectate to Fe^{III} through a cyano ion as a bridging ligand. Furthermore, large negative values of ΔS^\ddagger indicate that there is a decrease in the randomness during the oxidation process. This leads to the formation of compacted intermediate complex and such activated complex is more ordered than the reactants due to loss of degree of freedom. On the other hand, the positive value of ΔH^\ddagger indicates that the complex formation is endothermic. Also, the large positive value of ΔG^\ddagger suggests enhanced formation of the intermediate with increasing temperature as well as to the non-spontaneity of the complex formation [21].

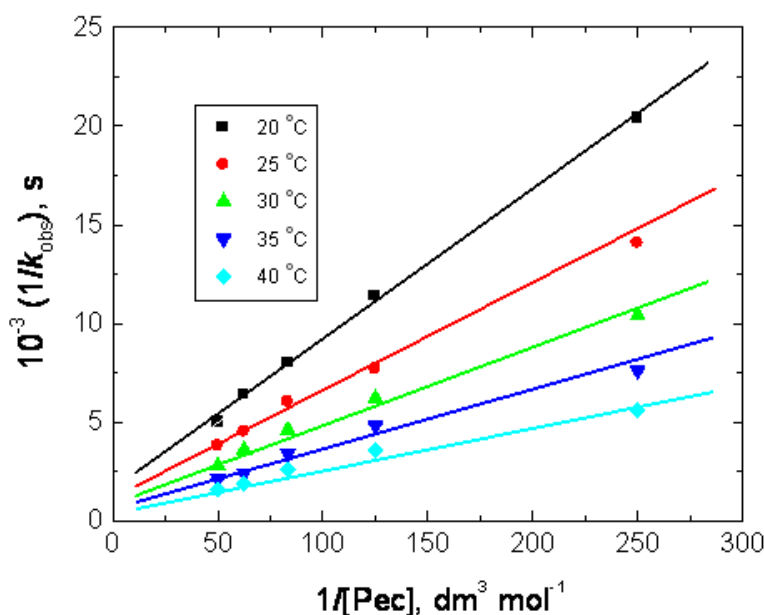


Figure 4 Plots of $1/k_{\text{obs}}$ versus $1/[\text{Pec}]$ in the oxidation of pectate by HCF in alkaline medium at different temperatures. $[\text{HCF}] = 7.0 \times 10^{-4}$, $[\text{OH}^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$.

The rate-law equation describing the dependence of the reaction rate on the substrate, oxidant and alkali concentrations has been deduced (Appendix A) to give the following,

$$\text{Rate} = \frac{k_1 K K_1 [\text{Pec}] [\text{HCF}] [\text{OH}^-]}{1 + K [\text{OH}^-] + K K_1 [\text{Pec}] [\text{OH}]} \quad (5)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k_{\text{obs}} [\text{HCF}] \quad (6)$$

Comparing Eqs. (5) and (6), the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K K_1 [\text{Pec}] [\text{OH}^-]}{1 + K [\text{OH}^-] + K K_1 [\text{Pec}] [\text{OH}]} \quad (7)$$

Eq. (7) can be verified by rearranging it to Eqs. (8) and (9),

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1 K K_1 [\text{OH}^-]} + \frac{1}{k_1 K_1} \right) \frac{1}{[\text{Pec}]} + \frac{1}{k_1} \quad (8)$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1 K K_1 [\text{Pec}]} \right) \frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_1 K_1 [\text{Pec}]} + \frac{1}{k_1} \right) \quad (9)$$

According to Eqs. (8) and (9), plots of $1/k_{\text{obs}}$ versus $1/[\text{Pec}]$ at constant $[\text{OH}^-]$, and $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ at constant $[\text{Pec}]$ should be linear with positive intercepts and were found to be so as shown in **Figures 4** and **5**, respectively. The values of the rate constant of the slow step (k_1) at different temperatures obtained as reciprocal of intercepts of $1/k_{\text{obs}}$ versus $1/[\text{Pec}]$ plots were listed in **Table 2**. The activation parameters of k_1 were calculated from the Arrhenius and Eyring plots, **Figure 6** (a, b), and were listed in **Table 3**. Also, the values of the equilibrium constants associated with the mechanistic Scheme 1 (K and K_1) at different temperatures were calculated from the slopes and intercepts of the $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ plots (and the calculated values of k_1) and were listed in Table 2. The thermodynamic parameters of K and K_1 were evaluated from van't Hoff plots (**Figure 7**) and were also inserted in **Table 4**.

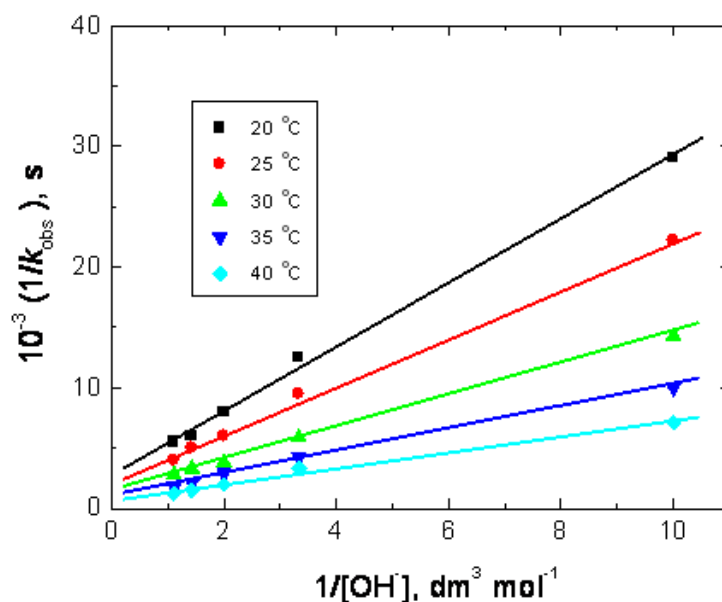


Figure 5 Plots of $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$ in the oxidation of pectate by HCF in alkaline medium at different temperatures. $[\text{HCF}] = 7.0 \times 10^{-4}$, $[\text{Pec}] = 12.0 \times 10^{-3}$ and $I = 1.0 \text{ mol dm}^{-3}$.

Table 2 Values of the rate constant of the slow step (k_1) and the equilibrium constants (K and K_1) in the oxidation of pectate by HCF in alkaline medium at different temperatures.

Constant	Temperature (°C)				
	20	25	30	35	40
$10^4 k_1 (\text{s}^{-1})$	5.39	7.92	12.40	17.29	25.71
$K (\text{dm}^3 \text{mol}^{-1})$	7.31	6.80	6.18	5.91	5.73
$10^{-2} K_1 (\text{dm}^3 \text{mol}^{-1})$	8.45	8.03	7.74	7.28	6.59

Experimental error = $\pm 4\%$

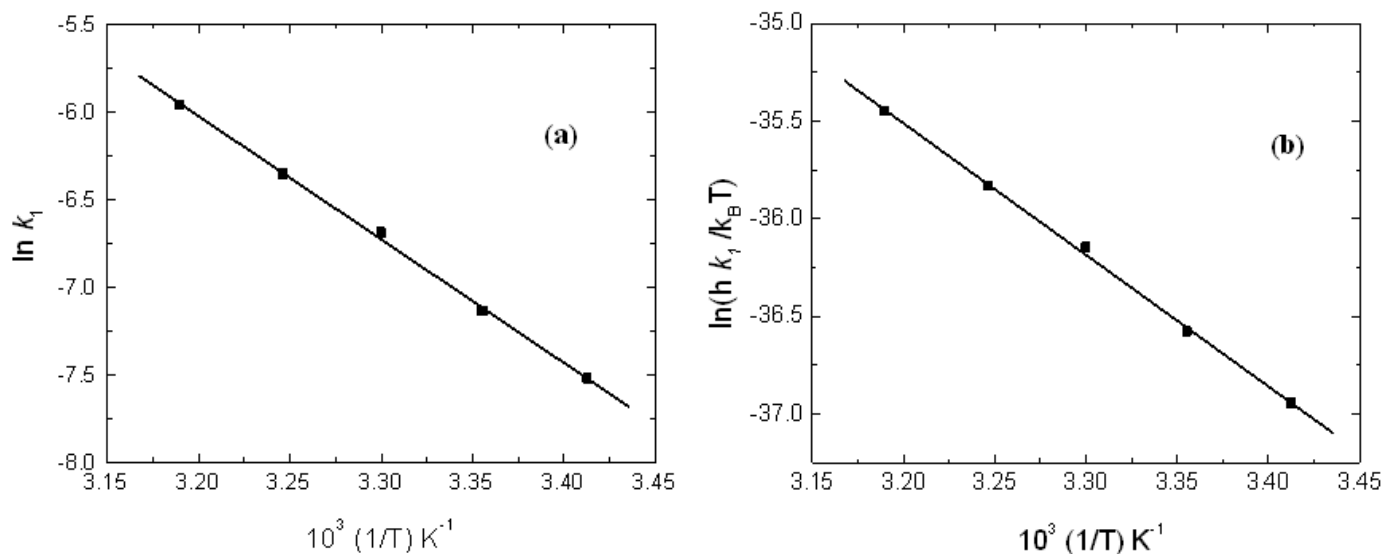


Figure 6 (a) Arrhenius and (b) Eyring plots of k_1 in the oxidation of pectate by HCF in alkaline medium. $[HCF] = 7.0 \times 10^{-4}$, $[Pec] = 12.0 \times 10^{-3}$, $[OH^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$

Table 3 Activation parameters of k_1 in the oxidation of pectate by HCF in alkaline medium. $[HCF] = 7.0 \times 10^{-4}$, $[Pec] = 12.0 \times 10^{-3}$, $[OH^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$

ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔG^\ddagger_{298} kJ mol ⁻¹	E_a^\ddagger kJ mol ⁻¹	A mol ⁻¹ s ⁻¹
-115.98	55.99	90.55	58.53	14.6×10^6

Experimental error = $\pm 4\%$

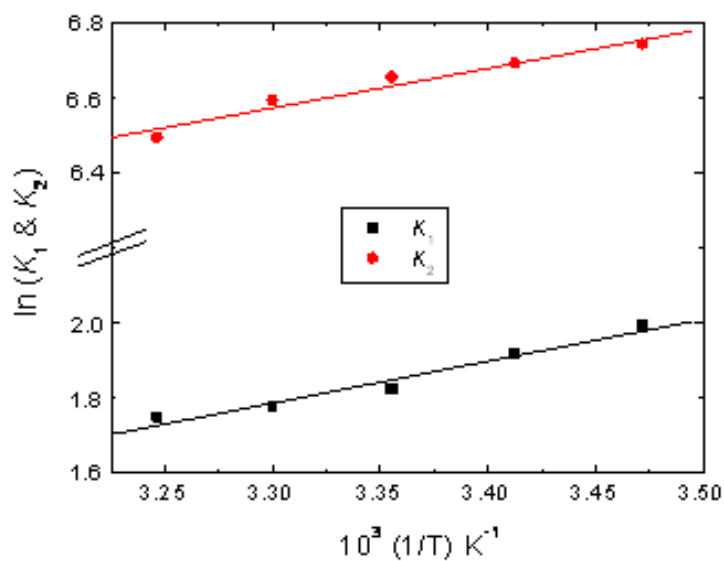


Figure 7 van't Hoff plots of K and K_1 in the oxidation of pectate by HCF in alkaline medium. $[HCF] = 7.0 \times 10^{-4}$, $[Pec] = 12.0 \times 10^{-3}$, $[OH^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$

Table 4 Thermodynamic parameters associated with K and K_1 in the oxidation of pectate by HCF in alkaline medium. $[\text{HCF}] = 7.0 \times 10^{-4}$, $[\text{Pec}] = 12.0 \times 10^{-3}$, $[\text{OH}^-] = 0.5$ and $I = 1.0 \text{ mol dm}^{-3}$

Equilibrium Constant	ΔH° kJ mol ⁻¹	ΔG°_{298} kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹
K	-9.28	-4.75	-15.2
K_1	-8.75	-16.57	26.24

Experimental error = $\pm 5\%$

Appendix A

Derivation of the rate law

According to the suggested mechanistic **Scheme 1**,

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k_1[\text{C}] \quad (\text{A1})$$

$$K = \frac{[\text{Pec}^-]}{[\text{Pec}][\text{OH}^-]}, \quad [\text{Pec}^-] = K[\text{Pec}][\text{OH}^-] \quad (\text{A2})$$

and

$$K_1 = \frac{[\text{C}]}{[\text{Pec}^-][\text{HCF}]}, \quad [\text{C}] = K_1[\text{Pec}^-][\text{HCF}] = KK_1[\text{Pec}][\text{HCF}][\text{OH}^-] \quad (\text{A3})$$

Substituting Eq. (A3) into Eq. (A1) leads to,

$$\text{Rate} = k_1KK_1[\text{Pec}][\text{HCF}][\text{OH}^-] \quad (\text{A4})$$

The total concentration of Pec is given by,

$$[\text{Pec}]_T = [\text{Pec}]_F + [\text{Pec}^-] + [\text{C}] \quad (\text{A5})$$

where 'T' and 'F' stand for total and free concentrations.

Substituting Eqs. (A2) and (A3) into Eq. (A5) and rearrangement gives,

$$[\text{Pec}]_T = [\text{Pec}]_F + K[\text{Pec}][\text{OH}^-] + KK_1[\text{Pec}][\text{HCF}][\text{OH}^-] \quad (\text{A6})$$

$$[\text{Pec}]_T = [\text{Pec}]_F (1 + K[\text{OH}^-] + KK_1[\text{HCF}][\text{OH}^-]) \quad (\text{A7})$$

Therefore,

$$[\text{Pec}]_F = \frac{[\text{Pec}]_T}{1 + K[\text{OH}^-] + KK_1[\text{HCF}][\text{OH}^-]} \quad (\text{A8})$$

In view of very small $[\text{HCF}]$, the third denominator term $KK_1[\text{HCF}][\text{OH}^-]$ in the above equation can be neglected. Therefore,

$$[\text{Pec}]_F = \frac{[\text{Pec}]_T}{1 + K[\text{OH}^-]} \quad (\text{A9})$$

Also,

$$[\text{HCF}]_T = [\text{HCF}]_F + [\text{C}] \quad (\text{A10})$$

Substituting Eq. (A3) into Eq. (A10),

$$[\text{HCF}]_T = [\text{HCF}]_F (1 + KK_1[\text{Pec}][\text{OH}^-]) \quad (\text{A11})$$

$$[\text{HCF}]_F = \frac{[\text{HCF}]_T}{1 + KK_1[\text{Pec}][\text{OH}^-]} \quad (\text{A12})$$

Regarding to the concentration of OH⁻

$$[\text{OH}^-]_F = [\text{OH}^-]_T \quad (\text{A13})$$

Substituting Eqs. (A9), (A12) and (A13) into Eq. (A4) (and omitting 'T' and 'F' subscripts) leads to,

$$\text{Rate} = \frac{k_1 K K_1 [\text{Pec}] [\text{HCF}] [\text{OH}^-]}{(1 + K [\text{OH}^-]) (1 + K K_1 [\text{Pec}] [\text{OH}])} \quad (\text{A14})$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (A15),

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k_{\text{obs}} [\text{HCF}] \quad (\text{A15})$$

Comparing Eqs. (A14) and (A15) and with rearrangement, the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K K_1 [\text{Pec}] [\text{OH}^-]}{1 + K [\text{OH}^-] + K K_1 [\text{Pec}] [\text{OH}] + K^2 K_1 [\text{Pec}] [\text{OH}]^2} \quad (\text{A16})$$

The term $K^2 K_1 [\text{Pec}] [\text{OH}]^2$ in the denominator of Eq. (A16) is negligibly small compared to unity in view of the low concentration of Pec used. Therefore Eq. (A16) can be written as,

$$k_{\text{obs}} = \frac{k_1 K K_1 [\text{Pec}] [\text{OH}^-]}{1 + K [\text{OH}^-] + K K_1 [\text{Pec}] [\text{OH}]} \quad (\text{A17})$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1 K K_1 [\text{OH}^-]} + \frac{1}{k_1 K_1} \right) \frac{1}{[\text{Pec}]} + \frac{1}{k_1} \quad (\text{A18})$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1 K K_1 [\text{Pec}]} \right) \frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_1 K_1 [\text{Pec}]} + \frac{1}{k_1} \right) \quad (\text{A19})$$

References

- [1] Aspinall GO, Cañas-Rodríguez A, J Chem Soc, 1958, 4020.
- [2] Mitchell J, Sommerville A, Speirs C, Int J Food Sci Technol, 1978, 13, 425.
- [3] Borzelleca JF, Filer LJ, Jr, Kinoshita FK, Gerrish TC, Kuo PK, La Du BN, Food Chem Toxicol, 1996, 34, 432.
- [4] Drury J, Mooney DJ, Biomaterials, 2003, 24, 4337.
- [5] Bouhadir KH, Kruger GM, Lee KY, Mooney DJ, J Pharm Sci, 2000, 89, 910.
- [6] Sutherland IW, In Biomaterials: Novel Materials from Biological Sources; Byron, D., Ed., Stockton Press, New York, 1991, p. 309.
- [7] Bellua SE, Gonzalez JC, Garc SI, Signorella SR, Sala LF, J Phys Org Chem, 2008, 21, 1059.
- [8] Khairou KS, Hassan RM, Eur Poly J, 2001, 36, 2021.
- [9] Shukla R, Upadhyay SK, Indian J Chem, 2008, 47A, 551.
- [10] Sharanabasamma K, Mahantesh A, Angadi MA, Tuwar SM, Open Cat J, 2011, 4, 1.
- [11] Farokhi SA, Nandibewoor ST, Tetrahedron, 2003, 59, 7595.
- [12] Nowdari A, Adari KK, Gollapalli NR, Parvataneni V, Eur J Chem, 2009, 6, 93.
- [13] Jose TP, Nandibewoor ST, Tuwar SM, J Sulfur Chem, 2006, 27, 25.
- [14] Kelson EP, Phengsy PP, Int J Chem Kinet, 2000, 32, 760.
- [15] Vovk AI, Muraveva IV, Kukhar VP, Baklan VF, Russ J Gen Chem, 2000, 70, 1108.
- [16] Speakman PT, Waters WA, J Chem Soc, 1955, 40.
- [17] Jose TP, Nandibewoor ST, Tuwar SM, J Solution Chem, 2006, 35, 51.
- [18] Singh VN, Singh MP, Saxena BBL, Indian J Chem, 1970, 8, 529.
- [19] Leal JM, Garcia B, Domingo PL, Coord Chem Rev, 1998, 173, 79.

- [20] Jose TP, Angadi MA, Salunke MS, Tuwar SM, J Mol Struct, 2008, 892, 121.
- [21] Hassan RM, Ibrahim SM, Zafarany IA, Fawzy A, Takagi HD, J Mol Cat A, 2011, 344, 93.
- [22] Pakai B, Shukla A, Santosh U, Int J Chem Kinet, 1995, 28, 713.
- [23] Narendra N, Singh MP, J Phys Chem, 1965, 69, 2038.
- [24] Olusanya SO, Odebumi EO, Pacific J Sci Technol, 2011, 12, 328.
- [25] Jeffery GH, Bassett J, Mendham J, Denney RC, Text Book of Quantitative Chemical Analysis, 5th ed.; ELBS Longman: Essex, 1996; (a) p. 399 and (b) p. 384.
- [26] Milazzo G, Caroll S, Tables of Standard Electrode Potential, Wiley, New York, 1978.
- [27] Vogel AI, Text Book of Practical Organic Chemistry including Quantitative Organic Analysis, third ed. ELBS, Longman, 1993, p. 332.
- [28] Feigl F, Spot Tests in Organic Analysis, Elsevier; New York, 1975, p. 195.
- [29] Leal JM, Domingo PL, Garcla B, Ibeas S, J Chem Soc Faraday Trans, 1993, 89, 3571.
- [30] Frost AA, Person RG, Kinetics and Mechanism, Wiley Eastern, New Delhi, 1970, p. 147.
- [31] Amis ES, Solvent Effect on Reaction Rates and Mechanism, Academic Press; New York, 1966, p. 28.
- [32] Michaelis L, Menten ML, Biochem Z, 1918, 49, 333.
- [33] Hicks KW, Toppen DL, Linck RG, Inorg Chem, 1972, 11, 310; Moore FM, Hicks KW, Inorg Chem, 1975, 14, 413; Hicks KW, Happelle GA, Inorg Chem, 1980, 19, 1623.
- [34] Sutin N, Acc Chem Res, 1968, 1, 225.
- [35] Freeman F, J Am Chem Soc, 1981, 103, 1154.

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