

Kinetics & Mechanism of Oxidation of *trans*-Cinnamic & *trans*-Crotonic Acids by Hexacyanoferrate(III) in Perchloric Acid Medium

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The kinetics of oxidation of cinnamic and crotonic acids (*trans*) by hexacyanoferrate(III) in perchloric acid show that the primary reaction is the direct attack of the protonated species of hexacyanoferrate(III) at the double bond by electron transfer with the formation of a cationic intermediate. This is supported by an inverse secondary kinetic isotope effect ($k_D/k_H = 1.2$) and a ρ^+ value of -4.0 . The cationic intermediate reacts with water to give a hydroxylic compound which is rapidly oxidized by the hexacyanoferrate(III) in successive stages until stable products are formed. A comparison of the rates of oxidation of crotonic acid ($k_{\text{obs}} = 7.0 \times 10^{-5} \text{ s}^{-1}$) and cinnamic acid ($k_{\text{obs}} = 13.0 \times 10^{-5} \text{ s}^{-1}$) indicates that phenyl conjugation accelerates the reaction. The activation energies for the reaction of the two substrates are comparable, indicating identical pathways for the oxidation process.

The oxidation of cinnamic acid by permanganate in aqueous neutral¹, acidic² and in alkaline media³ has earlier been shown to result in the cleavage of the carbon-carbon bond to yield benzaldehyde. However, permanganate oxidation of unsaturated acids in basic medium ($\text{pH} > 12$) has been reported to yield diols⁴. We have focussed our attention on the oxidation of cinnamic acid (and substituted cinnamic acids) and crotonic acid by potassium hexacyanoferrate(III) in acid medium. The carbon-carbon double bond in unsaturated acids is quite reactive, therefore abstraction of an electron by hexacyanoferrate(III) in acid medium can lead to cleavage of the carbon-carbon bond of cinnamic and crotonic acids to yield identifiable products.

Materials and Methods

All the substrates (Koch-Light) were purified and their purities were checked by melting points, IR and UV spectra. Perchloric acid (Baker), $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ (IDPL) were used as such. Acetic acid (E. Merck) was distilled under reduced pressure from acidic sodium dichromate⁵. *trans*-Cinnamic acid- α -*d* (m.p. 135°) and *trans*-cinnamic acid- β -*d* (m.p. 136°) were obtained from Isotopes Inc. (USA), and were checked for purity by IR and PMR spectra.

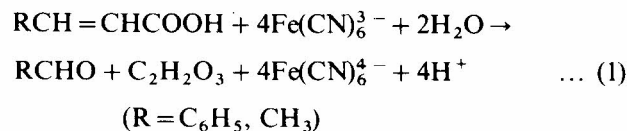
Temperature equilibrated solutions of the substrate with requisite amounts of HClO_4 , HOAc and $\text{K}_3\text{Fe}(\text{CN})_6$ solutions were mixed in equal volumes and the reaction was followed by observing the disappearance of $\text{Fe}(\text{CN})_6^{3-}$ at 420 nm, spectrophotometrically, as described in an earlier communication⁶. All the reactions were carried out under nitrogen atmosphere. All the values of rate constants were the average of two or more experiments, the accuracy being $\pm 1.5\%$ or better.

Product analysis—Using approximately the same experimental conditions that were employed for the kinetic determinations, a solution of the reaction mixture was kept under nitrogen atmosphere for 24 hr, for the completion of the reaction. The solution was extracted with chloroform, the organic layer washed with water, dried over anhydrous MgSO_4 , and then evaporated. Spotting on TLC plates showed two spots. The two products were separated by column chromatography using neutral alumina, and eluted with varying proportions (100:0 to 70:30, v/v) of hexane and chloroform, concentrated, and then identified.

Benzaldehyde (80% yield) and glyoxylic acid (10% yield) were identified (IR) as the two products from cinnamic acid oxidation. Glyoxylic acid was inferred by its 2,4-DNP derivative (m.p. 125°).

Acetaldehyde (75%) was identified (IR and UV) as one of the products in the crotonic acid oxidation. The other product was characterised as glyoxylic acid (10% yield).

Stoichiometric runs with an excess of hexacyanoferrate(III) when analysed, spectrophotometrically, gave a ratio of substrate: oxidant according to Eq. (1).



Results and Discussion

A detailed kinetic investigation revealed the following:

(i) The rate of the reaction was dependent on the first powers of the concentrations of the three

reactants, substrate, acid and oxidant (Table 1). Under the present experimental conditions, the rate law can be expressed as:

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_{\text{obs}}K[\text{Substrate}] \times [\text{Fe}(\text{CN})_6^{3-}][\text{H}^+] \quad \dots (2)$$

where K is the first protonation constant of $\text{Fe}(\text{CN})_6^{3-}$, whose value has been reported⁷ to be 10. The pseudo-first order rate constant, k_{obs} , was determined by keeping the concentrations of two of the three reactants (substrate, oxidant and acid) constant, and was calculated from Eq. (2)⁸,

$$k_{\text{obs}} = \frac{2.303}{t} \log \frac{D_0}{D_t} \quad \dots (3)$$

where D_0 is the initial optical density of the reaction mixture, and D_t is the optical density at time, t .

Cinnamic acid was oxidized at a faster rate, as compared to crotonic acid, indicating that phenyl conjugation was responsible for an acceleration in the rate of the reaction.

(ii) Increasing proportions of acetic acid from 80% to 90% (v/v) increased the rate constant, $10^5 k_{\text{obs}}$, s^{-1} , from 2.6 to 13.0 for cinnamic acid and from 2.1 to 7.0 for crotonic acid at $[\text{Substrate}] = 5 \times 10^{-2} M$, $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} M$, $[\text{HClO}_4] = 0.5 M$ and $\text{temp.} = 50^\circ$. This was probably due to the lowering of the dielectric constant of the medium, which favours a less polar transition state compared to more polar reactants. Plots of $\log k_{\text{obs}}$ versus the reciprocal of the dielectric constant were linear suggesting ion-dipole interaction.

(iii) An increase in the temperature resulted in an increase in the rate of the reaction. The activation energies for the oxidation of the two substrates were comparable (Table 2).

Table 1—Effect of Variation of [Substrate], [Oxidant] and [Acid] on the Rate of the Reaction

[HOAc] 90% (v/v); Temp. = 50°C			$10^5 \times k_{\text{obs}}$, s^{-1} for	
[Substrate] ($M \times 10^3$)	[Oxidant] ($M \times 10^3$)	[HClO ₄] (M)	cinnamic acid	crotonic acid
6.0	1.0	0.5	1.6	—
10.0	1.0	0.5	2.6	1.4
25.0	1.0	0.5	6.5	3.5
50.0	1.0	0.5	13.0	7.0
50.0	0.75	0.5	9.8	5.3
50.0	0.5	0.5	6.5	3.5
50.0	0.1	0.5	1.3	—
50.0	1.0	0.25	6.5	3.5
50.0	1.0	0.75	19.6	10.6
50.0	1.0	1.00	25.9	14.1

Table 2—Activation Parameters

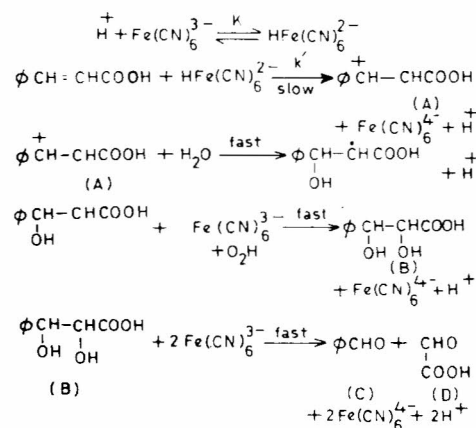
Parameter	Cinnamic acid	Crotonic acid
E_a (kJ mol ⁻¹)	70.0 ± 1.5	68.7 ± 1.5
A (s ⁻¹)	(2.7 ± 0.4) × 10 ⁷	(9.0 ± 0.3) × 10 ⁶
ΔH^\ddagger (kJ mol ⁻¹)	67.3 ± 1.5	66.0 ± 1.5
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-28.0 ± 0.6	-30.0 ± 0.6

(iv) The addition of hexacyanoferrate(II) ions ($5 \times 10^{-4} M$ to $1 \times 10^{-3} M$) to the reaction medium did not affect the rate of the reaction.

(v) The rate of the initial reaction was increased when either the α or β proton was replaced by deuterium ($k_D/k_H = 1.2$).

(vi) The effect of the introduction of substituents in the benzene ring affected the rate of the reaction $10^5 k_{\text{obs}}$ s^{-1} values at $[\text{Substrate}] = 5 \times 10^{-2} M$, $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3} M$, $[\text{HClO}_4] = 0.5 M$, $[\text{HOAc}] = 90\%$ (v/v), $\text{temp.} = 50^\circ$ for *p*-CH₃-, *p*-Cl-, *m*-Cl- and *p*-NO₂-cinnamic acids are 47.0, 8.3, 2.2 and 0.4 respectively. A Hammett type plot with σ^+ gave a ρ^+ value of -4.0 (correlation coefficient = 0.99) for cinnamic and substituted cinnamic acids. This ρ^+ value suggests that the transition state possesses a large degree of carbonium ion character resulting from a large amount of positive charge developed at the carbon atom adjacent to the benzene ring.

Mechanism—The observed dependence of the reaction on $[\text{H}^+]$ suggests that the first step is the protonation of $\text{Fe}(\text{CN})_6^{3-}$ to give $\text{HFe}(\text{CN})_6^{2-}$. The rate determining step of the reaction would be the abstraction of an electron, by $\text{HFe}(\text{CN})_6^{2-}$, from the carbon-carbon double bond of the substrate to give a cationic intermediate. The subsequent steps are fast as shown in Scheme 1. The ρ^+ value of -4.0 would support the formation of a cationic intermediate in the rate determining step, which is also supported by earlier work⁹ on the addition of chlorine to cinnamic acid ($\rho = -4.01$), indicating a fully developed benzylic carbonium ion-like transition state in the slow step of the reaction.



Scheme 1

The formation of a cationic intermediate is also supported by the inverse kinetic isotope effect $k_D/k_H = 1.2$. This suggests a change in the state of hybridization of one or more carbon atoms from sp^2 to sp^3 between the ground state and the transition state^{10,11}.

In the reaction of 1-propyl-1,4-dihydronicotinamide with hexacyanoferrate(III), the formation of an intermediate, (Int.)⁺, has been postulated in the rate determining step, supporting an initial electron transfer mechanism¹².

The formation of the products substantiates the proposed mechanism of the oxidation process, which involves a cleavage of the carbon-carbon bond in the final step of the reaction. Earlier reports have established that the cleavage of 1,2-glycols yields aldehydes as the major products¹³⁻¹⁶.

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