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Kinetic Studies on the Oxidation of Some *para* and *meta*-Substituted Cinnamic Acids by Pyridinium Bromochromate in the Presence of Oxalic Acid (A Co-oxidation Study)

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Abstract: The kinetics of oxidation of cinnamic acids by pyridinium bromochromate (PBC) in the presence of oxalic acid has been studied in acetic acid-water (60:40%) medium. The reaction shows unit order dependence each with respect to oxidant as well as oxalic acid [OX], the order with respect to $[H^+]$ and [CA] are fractional. The reaction is acid catalyzed and a low dielectric constant favours the reaction. Increase the ionic strength has no effect on the reaction rate. In the case of substituted cinnamic acids the order with respect to substrate vary depending upon the nature of the substituent present in the ring. In general, the electron withdrawing substituents retard the rate while the electron releasing substituents enhance the rate of reaction. From the kinetic data obtained the activation parameters have been computed and a suitable mechanism has been proposed.

Keywords: Kinetics, Oxidation of cinnamic acids, Activation parameters.

Introduction

In our earlier study, we have reported the kinetics of oxidation of cinnamic acids by pyridinium chlorochromate in the presence of oxalic acid has been studied in aqueous acetic acid medium^{1,2}. The mechanistic path ways and nature of the transition state in the oxidation of single and multiple C-C bonds with chromium(VI) still remains controversial. The oxidation of cinnamic acid by various Cr(VI) reagents such as acid dichromate^{3,4,5}, potassium dichromate in presence of picolinic acid⁶ and quinolium dichromate^{7,8} have been reported.

The substituents effects are very interesting because of possibility of the mechanism of the dual path, reported for stilbene bromination⁸, acid bromate oxidation⁹ of cinnamic acids and 1,10-phenanthroline catalysed Cr(VI) oxidation of some *trans*-cinnamic acids^{10,11} and hence, it was felt that it would be worthwhile to investigate the kinetics of oxidation of *trans* cinnamic acids by IDC by PBC and now we are here by presenting the results of the kinetics of oxidation of *trans*-cinnamic acids by PBC. Both the electron-releasing the electron withdrawing substituents facilitate the rate of oxidation. The oxidation of carbon-carbon multiple bonds by chromium(VI) reagents mainly leads to the formation of epoxides, glycols, aldehydes, ketones and carboxylic acids^{12,13,14}. Correlation with Hammett constants yields a 'V' shaped curve.

Experimental

Pyridinium bromochromate prepared as reported by Dhar *et al*¹⁵. Commercial samples of oxalic acid and substituted *trans*-cinnamic acids were collected (Merk) and used as such. All other chemicals were of AR grade. Acetic acid used as solvent was purified before use.

Kinetics measurements

The reactions were found under pseudo first order condition by maintaining always the substrate concentration in excess over that of PBC in presence of oxalic acid. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the desired volume and thermostated. The reaction was started by adding the oxidant to the mixture and aliquots were removed at definite time intervals and the unreacted PBC was estimated by standard iodometric titrations.

Stoichiometry and product analysis

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of PBC largely in excess over [CA]. The estimation of unreacted [PBC] showed that one mole of cinnamic acid react with one moles of PBC. The products were separated by column chromatography. An infrared spectrum exhibited a carbonyl band at 1705 cm⁻¹ and certain other bands below 900 cm⁻¹ characteristic of benzaldehyde. The IR spectrum of the other product sample have two sharp bands at 1680 and 1662 cm⁻¹ indicating the presence of two carbonyl groups. Bands at 3620 cm⁻¹ (OH stretching), 1360 cm⁻¹ (C-O stretching) and 1152 cm⁻¹ (OH bending) are characteristic of glyoxalic acid

Results and Discussion

Under pseudo first order conditions, the first order dependence on chromium(VI) was provided the linear semilogarithmic plots of log titre *versus* time ($r = 0.998$). The observed rate constant values (k_{obs}) did not vary appreciably with changing Cr(VI) concentrations. The effect of cinnamic acids on the reactivity 40 °C is shown in Table 1. A plot of k_{obs}^{-1} *versus* [CA]⁻¹ gave straight line with a slope of 0.68 ($r = 0.9974$; SD = 0.030). The same behaviour was observed in all substituted *trans*-cinnamic acids. The order dependence on acidity was < 1. Although the reaction is greatly affected by increase in acid concentration the plot of log k_{obs} *versus* H₀ gives slope 0.80. The catalytic activity of oxalic acid is shown in Table 2. In enhances the conversion of the unsaturated acids permittivity (D) value are calculated approximately from the values for pure solvents.

The low dielectric constant of the medium favors the reactivity as shown in Table 2. A plot of log k_{obs} *versus* D gave straight line ($r = 0.998$). The effect of ionic strength on the reactivity proved to be almost negligible Table 3. The insensitivity of rates on added acrylonitrile ruled out

a free radical process. The reaction rate increases tremendously with the increase in the concentration of added MnSO_4 (Table 3). In the rate determining step, Cr(VI) gets converted to Cr(IV). Further Cr(IV) oxidises Mn^{2+} to Mn^{3+} . The trivalent facilitates the oxidation rate. This type of reaction has been already studied Singh and Ghosh¹⁶ in the oxidation by mandelic acid. This confirms the formation of tetravalent chromium in the slow-step. The reaction rate is found to decrease by the addition of aluminium sulphate to the reaction mixture Table 4. This is obviously due to formation of complex between Al^{3+} and oxalic acid¹⁷. This observation leads to the assumption, that the ternary complex involving oxalic acid is intermediate in this type of co-oxidation reaction.

The rate of oxidation of *meta* and *para*-substituted *trans*-cinnamic acid are studied at four different temperature *viz.*, 25, 30, 35 and 40 °C. The activation parameters are calculated using Eyring's plot and the values are given in Table 4.

Table 1. Effect of [CA], [PBC] and [OX].

[CA] × 10 ² mol dm ⁻³	[PBC] × 10 ³ mol dm ⁻³	[OX] × 10 ² mol dm ⁻³	<i>k</i> _{obs} × 10 ⁴ s ⁻¹
0.5	-	-	1.19
1.0	-	-	1.88
1.5	-	-	2.54
2.0	-	-	3.13
2.5	-	-	3.47
-	0.50	-	1.84
-	0.75	-	1.79
-	1.00	-	1.88
-	1.25	-	1.81
-	1.50	-	1.75
-	-	0.50	0.98
-	-	1.00	1.88
-	-	1.50	3.12
-	-	1.75	3.67
-	-	2.00	4.25

[H⁺] = 11 × 10⁻² mol dm⁻³; Temp = 303 K; AcOH – 60% (v/v) CA = Cinnamic acid; OX = Oxalic acid.

Table 2. Effect of perchloric acid [H⁺] and acetic acid.

[H] × 10 ² mol dm ⁻³	AcOH, %	<i>k</i> _{obs} × 10 ⁴ s ⁻¹
2.75	60	0.75
5.50	60	1.01
8.25	60	1.34
11.00	60	1.88
12.58	60	2.31
-	50	0.41
-	55	1.12
-	60	1.88
-	65	2.45
-	70	3.61

[CA] = 1.0 × 10⁻² mol dm⁻³; [PBC] = 1.50 × 10⁻³ mol dm⁻³; [OX] = 1.0 × 10⁻² mol dm⁻³; Temp = 303 K.

Table 3. Effect of manganous sulphate and sodium perchlorate.

$[\text{Mn}^{2+}] \times 10$ mol dm^{-3}	$[\text{NaClO}_4] \times 10$ mol dm^{-3}	$k_{obs} \times 10^4$ s^{-1}
5.00	-	1.54
6.25	-	2.12
7.50	-	5.36
8.75	-	9.15
10.00	-	17.6
-	5.0	3.42
-	6.25	3.41
-	7.50	3.36
-	8.75	3.51
-	10.00	3.37

$[\text{CA}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{PBC}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{OX}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 11 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{AcOH} = 60\% (\text{v/v})$; $\text{Temp} = 303 \text{ K}$.

Table 4. Effect of aluminium sulphate and temperature.

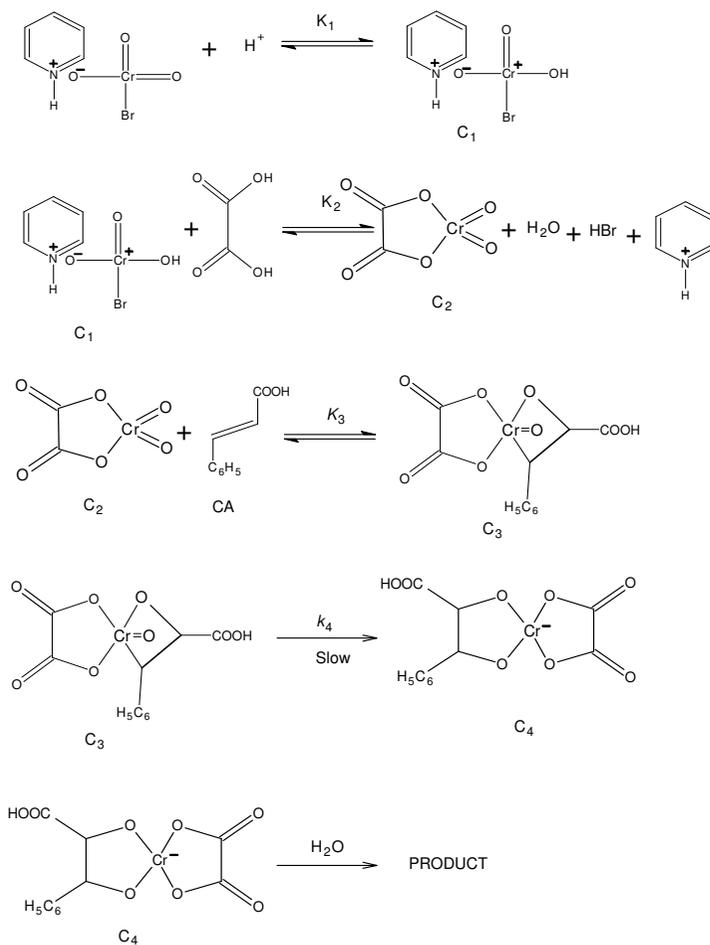
$[\text{Al}^{3+}] \times 10^3 \text{ mol dm}^{-3}$	Temp, °C	$k_{obs} \times 10^4 \text{ s}^{-1}$
5.00	-	3.89
6.25	-	3.42
7.50	-	2.99
8.75	-	2.18
10.00	-	1.98
-	25	0.76
-	30	1.88
-	35	2.05
-	40	4.28

$[\text{CA}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{PBC}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{OX}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 11 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{AcOH} = 60\% (\text{v/v})$.

Mechanism and rate law

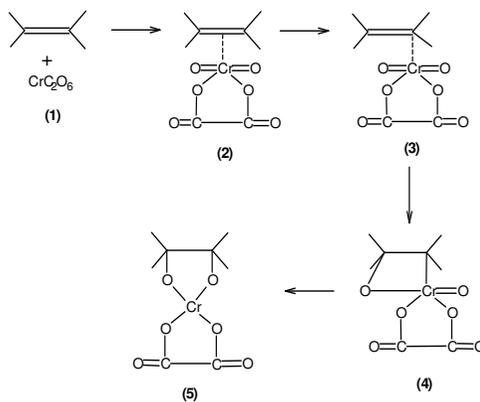
The kinetic of oxidation of cinnamic acid by PBC in the presence of oxalic acid in acid medium is first order with respect to [oxidant] as well as [oxalic acid], but the order in $[\text{H}^+]$ and [cinnamic acid] are fractional. In the absence oxalic acid, the rate of oxidation is very slow. The above facts reveal that there is a combined effect of oxidant, oxalic acid and H. One may presume that the increased rate of CA in the presence of oxalic acid is catalytic. The evolution of CO_2 confirms that the oxalic acid is one of the participants in the main reaction, in co-oxidation process. Such a phenomenon of a ternary system was already established. The absence of primary salt effect shows that the slow-step in this reaction is only between neutral species. This increase in the rate of oxidation by the addition of Mn(II) may be due to catalytic effect¹⁸.

The addition of Al^{3+} does affect the oxidation rate due to the formation of complex between Al^{3+} ion and oxalic acid. The possibility of radical formation is also ruled out by the absence of induced polymerization in the rate-determining step. Based on these observations the reaction mechanism, Scheme 1 has been proposed. Scheme 1 involved the formation of cyclic complex C_2 by the reaction between oxidant, oxalic acids and H which interaction with CA forms another complex (C_3). The complex (C_3) rearranges to form a cyclic chromium(IV) diester (C_4) in the slow step.



Scheme 1.

The complex (C₃) is formed by the following reaction (eq. 5) in which the double-bonds becomes η_2 ligand on chromium(VI) like MnO₄ oxidation of CA¹⁹.



Scheme 2.

When the chromium steps towards one end of the double bond (as in structure 3), acyclic organo-metallic compound is formed^{20,21}. The first three steps involve the bond formation, whereas the last step required to cleavage of a C-Cr bond. Consequently, it seems reasonable to consider the last step as the rate-limiting. From the above mechanism the rate law is derived as follows.

$$\begin{aligned} \text{Rate} = k_4 C_3 &= \frac{k_4 K_3 [\text{CA}] [C_2]}{\{1 + K_3 [\text{CA}]\}} \\ &= \frac{k_4 K_3 K_2 [\text{CA}] [C_1] [\text{OX}]}{\{1 + K_3 [\text{CA}]\}} \\ &= \frac{k_4 K_3 K_2 K_1 [\text{CA}] [\text{H}^+] [\text{Cr(VI)}] [\text{OX}]}{\{1 + K_3 [\text{CA}]\} \{1 + K_1 [\text{H}^+]\}} \\ &= \frac{K_1 K_2 K_3 k_4 [\text{CA}] [\text{H}^+] [\text{OX}] [\text{Cr(VI)}]}{\{1 + K_3 [\text{CA}] K_1 [\text{H}^+] + K_3 [\text{CA}] + K_1 [\text{H}^+]\}} \\ &= \frac{K_1 K_2 K_3 k_4 [\text{CA}] [\text{H}^+] [\text{OX}] [\text{Cr(VI)}]}{\{1 + K_1 [\text{H}^+] + K_3 [\text{CA}]\}} \\ k_{\text{obs}} &= \frac{K_1 K_2 K_3 k_4 [\text{CA}] [\text{H}^+] [\text{OX}]}{\{1 + K_1 [\text{H}^+] + K_3 [\text{CA}]\}} \end{aligned}$$

Where, CA = Cinnamic acid; OX = Oxalic acid

Effect of substituents on reaction rate

The effect of substituents on the rate of oxidation has been studied with a number of *ortho*, *meta* and *para*-substituted cinnamic acid at four different temperatures. The respective rate constants and the thermodynamic parameters are given in Table 5.

An analysis of the data has been made in respect of the linear free energy relationships. The Table 5 reveals that the entropy of activation is not constant throughout the series. In such cases, the variation in ΔS^\ddagger should be linearly related^{21,22} to changes in ΔS^\ddagger by equation.

$$\Delta H = \Delta H_0^\ddagger + \beta \Delta S^\ddagger$$

The plot of enthalpy of activation (ΔH^\ddagger) against entropy of activation (ΔS^\ddagger) gave a straight line (Figure 1) with an excellent correlation coefficient ($r = 0.99$). The isokinetic temperature obtained from slope is 343 K. The linear relationship shows that all the substituted cinnamic acids follow a common mechanism.

Exner^{23,24} criticised the validity of such a linear correlation between ΔH^\ddagger and ΔS^\ddagger as their quantities are dependent on each other. When measurements at two different temperatures have been made the data can be analysed by the following equation.

$$\log (k_2)_{T_2} = a + b \log (k_2)_{T_1}$$

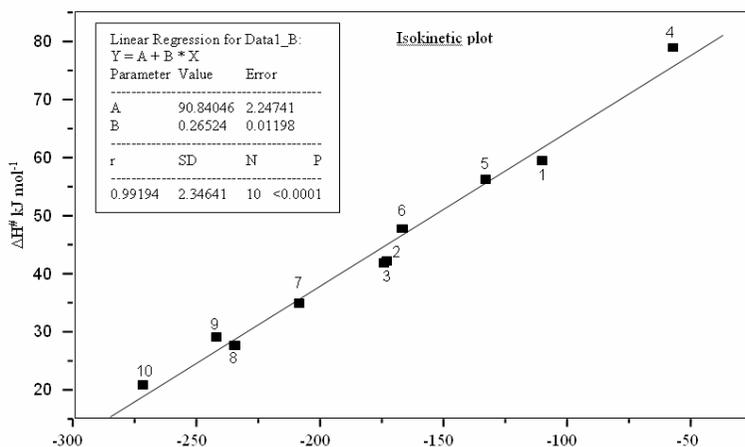
where, $T_2 > T_1$.

Table 5 thermodynamic parameters for the oxidation of substituted cinnamic acids by PBC in the presence of oxalic acid calculated from plots of $\ln (k_{\text{obs}}/T)$ versus $1/T$ ($r = 0.998$).

Table 5. Thermodynamic parameters of substituted *trans*-cinnamic acid.

S. No.	Substituted CA	$k_{\text{obs.}} \times 10^4 \text{ s}^{-1}$				ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	r	SD
		25 °C	30 °C	35 °C	40 °C				
1	<i>p</i> -OMe	4.29	6.11	10.6	13.5	59.450	-110.01	0.9899	0.08678
2	<i>p</i> -Me	2.03	2.85	4.42	5.32	41.863	-174.15	0.9826	0.08055
3	<i>m</i> -Me	2.23	3.26	4.48	5.23	42.180	-172.96	0.9852	0.0748
4	H	0.76	1.88	2.05	4.28	78.904	-57.258	0.9864	0.13418
5	<i>p</i> -F	0.99	1.35	2.25	2.98	56.263	-132.97	0.9927	0.06961
6	<i>p</i> -Br	0.52	0.69	1.08	1.32	47.785	-166.70	0.9897	0.07043
7	<i>p</i> -Cl	0.62	0.82	1.02	1.28	34.862	-208.45	0.9981	0.0217
8	<i>m</i> -Cl	0.51	0.63	0.75	0.91	27.611	-234.52	0.9996	0.00792
9	<i>m</i> -NO ₂	0.12	0.14	0.18	0.21	29.045	-241.98	0.9990	0.01297
10	<i>p</i> -NO ₂	0.09	0.11	0.12	0.14	20.828	-271.53	0.9903	0.02971

[PBC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$; [H⁺] = $11 \times 10^{-2} \text{ mol dm}^{-3}$; [OX] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$; AcOH = 60% (v/v).

**Figure 1.** The plot of ΔH^\ddagger versus ΔS^\ddagger .

The plot of $\log k_{\text{obs}}$ (35 °C) versus $\log k_{\text{obs}}$ (25 °C) gives straight line with $r = 0.998$. The good correlation indicates that all the investigated substituted compounds follow a common mechanism.

Hammett equation

The substituents when they are electron withdrawing retard the rate of reaction and when they are electron releasing, accelerate the rate of reaction. The ρ values calculated from the plots of $\log k_{\text{obs}}$ versus σ at different temperatures were found to be negative Table 6 from the negative sign of the ρ values it is inferred that an electron deficient transition state is formed during the oxidation.

Table 6. ρ Values obtained from Hammett equation.

Temperature °C	ρ	r	SD
25	-1.51	0.9840	0.1022
30	-1.59	0.9914	0.0787
35	-1.75	0.9947	0.0674
40	-1.78	0.9941	0.0724

Conclusion

In all the investigated oxidation reactions in the absence and in the presence of oxalic acid with various oxidants, the reaction rate is retarded by electron-withdrawing groups and accelerated by electron-releasing groups. The ρ values calculated from Hammett's plots of $\log k_{\text{obs}}$ against σ at different temperatures indicate the formation of deficient transition state during oxidation in the presence of oxalic acid and the reactions with Cr(VI) oxidant the reaction rate is found to be higher than that in the absence of oxalic acid.

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