

Kinetics and Mechanism of Oxidation of Some Substituted *trans* Cinnamic Acids by Pyridinium Bromochromate

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The kinetics of some substituted *trans* cinnamic acid by pyridinium bromochromate have been studied in 60 % acetic acid-water (v/v) medium. Increase in acidity increases the rate of the reaction. Increase in ionic strength has no effect on the reaction rate. Increase in dielectric constant decrease the rate of reaction. The added acrylonitrile has no effect on the reaction rate indicating the absence of free radical mechanism. From the kinetic data the enthalpy and entropy of activation are calculated and a suitable mechanism has been proposed.

Key Words: Pyridinium bromochromate, Cinnamic acids, Kinetics, Oxidation.

INTRODUCTION

The kinetics of oxidation of some *trans* cinnamic acids by several oxidants has been reported¹⁻⁶. Extensive kinetic and mechanistic studies on the oxidation of organic compounds with chromium reagents have revealed that such reactions ordinarily involve a three electron change, whereby Cr(VI) species are reduced to Cr(III), although some reports on two-electron oxidations were also made in the past. The relationship between the *m*- and *p*-*trans*-cinnamic acids and their reactivity towards oxidation by pyridinium bromochromate (PBC) is an important point of discussion. Though the literature survey reveals that there are some reports on the kinetics of oxidation of *trans*-cinnamic acids by few Cr(VI)⁷⁻⁹ and N-halao oxidants, no such efforts has been made with PBC. This prompted us to investigate the present work as a comparative study with view to get an insight into the nature of the reactivities of these *trans*-cinnamic acids with PBC. It is found that PBC always reacts slower than nicotinium dichromate (NDC) and isonicotinium dichromate (INDC).

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EXPERIMENTAL

PBC was prepared by literature procedure¹⁰ and *meta*, *para*-substituted *trans* cinnamic acids were purchased from Fluka. Other reagents *i.e.*, sodium perchlorate, perchloric acid, aluminium chloride, manganous sulphate and acrylonitrile were of AnalaR grade and used as such.

Kinetics measurements: The reaction was carried out under *pseudo*-first order conditions [substrate] \gg PBC in 60 % acetic acid-water (v/v) medium containing perchloric acid. The reaction mixture were kept in a thermostat and the progress of reaction was followed by estimating the consumption of PBC iodometrically to starch end point as described by Kolthoff and Carr¹¹ and rate constant k_1 computed from linear plot of log titre *vs.* time by the least square method was reproducible within ± 3 %.

Stoichiometry: Reaction mixture containing an excess of oxidant over *trans* cinnamic acid were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unchanged oxidant showed that one mole of PBC consumed one mole of substrate. The products are identified as benzaldehyde and glyoxalic acid.

RESULTS AND DISCUSSION

The order of reaction was found to be first with respect to the oxidant as evidenced by good linearity in the plot of log *vs.* time ($r = 0.99$). At constant [PBC], the rate constant increased with increase in the concentration of substrate. A plot of log k *vs.* log [substrate] gave a straight line with a slope of 1.00 indicating first order dependence of reaction with respect to substrate. A plot of log k_1 *vs.* $[H_0]$ gave straight line with slope 1.02 indicating the first order dependence with respect of $[H^+]$. The rate increases with decrease in the dielectric constant of medium and increase in ionic strength has negligible effect on the rate. The added acrylonitrile had no effect on the reaction rate, *i.e.* the reaction did not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The added Mn^{2+} ions decrease the rate considerably which may be taken as an evidence for a two-electron process¹².

Rate constants for the oxidation of *trans*-cinnamic acid (CA) by PBC with the experimental conditions are given Tables 1 and 2. The activation parameters were calculated using the Eyring's plot¹³ and the values are given in Table-1.

The kinetic runs were repeated at four different temperature *viz.*, 25, 30, 35, 40°C. The k_{obs} values are given in Table 2. The thermodynamic parameters *viz.*, enthalpy of activation and entropy of activation, are calculated from the linear plot of $\ln k_{obs}/T$ against $1/T$. The observed stoichiometry for this reaction 1:1 ([PBC] : [CA]) and major oxidation products are found to be benzaldehyde and glyoxalic acid. Based on the above

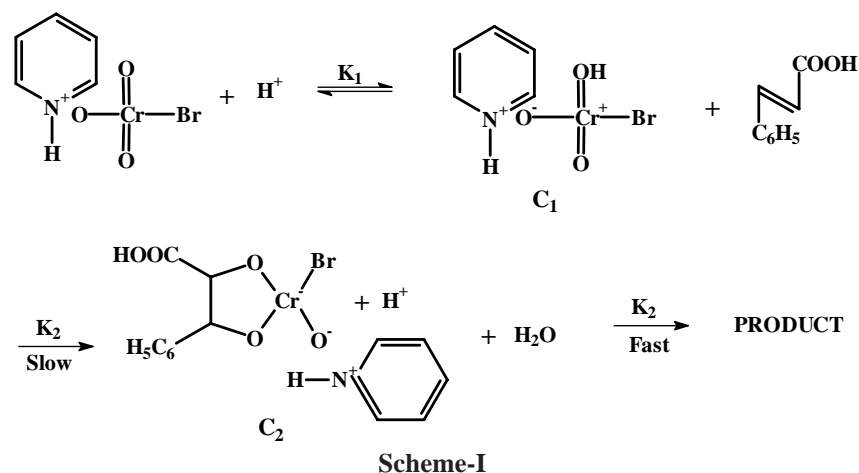
TABLE-1
EFFECT OF [PBC], [CA], [Ox] AND [H⁺]
Acetic acid = 60 % (v/v); Temp = 303 K

[PBC] × 10 ³ (mol dm ⁻³)	[CA] × 10 ² (mol dm ⁻³)	[H ⁺] × 10 ² (mol dm ⁻³)	k × 10 ⁴ (s ⁻¹)
0.50	-	-	1.81
0.75	-	-	1.92
1.00	-	-	1.82
1.25	-	-	1.78
1.50	-	-	1.82
-	0.5	-	0.81
-	1.0	-	1.82
-	1.5	-	2.64
-	2.0	-	3.32
-	2.5	-	4.19
-	-	8.25	1.08
-	-	11.00	1.82
-	-	12.58	2.25
-	-	13.75	2.65
-	-	16.50	3.94

TABLE-2
EFFECT OF NaClO₄, MnSO₄, SOLVENT AND TEMPERATURE
[PBC] = 1 × 10⁻² mol dm⁻³, [CA] = 1 × 10⁻³ mol dm⁻³, [H⁺] = 11 × 10⁻² mol dm⁻³

[NaClO ₄] × 10 (mol dm ⁻³)	[MnSO ₄] × 10 (mol dm ⁻³)	Solvent AcOH-H ₂ O (%)	Temp (°C)	k × 10 ⁴ (s ⁻¹)
5.00	-	-	-	2.88
6.25	-	-	-	2.75
7.50	-	-	-	2.79
8.75	-	-	-	2.83
10.00	-	-	-	2.81
-	5.00	-	-	0.15
-	6.25	-	-	0.13
-	7.50	-	-	0.11
-	8.75	-	-	0.10
-	10.00	-	-	0.08
-	-	50	-	0.91
-	-	60	-	1.31
-	-	70	-	1.82
-	-	80	-	3.52
-	-	90	-	4.23
-	-	-	25	1.21
-	-	-	30	1.82
-	-	-	35	3.88
-	-	-	40	4.93

observations, a probable mechanism for the oxidation of CA by PBC given in **Scheme-I**. In dilute aqueous solution, the oxidant exists as a monomer.



In aqueous solution PBC undergoes protonation^{14,15} at moderate acidic condition. This protonated species is more powerful than unprotonated species. Such protonation is not possible for CA of this concentration⁶. This oxidation kinetics is totally a third order one.

Rate law:

The above mechanism leads to the following rate equation,

$$\begin{aligned} \frac{-d[\text{Cr}(\text{VI})]}{dt} &= k_2[\text{C}_1][\text{CA}] \\ &= K_1k_2[\text{CA}][\text{H}^+][\text{Cr}(\text{VI})] \\ k_{\text{obs}} &= K_1k_2[\text{CA}][\text{H}^+] \end{aligned}$$

where $\text{C}_1 = [\text{PBCH}^+]$

Structural effects: The effect of substituents on the rate of oxidation has been studied with number of *meta*- and *para*-substituted cinnamic acids at four different temperatures. The respective rate constants and the thermodynamic parameters are given in Table-3.

An analysis of the data has been made in respect of the linear free energy relationships. The data in Table-3 reveal that the entropy of activation is not constant throughout the series. In such cases, the variation in ΔS^\ddagger should be linearly related^{16,17} to changes in ΔH^\ddagger by equation

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

ΔH^\ddagger is the enthalpy of activation, when $\Delta S^\ddagger = 0$ and usually has no physical significance and β is the isokinetic temperature.

A plot of ΔH^\ddagger against ΔS^\ddagger gave a straight line with a good correlation coefficient (Fig. 1) ($r = 0.9832$). The linear correlation between ΔH^\ddagger and

TABLE-3
THERMODYNAMIC PARAMETERS OF SUBSTITUTED
TRANS-CINNAMIC ACID

Substituted CA	$k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$				ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	r	SD
	25°C	30°C	35°C	40°C				
<i>p</i> -OMe	12.1	14.9	19.5	21.7	28.872	-203.83	0.9874	0.04721
<i>p</i> -Me	2.53	4.66	6.91	9.74	66.386	-90.539	0.9917	0.08793
<i>m</i> -Me	4.06	4.82	6.34	8.57	36.419	-188.01	0.9900	0.05289
H	1.21	1.82	3.88	4.93	74.694	-69.457	0.9821	0.14591
<i>p</i> -F	1.92	2.50	3.15	4.43	39.921	-182.30	0.9951	0.04026
<i>p</i> -Br	1.01	1.14	1.25	1.41	14.418	-273.03	0.9980	0.00928
<i>p</i> -Cl	0.91	1.06	1.14	1.24	12.871	-278.91	0.9821	0.02512
<i>m</i> -Cl	0.43	0.58	0.81	0.97	41.806	-188.22	0.9947	0.04400
<i>m</i> -NO ₂	0.11	0.14	0.17	0.21	31.102	-235.44	0.9968	0.02629
<i>p</i> -NO ₂	0.09	0.13	0.16	0.19	35.649	-221.56	0.9947	0.03744

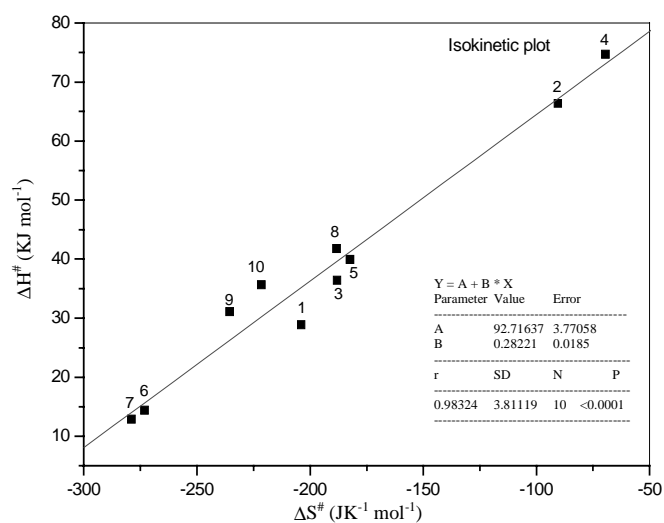


Fig. 1

ΔS^\ddagger indicates that all the substituted cinnamic acids follow a common mechanism. Exner^{18,19}, criticized the validity of such a linear correlation between ΔH^\ddagger and ΔS^\ddagger as their quantity are independent on each other. When measurement of two different temperatures have been made, the data can be analyzed by the following equation^{20,21}.

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

where $T_2 > T_1$

The plot of $\log k_{\text{obs}}(40^\circ\text{C})$ vs. $\log k_{\text{obs}}(25^\circ\text{C})$ and $\log k_{\text{obs}}(35^\circ\text{C})$ vs. $\log k_{\text{obs}}(25^\circ\text{C})$ gave straight line with $r = 0.9739$ and $r = 0.98872$, respectively.

Such a good correlation indicates that all the investigated, substituted compounds follow a common mechanism, at fixed concentration of CA and H⁺.

In general, the rate of the reaction is retarded by electron-withdrawing substituents and accelerated by electron releasing ones. The ρ values calculated from the plots of $\log k_{\text{obs}}$ vs. σ at different temperatures were found to be negative (Table-4; $r = 0.9712$). The negative ρ values indicate the formation of electron deficient transition state during oxidation.

TABLE-4
 ρ VALUES OBTAINED FROM HAMMETT EQUATION

Temperature (°C)	ρ	r	SD
25	-1.82	0.9713	0.1669
30	-1.85	0.9853	0.1196
35	-1.93	0.9917	0.0934
40	-1.96	0.9908	0.0999

For the oxidation of cinnamic acids and substituted cinnamic acid by PBC in aqueous acetic acid medium, the isokinetic plot ($r = 0.98$), Exner plot ($r = 0.99$) and Hammett plot ($r = 0.99$) gave straight lines indicating that all the substituted cinnamic acids follow a common mechanism.

REFERENCES

1. A. Gupta and M.K. Mahanti, *Oxid. Commun.*, **141**, 57 (1991).
2. L.I. Simandi and M. Jaky, *J. Am. Chem. Soc.*, **98**, 1996 (1976).
3. E.M. Stoddard, *J. Chem. Soc.*, 1874 (1931).
4. D.G. Lee and J.R. Brownridge, *J. Am. Chem. Soc.*, **95**, 3033 (1973).
5. K. Polgar, M. Jaky and L.I. Simandi, *React. Kinet. Catal. Lett.*, **5**, 489 (1976).
6. C.H.S. Reddy and E.V. Sundaram, *Tetrahedron*, **45**, 2109 (1989).
7. P.S. Radaakrishnamurthi and B.K. Panda, *Indian J. Chem.*, **21A**, 128 (1982).
8. P.S. Radhakrishnamurthi and B.K. Panda, *Indian J. Chem.*, **23A**, 766 (1984).
9. R.T.S. Mohan, M. Gopalakrishnan and M. Sekar, *Tetrahedron*, **50**, 10933 (1994).
10. A. Jagadhesan, K. Nambi and S.J. Arulraj, *Indian J. Chem.*, **28A**, 904 (1989).
11. I.M. Kolthoff and E.M. Carr, *Anal. Chem.*, **25**, 298 (1953).
12. G.T.E. Graham and F.H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958).
13. H. Eyring, *J. Chem. Phys.*, **33**, 103 (1935).
14. P.A. Nadar, V. Murugaesan and M. Chandramithula, *Indian J. Chem.*, **33A**, 10933 (1994).
15. K.B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York, p. 42 (1997).
16. W.R. Gilkerson, C.A. Gallup and M.M. Jones, *Trans. Kaisam Acad. Sci.*, **57**, 391 (1954).
17. J.E. Leffler, *J. Chem. Phys.*, **23**, 2199 (1955); **27**, 981 (1957).
18. O. Exner, *Coll. Czech. Chem. Commun.*, **29**, 1094 (1964).
19. O. Exner, *Nature*, **201**, 488 (1964).
20. F. Hasan and J. Rocke, *J. Am. Chem. Soc.*, **94**, 3181 (1972).
21. M.J. Malawski, *Roczniki. Chem.*, **38**, 1129 (1964).

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