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Kinetics and Mechanism of Oxidation of some Substituted trans-Cinnamic Acids by Pyridinium Chlorochromate — A Non-Linear Hammett Plot

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Abstract: Kinetics and mechanism of oxidation of some ortho-, para- and meta-substituted trans-cinnamic acids by pyridinium chlorochromate (PCC) in presence of oxalic acid has been studied. The main product of oxidation is corresponding benzaldehyde and glyoxalic acid. The reaction is first order with respect to [PCC] and [oxalic acid]. The oxidation follows fractional order in [substrate] and [H^+]. The thermodynamic parameters are also determined. Both the electron-releasing and electron-withdrawing substituents, facilitate the rate of oxidation. Correlation with Hammett constants yields a 'V' shaped curve. A suitable mechanism is proposed. In the transition state the formation of carbanion, for electron-withdrawing and carbonium ion for electron releasing substituents is discussed.

Kinetics and mechanism of oxidation of several organic substrates by PCC[1-3] are well documented. Only few studies[4-6] are available for oxidation of substrates by Cr(VI) in presence of oxalic acid. But there is no systematic kinetic reports on the oxidation of trans-cinnamic acid by Cr(VI) complexes.

Chromium(VI) functions both a one and two-electron oxidant depending on the substrate and experimental conditions. The intermediate valency states Cr(V) and Cr(IV) are involved in these process. Hasan and Rocek[7] reported the concept of a "three-electron transfer" process in the cooxidation study of isopropyl alcohol and oxalic acid by chromic acid, when Cr(VI) get directly reduced to Cr(III). Interestingly both substrates undergo oxidation and the process was termed co-oxidation. This prompted us to undertake the title for investigation.

EXPERIMENTAL

Reagents. Pyridinium chlorochromate was prepared by the method of Corey and Suggs[8]. Trans-cinnamic acid and most of the substituted cinnamic acids were obtained commercially (AR, Aldrich/Fluka) and their purity was checked by IR and TLC. Some of the substituted trans-cinnamic acids (p-fluoro, m-fluoro-, p-bromo-, o-methyl, m-chloro-and o-bromo) were prepared by literature method[9]. Doubly distilled water was used throughout the course of investigation. All other chemicals used were of analytical grade.

Kinetic measurements. The kinetic studies were made in glass stoppered conical flask under pseudo-first order conditions where [CA] > [oxidant]. The reactions were initiated by the rapid addition of requisite amounts of oxidant solution, thermally equilibriated at a desired temperature, to a mixture containing known amounts of CA, $HClO_4$, oxalic acid solutions and water and acetic acid (to maintain 50% (v/v) aqueous acetic acid), pre-equilibriated at the same temperature. The progress of the reactions was monitored for atleast two half lives by iodometric determination of unreacted oxidant at regular intervals of time. The pseudo-first order rate constants (k_{obs}) were computed by the method of least squares and were reproducible within ±3%.

Stoichiometry and product analysis. The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [PCC] largely in excess over [CA]. The estimations of unreacted [PCC] showed that one mole of cinnamic acid reacts with two moles of PCC.

$$\text{Ph-CH=CH-CO}_2\text{H} + 2\text{PyHOCrO}_2\text{Cl} + (\text{CO}_2\text{H})_2 \xrightarrow{H^+} \text{PhCHO} + \text{OHCCO}_2\text{H} + 2\text{CO}_2 + 2\,\text{PyHCl} + \text{H}_2\text{O} + \text{Cr}_2\text{O}_3 \qquad (1)$$

For identifying the product, substrate was mixed with excess of oxidant, under kinetic conditions in an inert atmosphere (under nitrogen atmosphere). After the reaction was completed, a current of nitrogen passed through the reaction mixture and collected. The gas product was analysed for carbon dioxide. 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 products were separated by column chromatography using neutral alumina and eluted with varying proportions of hexane and chloroform, concentrated and then identified. An infrared spectrum exhibited a carbonyl band at 1705cm^{-1} and certain other bands below 900cm^{-1} characteristic of benzaldehyde. The IR spectrum of the other product sample have two sharp bands at 1680 and 1662cm^{-1} indicating the presence of two carbonyl groups. Bands at 3620cm^{-1} (OH streching), 1360cm^{-1} (C-O streching) and 1152cm^{-1} (OH bonding) are characteristic of glyoxalic acid. The substituents also gave their respective benzaldehydes. The obtained 2,4-DNP devivatives of the products were checked and identified by Co-TLC method.

RESULTS AND DISCUSSION

The reaction has been found to be first order with respect to the disapperance of PCC as evidenced by a good linearity in the plot of log[PCC] vs time. The pseudo-first order rate constants ($k_{obs}\,s^{-1}$) with respect to PCC are also fairly constant over a wide range in PCC (Table 1).

The pseudo-first order rate constant increases on increasing the substrate concentration (Table 1). The plots of log k_{obs} versus log [S] for all the compounds have been found to be linear with slopes less than unity indicating fractional order dependence on [substrate]. The double reciprocal plot of $1/k_{obs}$ versus 1/[S] is linear with finite intercept on the inverse rate axis indicating complex formation between PCC and substrate.

Some important substituents were studied under the same condition. It showed that all the substituents follow same Michaelis-Menten type (Table 2). So the mechanism is common in all substituents.

Table 1. Pseudo-first Order Rate Constants (k_{obs}) for different Concentration of PCC and Cinnamic acid at 35°C

10^2[CA] mol dm^{-3}	10^3[PCC] mol dm^{-3}	$10^4 k_{obs}/s^{-1}$
1.90	0.50	3.98
1.90	0.75	3.97
1.90	1.00	4.01
1.90	1.25	4.60
1.90	1.50	4.37
0.70	1.00	2.59
0.94	1.00	3.20
1.90	1.00	4.01
2.84	1.00	5.10
3.79	1.00	6.23

$[H^+] = 0.2$ mol dm^{-3}, $[OxH_2] = 2.0 \times 10^{-2}$ mol dm^{-3}, HOAc = 50% (v/v)

Table 2. Pseudo-first Order Rate Constants for different Concentration of some Substrate (substituents)

		$10^4 \times k/s^{-1}$ at $10^3 \times$ [CA]/mol dm^{-3}			
	Cinnamic acids [CA]	2.0	4.0	5.0	6.0
1	-H	1.39	1.96	2.15	
2	p-NO_2	12.52	16.67	18.41	20.92
3	p-Cl	3.75	5.02	5.40	5.90
4	m-NO_2	12.41	16.19	18.58	20.69
5	p-CH_3	2.79	3.71	4.11	4.59
6	p-OCH_3	6.41	8.50	9.67	10.51
7	o-Cl	3.61	4.80	5.38	6.67
8	o-NO_2	15.27	20.15	22.70	25.73
9	o-OCH_3	9.10	12.26	14.01	15.15

[PCC] = $(0.25\text{-}1.00) \times 10^{-3}$ mol dm^{-3}; $[HClO_4] = 0.2$ mol dm^{-3};
$[OxH_2] = 2.00 \times 10^{-2}$ mol dm^{-3}; [HOAc] = 50%(v/v).

The effect of oxalic acid has been studied by varying the concentration of oxalic acid at a given substrate concentration (Table 3). The rate is greatly affected by an increase in oxalic acid concentration. The plot of log k_{obs} versus log[oxalic acid]is linear with a slope of unity. It reveals that the order in [oxalic acid] is one.

The effect of acidity has been studied by varying the concentration of perchloric acid at a given substrate concentration (Table 3). Although the reaction is greatly affected by an increase in acid concentration the plot log k_{obs} versus log $[H^+]$ gives a slope 0.44.

The reaction is studied in acetic acid-water mixtures of varying compositions. An increase in acetic acid content accelerates the reaction rate (Table 3). A plot of log k_{obs} versus 1/D (where D is dielectric constant of the medium) was linear with a positive slope.

Variation of the ionic strength of the medium (0.01 - 0.04 mole dm^{-3}) has no significant effect on the rate (Table 3). It indicates that the absence of ion-ion (or) ion-dipole interaction in the slow-step.

Table 3. Pseudo-first Order Rate Constants for different Concentration of Oxalic acid, Perchloric acid, Acetic acid and Sodium perchlorate at 35°C

$10^2[OxH_2]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	[HOAc] %	$10^2[NaClO_4]$ mol dm^{-3}	10^4k_{obs} s^{-1}
1.0	0.2	50	-	2.10
2.0	0.2	50	-	4.01
3.0	0.2	50	-	6.90
4.0	0.2	50	-	9.60
2.0	0.1	50	-	3.10
2.0	0.2	50	-	4.01
2.0	0.3	50	-	5.20
2.0	0.4	50	-	5.60
2.0	0.2	55	-	4.62
2.0	0.2	60	-	5.26
2.0	0.2	65	-	5.86
2.0	0.2	70	-	6.75
2.0	0.2	50	1.0	4.22
2.0	0.2	50	2.0	4.10
2.0	0.2	50	3.0	4.25
2.0	0.2	50	4.0	4.21

[PCC] = 1.00×10^{-3} mol dm^{-3}; [CA] = 1.90×10^{-2} mol dm^{-3}.

The reaction rate increases tremendously with the increase in the concentration of added $MnSO_4$ (Table 4). In the rate determining step, Cr(VI) gets converted to Cr(IV). Further Cr(IV) oxidises Mn^{+2} to Mn^{+3}. The trivalent manganese facilitates the oxidation rate. This type of reaction has been already studied by Singh and Ghosh[10] in the oxidation by mandellic 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 the formation of complex between Al^{3+} and oxalic acid[11]. This observation leads to the assumption, that the ternary complex involving oxalic acid is intermediate in this type of co-oxidation reaction.

Table 4. Pseudo-first Order Rate Constants for different Concentration of Manganese Sulphate and Aluminium sulphate at 35°C

10^3 [$MnSO_4$] mol dm^{-3}	10^4[Aluminium sulphate] mol dm^{-3}	10^4 k_{obs} s^{-1}
0.00	-	4.01
0.25	-	7.01
0.50	-	14.85
1.00	-	21.20
-	-	4.01
-	0.55	3.75
-	1.10	3.51
-	2.20	3.05
-	3.30	2.81
-	3.85	2.17

[PCC] = 1.00×10^{-3} mol dm^{-3}; [CA] = 1.90×10^{-2}mol dm^{-3}; [H^+] = 0.2 mol dm^{-3}; [OxH_2] = 2.0×10^{-2} mol dm^{-3}.

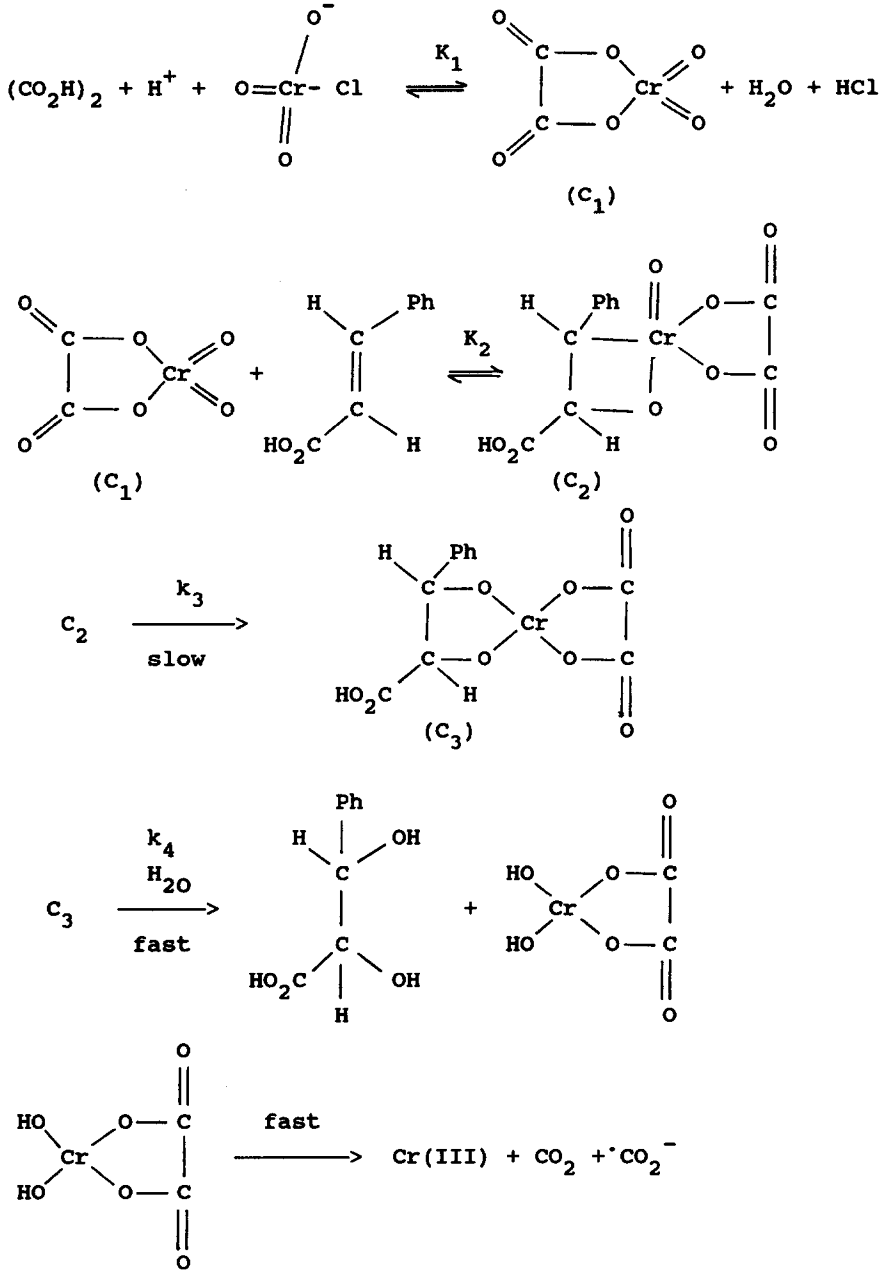
The rate of oxidation of some ortho-, meta- and para-substituted trans-cinnamic acids are studied at four different temperatures viz, 30,35,40 and 45°. The activation parameters are calculated using Eyring's plot and the values are given in the Table 5.

Mechanism and Rate Law. The kinetics of oxidation of cinnamic acid by PCC 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 [H^+] and [cinnamic acid] are fractional. In the absence of oxalic acid, the rate of oxidation is very slow. The above fact reveals 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 oxalic acid as one of the participants in the main reaction, in co-oxidation process. Such a phenomenon of a ternary system was already established[7]. 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 effect[12].

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 polymerisation in the rate-determining step.

Based on these and other facts the reaction mechanism, Scheme-1 has been proposed. Scheme-1 involves the formation of a cyclic complex (C_1) by the reaction between oxidant, oxalic acid and H^+ which on interaction with CA forms another complex (C_2). The complex (C_2) rearranges to form a cyclic chromium (IV) diester (C_3) in the slow-step.

Scheme-1



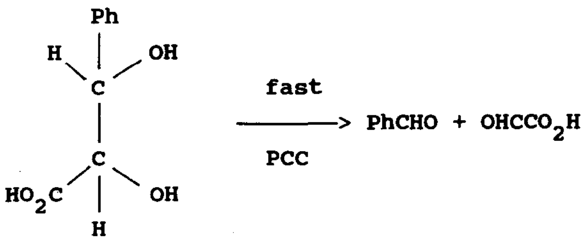
(2)

(3)

(4)

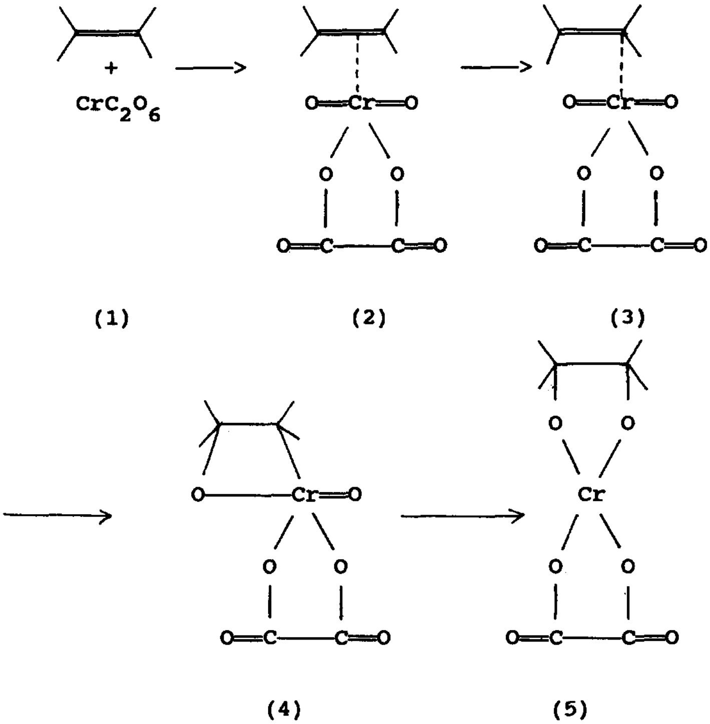
(4a)

(4b)



(4c)

The complex (C_2) is formed by the following reaction (eq.5) in which the double bond becomes η^2 ligand on chromium (VI) like MnO_4^- oxidation of CA[13].



(5)

When the chromium slips towards one end of the double bond (as in structure 3), a cyclic organometallic compound is formed[14,15]. The first three steps given in (eq.5) involve bond formation, whereas the last step required 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.

$$\text{rate} = k_3C_2$$

$$\frac{-d[PCC]}{dt} = \frac{k_3K_2[CA][C_1]}{1 + K_2[CA]} \tag{7}$$

$$= \frac{k_3\ K_2[CA]k_1[PCC][Ox][H^+]}{1 + K_2[CA][1 + K_1[H^+]]}$$

$$= \frac{K_1\ K_2k_3[CA][PCC][Ox][H^+]}{1 + K_1K_2[CA][H^+] + K_2[CA] + K_1[H^+]}$$

$$k_{obs} = \frac{K_1\ K_2k_3[CA][Ox][H^+]}{1 + K_1K_2[CA][H^+] + K_2[CA] + K_1[H^+]} \tag{8}$$

where [Ox] represents 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 acids 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 $\Delta S^{\#}$ should be linearly related[16,17] to changes in $\Delta H^{\#}$ by equation 9.

$$\Delta H^{\#} = \Delta H^{\#}_0 + \beta\, \Delta S^{\#} \tag{9}$$

A plot of enthalpy of activation ($\Delta H^{\#}$) against entropy of activation ($\Delta S^{\#}$) gave a straight line with an excellent correlation coefficient (r=0.995). The isokinetic temperature obtained from the slope is 343K. The linear relationship shows that all the substituted cinnamic acids follow a common mechanism.

Exner[18,19] criticised the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ 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,[20,21]

$$\log(k_2)_{T_1}\ a + b \log (k_2)_{T_2} \tag{10}$$

where $T_2 > T_1$

Table 5. Thermodynamic Parameters for the Oxidation of Substituted Cinnamic acids by PCC in presence of Oxalic acid calculated from plots of ln(k_{obs}/T) versus 1/T

S.No.	Substituent	$k_{obs} \times 10^4\ s^{-1}$				$\Delta H^{\#}$ ($kJmol^{-1}$)	$-\Delta S^{\#}$ ($JK^{-1}mol^{-1}$)	r	sd
		30°	35°	40°	45°				
1	- H	1.58	2.15	3.03	4.01	47.7	160.1	0.999	0.015
2	p-CH_3	2.70	3.75	4.57	5.90	38.2	187.2	0.995	0.035
3	p-OCH_3	5.95	8.45	10.45	14.25	42.8	165.4	0.995	0.038
4	o-CH_3	2.97	3.61	4.45	5.11	26.9	223.9	0.996	0.020
5	o-OCH_3	8.42	12.10	15.55	21.42	46.4	150.9	0.997	0.029
6	p-NO_2	10.41	16.49	24.10	36.44	63.8	91.8	0.999	0.019
7	p-Cl	4.20	5.00	5.96	7.01	24.9	227.7	0.999	0.002
8	p-Br	4.60	5.80	6.60	8.01	26.2	222.6	0.994	0.028
9	p-F	2.35	3.10	3.51	4.70	32.7	206.6	0.987	0.051
10	m-NO_2	8.97	16.03	20.99	33.00	64.4	90.5	0.990	0.085
11	m-Cl	7.98	9.01	9.98	10.99	14.5	256.7	0.998	0.006
12	m-F	5.14	6.65	8.18	10.21	33.8	196.7	0.999	0.012
13	o-NO_2	12.42	19.98	26.47	39.20	57.2	111.7	0.995	0.052
14	o-Cl	3.19	4.65	6.08	8.16	46.9	157.1	0.997	0.030
15	o-Br	2.91	4.56	6.14	9.01	56.6	126.0	0.997	0.040

The plot of log$k_{obs(45°)}$ versus log $k_{obs(30°)}$ gives straight line with r = 0.930. The good correlation indicates that all the investigated substituted compounds follow a common mechanism.

Deviation from the Hammett Relationship. On applying Hammett equation, the usual substituent constant σ and k_{obs} data of ortho-,meta- and para-substituted cinnamic acids, a 'V' shaped curve is obtained (Fig.1). The electron-releasing substituents fall on the one side of the curve with a negative slope and the electron-withdrawing substituents on the other side with a positive slope (Fig.1). The values of ρ_+ and ρ_- at different temperatures are given in Table 6.

Table 6. Reaction Constant for Oxidation of Substituted Cinnamic acids by PCC

Temp.°C	ρ_+	ρ_-
30	0.95	1.97
35	1.09	2.13
40	1.13	1.95
45	1.22	2.03

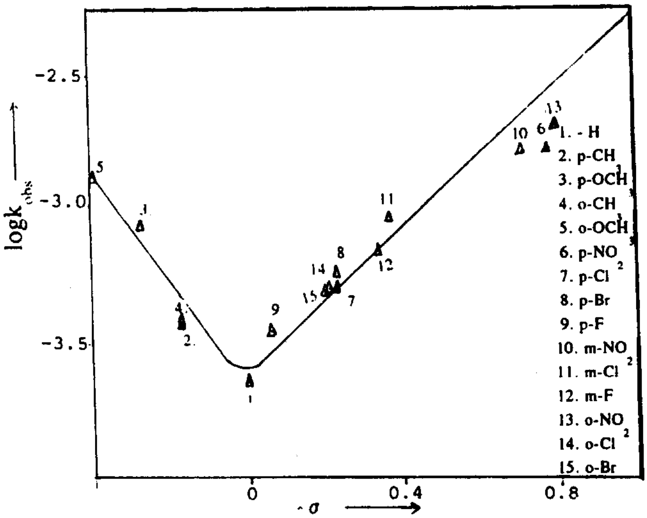


Fig. 1. Hammett plot for oxidation of some substituted trans-cinnamic acids by PCC

This type of U (or) V-shaped curve in Hammett plot is reported earlier [22-24].

The break in the Hammett plot may be due to the following three factors.

1. A change in the machanism when one passes from electron donors to electron attractors.
2. A change in the rate-determining step with change in the nature of substituent and
3. A change in the nature of the transition state.

The break in the Hammett plot can't be due to the change in the rate-determining step, since the Michaelis-Menten's plot with some important substrates does yield an intercept (Fig 2). The isokinetic plot

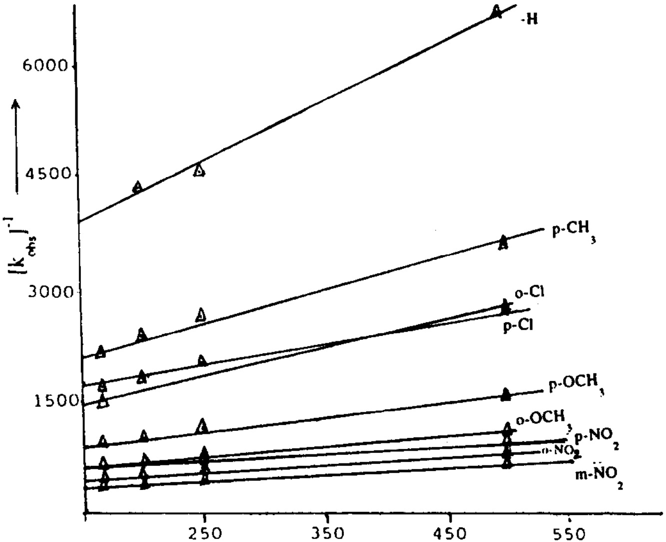
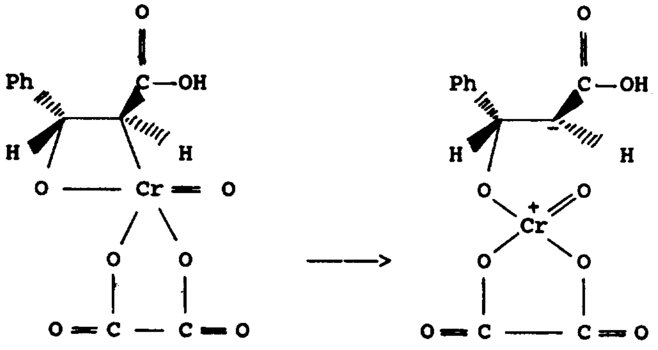


Fig. 2. Michaelis-Menten plot for oxidation of some substituted trans-cinnamic acids by PCC

and Exner plot reveal that there is no change in reaction mechanism with respect to substituents. Hence the observe versus σ is attributed to the change in the transition state.

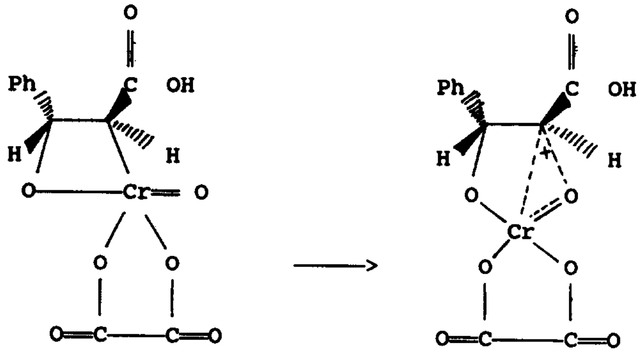
The foregoing proposal would accomadate the experimental observation if one assumes a complex formation by an interaction of the substrate and oxalatochromium complex (eq. 3). The unsubstituted CA is least reactive in this series. But both the electron releasing and withdrawing substituents facilitate the rate of the reaction considerably. The electron attractors accelerate the reaction rate only when the rate-determining step proceeds with the development of negative charge on the α-or ß- carbon (eq. 11) in cinnamic acid.



(11)

A similar observation was noticed in the case of oxidation of CA by methyl tributyl ammonium permanganate.[13]

Since the electron releasing substituents also (a carbonium ion in the transition state) accelarate the rate of the reaction, the transition state may be a carbonium ion. The development of positive charge may be suggested by the following equation.



(12)

This type of transition state has already been suggested in the oxidation of sulphides by PCC[25] and PDC[26].

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