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Kinetics of Oxidation of Some Substituted Cinnamic Acids by Imidazolium Dichromate in the Presence of Oxalic Acid

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The kinetics of oxidation of some substituted cinnamic acids has been studied in 60 % acetic acid medium. The order of the reaction is found to be one with respect to [oxidant] as well as [oxalic acid] and fractional with respect to substrate concentration and the reaction is acid catalyzed one. Decrease in dielectric constant of the medium decrease the rate of the reaction. The reaction shows zero salt effect. The reaction rate incerases with increase of concentration of manganous sulfate, reaction rate decreases with increase of concentration of aluminium sulphate due to the formation of complex between Al^{3+} and oxalic acid. The reaction does not induce the polymerization of acrylonitrile. The reactions are carried out at five different tempeatures and the activation parameters have been calculated.

Key Words: Kinetics, Oxidation, Imidazolium dichromate, Cinnamic acids.

INTRODUCTION

In the recent, years a variety of Cr(VI) complexes have been prepared and tested to be effective oxidants[1-4]. Imidazolium dichromate (IDC) is reported to be neutral and mild oxidant for selective oxidation. Kinetics of oxidation of some substrates by IDC have already been reported[5-7]. The oxidation of reactive substrate, cinnamic acids has been studied with a wide variety of oxidants[8-10]. The present work deals with the kinetics of oxidation of *trans* cinnamic acids by IDC. Chromium(VI) function both as one and two electron oxidant depending on the substrate and experimental conditions. The intermediate valence state Cr(VI) and Cr(IV) are introduced in these parameters. Hasan and Rocek[11] concept of a “three electron transfer” process in the study of oxidation of isopropyl alcohol and oxalic acid by chromic acid, when Cr(VI) gets directly reduced to Cr(III). Interestingly both substrates undergo oxidation and the process was termed as co-oxidation.

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EXPERIMENTAL

Imidazolium dichromate was prepared by the literature method[12]. Cinnamic acid and most of the substituted cinnamic acid were obtained commercially (Fluka AnalaR and their purity was checked by IR and TLC. Some of the substituted *trans* cinnamic acids (*p*-chloro, *p*-bromo, *m*-chloro) were prepared by literature method[13]. All other chemicals used were of AR grade (E-Merck). Triply distilled water was used for preparation of solution.

Kinetic measurements: The reaction was carried out under *pseudo*-first order conditions [cinnamic acid] >> [IDC] in 60% acetic acid-water (v/v) medium containing perchloric acid. The reaction mixture were kept in thermostat and the progress of reaction was followed by estimating the consumption of IDC iodometrically to starch end point as described by Kolthoff and Carr[14] and rate constant k_1 computed from the linear plot of log titre *vs.* time by the least square method, was reproducible ± 2%.

Stoichiometry: Reaction mixture containing an excess of the oxidant over cinnamic acid were kept at room temperature in presence of perchloric acid for 24 h. Estimation of the unchanged oxidant showed that one mole of IDC consumed by one mole of substrate. The product benzaldehyde and glyoxalic acid was confirmed by infrared spectra and spot test.

RESULTS AND DISCUSSION

Kinetics and mechanism of oxidation of several organic substrates by IDC[8-10] is well documented. But there is no systematic kinetic report on the oxidation of cinnamic acids by Cr(VI) complex, IDC in the presence of oxalic acid. The present investigation indicates that the rate of oxidation of cinnamic acid (CA) with IDC in the presence of oxalic acid is several times higher than the independent oxidation rate of cinnamic acid and oxalic acid by Cr(VI).

The order with respect to oxidant was found to be one as evidenced by the linear plot log titre *vs.* time. The *pseudo*-first order rate constnat with respect to [IDC] are fairly constant wide range in [IDC].

The order with respect to substrate was found to be fractional as evidenced by the linear plot of log k_{obs} *vs.* log [substrate] (r = 0.9980 with slope of 0.69) also verified by Michalies-Menten plot. The rate constant k_1 increased with the incerase in the [substrate]. The order with respect to oxalic acid was found to be one as evidenced by linear plot of log k *vs.* log [oxalic acid] (Table-1).

There was no appreciable change in the rate with change of ionic strength indicating the involvement of neutral molecule in the rate-determining step, when the reaction was studied at various initial [H^+] keeping [oxidant], [substrate], [oxalic acid] and temperature constant, rate of the reaction was increased appreciably. The rate increases with decrease in ionic strength has negligible effect on the rate.

TABLE-1
EFFECT OF [IDC], [CA], [OX] AND [H^+]

[IDC] × 10^3 (mol dm^{-3})	[CA] × 10^2 (mol dm^{-3})	[OX] × 10^2 (mol dm^{-3})	[H^+] × 10^2 (mol dm^{-3})	k × 10^4 (s^{-1})
0.50	–	–	–	3.33
0.75	–	–	–	3.29
1.00	–	–	–	3.04
1.25	–	–	–	3.35
1.50	–	–	–	3.19
–	0.5	–	–	1.99
–	1.0	–	–	3.04
–	1.5	–	–	4.13
–	2.0	–	–	5.22
–	2.5	–	–	6.06
–	–	0.50	–	1.59
–	–	1.00	–	3.04
–	–	1.50	–	5.19
–	–	1.75	–	6.68
–	–	2.00	–	7.35
–	–	–	2.75	1.21
–	–	–	5.50	1.72
–	–	–	8.25	2.41
–	–	–	11.00	3.04
–	–	–	12.58	4.41

Acetic acid = 60 % (v/v); Temp = 303 K
IDC = Imidazolium dichromate; CA = Cinnamic acid; OX = oxalic acid

Mechanism and rate law: The above facts revealed that there is a combined effect of oxidant, oxalic acid and H^+. One may presume that the increased rate of cinnamic acid in the presence of oxalic acid is catalytic. The evaluation of CO_2 confirms oxalic acid as one of the participants in the main reaction, in co-oxidation process. Such a phenomenon of ternary system was already established. The absence of primary salt effect shows that the slow-step in this reaction is only between the neutral species. This increase in the rate, by the addition of Mn(II) may be due to catalytic effect[15-17].

The adition of Al^{3+} does not 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. When we compare the k_{obs} value of oxidaton of cinnamic acid by IDC, they are almost one and the same, and this indicates that there is a common species involved in these reactions.

TABLE-2

EFFECT OF $NaClO_4$, $MnSO_4$, $Al_2(SO_4)_3$, SOLVENT AND TEMPERATURE

$[NaClO_4] \times 10^3$ (mol dm^{-3})	$[MnSO_4] \times 10$ (mol dm^{-3})	$Al_2(SO_4)_3 \times 10^3$ (mol dm^{-3})	Solvent AcOH-H_2O (%)	Temp. (ºC)	$k \times 10^4$ (s^{-1})
5.00	–	–	–	–	4.04
6.25	–	–	–	–	4.01
7.50	–	–	–	–	3.98
8.75	–	–	–	–	4.10
10.00	–	–	–	–	4.13
–	5.00	–	–	–	1.97
–	6.25	–	–	–	2.99
–	7.50	–	–	–	6.41
–	8.75	–	–	–	12.4
–	10.00	–	–	–	21.5
–	–	5.00	–	–	46.8
–	–	6.25	–	–	42.1
–	–	7.50	–	–	38.5
–	–	8.75	–	–	31.2
–	–	10.00	–	–	28.9
–	–	–	50	–	1.05
–	–	–	60	–	2.49
–	–	–	70	–	3.04
–	–	–	80	–	5.98
–	–	–	90	–	6.74
–	–	–	–	25	2.10
–	–	–	–	30	3.04
–	–	–	–	35	4.11
–	–	–	–	40	5.10

Based on these and other facts the reaction mechanism **Scheme-I** has been proposed. **Scheme-I** involves the formation of a cyclic complex (C_2) by the reaction between oxidant, oxalic acid and H^+, which on interaction with cinnamic acid forms another complex (C_3). The complex (C_3) rearranges to form a cyclic chromium(IV) diester (C_4) in the slow step which decomposes to give the product.

From the above mechanism the rate of law is derived as follows:

Rate law:

$$\text{Rate} = k_4 C_3$$

$$= \frac{k_4 K_3 [CA] [C_2]}{\{1 + K_3 [CA]\}}$$

$$= \frac{k_4 K_3 K_2 [CA] [C_1] [OX]}{\{1 + K_3 [CA]\}}$$

$$= \frac{k_4 K_3 K_2 K_1 [CA] [H^+] [Cr(VI)] [OX]}{\{1 + K_3 [CA]\} \{1 + K_1 [H^+\}}$$

$$= \frac{K_1 K_2 K_3 k_4 [CA] [H^+] [OX] [Cr(VI)]}{\{1 + K_3 [CA] K_1 [H^+] + K_3 [CA] + K_1 [H^+]\}}$$

$$= \frac{K_1 K_2 K_3 k_4 [CA] [H^+] [OX] [Cr(VI)]}{\{1 + K_1 [H^+] + K_3 [CA]\}}$$

$$k_{obs} = \frac{K_1 K_2 K_3 k_4 [CA] [H^+] [OX]}{\{1 + K_1 [H^+] + K_3 [CA]\}}$$

where CA = Cinnamic acid
OX = Oxalic acid

Structural effects: The effect of substituents on the rate of oxidation has been studied with number of *m*- and *p*-substituted cinnamic acids at four different temperatures. The respective rate constant and thermodynamic parameter are presented in Table-3.

TABLE-3
THERMODYNAMIC PARAMETERS OF SUBSTITUTED *TRANS*-CINNAMIC ACID

S. No.	Substituted CA	k_{obs} x 10_4 (s^{-1})				$\Delta H^\#$ (KJ mol^{-1})	$\Delta S^\#$ (J K^{-1} mol^{-1})	r	SD
		25°C	30°C	35°C	40°C				
1	*p*-OMe	7.54	9.69	13.3	15.00	34.315	-189.46	0.9869	0.05718
2	*p*-Me	3.92	4.61	6.28	7.94	35.090	-192.70	0.9915	0.04687
3	*m*-Me	3.14	4.08	5.17	6.62	35.813	-191.83	0.9999	0.00568
4	H	2.10	3.04	4.11	5.10	43.384	-169.52	0.9944	0.04686
5	*p*-F	2.02	2.90	3.63	4.47	37.849	-188.35	0.9912	0.05147
6	*p*-Br	1.32	1.74	2.51	3.02	41.796	-178.97	0.9928	0.05139
7	*p*-Cl	0.99	1.68	2.35	2.88	52.294	-145.50	0.9804	0.10708
8	*m*-Cl	0.88	1.10	1.72	2.39	51.044	-151.77	0.9919	0.06649
9	*m*-NO_2	0.35	0.52	0.71	1.09	55.017	-145.69	0.9977	0.03824
10	*p*-NO_2	0.30	0.38	0.63	0.91	57.078	-140.56	0.9879	0.09122

[IDC] = 1.00 x 10^{-3} mol dm^{-3}; [OX] = 1.00 x 10^{-2} mol dm^{-3}; [H^+] = 11 x 10^{-2} mol dm^{-3}; AcOH = 60% (v/v).

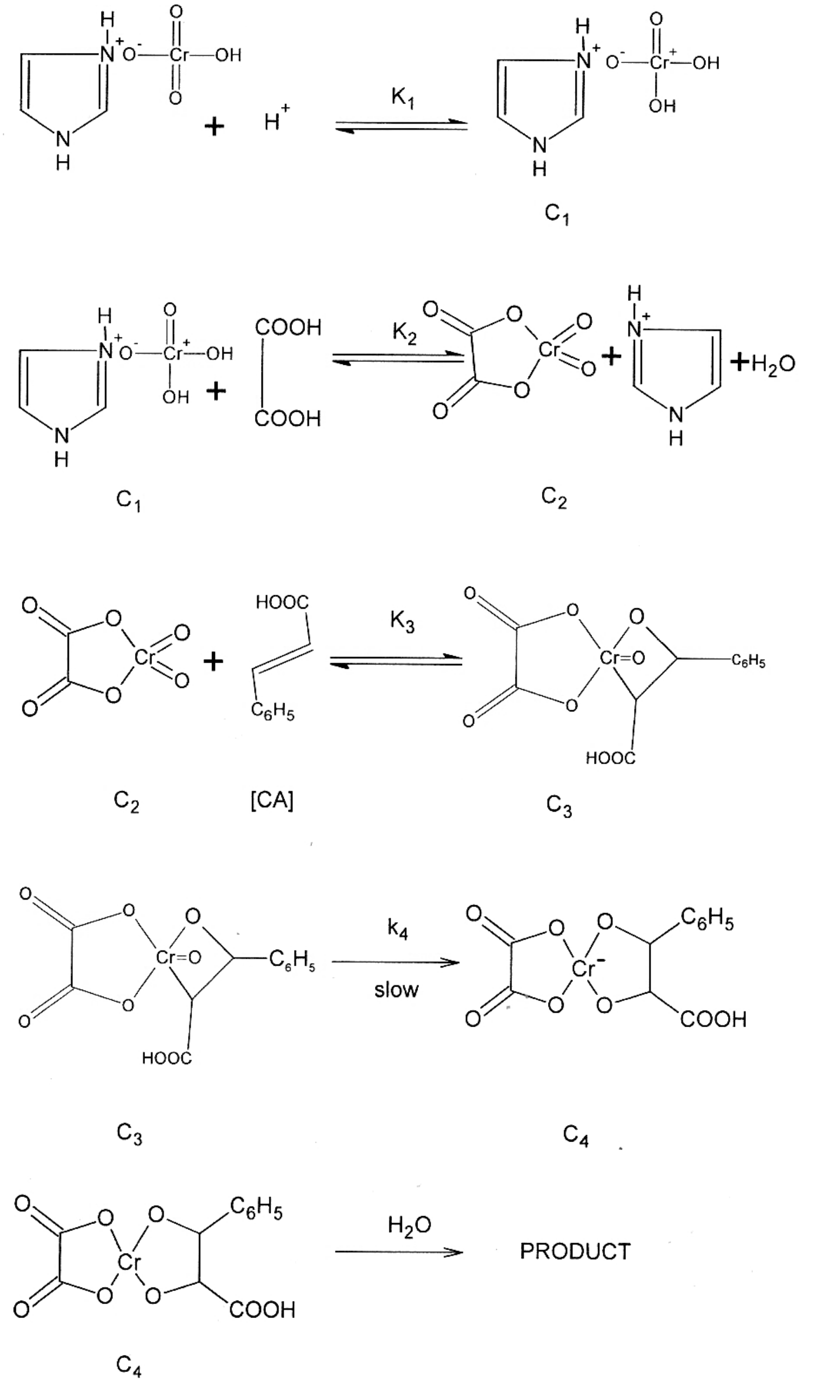
TABLE 4
ρ VALUES OBTAINED FROM HAMMETT EQUATION

Temp. (°C)	ρ	r	SD
25	-1.45	0.9935	0.0605
30	-1.49	0.9929	0.0666
35	-1.54	0.9956	0.5420
40	-1.56	0.9859	0.0523

An analyis of the data has ben made in respect of the lienar free-energy relationships. The data (Table-3) reveal that the entropy of activation is not constant throughout the series. In such cases, the variation in $\Delta S^\#$ should be linearly related[18,19] to changes in by $\Delta H^\#$ equation

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

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



Scheme - I

The linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ is observed from a plot of $\Delta H^{\#}$ against $\Delta S^{\#}$ (Fig. 1) with fair correlation coefficient ($r = 0.99$) which indicates that all the substituted cinnamic acids follow a common mechanism.

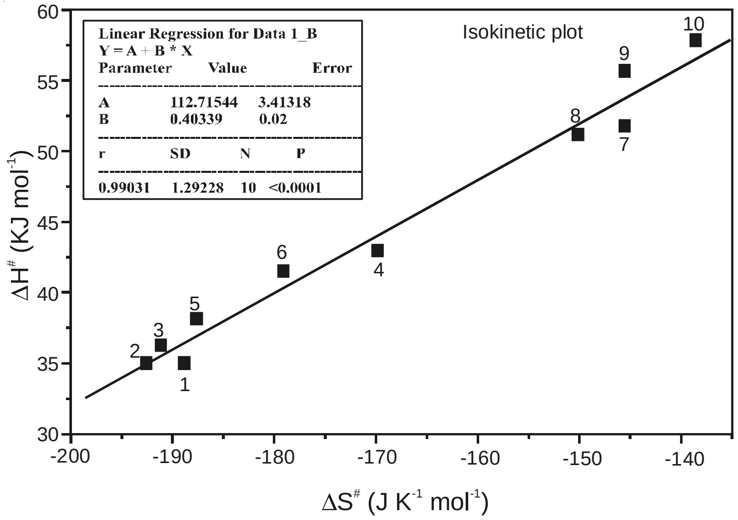


Fig. 1. Plot of $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$

The validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ was criticized by Exner[20,21] as their quantities are dependent on each other. When measurments at two different temperature have been made, the data can be analyzed by the following equation[22,23].

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

where $T_2 > T_1$

The plot of log k_{obs} (40ºC) *vs.* log k_{obs} (25ºC) and log k_{obs} (35ºC) *vs.* log k_{obs} (25ºC) gave straight line with $r = 0.99$ and $r = 0.99$, respectively. Such a good correlation indicates that all the investigated, substituted compounds follow common mecahnism at fixed concentration of cinnamic acid and H^+.

Electron-withdrawing substituents retard the rate of reaction while electron-releasing groups accelerate the rate of reaction. The ρ values calculated from the plots of k_{obs} *versus* σ at different temperature were found to be negative sign of the ρ values.

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