Kinetics and mechanism of the oxidation of alkenes by chromium(VI) in the presence of complexing agents

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The catalytic activities of 2,2′-bipyridyl (bipy) and oxalic acid (Oxa) in the $HCrO_4^-$ oxidation of some substituted *trans*-cinnamic acids have been investigated in acidic solutions. The Cr(VI)–bipy and Cr(VI)–Oxa complexes are believed to be the probable reactive electrophiles in this redox process. The kinetic data reveal that electron-releasing groups enhance the reactivity to a significant extent while the electron-withdrawing ones reduce the rate marginally. It appears that the mechanism of bipy/Oxa catalysed chromium(VI) oxidation of unsaturated systems to the corresponding cleavage products involves an electrophilic attack of the reactive complex at the C–C double bond. The formation of a ternary complex as an intermediate is envisaged to describe the redox process. In this paper, we also report on the kinetic form of the oxidation of *trans*-stilbene to methyl 3-hydroxy-2,3-diphenylpropanoate. The mechanistic pathway has been determined based on the kinetic behaviour and the product assignment.

Keywords: *trans*-cinnamic acid, *trans*-stilbene, 2,2'-bipyridyl, oxidation, chromium(VI)

Among the oxo derivatives of variable valance metals, chromium compounds play the most important role because the oxidative reactions based on them can be readily carried out. The oxidation of carbon–carbon multiple bonds by chromium(VI) reagents mainly leads to the formation of epoxides, glycols, aldehydes, ketones and carboxylic acids.[1] The mechanistic pathways and the nature of the transition states in the oxidation of single and multiple carbon–carbon bonds with chromium(VI) still remain controversial. The oxidation of cinnamic acids by chromium(VI) reagents in the presence of complexing agents such as oxalic acid,[2] picolinic acid[3] and 1,10-phenanthroline[4] have been reported. The substituent effects in this type of reaction are very interesting because of the possibility of the dual-path mechanism, reported for stilbene bromination[5] and acid bromate oxidation[6] of cinnamic acids. In the present study we have undertaken chromium (VI) oxidation kinetics investigations in the presence of complexing agents 2,2'-bipyridyl and oxalic acid since they can form a more reactive complex with chromium(VI) analagous than picolinic acid[7, 8] and 1,10-phenanthroline complexes with chromium(VI).[9]

Experimental

All the chemicals used were reagent grade products. 2,2'-Bipyridyl (E. Merck) was used as supplied without further purification. *trans*-Cinnamic acid (Loba Chem) was recrystallised from a $CHCl_3$–hexane mixture (m.p. 131–133°C). Substituted cinnamic acids (Aldrich), *trans*-stilbene (Aldrich) and potassium dichromate (E. Merck) were used as such. Heavy water (99.4%) was supplied by Bhaba Atomic Research Centre, India and was used for solvent isotope effect studies.

Purification of acetic acid

Acetic acid of AR grade was first refluxed with chromium trioxide (20 g l^{-1}) for 4 h and then distilled. It was refluxed again with chromium trioxide (2 g l^{-1}). Then it was fractionated through a Dufton column and the fraction at 117–118°C was collected.

Purification of water

De-ionised water was distilled twice over potassium permanganate in an all glass Corning vessel. All the aqueous solutions were prepared using this double-distilled water.

The reactions were performed in aqueous acetic acid medium under pseudo-first order conditions by maintaining a large excess of substrate over chromium(VI). The reaction mixture was homogeneous throughout the course of the reaction. The progress of the reaction was monitored for at least two half-lives by iodometric estimation of unchanged oxidant at regular time intervals. The pseudo-first order rate constants were evaluated from the slopes of linear plots of log titre versus time. The least squares method was adopted. All the rate constants are the average of two or more determinations.

Stoichiometry and product analysis

The stoichiometry of the reaction was determined for a number of reaction mixtures at 308 K, under the conditions of $[Cr^{VI}]_{initial} > [substrate]_{initial}$ at constant acidity. The disappearance of chromium(VI) was followed until the titre values became constant. The estimation of unreacted chromium(VI) shows that 4 mol of oxidant is consumed by 3 mol of substrate.

Chromium(VI) (0.15 mol), trans-cinnamic acid (0.05 mol), catalyst (0.004 mol) and perchloric acid (0.32 mol) were mixed. The reaction mixture was kept for 48 h to ensure completion of the reaction. The solution was extracted with chloroform and the organic layer was washed with water, dried over anhydrous Na_2SO_4 and then evaporated. A white solid residue was obtained (m.p. 119–122°C) (lit. 122°C); yield 60%. The product was identified by FT-IR. A band at ~ 1690 cm^{-1} [$\nu_{(C=O)}$] is characteristic of benzoic acid. ^{13}C NMR studies further confirm the above product (C=O 167 ppm; other carbons 130–128 ppm). The product analysis studies with p-CH_3 and p-Cl substituents give p-methylbenzoic acid (m.p. 178–181°C) (lit. 181°C) (yield 55%) (C=O 168.2 ppm, other carbons 129–127 ppm) and p-chlorobenzoic acid (m.p. 240–243°C) (lit. 243°C) (yield 50%) (C=O 166.2 ppm; other carbons 137–128 ppm) as the respective products.

It appears that benzaldehyde was the initial product of cinnamic acid which then undergoes further oxidation to the product reported from this reaction, benzoic acid in the presence of excess oxidant. The presence of benzaldehyde in the presence of reduced oxidant concentration was confirmed by the formation of the 2,4-dinitophenylhydrazone derivative. The gas evolved from the reaction mixture, when passed through an aq-barium(II) solution gives a white precipitate implying the formation of carbon dioxide.

Trans-stilbene oxidation

The reactants in the ratio trans-stilbene: chromium(VI) (1:3) in aqueous acetic acid medium were mixed. The reaction mixture after 48 h, was extracted with chloroform, dried over anhydrous Na_2SO_4 and then evaporated. The product was separated by column chromatography using neutral alumina and eluted with varying proportions of hexane and chloroform, concentrated and then identified by FT-IR. The major product of the oxidation was identified tentatively as methyl 3-hydroxy-2,3-diphenylpropanoate (yield 50%) [–O–H (str) (broad 3431 cm^{-1}); aromatic –C–H (str) 2958 and 2926 cm^{-1}; –CH_3 (str) 2886 cm^{-1}; C=O (str) 1723 cm^{-1}; aromatic $C \overset{---}{=} C$ 1602 cm^{-1}; C–O 1276 cm^{-1}; aromatic –C–H bend 702 cm^{-1}]. Normally ester carbonyls absorb at 1740 cm^{-1}. Owing to hydrogen bonding with –OH at C-3 carbon, the carbonyl absorption frequency decreases.

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Results and discussion

2,2′-Bipyridyl catalysis in the Cr(VI) oxidation of trans-*cinnamic acids*

2,2′-Bipyridyl ($C_{10}H_8N_2$) is well known as a chelating agent for metals[10] and used in the analysis of heavy metals. It forms complexes with many metal ions in normal (*e.g.* +2, +3) oxidation states. It has been reported that the ligand 2,2'-bipyridyl is oxidation resistant.[11] 2,2'-Bipyridinium chromate (BPC) has been proposed as an oxidant for the oxidation of the hydroxy group to the carbonyl group.[1] Kinetic investigations of the oxidation of various inorganic substrate ligands by $[Ni(bipy)_3]^{3+}$ have been reported.[12,13]

Under pseudo-first-order conditions the first order dependence on chromium(VI) was provided by the linear semilogarithmic plots of titre *versus* time ($r \approx 0.993$; $s \approx 0.013$). The observed rate constants k_{obs} did not vary appreciably with changing chromium(VI) concentrations. The linear increase in the rate of oxidation with [cinnamic acid] is shown in Fig. 1 ($r = 0.999$; $s = 0.410$). The catalytic activity of bipy is significant and this conversion exhibits fractional order dependence on [bipy] (Table 1). It enhances the conversion of the unsaturated acids and the system can be characterised as,

$$k_{obs} = a + b\,[\text{bipy}]$$

where a and b are rate constants for the uncatalysed and acid catalysed reactions respectively. It is clear from the data that the second term becomes more pronounced at higher concentrations of the catalyst. The catalyst increases the electrophilic activity of the oxidant and, hence, enhances the rate.

Permittivity (D) values are calculated approximately from the values of pure solvents. The low dielectric constant of the medium favours the reaction as shown in Table 2. A plot of log k_{obs} *versus* D^{-1} is fairly linear with a positive slope ($r = 0.993$; $s = 0.244$). Variation of pH does affect the reactivity by the catalysed reaction pathway and the order dependence on acidity was > 1 and < 2 as shown in Fig. 2 ($r = 0.992$; $s = 0.077$). The effect of ionic strength on the reactivity proved to be almost negligible. The kinetic data are summarised in Table 2.

The insensitivity of rates to added acrylonitrile (5% aqueous solution) ruled out a free radical process. Initial addition of manganese(II) depressed the reactivity but further additions have no significant effect in the conversion of unsaturated acids. This clearly indicates the involvement of intermediate valence states of chromium, particularly chromium(IV). Direct oxidation of manganese(II) with chromium(VI) is thermodynamically unfavourable.[14] Retardation of rate was observed in the presence of an excess of $Co(NH_3)_5Cl^{2+}$, a specific trapping agent for chromium(II) (Table 3).

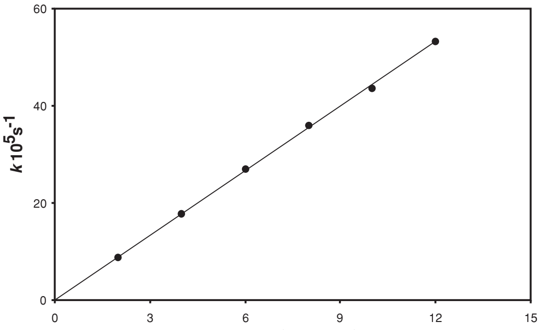


Fig. 1 First order dependence on [CA].

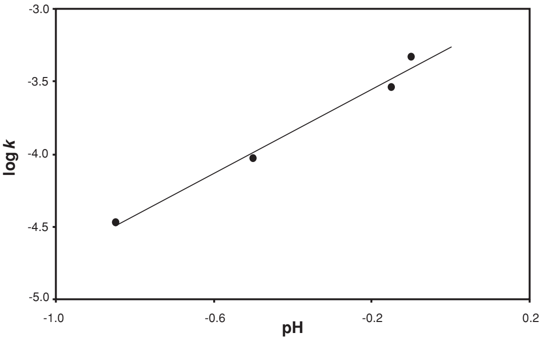


Fig. 2 A Plot of log k_{obs} *versus* pH.

Table 1 Effect of reactants on the reaction rate of oxidation at 308 K

[CA] 10^2 /mol dm^{-3}	[bipy] 10^3 /mol dm^{-3}	[Cr(VI)] 10^3 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
2.0	4.0	2.0	8.8
4.0	4.0	2.0	17.7
6.0	4.0	2.0	26.9
8.0	4.0	2.0	35.9
10.0	4.0	2.0	43.7
12.0	4.0	2.0	53.3
4.0	0	2.0	5.9
4.0	1.5	2.0	12.1
4.0	2.0	2.0	13.9
4.0	4.0	2.0	17.7
4.0	4.0	1.0	19.0
4.0	4.0	1.5	16.8
4.0	4.0	2.0	17.7
4.0	4.0	3.0	18.6

$[H^+] = 0.32$ mol dm^{-3}; AcOH : Water = 50 : 50 (v/v)

Table 2 Effect of dielectric constant and ionic strength on the reaction rate of 308 K

% AcOH	% H_2O	D	[$NaClO_4$]10^3 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
30	70	57.9	–	15.8
40	60	50.5	–	16.6
50	50	43.1	–	17.7
60	40	35.7	–	24.5
70	30	25.9	–	44.7
50	50	43.1	0.0	17.7
50	50	43.1	1.0	17.9
50	50	43.1	2.0	16.0
50	50	43.1	3.0	17.2
50	50	43.1	4.0	18.8

[Cr(VI)] = 2.0×10^{-3} mol dm^{-3}; [CA] = 4.0×10^{-2} mol dm^{-3}; [bipy] = 4.0×10^{-3} mol dm^{-3}; $[H^+] = 0.32$ mol dm^{-3}.

Table 3 Effect of acrylonitrile, Mn(II) and Co(III) on the reaction rate in the oxidation of cinnamic acid at 308 K

[Acrylonitrile] 10^3 /mol dm^{-3}	[Mn(II)] 10^3 /mol dm^{-3}	[Co(III)] 10^3 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
0.0	–	–	17.7
1.0	–	–	19.2
2.0	–	–	18.5
3.0	–	–	19.2
4.0	–	–	20.8
–	0.0	–	17.7
–	1.0	–	15.1
–	2.0	–	14.6
–	3.0	–	15.0
–	4.0	–	15.9
–	–	0.0	17.7
–	–	1.0	15.8
–	–	3.0	14.9
–	–	4.0	13.2

[Cr(VI)] = 2.0×10^{-3} mol dm^{-3}; [CA] = 4.0×10^{-2} mol dm^{-3}; [bipy] = 4.0×10^{-3} mol dm^{-3}; $[H^+] = 0.32$ mol dm^{-3}; AcOH: H_2O = 50:50 (v/v).

Addition of benzaldehyde, the suspected intermediate oxidation product in this conversion, enhances the reactivity considerably and this is well reflected in the product assignment. The large excess of substrate concentration ensures that the rates of oxidation of intermediate products are kinetically insignificant. Marginally enhanced reactivity is observed with chromium(III) (Table 4). Significant rate enhancement was observed when the reaction was conducted in AcOH–D_2O–H_2O medium in place of AcOH–H_2O medium (Table 5). This would imply a proton catalysed reaction, an observation which has been reflected in the acid dependence on the rate of the reaction. The rate constants were measured at 298, 308, 318 and 328 K. The activation parameters evaluated from the Eyring's plot (r = 0.990; s = 0.119) are listed in Table 6.

Structure–reactivity relationships are ascertained by employing some substituted *trans*-cinnamic acids at different temperatures and although more studies on substituent effects are required, it can be seen from the kinetic data (Table 6) that electron-releasing groups enhance the reactivity to a significant extent while electron-withdrawing ones reduce the rate marginally. This type of situation generally will result in a continuously changing Hammett[15] curve (Fig. 3) (r = 0.794; s = 0.315). The correlation doses improve with Brown–Okamoto constants[15] ($\sigma^{+}_{B.O}$) (r = 0.919; s = 0.219) but the shape of the curve remains almost same. Non-linearity in the Hammett plot can be removed to a considerable extent by using the σ_R^+ value[15] (–1.1) for the p-OCH_3 substituent (r = 0.988; s = 0.078). Since the number of substituents are limited, no detailed correlation analysis studies have been carried out. This type of curvature has been reported in the literature.[4,16-18] The observed slopes of the ρσ correlation curves (–3.1 and –0.5 for two limbs) very much suggest the involvement of a positively charged species and the dispersal of positive charge in the reaction prior to or after the rate-determining step. The curved plot is explained by mechanistic pathways involving a fully developed carbonium ion like activated complex for electron-donors and its dispersal for electron-acceptors.

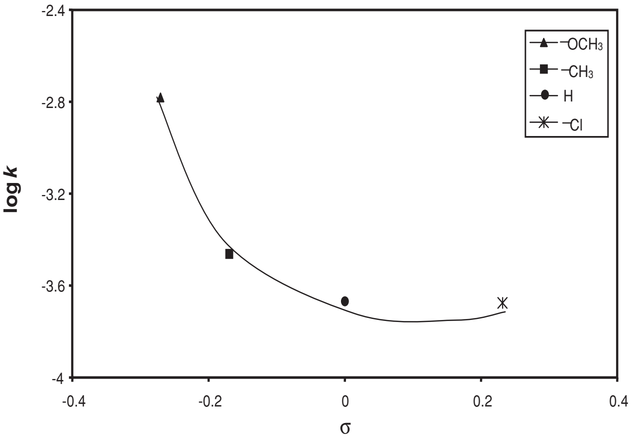


Fig. 3 The Hammett plot

Table 4 Effect of Cr(III) and benzaldehyde on the reaction rate at 308 K

[Cr(III)] 10^3 /mol dm^{-3}	[C_6H_5CHO] 10^3 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
0.0	–	17.7
2.0	–	19.0
3.0	–	20.8
4.0	–	21.0
–	0.0	17.7
–	1.0	21.0
–	4.0	23.2

[Cr(VI)] = 2.0 × 10^{-3} mol dm^{-3}; [CA] = 4.0 × 10^{-2} mol dm^{-3}; [bipy] = 4.0 × 10^{-3} mol dm^{-3}; [H^+] = 0.32 mol dm^{-3}; AcOH: H_2O = 50:50 (v/v)

Table 5 Effect of D_2O on the reaction rate at 308 K

% AcOH	% H_2O	% D_2O	k_{obs} 10^5 /s^{-1}
50	50	0	17.7
50	47.5	2.5	22.4
50	40.0	10.0	24.0
50	35.0	15.0	25.7
50	30.0	20.0	29.1

[Cr(VI)] = 2.0 × 10^{-3} mol dm^{-3}; [CA] = 4.0 × 10^{-2} mol dm^{-3}; [bipy] = 4.0 × 10^{-3} mol dm^{-3}; [H^+] = 0.32 mol dm^{-3}.

Mechanism and rate law: It is believed that the catalytic activity of the complexing agent 2,2'-bipyridyl depends on its ability to stabilise intermediate chromium valence states. Substantial acid catalysis in the present study can be attributed to the facile formation of a Cr^{VI}–bipy complex in acidic solutions.

Generally a one-electron transfer process is characterised by low ρ-values.[19-21] The small ρ-values[19-25] observed in the present study cannot be associated with a free radical mechanism since the studies with acrylonitrile do not support this pathway.

The formation of a 2:1 complex between chromium(VI) and 2,2'-bipyridyl is ruled out in the present study since the reaction exhibits a clean first-order dependence on the concentration of oxidant. It appears that the Cr^{VI}–bipy complex is the probable electrophile in this conversion. The catalysis by bipy may be explained as being due to a more favourable electron transfer through its π-electron cloud.[26] This view is similar to the one proposed in the case of 1,10-phenanthroline catalysed chromium(VI) oxidation of unsaturated acids.[4]

The absorption spectrum recorded in the presence of chromium(VI), bipy and cinnamic acid shows spectral changes supporting complex formation (Fig. 4). The available kinetic data can be rationalised by the following two-pathway mechanism *i.e.*, non-catalysed and 2,2'-bipyridyl catalysed schemes.

Table 6 Rate constants and activation parameters for the 2,2′-bipyridyl catalysed Cr(VI) oxidation of cinnamic acids

Substrate	k_{obs} 10^5 /s^{-1}				ΔH≠ /kJ mol^{-1}	–ΔS≠ /J K^{-1} mol^{-1}	r^a	s^b
	298 K	308 K	318 K	328 K				
H	12.6	21.2	45.1	59.7	42.4 ± 6.8	179.6 ± 11.0	0.985	0.139
p-CH_3	23.3	42.1	83.0	110.5	42.0 ± 6.1	175.3 ± 13.0	0.987	0.134
p-OCH_3	94.9	165.3	264.8	439.0	39.6 ± 7.2	172.1 ± 13.2	0.999	0.028
p-Cl	8.6	20.5	27.1	51.9	46.8 ± 7.1	168.4 ± 12.8	0.999	0.037

[Cr(VI)] = 1.0 × 10^{-3} mol dm^{-3}; [S] = 1.0 × 10^{-2} mol dm^{-3}; [bipy] = 4.0 × 10^{-3} mol dm^{-3}; [H^+] = 0.32 mol dm^{-3}; AcOH: H_2O = 75:25 (v/v).
[a] Correlation coefficient.
[b] Standard deviation.

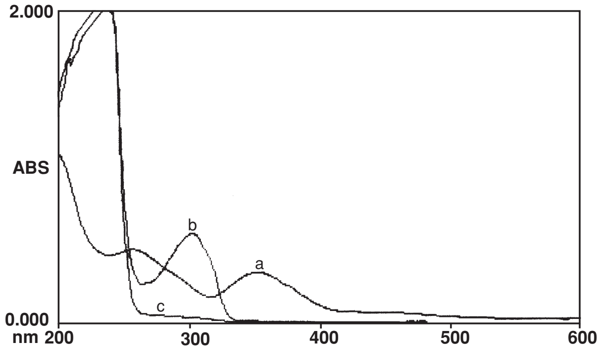


Fig. 4 The absorption spectra of: a, 10^3[Cr(VI)] = 0.2 mol dm^{-3}; b, 10^3[Cr(VI)] = 0.2 mol dm^{-3} and 10^3[bipy] = 0.4 mol dm^{-3}; c, 10^3[Cr(VI)] = 0.2 mol dm^{-3}, 10^3 [bipy] = 0.4 mol dm^{-3} and 10^3[CA] = 4.0 mol dm^{-3}

(i)

$$\text{bipy} + Cr^{VI} + 2H+ \overset{K}{\rightleftharpoons} Cr^{VI}\text{-bipy} \tag{1}$$

$$C_1 + S \xrightarrow[\text{slow}]{k_1} C_2 \tag{2}$$

where S stands for substrate

$$C_2 \xrightarrow{k_2} Cr^{IV}\text{–bipy} + \text{intermediates} \xrightarrow[\text{several steps}]{} \text{products} \tag{3}$$

(ii)

$$Cr^{VI} + H^+ \overset{K_3}{\rightleftharpoons} H_2CrO_4 \tag{4}$$

$$H_2CrO_4 + S \xrightarrow[\text{slow}]{K_4} C_3 \tag{5}$$

$$C_3 \xrightarrow{K_5} \text{products} \tag{6}$$

This reaction system can be characterised by the combined rate law,

$$\frac{-d[Cr^{IV}]}{dt} = k_1K[S]\{Cr^{VI}][bipy][H^+]^2 + k_4K_3[S][H^+][Cr^{VI}]$$

The initial inhibitory effect on the rate with manganese (II) supports steps (7) and (8).

$$Cr^{IV}\text{–bipy} + Cr^{VI}\text{–bipy} \longrightarrow 2Cr^{V}\text{–bipy} \tag{7}$$

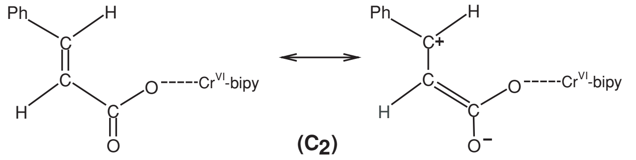
$$\begin{aligned} &2Cr^{V}\text{–bipy} + Ph\text{–}CH{=}CHCOOH \longrightarrow \\ &\quad PhCHO + OHC.COOH + 2Cr^{III}\text{-bipy} \end{aligned} \tag{8}$$

$$PhCHO \xrightarrow{(O)} PhCOOH \tag{9}$$

The protonated chromium(VI) would be a more reactive electrophilic species than chromium(VI) itself and is sufficiently reactive to attack an activated ethylenic system. The possibility of 2,2'-bipyridyl existing in protonated form is not entirely ruled out.

$$\text{bipy} + H^+ \rightleftharpoons \text{H bipy}^+ \tag{10}$$

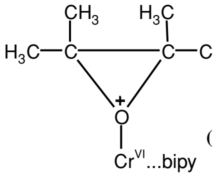
Sharpless *et al.*[1] believed that reactions involving oxidation by metal oxo compounds proceed with the attack by the organic reductant on the metallic centre. Nucleophilic attack of the double bond on electropositive chromium is not a favoured process. C_2 and C_3 could be chromate esters.



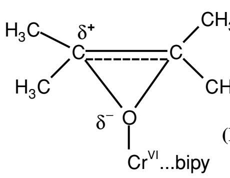
(C2)

This type of interaction between carboxylic acid group and chromium(VI) is well reported in the literature.[4,27,28]

The kinetic data are also consistent with a mechanism which involves an electrophilic attack of Cr^{VI}–bipy complex at the carbon–carbon double bond. Structure (I) (or) (II) could be the intermediates for this conversion.



(I)



(II)

Analogous structures have been postulated in the chromyl chloride oxidation of C–C double bonds.[1,29] The formation of a rigid activated complex from two acyclic reactants is indicated by the large negative values of entropies of activation.

In this mechanism, formation of C_2 (step 2) is slow and rate-limiting for electron-withdrawing groups and step (3), decomposition of complex C_2, slow for electron-releasing groups. This conversion can be described by shifts in the rate-limiting step with the nature of the substituent within the same overall reaction pathway. The point of view of the direction of opening of the double bond[4] can also account for the experimental observations. The electron-attracting effect of –COOH may encourage the movement of electrons away from the ring and presumably this would also be encouraged by electron-releasing groups in the ring. Electron-attracting groups in the ring would presumably favour opening of the double bond in the other direction.

Charge separation in the transition state is generally supported by the marked increase in the rate of conversion with decrease in the dielectric constant of the medium. Also, the rate enhancement in a medium of low permittivity is probably due to the facile formation of the Cr^{VI}–bipy complex. The insignificant rate variation with ionic strength (Table 2) may be attributed to the absence of ion–ion interactions in the rate-determining step.

The reduced reactivity in the presence of cobalt(III) is quite likely to be due to the formation of Co^{III}–bipy complex, since the ligand bipy can form complexes with a variety of metal atoms in a great range of oxidation states.[30]

The marginal enhancement in reactivity with chromium(III) (Table 4) observed in the presence of 2,2'-bipyridyl in the redox process can be explained by complexation of chromium (III) with 2,2'-bipyridyl. Initial addition of chromium(III) along with 2,2'-bipyridyl has a rate accelerating influence in the chromium(VI) oxidation[31] of lactic and malic acids.

Near constancy in $\Delta G^{\neq}$ values ($\approx$ 95 kJ mol^{-1}) implies that a common mechanism is operating in all the unsaturated acids studied. High negative $\Delta S^{\neq}$ values imply a structured transition state. The $\Delta S^{\neq}$ values reported in this work are comparable to those for oxidation of unsaturated acids catalysed by 1,10-phenanthroline.[4]

The reactivity pattern for 2,2'-bipyridyl catalysed chromium(VI) oxidation of cinnamic acids bears a strong resemblance to the related 1,10-phenanthroline catalysed oxidation reported[4] earlier from our laboratories.

Oxalic acid catalysis in the Cr(VI) oxidation of trans-*cinnamic acids*

Oxalic acid accelerates the rates of many chromium(VI) oxidations. In the presence of oxalic acid *trans*-substituted cinnamic acids react with pyridinium chlorochromate (PCC) in a cooxidation process yielding benzaldehyde, glyoxylic acid and carbon dioxide with chromium(VI) being directly reduced to chromium(III). On the other hand, it has been reported[32,33] that oxalic acid can also increase the rate of chromium(VI) oxidations without undergoing oxidation itself; it thus can act as an oxidation catalyst. In the present study, we examine the mechanism of oxalic acid catalysed chromium(VI) oxidation of some substituted *trans*-cinnamic acids at low oxalic acid concentrations. Under the experimental conditions, oxalic acid does not undergo any significant reaction. Product analysis studies reveal the absence of carbon dioxide as one of the reaction products. One may presume that the enhanced reactivity of unsaturated acids in the presence of oxalic acid is due to its role as an oxidation catalyst.

The catalytic pathway is first order in chromium(VI). The redox process has a non-integral kinetic order for both substrate (< 1) and catalyst (< 1). Michaelis–Menten dependence on the concentration of substrate was observed. The catalytic activity of oxalic acid is depicted in Fig. 5. The reaction rate is not significantly affected by an increase in acid concentration. The kinetic data are listed in Table 7.

Structure–reactivity relationships are ascertained by employing some *para*-substituted unsaturated acids at four different temperatures and the kinetic observations reveal that electron-releasing groups enhance the reactivity while electron-withdrawing ones reduce the rate. The rate coefficients and activation parameters evaluated from the plots of ln k/T *versus* $1/T$ are listed in Table 8. The rate data are well correlated with a Hammett ρσ relationship ($r = 0.989$; $s = 0.075$) with a reaction constant (ρ) value of –1.98. The kinetic data can be reconciled with the following reaction scheme.

$$\mathrm{Cr^{VI} + H^+ \overset{K_6}{\rightleftharpoons} H_2CrO_4} \tag{12}$$

$$\mathrm{H_2CrO_4 + Oxa \overset{K_7}{\rightleftharpoons} C_5} \tag{13}$$

$$\mathrm{C_5 + S \overset{K_8}{\rightleftharpoons} C_6} \tag{14}$$

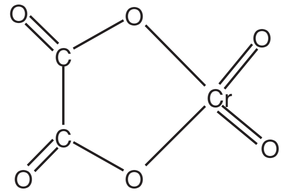
$$\mathrm{C_6 \underset{slow}{\overset{k_9}{\rightleftharpoons}} Cr^{IV}\text{-}Oxa + intermediates} \tag{15}$$

$$\xrightarrow{\text{several steps}} \text{products} \tag{16}$$

The reaction system can be characterised by the rate expression,

$$\frac{-\mathrm{d[Cr^{VI}]}}{\mathrm{d}t} = \frac{k_9K_8K_7K_6[\mathrm{S}][\mathrm{Oxa}]\mathrm{H^+}][\mathrm{Cr^{VI}}]\mathrm{t}}{1+K_6K_7[\mathrm{H^+}]+K_6K_7K_8[\mathrm{S}][\mathrm{Oxa}][\mathrm{H^+}]} \tag{17}$$

The structure of C_5, oxalatochromate(VI) is well established in the literature.[33]



$$\mathrm{Cr^{IV}\text{–}Oxa + Cr^{VI}\text{–}Oxa \longrightarrow 2\,Cr^{V}\text{–}Oxa} \tag{18}$$

$$\mathrm{2Cr^{V}\text{–}Oxa + Ph\text{–}CH{=}CH\text{–}COOH \longrightarrow PhCHO + OHC.COOH + 2Cr^{III}\text{–}Oxa} \tag{19}$$

$$\mathrm{PhCHO \xrightarrow{(O)} PhCOOH} \tag{9}$$

The negative reaction constant value very much implies an electron-deficient transition state. C_6 could be a cyclic complex and the development of positive charge can be envisaged.

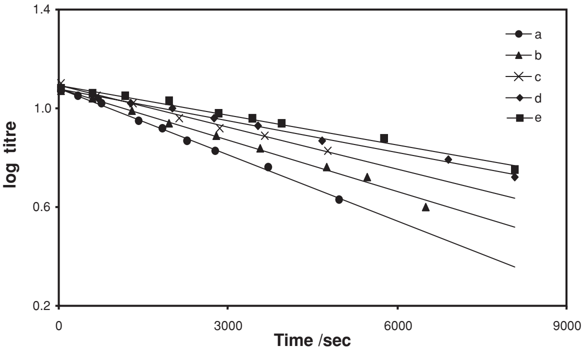


Fig. 5 Catalytic activity of oxalic acid: a, 10^3[Oxa] = 4.0 mol dm^{-3}; b, 10^3[Oxa] = 3.0 mol dm^{-3}; c, 10^3[Oxa] = 2.0 mol dm^{-3}; d, 10^3 [Oxa] = 1.0 mol dm^{-3}; e, 10^3[Oxa] = 0.0 mol dm^{-3}

Table 7 Effect of reactants on the reaction rate at 308 K

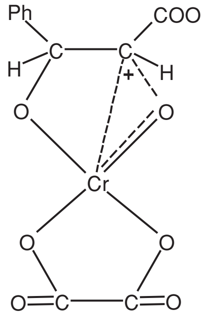
[CA] 10^2 /mol dm^{-3}	[Oxa] 10^3 /mol dm^{-3}	[Cr(VI)] 10^3 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
2.0	4.0	2.0	10.7
4.0	4.0	2.0	21.8
6.0	4.0	2.0	27.4
8.0	4.0	2.0	34.1
10.0	4.0	2.0	37.7
4.0	0.0	2.0	9.3
4.0	1.0	2.0	9.9
4.0	2.0	2.0	13.3
4.0	3.0	2.0	17.6
4.0	4.0	2.0	21.8
4.0	4.0	0.5	20.6
4.0	4.0	1.0	20.9
4.0	4.0	1.5	20.8
4.0	4.0	2.0	21.8

[H$^+$] = 0.32 mol dm^{-3}; AcOH : Water = 50 : 50 (v/v).

Table 8 Rate constants and activation parameters for the oxalic acid catalysed Cr(VI) oxidation of cinnamic acids

Substrate	k_{obs} 10^5 (s^{-1})				$\Delta H^{\neq}$	$-\Delta S^{\neq}$	r	s
	298 K	308 K	318 K	328 K	/kJ mol^{-1}	/J K^{-1} mol^{-1}		
H	9.8	25.5	39.8	86.6	47.9 ± 7.1	158.9 ± 18.2	0.991	0.098
p-CH3	17.7	41.9	71.8	111.3	47.6 ± 5.4	158.6 ± 16.2	0.987	0.153
p-OCH3	48.3	88.3	168.3	255.5	44.2 ± 6.1	162.2 ± 16.4	0.996	0.081
p-Cl	4.2	8.2	15.7	23.2	45.3 ± 6.7	178.8 ± 14.1	0.993	0.103

[Cr(VI)] = 1.0 × 10^{-3} mol dm^{-3}; [S] = 1.0 × 10^{-2} mol dm^{-3}; [Oxa] = 4.0 × 10^{-3} mol dm^{-3}; [H$^+$] = 0.32 mol dm^{-3}; AcOH: H$_2$O = 75:25 (v/v).



This type of transition state has already been suggested in the literature.[2] Activation parameters are close to the values observed for typical reactions involving a termolecular complex.

Chromium(IV) is known to be reduced by oxalic acid. Under the experimental conditions it appears that the unsaturated acids are more reactive toward chromium(IV) than oxalic acid.

Contrasting kinetic behaviours are observed in the cooxidation and catalysed oxidation processes. The oxalic acid catalysed redox process is found to obey a LFER whereas the available literature[2] on oxalic acid involved cooxidation process shows that the reaction species can be characterised by a 'V' shaped Hammett curve. The oxalic acid catalysed reaction was rationalised by a mechanism in which there is a development of electron-deficient benzylic carbon in the transition state. Electron-releasing groups facilitate the rate of conversion while electron-attractors retard the reactivity. In contrast, the reaction proceeds *via* either an electron-deficient or electron-rich transition state in the cooxidation process depending on the nature of the substrate. The catalytic activity of oxalic acid is described by assuming the formation of a termolecular complex and its decomposition in a slow rate-limiting step.

2,2'-Bipyridyl catalysis in the Cr(VI) oxidation of trans-*stilbene*

2,2'-Bipyridyl has the ability to accelerate the chromium(VI) oxidation of unsaturated systems. It could be expected to form a relatively stable complex with chromium(IV). It is believed that the reason for the catalytic activity of bipy depends on its ability to stabilise intermediate chromium valence states, probably chromium(IV), through complex formation.

The reaction exhibits first order dependence each in chromium(VI), substrate and catalyst. The kinetic studies show that the order dependence on acidity is <1. Low dielectric constant of the medium favours this redox process. Temperature dependence studies were carried out between 298 and 328 K. The kinetic data are summarised in Tables 9–11.

$$\mathrm{Cr^{VI} + H^+ \overset{K_6}{\rightleftharpoons} H_2CrO_4} \qquad (12)$$

$$\mathrm{H_2CrO_4 + bipy \overset{K_{10}}{\rightleftharpoons} C_7} \qquad (20)$$

Table 9 Effect of reactants on the reaction rate at 308 K

[Stilbene] 10^3 /mol dm^{-3}	[bipy] 10^4 /mol dm^{-3}	[Cr(VI)] 10^4 /mol dm^{-3}	k_{obs} 10^5 /s^{-1}
2.0	4.0	2.0	5.3
4.0	4.0	2.0	6.4
6.0	4.0	2.0	11.5
8.0	4.0	2.0	17.0
10.0	4.0	2.0	23.2
4.0	0	2.0	4.8
4.0	3.0	2.0	5.7
4.0	4.0	2.0	6.4
4.0	5.0	2.0	8.7
4.0	6.0	2.0	10.7
4.0	7.0	2.0	12.1
4.0	4.0	1.5	6.4
4.0	4.0	2.0	6.4
4.0	4.0	2.5	6.2
4.0	4.0	3.0	6.4

[H$^+$] = 0.032 mol dm^{-3}; AcOH : Water = 80:20 (v/v).

Table 10 Effect of dielectric changes on the oxidation of *trans*-stilbene at 308 K

% AcOH	% H$_2$O	*D*	k_{obs} 10^5 /s^{-1}
70	30	28.3	4.7
75	25	24.7	5.9
80	20	20.9	6.4
85	15	17.3	16.5

[Cr(VI)] = 2.0 × 10^{-4} mol dm^{-3}; [Stilbene] = 4.0 × 10^{-3} mol dm^{-3}; [bipy] = 4.0 × 10^{-4} mol dm^{-3}; [H$^+$] = 0.032 mol dm^{-3}.

$$\mathrm{C_7 + S \xrightarrow[slow]{k_{11}} Cr^{IV}\text{–}bipy + intermediates} \qquad (21)$$

$$\Big\downarrow \text{ several steps}$$

$$\mathrm{Cr^{III}\text{–}bipy + other\ products} \qquad (22)$$

Equilibrium treatment may be applied to deduce the rate expression which can characterise the reaction system.

$$\frac{-\mathrm{d[Cr^{VI}]}}{\mathrm{d}t} = \frac{k_{11}K_{10}k_6[\mathrm{S}][\mathrm{biby}][\mathrm{Cr^{VI}}][\mathrm{H^+}]}{1+K_6[\mathrm{H^+}]} \qquad (23)$$

The major product in this redox process is believed to be methyl 3-hydroxy-2,3-diphenylpropanoate. In the oxidation of olefins by various chromium(VI) complexes, an epoxide has been suspected as the prime intermediate.[34] Hence, in the present investigations, we expect the reaction to proceed *via* an epoxide intermediate. As we have seen earlier, the complex formation is a facile process in a medium of low dielectric constant. Activation parameters are close to the values observed for *trans*-cinnamic acid oxidation revealing the similarity in the nature of transition states in both the reaction systems.

Comparison of oxidation rates of *trans*-cinnamic acid and *trans*-stilbene (Table 12) reveals that, even though the difference is small, a slightly higher reactivity is observed in the case of *trans*-stilbene. This very much suggests that the transition state is well stabilised in the case of *trans*-stilbene. High negative $\Delta S^{\neq}$ values imply a structured transition state.

Table 11 Effect of temperature on the reaction rate in the oxidation of *trans*-stilbene

k_{obs} 10^5 /s^{-1}				$\Delta H^{\neq}$ /kJ mol^{-1}	$-\Delta S^{\neq}$ /J K^{-1} mol^{-1}	*r*	*s*
298 K	308 K	318 K	328 K				
3.6	6.4	12.0	24.5	49.9 ± 8.1	165.6 ± 13.2	0.999	0.049

[Cr(VI)] = 2.0 × 10^{-4} mol dm^{-3}; [Stilbene] = 4.0 × 10^{-3} mol dm^{-3}; [bipy] = 4.0 × 10^{-4} mol dm^{-3}; [H$^+$] = 0.032 mol dm^{-3}; AcOH: H$_2$O = 80:20 (v/v).

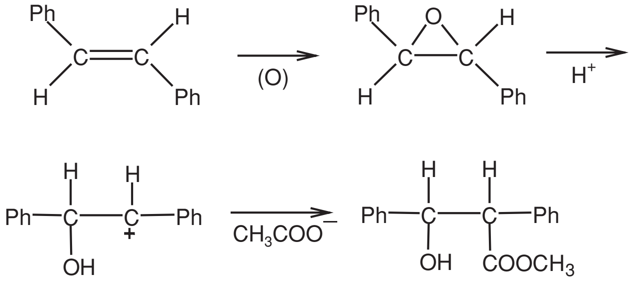


Table 12 Comparison of oxidation rates at 308 K

Substrate	k_{obs} 10^5 /s^{-1}
Stilbene	6.4
CA	4.5

[Cr(VI)] = 2.0×10^{-4} mol dm^{-3}; [bipy] = 4.0×10^{-4} mol dm^{-3}; [Substrate] = 4.0×10^{-3} mol dm^{-3}; [H^+] = 0.032 mol dm^{-3}; AcOH: H_2O = 80:20 (v/v).

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References

1 Sh.O. Badanyan, T.T. Minasyan and S.K. Vardapetyan, *Russ. Chem. Rev.,* 1987, **56(8),** 740.
2 R.T. Sabapathy Mohan, M. Gopalakrishnan and M. Sekar, *Tetrahedron,* 1994, **50,** 10933.
3 R. Vinothini, Catalysed Cr(VI) oxidation of cinnamic acids and methionine, MPhil thesis, Annamalai University, 2001.
4 Subbiah Meenakshisundaram and R. Markkandan, *Trans. Met. Chem.,* 2004, **29,** 308.
5 M.F. Ruasse and J.E. Dubois, *J. Org. Chem.,* 1973, **38,** 493.
6 C.H. Sanjeeva Reddy and E.V. Sundaram, *Tetrahedron,* 1989, **45,** 2109.
7 T.Y. Peng and J. Roček, *J. Am. Chem. Soc.,* 1976, **98,** 1026; 1977, **99,** 7622.
8 C. Srinivasan, S. Rajagopal and A. Chellamani, *J. Chem. Soc. Perkin Trans. 2*, 1990, 1839.
9 P.M. Reddy, V. Jagnnadhan, B. Sethuram and T.N. Rao, *Pol. J. Chem.,* 1982, **56,** 865.
10 F.S. Guziec, Jr. and F.A. Luzzio, *Synthesis,* 1980, 691.
11 J.E. Sarnaski, D. Michos, H.H. Thorp, M. Didiuk, T. Boon, J. Blewitt, G.W. Brudvig and R.H. Crabtree, *Tetrahedron Lett.,* 1991, **32,** 1153.
12 C.F. Wells and D. Fox, *J. Chem. Soc. Dalton Trans,* 1977, 1498; 1977, 1502.
13 J.K. Brown, D. Fox, M.P. Heyward and C.F. Wells, *J. Chem. Soc. Dalton Trans.,* 1979, 735.
14 J.K. Beattie and G.P. Haight, Inorganic Reaction Mechanism, Part-II, ed. J.O. Edwards, J. Wiley, New York, 1972, 93.
15 J. Shorter, *Correlation Analysis of Organic Reactivity*, Research Studies Press, Chap. 3, 1982.
16 G.S. Hammond, C.E. Reeder, F.T. Fang and J.K. Kochi, *J. Am. Chem. Soc.,* 1958, **80,** 563.
17 C.G. Swain and W.P. Langsdorf Jr, *J. Am. Chem. Soc.,* 1951, **73,** 2813.
18 K. Aruna and P. Manikyamba, *Ind. J. Chem.,* 1994, **33A,** 854.
19 P.D. Bartlett and C. Ruchard, *J. Am. Chem. Soc.,* 1960, **82,** 1756.
20 C.A. Bunton, H.J. Foroudian and A. Kumar, *J. Chem. Soc. Perkin Trans. 2,* 1995, 33.
21 S.B. Hanna and S.A. Sarac, *J. Org. Chem.,* 1977, **42,** 2069.
22 G.A. Russel and R.C. Williamson, *J. Am. Chem. Soc.,* 1964, **86,** 2357.
23 R.L. Huang and K.H. Lee, *J. Chem. Soc.,* 1966, 935.
24 V. Baliah and P.V.V. Satyanarayana, *Ind. J. Chem.,* 1978, **16A,** 966.
25 S. Nagarajan and M. Gopalakrishnan, *React. Kinet. Catal. Lett.,* 1993, **51,** 423.
26 M.S. Frank and P.V. Krishna Rao, *Ind. J. Chem.,* 1979, **17A,** 632.
27 K. Karim and M.K. Mahanti, *Pol. J. Chem.,* 1992, **66,** 1471.
28 P. Uma, P. Kanta Rao and M.N. Sastry, *React. Kinet. Catal. Lett.,* 1989, **39,** 255.
29 F. Freeman, Perry, D. McCart and Nira J. Yamachika, *J. Am. Chem. Soc.,* 1970, **92,** 4621 and references cited therein.
30 F.A. Cotton, *Advanced Inorganic Chemistry,* 3rd edn. Wiley Eastern Ltd., New Delhi, 1972, 723–727.
31 N. Venkatasubramanian and S. Sundaram, *J. Inorg. Nucl. Chem.,* 1969, **31,** 1761.
32 G.F. Vandegrift and J. Roček, *J. Am. Chem. Soc.,* 1976, **98** 1371.
33 R.E. Hintze and J. Roček, *J. Am. Chem. Soc.,* 1977, **99,** 132 and references cited therein.
34 N. Miyaura and J.K. Kochi, *J. Am. Chem. Soc.,* 1983, **105,** 2368.