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MECHANISM OF ACID BROMATE OXIDATION OF TRANS MONO-SUBSTITUTED CINNAMIC ACIDS: STRUCTURE REACTIVITY CORRELATION - A NON-LINEAR HAMMETT'S PLOT

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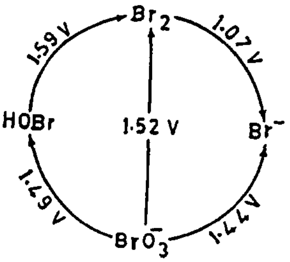
Abstract — Oxidation of cinnamic and trans mono-substituted cinnamic acids with Br(V), unmixed by generated molecular bromine addition, has been studied from the kinetic and mechanistic aspects. Acid bromate, in the presence of mercury(II), oxidises cinnamic acids smoothly and quantitatively to the respective benzaldehydes. Reactions are catalysed by mineral acids and they exhibit first, fractional orders in [Br(V)] and [substrate] respectively. An inverse secondary deuterium kinetic isotope effect characterises the oxidation and reaction rates increase when deuterium replaces either α or β-proton of cinnamic acids. Oxidation rate is not much affected by electron attractors whereas it is susceptible to electron demand at the seat of the reaction. The free energy relationship is characterised by two distinct lines in the Hammett's plot with ρ^+ values of -3.7 and -0.8 for the two limbs. Two alternative mechanistic pathways have been proposed involving (i) a partially and a fully developed benzylic carbonium ion like activated complex for electron attractors and donors respectively in the slow and the rate determining step, or (ii) two discrete centres viz. C_α and C_β passing via C_α^+ and C_β^+ carbonium ion intermediate for electron attractors and donors respectively. Mercury(II) role is only in scavenging bromide ions.

Despite many publications and potential utility of the oxidation of unsaturated compounds with different oxidants, their mechanisms have been less clarified except in a few cases. On the other hand, oxidation of cinnamic acid by permanganate in neutral[1], acidic[1-4] and alkaline media[5] has shown earlier to result in the cleavage of carbon-carbon bond to yield benzaldehyde. However, in basic medium (pH > 12), oxidation of unsaturated acids by the same oxidant, has been reported to yield diol[6].

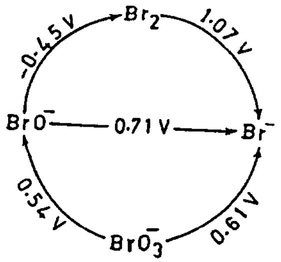
Bromate, Br(V), is also known to be a powerful oxidising agent with redox potentials[7] of 1.44 V in acid medium and 0.61 V in basic medium. The potentials show that Br_2 in basic solutions [Ib] can disproportionate spontaneously to BrO^- and Br^-. However, in acidic solutions [Ia] Br_2 does not disproportionate but infact it accumulates [2] by an auto-catalytic reaction. Therefore in the presence of acid and excess bromide ions, bromate can exclusively act as bromine generator and the resulted bromine can either brominate or oxidise the organic compound under study depending on its nature.

$$BrO_3^- + Br^- + 6\,H^+ \rightleftharpoons 3\,Br_2 + 3\,H_2O; \quad K = 10^{33} \qquad [2]$$

Early literature reveals that olefin-bromate reactions are essentially Br_2 additions liberated by an auto-catalytic reaction [2]. But, the present interest stemmed from a desire to study an oxidation of olefins by Br(V) alone, unmixed by competing/faster addition by liberated bromine. Literature has not recorded any kinetic and mechanistic study of this practically important and useful oxidation in synthetic organic chemistry. Hence the mechanism of the hitherto unreported olefin-bromate reaction is probed and reported with unsaturated compounds in general and cinnamic acids in particular.



In acid medium [Ia]



In basic medium [Ib]

The use of trans-cinnamic acids as substrates offers several distinct advantages. (a) The carboxylic group gives the molecule sufficient solubility in aq-acetic acid solutions. (b) Aromatic ring permits a study of substituent effect on the rates of formation and decomposition of the intermediate bromate ester and (c) the vinyl hydrogens can easily be replaced by deuterium.

EXPERIMENTAL

Most of the unsaturated acids were obtained commercially (AR,BDH/Fluka) and their purity was checked by NMR, IR and Mass spectra. Trans p-chlorocinnamic acid was prepared by heating a mixture of 75 g (0.5 mole) of p-chlorobenzaldehyde with 52 g (0.5 mole) of malonic acid and 2 ml pyridine on a steam bath for 24 hrs, 84 g (82%) of almost pure acid was obtained when the solid was washed twice with methanol and was used after three times of recrystallization from methanol (mp 244-245°C),p-tolualdehyde was used to prepare trans p-methylcinnamic acid in the same way (78% yield) and had the mp 197-198°C after three recrystallizations. Trans cinnamic acid (Loba Chem) was recrystallized three times from a chloroform - hexane mixture and had the mp 132-133°C. Trans cinnamic acid α-d (mp 135°) and trans cinnamic acid β-d (mp 136°) were obtained from isotope Inc (USA) and checked for purity by NMR and IR. All the inorganic chemicals used were of AR grade (BDH/Fluka/Merck). Acetic acid (AR, BDH) was used after refluxing over CrO_3. Solutions of cinnamic acids were prepared in aq-acetic acid mixture.

Kinetic Measurements — Under subdued light and nitrogen atmosphere the solutions were thermostated for an hour at a desired temperature. Temperature equilibriated solutions of the substrate were mixed with requisite amounts of other reagents. The course of the reaction was followed iodometrically for over three-half lives. However, before adopting iodometric method, it was ensured that the presence of cinnamic acids in the quenching solution of KI did not change the bromate titre value.

The reactions were carried out under pseudo first-order conditions using 10-fold excess of $[\text{substrate}]_0$ over $[\text{Br(V)}]_0$. The pseudo first-order rate constants (k') with respect to Br(V) were computed from the linear plots ($r > 0.99$) of log $[\text{bromate}]_t$ against time. The reproducibility of k' was within ± 5% and the mean values are reported.

Stoichiometry — Attempts made to determine the stoichiometry of the reaction, under the conditions $[\text{Br(V)}]_0 < [\text{substrate}]_0$, in the presence of an acid and mercury(II), revealed that three moles of substrate consumed two moles of bromate giving benzaldehyde and

$$3\ \text{X-C}_6\text{H}_5\text{-CH} = \text{CHCOOH} + 2\ \text{BrO}_3^- \rightleftharpoons 3\ \text{X-C}_6\text{H}_5\text{CHO} + 3\ \text{OHC-COOH} + 2\ \text{Br}^- \quad [3]$$

$$3\ \text{X-C}_6\text{H}_5\text{-CH} = \text{CHCOOH} + 5\ \text{BrO}_3^- \rightleftharpoons 3\ \text{X-C}_6\text{H}_5\text{COOH} + 6\ \text{CO}_2 + 5\ \text{Br}^- + 3\ \text{H}_2\text{O} \quad [4]$$

glyoxylic acid **[3]**. However, the volumetric analysis of the same runs with an excess of $[\text{Br(V)}]_0$ gave the substrate to oxidant mole ratio as in eq **[4]**. The same stoichiometries were observed with all the substituted cinnamic acids (except nitro compounds where benzoic acid (40-60%,yield) was also obtained under kinetic conditions).

Product Analysis — Using approximately the same conditions as in the kinetic determinations, a solution of the reaction mixture was kept under nitrogen (oxygen free) atmosphere and subdued light for 60 hrs to ensure completion of the reaction. Lateron it 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 (100:0 to 70:30 v/v) of hexane and chloroform, concentrated and then identified. An infrared spectrum exhibited a carbonyl band at 1700 cm^{-1} and certain other bands below 900 cm^{-1} characteristic of benzaldehyde. The IR spectrum of the other product sample gave two sharp bands at 1680 and 1660 cm^{-1} indicating the presence of two carbonyl groups. Bands at 3620 cm^{-1} (O-H stretching), 1360 cm^{-1} (C-O stretching) and 1150 cm^{-1} (O-H bending) are characteristic of glyoxylic acid. Benzaldehyde (~75%, yield), and glyoxylic acid (20-30%, yield) the products of cinnamic acid were also inferred by their 2,4-DNP derivatives (mp 241 and 125±1 $^\circ$C respectively). Chloro, bromo, methyl and methoxy substituted cinnamic acids also resulted in their respective benzaldehydes (60-80%, yield). The obtained 2,4-DNP derivatives of the products were checked and identified by CO-TLC, mixed melting point and super imposable IR with authentic samples obtained from the condensation of the corresponding benzaldehydes with 2,4-DNP.

The only product obtained was benzoic acid (the chloroform layer was dried over anhydrous $MgSO_4$ and evaporated to dryness, leaving a white solid residue which was found to be benzoic acid, mp 121°C) when bromate was in stoichiometric excess. Thus it appears that benzaldehyde was the initial product of cinnamic acid which must have undergone further oxidation to benzoic acid in the presence of excess bromate. Similar experiments with substituted cinnamic acids yielded respective benzoic acids in 85-90% yields after recrystallization. The white precipitate implies the formation of CO_2, when the gas evolved from the reaction mixture was passed through an aq-barium(II) solution. In all the cases $[Br^-]$ was estimated as usual with $AgNO_3$ solution.

RESULTS

Effect of concentrations - In the presence of mercury(II), a bromide ion scavenger, the oxidation of cinnamic and trans mono-substituted cinnamic acids by bromate in acid medium proceeds smoothly and is found to be clearly of first-order both with respect to time (as evidenced by good fits of log $[BrO_3^-]_t$ versus time plots) and concentration as shown by the time order rate coefficient (**k'**) which is independent of $[\text{bromate}]_0$, Table 1. Dependence of $\mathbf{k_{obs}}$ values on the $[\text{substrate}]_0$ is consistent with the Michaelis-Menten's kinetics in each case (Fig.1). $\mathbf{k_{obs}}$ values also increased with an increase in [acid] and follow Hammett's acidity ($-\mathbf{H_0}$) function (Table 2). A change in the concentration of added salts like $NaClO_4$ and $NaHSO_4$ had a marginal effect on the reaction rate.

Effect of temperature - The rate data on temperature effect in aq-acetic acid media have been studied in the range 278 to 333 K and the activation parameters calculated from the least-square slopes of log **k'** versus 1/T are presented in Table 3. The average error limits in the values of $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ (at 313 K) are ± 3 kJ/mole, ±5 J/K mole and ±4 kJ/mole respectively.

Effect of solvent polarity - The reaction rate is enhanced by increasing the volume percentage of acetic acid in $HOAc-H_2O$ mixture (Table 4).

Kinetic isotope effect - Table 5 shows α and β secondary deuterium kinetic isotope effect for the acid bromate oxidation of trans cinnamic α-d and β-d acids.

Structural effect - Structural modifications in the phenyl moiety result in varied reactivity; while electron releasing substituents (donors) acelerate the rate of oxidation to a very large extent, the rate ratardation by electron withdrawing substituents (attractors) though perceptible is not very much. The free energy relationship is characterised by two distinct lines in the Hammett's plot (Fig.2) with ρ^+ values of -3.7 and -0.8 for the two limbs.

Table 1. Effect of [bromate]$_0$ on the rate of reaction at 40 ± 0.1°C

Cinnamic acid(CA)	$10^5 \times {}^a k'/s^{-1}$ at $10^4 \times [Br(V)]_0$ / M					
	2.5	5.0	10.0	15.0	20.0	25.0
-H	21.13 (11.14)	20.88 (10.95)	20.89 (10.95)	20.88 (10.92)	20.82 (10.96)	20.87 (10.96)
	20.36^p (10.77)^p	20.30 (10.75)	20.32 (10.75)	20.37 (10.72)	20.30 (10.74)	20.29 (10.75)
p-NO_2	3.85	3.84	3.84	3.85	3.82	3.83
m-NO_2	5.05	5.02	5.03	5.03	5.00	5.06
o-NO_2	4.00	3.96	3.98	3.96	3.98	3.98
p-Cl	14.22	14.20	14.20	14.24	14.25	14.20
m-Cl	8.23	8.22	8.23	8.23	8.20	8.23
o-Cl	7.22	7.20	7.21	7.23	7.23	7.22
p-Br	12.60	12.52	12.59	12.60	12.58	12.56
m-CH_3	25.18	25.13	25.13	25.10	25.14	25.15
p-CH_3*	10.44	10.47	10.47	10.41	10.42	10.47
o-$CH*_3$	5.28	5.25	5.25	5.27	5.24	5.25
o-OCH_3^*	165.83	165.79	165.70	166.00	164.80	166.00

(a) Rate constants are accurate to ± 5%.(*) Reactions are carried out at 10°C.
Values in parentheses are obtained in 1:1 HOAc-H_2O and molar mineral acid solutions.
(p) Values obtained in perchloric acid solutions.
[Substrate] = 0.01M; [H_2SO_4] = 0.5M; [$Hg(OAc)_2$] = 0.005M; H_2O-HOAc = 20-80%(v/v)

Table 2. Effect of [acid] on the rate ($10^5 \times k's^{-1}$) of acid bromate oxidation of Trans Mono-Substituted Cinnamic acids.

[H_2SO_4] /M	$-H^b$	p-Cl	m-Cl	p-NO_2	m-NO_2	p-CH_3*
0.25	1.17 (1.05)	7.08	3.95	1.89	2.51	5.01
0.50	3.11 (2.89)	14.20	8.22	3.84	5.03	10.47
0.75	5.72 (5.11)	23.99	12.87	5.62	7.88	17.35
1.00	10.96 (10.75)	35.48	19.98	8.91	12.59	26.91
1.50	25.44 (24.32)	70.79	39.81	17.78	25.12	56.23
2.00	54.22 (48.00)	144.55	85.11	35.48	48.96	120.89
2.50	155.50	234.03	158.49	63.09	89.12	257.33
3.00	286.82	-	314.73	112.20	158.48	-

[Substrate]=0.01M; [Br(V)]=0.001M; [$Hg(OAC)_2$]=0.005M; temp=40°C; H_2O-HOAc=20-80%(v/v);
(b) at 1:1 HOAc-H_2O; * at 10°C. Values in parentheses are obtained in perchloric acid media.

Table 3. Temperature effect and Thermodynamic parameters of acid bromate oxidation of Trans Mono-Substituted Cinnamic acids

Cinnamic acid	k x $10^5 (s^{-1})$ at ° C 30	40	45	50	60	$\Delta H^\#$ kJ/mole	$\Delta S^\#$ J/K mole	$\Delta G^\#$ kJ/mole
-H	7.94	20.80	31.41	52.78	120.22	75.89	73.5	98.89
p-NO_2	1.32	3.84	6.31	11.19	26.80	85.46	57.0	103.31
m-NO_2	1.99	5.03	7.95	13.80	28.84	72.07	97.5	102.59
o-NO_2	1.51	3.98	6.31	10.96	25.58	77.81	72.8	100.61
p-Cl	6.00	14.20	23.98	40.12	91.20	77.62	71.2	100.00
m-Cl	3.19	8.22	12.58	19.20	40.38	70.02	90.4	101.32
o-Cl	2.52	7.20	-	18.33	44.67	81.64	64.0	101.67
p-Br	4.89	12.59	19.95	33.14	85.17	78.77	68.4	99.19
m-CH_3	10.02	25.12	39.82	67.61	-	77.81	57.6	95.84
	5	10	15	20	40			
o-CH_3	3.50	5.25	12.79	24.23	83.17	64.41	98.7	95.30
p-CH_3	6.30	10.47	17.80	31.60	199.53	70.15	73.0	93.08
p-OCH_3	870 630a	1258	1995*	-	10220*	40.06	136.6	82.76
o-CH_3O	125.9	165.7	239.9	338.3	1096*	40.51	153.6	88.58

Thermodynamic parameters are calculated at 40°C (*) Values obtained on extrapolation. [Br(V)] = 0.001 M; [Substrate] = 0.01 M ; $[H_2SO_4]$ = 0.5 M; HOAc-H_2O = 80-20% (v/v); $[Hg(OAc)_2]$ = 0.005 M. (a) Rate constant obtained at 0°C.

Table 4. Rate dependence on dielectric constant of the medium

Cinnamic acid	k' x 10^5 (s^{-1}) at HOAc-H_2O% (v/v) 50-50 (39.76)a	60-40 (33.08)	70-30 (26.38)	80-20 (20.19)	90-10 (13.56)
-H	7.41	9.55	12.98	20.89	70.79
p-NO_2		1.58	2.23	3.84	10.74
p-Cl		5.37	7.59	14.20	39.81
m-Cl		-	2.95	8.22	15.11
p-CH_3^*		3.58	4.47	10.47	31.62

(a) Dielectric constant of the medium (calculated by an approximate validity method at 40°C). Experimental conditions as in Table 1 & 2.

DISCUSSION

In acid solutions bromine, resulted from an auto-catalytic reaction [2], reacts rapidly and irreversibly with unsaturated acids. Spectroscopic data and product analysis also confirmed the same.

Under pseudo first-order conditions, the plot of log $[BrO_3^-]$ against time gives two intersecting lines (Fig.3), supporting two successive reactions, an initial slow reaction followed by a fast reaction, which are attributed to Br(V) oxidation and molecular bromine addition respectively. This is proved by three independent ways. (i) Under similar conditions the observed rate constants (k', s^{-1}) of Br_2 addition of these cinnamic acids are very close to the rate constants of the second part of the bromate oxidation. (ii) Initial KBr addition completely suppressed the first part of the reaction, and the reaction followed a simple first-order kinetics right from the beginning. The rate constants were nearly the same as those obtained either for the second stage of the reaction or for bromine addition under identical conditions [for example, for the oxidation of cinnamic acid at 30°C, 1.0 M $HClO_4$ and 1:1 $HOAc-H_2O$; $k(s^{-1})$ for Br_2 addition = 10.82×10^{-3}; for Br(V) oxidation in the presence of 0.005 M KBr = 10.68×10^{-3}; for the second part of bromate oxidation = 10.03×10^{-3}]. (iii) When elemental bromine is scrubbed from the reaction mixture by a stream of inert gas, a simple first-order plot is observed without any break upto 80% completion of the reaction, $k'(s^{-1})$ is very close to that of the first of the bromate oxidation.

By the initial addition of mercury (II), a bromo complex-forming metal ion, Br_2 evolution and its subsequent reaction were suppressed leaving only this slower first part from the beginning to over three half-lives. In the presence of mercuric acetate, Br^- ions formed in the bromate – cinnamic acid(s) reaction, react with mercury(II) forming stable mercury(II)-bromocomplexes [5-8][8,9]. Since bromide ions bound in the complex donot react with bromate, bromide ions accumulate in the presence of mercury(II)[9].

$$Hg^{2+} + Br^- \rightleftharpoons HgBr^+ \quad ; \quad K_5 = 2.5 \times 10^8 \ M^{-1} \quad [5]$$

$$HgBr^+ + Br^- \rightleftharpoons HgBr_2 \quad ; \quad K_6 = 3.81 \times 10^8 \ M^{-1} \quad [6]$$

$$HgBr_2 + Br^- \rightleftharpoons HgBr_3^- \quad ; \quad K_7 = 5.75 \times 10^2 \ M^{-1} \quad [7]$$

$$HgBr_3^- + Br^- \rightleftharpoons HgBr_4^{2-} \quad ; \quad K_8 = 3.10 \times 10^2 \ M^{-1} \quad [8]$$

Before further discussion, it is necessary to clarify that in the present study of cinnamic acid(s)-bromate system no free radicals were obtained (with and without Hg^{II}) as is evidenced in Hg(II) oxidations[10] and the initial rates were similar even in the presence and absence of mercuric acetate. The above considerations confirm only the complex forming ability of Hg(II) with Br^- ion in this reaction. Different concentrations of added $Hg(OAc)_2$ over a ten-fold range did not effect the rate constant (Fig.3). However, concentrations below 0.001 M Hg(II) are not sufficiently high to keep back all the Br^- ions produced, with the result that Br_2 evolution sets in slowly. Because of this complexity, the reactions were carried out with an optimum mercuric acetate of 0.005 M. The reported rate constants, therefore stand for pure bromate oxidation.

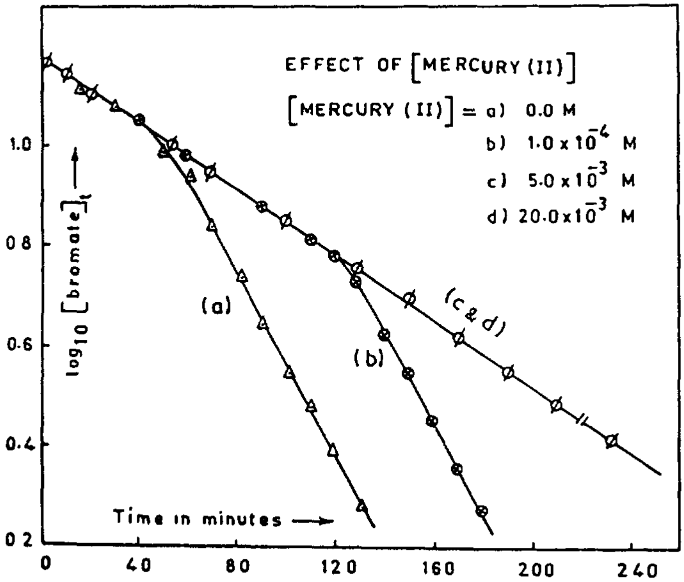


Fig.3 Effect of [Mercury(II)] on the rate of acid bromate -cinnamic acid reaction at 30° C.

In acid solution of bromate the reactive species are likely to be BrO_3^- and protonated bromate [$HBrO_3$ and/or $H_2^+BrO_3$ (BrO_2^+)], hence the oxidation in the reaction may be a reaction between olefinic acid and one of the oxidant species. The effect of solvent polarity and the rate acceleration with an increase in [acid], mitigate the chances of BrO_3^- to be the reactive species. Amis et al[11] proposed BrO_2^+ as the oxidising species, shown as: $BrO_3^- + 2H^+ \rightleftharpoons BrO_2^+ + H_2O$. Anbar and Guttmann[12], Wright and Barton[13] on the other hand, suggested that in moderately strong acid solutions $H_2^+XO_3$ is the existing form of halate ion and in case of bromate $H_2^+BrO_3$ is the existing form. Beck and co-workers[14] and the authors[15], however, have shown that both $HBrO_3$ and $H_2^+BrO_3$ are the existing forms [9,10] of bromate in moderately strong acid solutions.

$$BrO_3^- + H^+ \overset{Kp1}{\rightleftharpoons} HBrO_3 \qquad [9]$$

$$HBrO_3 + H^+ \overset{Kp2}{\rightleftharpoons} H_2^+BrO_3 \qquad [10]$$

Cinnamic acids easily undergo acid bromate oxidation and result in identifiable products whereas the analogous saturated carboxylic acids were not at all oxidised. This indicates the active participation of the ethylenic bond in the oxidation and the oxidant attack at the double bond.

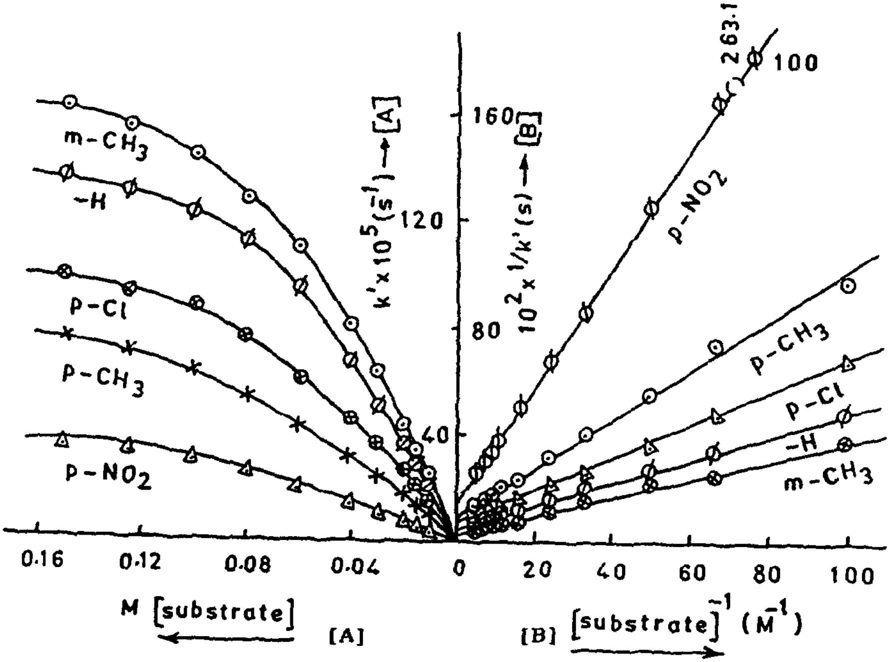


Fig.1 [A] Rate dependence on substrate concentration.
[B] Representative Michaelis-Menten plots and kinetic evidence for complex formation
Experimental conditions are as in Table 1 & 2.

The non-linear increase in k_{obs} towards a limiting value (Fig.1) at high [substrate], a definite intercept in the Michaelis-Menten's plot provides a kinetic evidence for the formation of an intermediate-complex prior to the rate-determining step(intermediate complex could not be isolated). Further UV spectra of the reaction mixture of cinnamic and substituted cinnamic acids at 275 nm, compared to the spectrum of pure compounds is also consistent with a complex formation. The results of deuterium substitution are also entirely consistent witha mechanism in which an ester is the intermediate in the bromate oxidation of cinnamic acids. An increase in rate when vinyl hydrogens are replaced by deuterium, indicates that the initial step of the reaction involves a change in hybri-

Table 5. Kinetic isotope effect

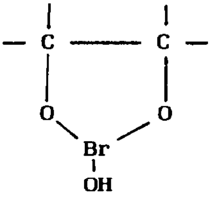
Substrate	Rate constant(s^{-1})
Cinnamic acid α -H	1.119×10^{-4}
Cinnamic acid β -d	1.419×10^{-4}
Cinnamic acid α -d	1.418×10^{-4}

dization of the α and β- carbon from sp^2 to sp^3 (ref.16) and the intermediate is symmetrical with respect to the extent of rehybridization of both the carbons. If attack had taken place at only one of the carbons before transition state is achieved, it is expected to produce an inverse isotope effect only at that carbon. For example in CrO_2Cl_2 oxidation of styrene, only β-carbon isotopic effect was exhibited[17] which suggested that the rate determining reaction produced a carbonium ion (β) where α-carbon remained sp^2. On the other hand, the identical effects observed in the oxidation of cinnamic acid α-d and cinnamic acid β-d by acid bromate (Table 5) are more consistent with the formation of symmetrical complex.

The kinetic and spectroscopic data are not consistent with the formation of the charge-transfer complex or the π-complex.

The other possibility, which also explains the isotopic effect, is the formation of a diester but, this intermediate is eliminated on the basis of bromate dependence which indicates that the transition state of the reaction involves only single bromate molecule.

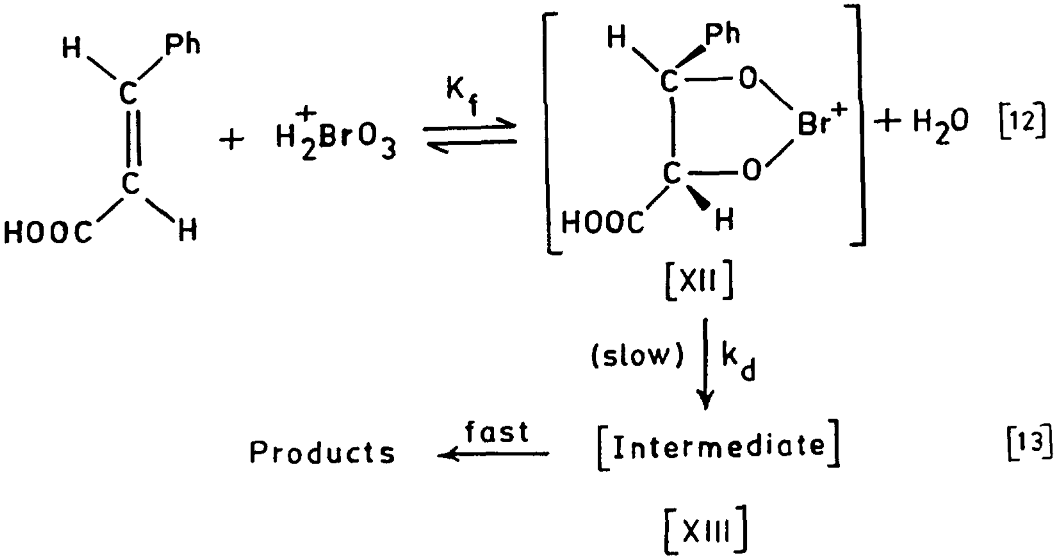
Possibly the intermediate of a concerted cis 1,3-cyclo addition of $HBrO_3$ to the carbon-carbon double bond of olefinic acid could be represented by [**XI**]. However,the intermediate complex for the formation of the bromate-cinnamic acid cannot have a very close resemblance to [**XI**] since, the rate of oxidation is increased by electron releasing substituents (donors) and decreased by electron withdrawing substituents (attractors). Wiberg and Geer[6] have shown that permanganate oxidation of substituted cinnamic acids proceeds via cis-cyclo addition mechanism where the ρ value is close to zero. Furthermore, 1,3-dipolar cyclo addition reactions are generally characterised by low positive ρ values[18] ($\sim$0.5). Consequently the magnitude of the observed ρ^+ values (-3.7 and-0.8) makes [**XI**] as unreasonable intermediate complex for the bromate oxidation of unsaturated acids.



[XI]

As expected for an electrophilic addition the oxidation rate of cinnamic acids is increased by electron-donors. Therefore it is assumed that the reaction is between $H_2^+BrO_3$ and cinnamic acid molecule, since $H_2^+BrO_3$ is more electrophilic than $HBrO_3$.

Consistent with the above data, the following mechanism is proposed. There is no evidence for the protonation of cinnamic acids in moderate mineral acid solutions[19,20].



Cinnamic acids dissociate slightly and it is probable that acid bromate in the medium of $H_2SO_4/HClO_4$ reacts prevailingly with the undissociated molecule. Therefore the formation of bromate ester is visualised [12] as occuring through an electrophilic attack of $H_2^+BrO_3$ at the ethylenic bond of the unprotonated and undissociated cinnamic acid.

If the equilibrium concentrations of ester intemediate is invoked the proposed mechanism [12,13] leads to the rate expression.

$$\text{Rate} = -\frac{d[Br(V)]_T}{dt} = -\frac{d[\text{complex}]_{XII}}{dt}$$

$$= k_d\ [\text{complex}]_{XII}$$

$$= K_f k_d\ [\text{substrate}]\ [H_2^+BrO_3]$$

$$= K_{p1}\ K_{p2} K_f k_d [\text{substrate}][H^+]^2[Br\bar{O}_3] \qquad \dots\ 14$$

But bromate is present in complexed and uncomplexed form. Hence, the total bromate concentration is given by

$$[Br(V)]_T = [BrO_3^-] + [HBrO_3] + [H_2^+BrO_3] + [\text{complex}]_{XII}$$

$$= [BrO_3^-]+K_{p1}[H^+][BrO_3^-]+K_{p1}K_{p2}[H^+]^2[BrO_3^-]+K_{p1}K_{p2}[\text{Sub}][H^+]^2[BrO_3^-]\ K_f$$

$$= [BrO_3^-]\ (\ 1+K_{p1}[H^+]+K_{p1}K_{p2}[H^+]^2+K_{p1}K_{p2}K_f[\text{sub}][H^+]^2\ )$$

Substituting $[BrO_3^-]$ value in the rate equation [**14**].

$$\text{Rate} = -\frac{d[Br(V)]_T}{dt} = \frac{K_{p1}K_{p2}K_f k_d[\text{Substrate}][H^+]^2\ [Br(V)]_T}{1+K_{p1}[H^+]+K_{p1}K_{p2}[H^+]^2+K_{p1}K_{p2}K_f[\text{Sub}][H^+]^2} \qquad \ldots [15]$$

The mechanism is supported by the observed rate law, first order in [Br(V)] and fractional order in [substrate] and the kinetic isotopic effet. This is further corro borated by the solvent influence on the reaction rate. The intermediate ester is less polar than the reactants due to dispersal of charge, hence decreasing polarity of the solvent is expected to stabilise the bromate ester-intermediate inpreference to the reactants thereby enhancing the rate. Once again fact is in accord with prediction (Table 4).

Dividing the rate with $[Br(V)]_T$

$$\frac{\text{Rate}}{[Br(V)]_T} = k' = \frac{K_{p1}K_{p2}K_f k_d\ [\text{substrate}]\ [H^+]^2}{1+K_{p1}[H^+] + K_{p1}K_{p2}[H^+]^2 + K_{p1}K_{p2}K_f[\text{sub}][H^+]^2} \qquad \ldots [16]$$

Taking reciprocal and rearranging eq [**16**] we get:

$$\frac{1}{k'} = \frac{1}{k_d K_f K_{p2}[H^+]\ (1+K_{p1}[H_p^+]\ )\ [\text{substrate}]} + \frac{1}{k_d} \qquad \ldots [17]$$

Where **Kp1** and **Kp2** are the first and second protonation constants of bromate and are 0.51 $dm^3\ mol^{-1}$ and 0.209 $dm^6 mol^{-2}$ respectively at 40°C (ref.15). At constant (molar) acid if **Kp1** and **Kp2** are substituted, eq[**17**] can be reduced to eq[**18**].

$$\frac{1}{k'} = \frac{1}{0.315\ k_d K_f\ [\text{substrate}]} + \frac{1}{k_d} \qquad \ldots [18]$$

According to eq[**18**] 1/k' against 1/[substrate] should be linear with a definite intercept and this is found to be the case. It is also evident from eq[**18**] that, from slope intercept data, K_f and k_d, formation and decomposition constants of the intermediate complex respectively can be calculated.

Structural effects

In the hope that the effect of substituent might reveal something about the nature of the intermediate complex and its mode of decomposition, the oxidation of substituted cinnamic acids were studied. It is seen that structural modifications in the phenyl moiety result in varied reactivity; while electron donors accelerate the oxidation rate to a very large extent, the rate retardation by electron attractors though perceptible is not very high. For instance, the acceleration by the p-methoxy substituent is a factor

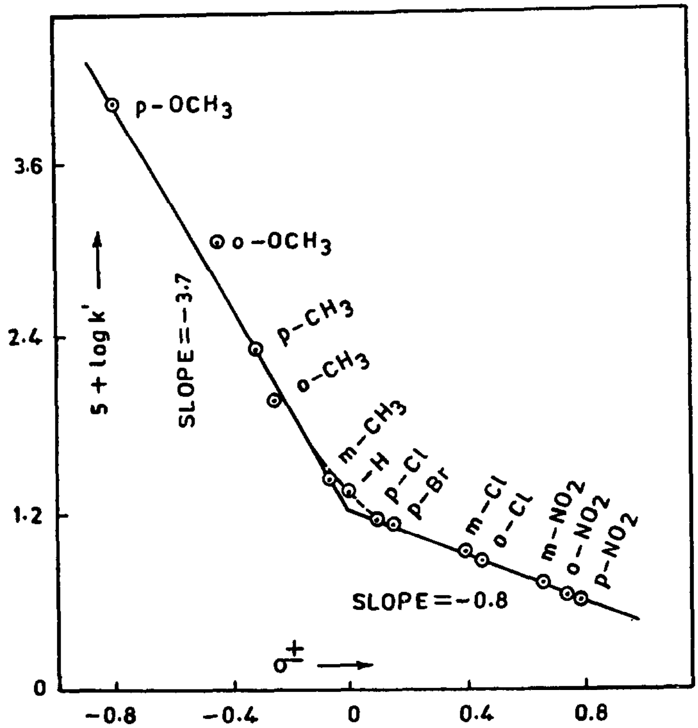


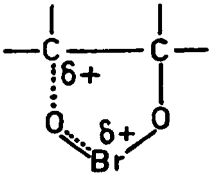
Fig.2 Structure - Reactivity relationship for the acid bromate oxidation of Trans-Mono-Substituted Cinnamic acids. Experimental conditions are as in Table 4.

by ~2800, and the retardation by the p-NO_2 group, whose absolute value of σ^+ equals to that of p-methoxy, is only 30. Thus no linear relationship of the type log $k/k_0 = \rho\sigma$ exists, neither with Brown's σ^+ nor with Hammett's σ constants. The Hammett's plot shows two distinct lines, where each has a good correlation between the substituent constant and the log k', particularly when Brown's constant[21] is used for electron donors: of these one has a much large ρ^+ of -3.7 and the other, a relatively low $\rho^+$of-0.8 at 40°C(Fig.2). Such a curve is obtained at all temperatures studied and it remains unchanged in shape even when log k' is correlated with either σ^- or σ instead of σ^+. Hence the deviation from linearity in Hammett's plot is not due to change in σ values.

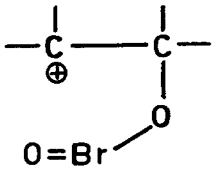
The break in the Hammett's plot may be due to any of the following factors. (i) A change in the rate determining step with change in the nature of substituent. (ii) A change in the reaction mechanism when one passes from electron donors to electron attractors and/or (iii) a change in the nature of the transition state.

The break in the Hammett's plot cannot be attributed to the change in the rate-determining step since, the Michaelis-Menten's plot with all the substrates does yield an intercept (Fig.1) and no evidence for free radicals was obtained for electron donors and electron attractors. The observed break in the log k versus σ^+ plot may be due to a change in the reaction mechanism/nature of the transition state.

The foregoing proposal would accommodate the experimental observations if one assumes a symmetrical complex formation by an interaction of the substrate and $H_2^+BrO_3$ is the fast step and its subsequent breakdown is the slow step. Formation of carbonium ion in the latter step would be governed by the presence or absence of electron donors and the concentration of the cation will be related directly to the nature of such a substituent. Whereas, electron attractors in meta or para positions would not facilitate the formation of the fully developed benzylic carbonium ion and would lead to a small ρ^+ value.



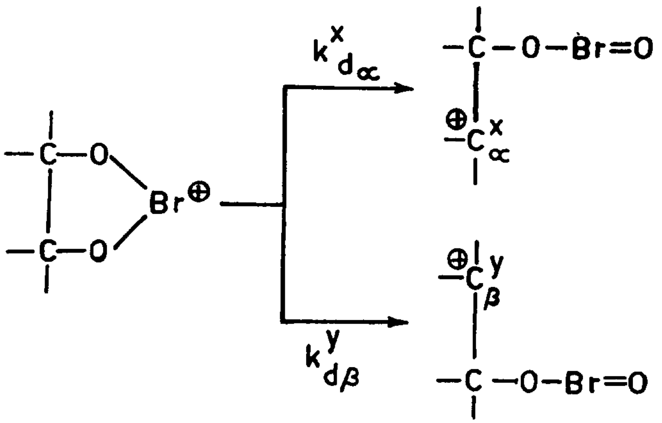
[XIX]



[XX]

ρ values larger than -3.0 generally suggest a fairly large degree of carbonium ion character in the activated complex. Consequently the partial, the partially bridged resonance stabilized five membered activated complex [XIX] is entirely compatible with the kinetic data for cinnamic acids with electron attractors. On the other hand, ρ^+ value of more than -3.0 for the electron donors supports the reaction involving a fairly large degree of carbonium ion character in the activated complex, the relatively low ρ^+ value of -0.8 (for electron attractors) mitigates against a fully developed positive charge on the benzylic carbon atom which would resemble [XIX]. Therefore it is assumed that cinnamic acids with electron attractors pass through the activated complex like [XIX] and with electron donors through an activated complex of [XX]. A small value of ρ would be expected for the formation of [XIX] in the slow step.

An alternative proposal also accommodating the observed results is the indication of a considerable magnitude of carbonium ion character in the transition state by the negative reaction constant. The rate-determining step is the transformation of the symmetrical complex into an ionic intermediate by C-O bond rupture. Then there exist, two modes of dissociation, [XXI] and [XXII], of the symmetrical complex, leading to two discrete intermediates.



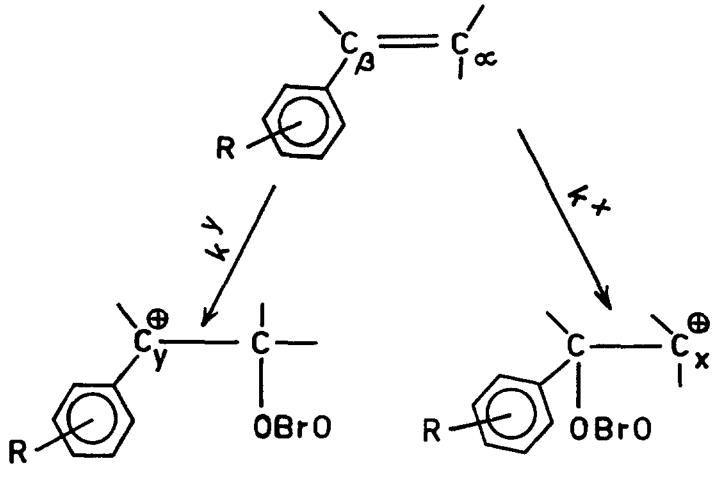
[XXI]

[XXII]

For the structural effects interpretation, the simplified scheme is sufficient if the rate-determining step is not reversible.

For a reaction at two independent centers, the measured rate constant is the sum of two partial rate constants k^x and k^y (k^x/k^y is the rate constant of the C_x/C_y path leading to the carbonium ion C_x^+/C_y^+). It is assumed that each partial rate constant obeys the Hammett's equation. Then, the effect of substituent (R), which may be directly conjugated to the incipient carbonium ion **[XXIII]**, is expressed as $\rho_\beta\sigma^{+}$. The effect of substituent (R) on **[XXIV]**, transmitted by COBrO will be given by $\rho_\alpha\sigma$. The reaction constants ρ_β represents the effect of the substituent on the ring in the α position with respect to the charged centre i.e. the C_y atom in case of substituted cinnamic acids, and ρ_α for substituents in the α position. For the C_y path the proper substituent constant is the Brown's σ^+. While for C_x path, the substituent constant is the Hammett's σ ($\sigma \simeq \sigma^+$ for electron withdrawing groups). In the latter case, the substituted ring is insulated from the carbonium ion center by the COBrO group, hindering the transmission of the resonance effects, resulting in a low vaue of ρ . In the same way, it can be assumed that ρ_β is greater than ρ_α since the substituents are nearer to the ionic center in the intermediate [**XXIII**] than in the intermediate [**XXIV**].

In case where $k^x \gg k^y$ or $k^y \gg k^x$, the reaction passes through a unique transition state since the other one is strongly disfavoured, but, when k^x and k^y are in the same range the two transition states co-exist and there is not a single transition state whose charge would be distributed between the carbon centers. This model is some what similar to the addition reactions[22].

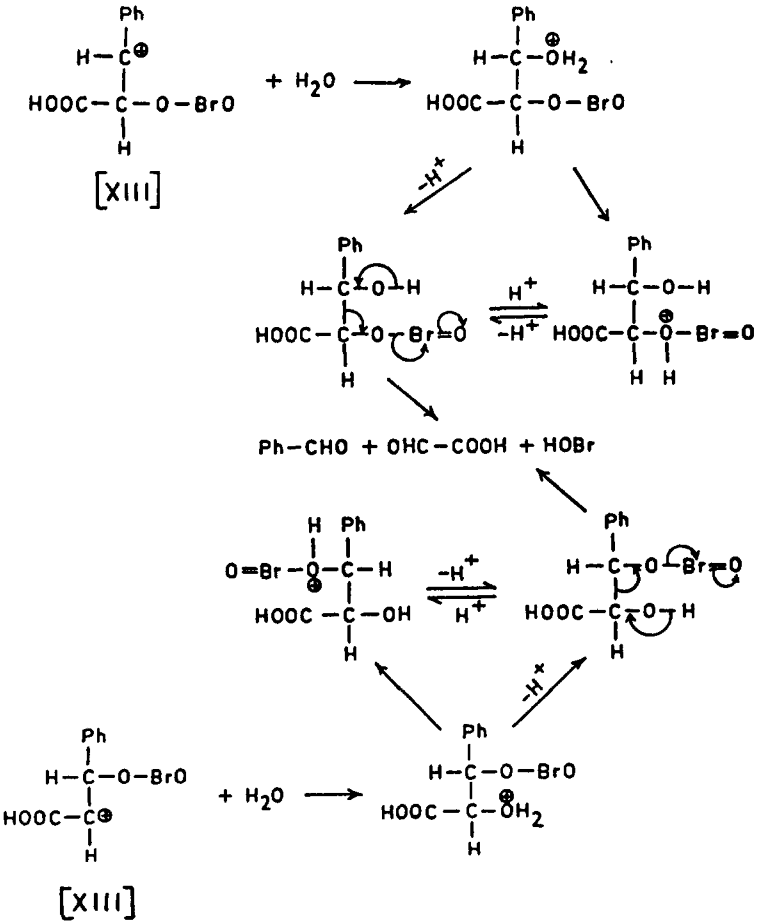


[XXIII] [XXIV]

The formed carbonium ion, irrespective of the way in which it is formed, reacts with water molecule and finally gives cleavage products as is assumed in scheme-I. When attempts were made to identify the intermediates by quenching the reaction with an excess of sodium arsenite solution, the expected diol was not detected. On the other-hand benzaldehyde(s) was major product of cinnamic acid(s) oxidation.

Benzaldehydes were identified and measured quantitatively (~60-80% yield). It is worth to mention that the oxidation rate of benzaldehyde, and methyl, methoxy and chloro-substituted benzaldehydes is comparatively less than the respective cinnamic acids, and hence a major yield of benzaldehyde. But, in the case of nitro substituted benzaldehydes the oxidation rate was a bit faster than that of the respective cinnamic acids, hence, the formed benzaldehyde was further oxidised to benzoic acid and it was the major product (~60% yield). It was also observed that benzaldehydes with electron donors had a lower rate while it was reverse for those with electron attractors. The order of reactivity among the substituted benzaldehydes was : p-NO_2 > m-NO_2 > o-NO_2 > m-Cl > p-Cl > H > m-CH_3 > p-CH_3 > p-OCH_3 and a linear Hammett's plot was obtained with a slope of +0.86.

Four different test reactions for glyoxylic acid (with 2,7-dihydroxynaphthalene, pyrogallol carboxylic acid, phenylhydrazine and β,β'-dinaphthol) gave strongly positive results whereas those for oxalic acid were negative or weakly positive.



Scheme -I

Hypobromous acid, HOBr, is a two equivalent oxidant strong enough to consume many organic substrates, but is a relatively weak one equivalent oxidant. One equivalent reduction of HOBr, produces a bromine atom which easily oxidises the substrates or undergoes addition to the ethylenic bond. Therefore, HOBr can behave both as an oxidant and as a brominating agent.

In the presence of mercury(II), a bromide ion scavenger, there were no free radicals and no evidence for bromo products. Therefore it is assumed that HOBr acts as an oxidising agent only. HOBr thus formed (**scheme-I**) further involves in oxidation either with the substrate or with intermediate and is finally converted to Br^-. Since Br^- ion can react with the unreacted bromate to form molecular bromine, initial addition of bromo complex-forming-metal ion like Hg(II) is justified.

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