KINETICS AND MECHANISM OF OXIDATION OF SOME UNSATURATED ACIDS BY BENZYLTRIETHYLAMMONIUM CHLOROCHROMATE

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ABSTRACT

The oxidation of maleic, fumaric, crotonic and cinnamic acids by benzyltriethylammonium chlorochromate (BTEACC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding epoxide. The reaction is of first order with respect to BTEACC and the acid. The reaction is catalysed by hydrogen ions. The hydrogen–ion dependence has the form: $k_{obs} = a + b [H^+]$. The oxidation of these acids was studied in nineteen different organic solvents. The solvent effect was analysed by Kamlet's and Swain's multiparametric equations. Solvent effect indicated the importance of the cation solvating power of the solvent. A mechanism involving a three–centre transition state has been postulated.

Key words : Unsaturated acids, Benzyltriethylammonium Chlorochromate, Oxidation, Kinetics.

INTRODUCTION

Pyridinium and quinolinium halochromates have long been used as mild and selective oxidizing reagents in synthetic organic chemistry[1–5]. Benzyltriethylammonium chlorochromate (BTEACC) is also one of such compounds used for the oxidation of benzylic alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several reports, by halochromates have already been reported[7–10]. Though the oxidation of alkenes by chromyl chloride and chromic acid has received much attention[11,12]. There seems to be no report on the oxidation of alkenes by benzyltriethylammonium chlorochromate (BTEACC) and therefore, an investigation of the oxidation of fumaric (FA) maleic (MA), crotonic (CrA) and cinnamic (CiA) acids by BTEACC has been undertaken in dimethylsulphoxide (DMSO) as a solvent. Mechanistic aspects are discussed.

EXPERIMENTAL

Materials

The unsaturated acids were commercial products and were used as supplied. BTEACC was prepared by the reported method[6] and its purity was ascertained by an iodometric method. Solvents were purified by the usual methods[13]. Due to non–aqueous nature of the medium, toluene–p–sulphonic acid (TsOH) was used as a source of hydrogen ions.

Product analysis

Product analysis was carried out under kinetic conditions i.e. with an excess of the reductant over BTEACC. In a typical experiment, the unsaturated acid (0.2 mol) and BTEACC (3.27 g, 0.01 mol) were dissolved in 100 mL of DMSO and was allowed to stand for ca. 12 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm^3) of a saturated solution of 2,4–dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4–dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.55 g (89%) and 2.32 g (79%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetophenone, acetone and pyruvic acid in the oxidation of cinnamic, crotonic and maleic/fumaric acids, respectively. The oxidation state of chromium in completely reduced reaction mixtures, as determined by an iodometric method, was 3.95 ± 0.06.

Kinetic measurements

The pseudo–first order conditions, were attained by keeping an excess (x 10 or greater) of the reductant over BTEACC. The solvent was DMSO, unless specified otherwise. The reactions were followed at constant temperature (± 0.1 K). The reactions were followed by monitoring the decrease in the concentration of BTEACC spectrophotometrically at 356 nm for at least three half–lives. The pseudo–first order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) plots of log [BTEACC] against time. Duplicate kinetic runs indicated that the rate constants are reproducible within $\pm 3\%$. The second order rate constant, k_2, was evaluated from the relation: $k_2 = k_{obs}$ / [reductant]. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

RESULTS

The rate and other experimental data were obtained for all the unsaturated acids studied. Since the results are similar, only representative data are reproduced here.

Stochiometry

After the workout of the product, the final product, in the oxidation of crotonic, cinnamic and maleic/fumaric acids is acetone, acetophenone and pyruvic acid, respectively. These must have arisen from the corresponding epoxides by rearrangement and decarboxylation as shown in equation (1).

$$R - CH - CH - COOH \longrightarrow R - C - CH_2COOH \longrightarrow R - C - CH_3 + CO_2 \qquad ...(1)$$

(R = Ph, Me or COOH)

Epoxides are known to rearrange to ketones[14]. β–Ketoacids readily decarboxylate in acidic solutions[15]. Therefore, the overall oxidation process may be written as follows.

$$R - CH = CH - COOH + O_2CrClO^-bteN^+ \longrightarrow$$
$$R - CH - CH - COOH + CrOClO^-bteN^+ \qquad ...(2)$$
$$\diagdown O \diagup$$
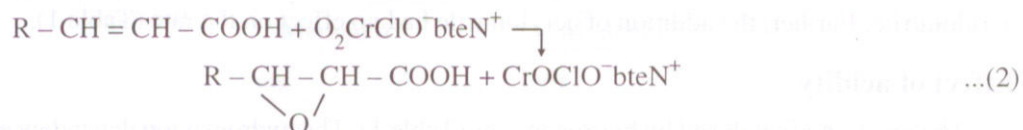
BTEACC undergoes a two–electron change. This is in accordance to the earlier observations with BTEACC[10] and with other halochromates[16, 17] also.

Rate laws

The reactions are first order with respect to BTEACC. Individual kinetic runs were strictly first order in BTEACC. Further, the pseudo–first order rate constants do not depend on the initial [BTEACC]. The reaction rate increases linearly with an increase in the concentration of the reductant (Table 1).

Table 1. Rate constants for the oxidation of cinnamic acid by BTEACC at 298 K

10^3 [BTEACC] (mol dm^{-3})	[Cia] (mol dm^{-3})	[TsOH] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
1.00	0.10	0.00	14.4
1.00	0.20	0.00	29.6
1.00	0.40	0.00	61.2
1.00	0.60	0.00	90.3
1.00	0.80	0.00	122
1.00	1.00	0.00	153
2.00	0.20	0.00	30.3
4.00	0.20	0.00	28.8
6.00	0.20	0.00	29.2
8.00	0.20	0.00	31.0
1.00	0.10	0.10	19.2
1.00	0.10	0.20	24.3
1.00	0.10	0.40	34.7
1.00	0.10	0.60	46.6
1.00	0.10	0.80	55.7
1.00	0.10	1.00	66.5
1.00	0.40	0.00	61.8*

*Contained 0.001 mol dm^{-3} acrylonitrile

Induced polymerization test

The oxidation of acids in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table 1).

Effect of acidity

The reaction is catalysed by hydrogen ions (Table 1). The hydrogen ion dependence has the following form as given in equation (3). The values of a and b, for the oxidation of cinnamic acid are $1.39 \pm 0.05 \times 10^{-3}$ s^{-1} and $5.27 \pm 0.08 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} ($r^2 = 0.9992$).

$$k_{obs} = a + b\ [H^+] \qquad \qquad ...(3)$$

Effect of solvents

The rates of the oxidation of the unsaturated acids were obtained in nineteen different organic solvents. The solubility of reagents and reaction of BTEACC with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. Kinetics was similar in all the solvents. The values of k_2 are recorded in Table 2.

Table 2. Effect of solvents on the oxidation of cinnamic acid by BTEACC at 298 K

Solvents	$10^4\ k^2$ (dm^3 mol^{-1} s^{-1})	Solvents	$10^4\ k^2$ (dm^3 mol^{-1} s^{-1})
Chloroform	57.5	Acetic acid	14.8
1,2–Dichloroethane	64.6	Cyclohexane	3.47
Dichloromethane	53.7	Toluene	17.4
DMSO	153	Acetophenone	77.6
Acetone	59.0	THF	28.2
N,N–Dimethylformamide	81.2	*t*–Butyl alcohol	26.3
Butanone	44.7	1,4–Dioxane	33.1
Nitrobenzene	63.1	1,2–Dimethoxyethane	19.9
Benzene	24.5	Carbon disulfide	10.2
Ethyl acetate	27.5		

Effect of temperature

The rates of oxidation of the unsaturated acids were determined at different temperatures and the activation parameters were calculated (Table 3).

Table 3. Rate constants and activation parameters of the oxidation of unsaturated acids by BTEACC

Subst.	$10^4 k_2 / (dm^3 mol^{-1} s^{-1})$				ΔH^* (kJ mol^{-1})	ΔS^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
	288 K	298 K	308 K	318 K			
FA	4.41	7.74	13.5	23.4	39.8 ± 0.5	-171 ± 2	90.7 ± 0.4
CrA	13.5	23.4	39.6	68.4	38.5 ± 0.6	-167 ± 2	88.0 ± 0.4
MA	17.1	28.8	47.7	79.2	36.3 ± 0.4	-172 ± 1	87.5 ± 0.3
CiA	92.7	153	252	423	25.9 ± 0.7	-160 ± 2	83.3 ± 0.5

DISCUSSION

The observed acid–dependence of the reaction rate may be explained on the basis of a protonation of BTEACC in a pre–equilibrium (14), with both the protonated and deprotonated forms being active oxidizing species.

$$[O_2CrClO^- bteN^+] + H^+ \rightleftharpoons [HOCr^+OClO^- bteN^+] \qquad ...(4)$$

Solvent effect

The rate constants, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (5) of Kamlet et al.[18]

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad ...(5)$$

In this equation, $p\pi^*$ represents the solvent polarity, β the hydrogen bond acceptor bascities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α. The results of correlation analysis in terms of equation (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below as equations (6)–(9).

$$\log k_2 = -3.37 + 1.34 (\pm 0.17) \pi^* + 0.15 (\pm 0.15) \beta - 0.07 (\pm 0.14) \alpha \qquad ...(6)$$
$$R^2 = 0.8423; \ sd = 0.16; \ n = 18; \ \psi = 0.44$$

$$\log k_2 = -3.28 + 1.37 (\pm 0.16) \pi^* + 0.13 (\pm 0.13) \beta \qquad ...(7)$$
$$R^2 = 0.8396; \ sd = 0.34; \ n = 18; \ \psi = 0.43$$

$$\log k_2 = -3.36 + 1.40 (\pm 0.16) \pi^* \qquad ...(8)$$
$$r^2 = 0.8298; \ sd = 0.83; \ n = 18; \ \psi = 0.42$$

$$\log k_2 = -2.59 + 0.37 (\pm 0.30) \beta \qquad ...(9)$$
$$r^2 = 0.0873; \ sd = 0.36; \ n = 18; \ \psi = 0.98$$

Here n is the number of data points and is the Exner's statistical parameter[19].

Kamlet's[18] triparametric equation explains *ca.* 84% of the effect of solvent on the oxidation. However, by Exner's criterion[19], the correlation is not even satisfactory (cf. equation 6). The major contribution is of solvent polarity. It alone accounted for *ca.* 83% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation[20] of cation–and anion–solvating concept of the solvents also using equation (10).

$$\log k_2 = aA + bB + C \qquad\qquad ...(10)$$

Here A represents the anion–solvating power of the solvent and B the cation–solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (10), separately with A and B and with (A + B).

$$\log k_2 = 0.60 \, (\pm 0.04) \, A + 1.43 \, (\pm 0.03) \, B - 3.57 \qquad\qquad ...(11)$$
$$R^2 = 0.9940; \, sd = 0.03; \, n = 19; \, \psi = 0.01$$

$$\log k_2 = 0.40 \, (\pm 0.47) \, A - 2.58 \qquad\qquad ...(12)$$
$$r^2 = 0.0396; \, sd = 0.38; \, n = 19; \, \psi = 1.00$$

$$\log k_2 = 1.38 \, (\pm 0.11) \, B - 3.37 \qquad\qquad ...(13)$$
$$r^2 = 0.9042; \, sd = 0.12; \, n = 19; \, \psi = 0.32$$

$$\log k_2 = 1.15 \pm 0.11 \, (A + B) - 3.54 \qquad\qquad ...(14)$$
$$r^2 = 0.8690; \, sd = 0.87; \, n = 19; \, \psi = 0.37$$

The rates of oxidation of cinnamic acid in different solvents showed an excellent correlation in Swain's equation [cf. equation (10)] with the cation–solvating power playing the major role. In fact, the cation–solvation alone accounts for *ca.* 90% of the data. The correlation with the anion–solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 87% of the data. In view of the fact that solvent polarity is able to account for *ca.* 87% of the data, an attempt was made to correlate rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.5062$; sd = 0.27; $\psi = 0.72$).

MECHANISM

The reactions of alkenes with various Cr (VI) derivatives have been widely studied. The most extensively studied derivative is chromyl chloride. The results of the present study are comparable with those obtained with chromyl chloride.
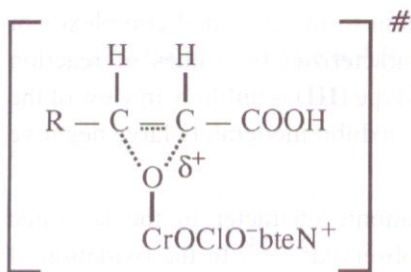
The low values of the enthalpies of activation indicate that bond–cleavage is not extensive in the formation of the activated complex. The formation of a rigid cyclic activated complex is indicated by the large negative values of the entropies of activation. The probable structures, if the activated complex are (**I**), (**II**), (**III**) and (**IV**), **III** is akin to the activated complexes of concerted *cis*–1, 3–cycloaddition reactions, which are characterized by values of reaction constants close to zero[21]. Therefore, an activated complex of type (**III**) is unlikely in view of the fact that the reactions of substituted styrenes[22] and alkenes[23] exhibit moderately large negative reaction constants (i.e. –1.99 and –2.63, respectively).

In reactions involving fairly large degree of carbocationic character in the activated complex, reaction constant values of –3 to –5 have been observed[24, 25]. In the oxidation of *trans*– monosubstituted cinnamic acid by acid borate, Reddy and Sundaram[26] observed that electron– withdrawing groups have a little effect on the rate of oxidation while electron–donating groups have substantial effect on the reactivity. They obtained a reaction constant of –3.7 for the electron–donating groups. The activated complex is proposed to be a benzylic carbocation in character. Therefore, the reported value of *ca.* –2 in the oxidation of styrenes[21] by chromyl chloride mitigates against an activated complex with a fully developed positive charge (**IV**). In the present reaction also, replacement of a methyl group by a phenyl group results in a modest rate enhancement (*ca.* 7 times).
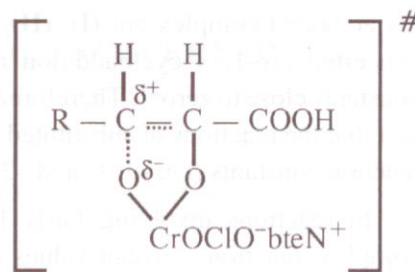
A perusal of the relative rates of the oxidation (*cf.* Table 2) showed that maleic acid is oxidized at a rate *ca.* 3 times that of fumaric acid. This mitigates against the formation of the activated complex (**II**). The formation of a four–membered cyclic activated complex is likely to be more vulnerable to steric factors. Sterically the attack of BTEACC on the open face of maleic acid (having two hydrogens) is more facile than on fumaric acid. Had the activated complex been a four–membered cyclic structure, the difference in the rates of maleic and fumaric acids would have been much sharper. A formation of even the three–membered cyclic activated complex (**I**) is less hindered in the oxidation of the *cis*–acid. However, the data against an involvement of the activated complex (**II**) is not conclusive. Freeman *et al.*[11, 22, 23] also have not been able to show conclusively whether the activated complex had a three– or a four–membered cyclic structure.

The analysis of the solvent effect also supports the proposed mechanism. The fact that the reaction proceeds faster in more polar solvents is in accordance with the formation of a partially charged activated complex from two neutral molecules. The relatively major contribution of the cation–solvating power of the solvents supports the generation of an electron–deficient carbon centre in the transition state. Further, the relatively low magnitude of the regression coefficient, b, is consistent with the development of a partial positive charge in the activated complex. In the oxidation of benzaldehyde by pyridinium fluorochromate[7], where the formation of a carbocationic activated complex has been postulated, the value of b is 1.73. To conclude, though
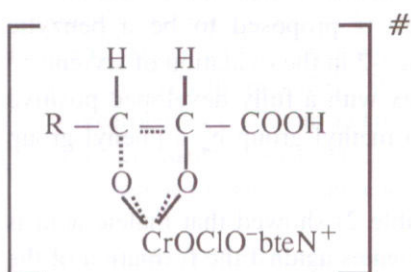
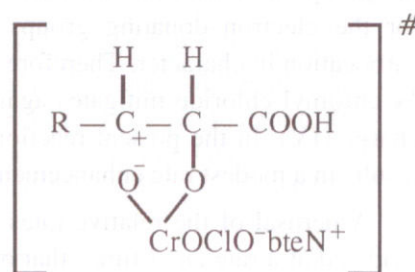both structures (**I**) and (**II**) are possible for the activated complex, the balance of evidence is in favour of (**I**).

$$
\left[\begin{array}{c} \underset{\substack{|\\ R-C}}{\overset{\substack{H\\ |}}{}} =\overset{\substack{H\\ |}}{\underset{\substack{|\\ }}{C}}-COOH \\ \underset{CrOClO^-bteN^+}{\overset{\delta^+}{O}} \end{array}\right]^{\#}
$$

(I)

$$
\left[\begin{array}{c} R-\overset{\substack{H\\ |}}{\underset{\substack{\delta^+}}{C}} =\overset{\substack{H\\ |}}{\underset{\substack{|}}{C}}-COOH \\ \overset{\delta^-}{O}\quad O \\ CrOClO^-bteN^+ \end{array}\right]^{\#}
$$

(II)

$$
\left[\begin{array}{c} R-\overset{\substack{H\\ |}}{C} =\overset{\substack{H\\ |}}{C}-COOH \\ O\quad O \\ CrOClO^-bteN^+ \end{array}\right]^{\#}
$$

(III)

$$
\left[\begin{array}{c} R-\overset{\substack{H\\ |}}{\underset{+}{C}}-\overset{\substack{H\\ |}}{C}-COOH \\ O^-\quad O \\ CrOClO^-bteN^+ \end{array}\right]^{\#}
$$

(IV)

ACKNOWLEDGEMENTS

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