

# Oxidation of some unsaturated acids by diethylammonium chlorochromate: A kinetics and mechanistic approach

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## Abstract

The oxidation of maleic, fumaric, crotonic and cinnamic acids by diethylammonium chlorochromate (DEACC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding epoxide. The reaction is of first order with respect to DEACC and the acid. Due to non-aqueous nature of the solvents toluene-p-sulphonic acid (TsOH) was used the source of hydrogen ions. 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 analyzed 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:** Halochromates, kinetics, mechanism, oxidation, unsaturated acids.

## 1. INTRODUCTION

Selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. For this a number of different chromium (VI) derivatives have been reported[1-5]. Diethylammonium chlorochromate (DEACC) is one such compound used for the oxidation of phenylic alcohols and oximes[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 available on the oxidation aspects using diethylammonium chlorochromate (DEACC). In continuation of our earlier work with halochromates, We have, therefore, undertaken an investigation of the oxidation of fumaric (FA), maleic (MA), crotonic (CrA) and cinnamic (CiA) acids by DEACC in dimethylsulphoxide (DMSO) as a solvent. Mechanistic aspects are discussed.

## 2. MATERIALS AND METHODS

### 2.1 Materials:

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

### 2.2 Product analysis:

Product analysis was carried out under kinetic conditions i.e. with an excess of the reductant over DEACC. In a typical experiment, the unsaturated acid (0.2 mol) and DEACC (1.58 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<sup>3</sup>) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm<sup>-3</sup> 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 re-crystallization were 2.52 g (88%) and 2.49 g (85%) 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, determined by an iodometric method, was 3.90±0.15.

### 2.3 Kinetic measurements:

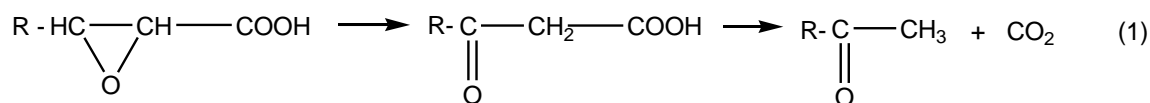
The pseudo-first order conditions, were attained by keeping an excess ( $\times 10$  or greater) of the reductant over DEACC. The solvent was DMSO, unless specified otherwise. The reactions were followed at constant temperature ( $\pm 0.1$  K). The reactions were followed by monitoring the decrease in the concentration of DEACC spectrophotometrically at 352 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  $\log [DEACC]$  against time. Duplicate kinetic runs indicated that the rate constants are reproducible to within  $\pm 3\%$ . The second order rate constant,  $k_2$ , was evaluated from the relation:  $k_2 = k_{obs} / [\text{reductant}]$ . All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

### 3. RESULTS AND DISCUSSION

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

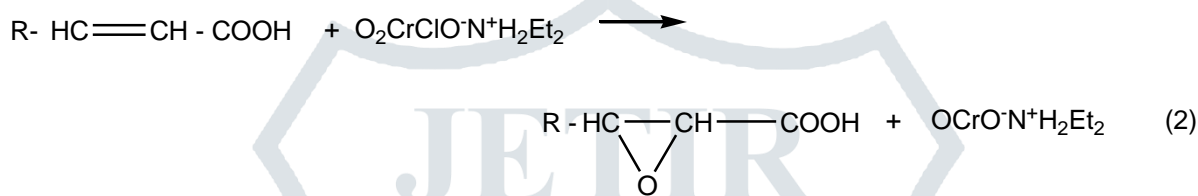
#### 3.1 Stoichiometry:

After the workout of the product, the final product, in the oxidation of crotonic, cinnamic, 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 = Ph, Me or COOH)

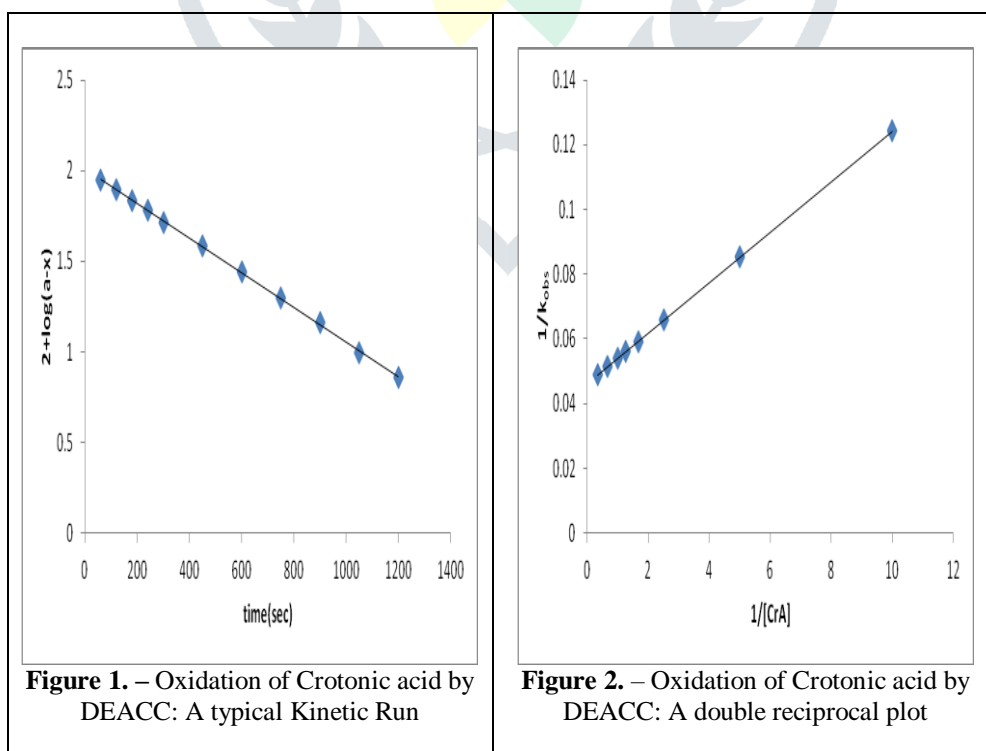
Epoxies are known to rearrange to ketones[14].  $\beta$ -Ketoacids readily decarboxylate in acidic solutions[15]. Therefore, the overall oxidation process may be written as follows.



DEACC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both PFC[16] and PCC[17] act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.

#### 3.2 Kinetic dependence:

The reactions are of first order with respect to DEACC (Figure 1). Further, the pseudo-first order rate constant,  $k_{\text{obs}}$  is independent of the initial concentration of DEACC. The reaction rate increases with increase in the concentration of the hydroxy acid but not linearly (Table 1). A plot of  $1/k_{\text{obs}}$  against  $1/[\text{USA}]$  is linear ( $r > 0.995$ ) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the unsaturated acids. This leads to the postulation of following overall mechanism (3) and (4) and rate law (5).



**Table 1:** Rate constants for the oxidation of Crotonic acid by DEACC at 288 K

$10^3$ [PDC] (mol dm <sup>-3</sup> )	[CrA] (mol dm <sup>-3</sup> )	[TsOH] (mol dm <sup>-3</sup> )	$10^4 k_{obs}$ (mol dm <sup>-3</sup> )
1.0	0.10	0.00	8.05
1.0	0.20	0.00	11.7
1.0	0.40	0.00	15.2
1.0	0.60	0.00	16.9
1.0	0.80	0.00	17.8
1.0	1.00	0.00	18.5
1.0	1.50	0.00	19.4
1.0	3.00	0.00	20.5
2.0	0.40	0.00	16.2
4.0	0.40	0.00	15.3
6.0	0.40	0.00	14.4
8.0	0.40	0.00	16.0
1.0	0.20	0.00	12.6 <sup>a</sup>

<sup>a</sup> contained 0.001 M acrylonitrile



$$\text{Rate} = k_2 K [\text{USA}] [\text{DEACC}] / (1 + K [\text{USA}]) \quad (5)$$

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and  $k_2$  were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and  $k_2$  respectively at different temperatures (Tables 2 and 3).

**Table 2:** Rate constants for the decomposition of DEACC–USA complexes and their activation parameters

USA	$10^3 k_2 / (\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1})$				$\Delta H^*$	$-\Delta S^*$	$\Delta G^*$
	288 K	298 K	308 K	318 K	(kJ mol <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )	(kJ mol <sup>-1</sup> )
FA	5.58	9.54	16.2	26.1	36.7±0.2	180±1	90.2±0.2
CrA	21.6	37.8	66.6	108	38.6±0.3	162±1	86.8±0.2
MA	17.1	28.8	49.5	81.0	37.1±0.4	169±1	87.5±0.3
CiA	117	171	261	387	28.0±0.6	185±2	83.0±0.5

**Table 3:** Formation constants for the decomposition of DEACC–USA complexes and thermodynamic parameters

USA	K / ( dm <sup>3</sup> mol <sup>-1</sup> )				- ΔH* (kJ mol <sup>-1</sup> )	- ΔS* (J mol <sup>-1</sup> K <sup>-1</sup> )	- ΔG* (kJ mol <sup>-1</sup> )
	288 K	298 K	308 K	318 K			
FA	6.57	5.78	4.85	4.92	14.2±0.6	25±2	6.79±0.4
CrA	5.94	5.15	4.32	3.48	16.0±0.8	32±2	6.50±0.6
MA	6.48	5.65	4.82	4.07	14.3±0.4	26±1	6.75±0.3
CiA	5.76	4.88	4.07	3.26	16.8±0.6	36±2	6.38±0.5

### 3.3 Test for free radicals:

The oxidation of unsaturated acids, by DEACC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (Table 1). We further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm<sup>-3</sup> of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

### 3.4 Effect of Acidity:

Due to the non-aqueous nature of the solvents, TsOH was used as a source of hydrogen ions. The reaction is catalysed by hydrogen ions (Table 4). The hydrogen ion dependence has the following form as equation (6). The values of a and b, for the oxidation of maleic acid are  $10.4 \pm 0.57 \times 10^{-4} \text{ s}^{-1}$  and  $18.5 \pm 0.94 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $r^2 = 0.9897$ ).

$$k_{\text{obs}} = a + b [\text{H}^+] \quad (6)$$

**Table 4:** Dependence of the reaction rate on hydrogen-ion concentration

[PDC] = 0.001 mol dm <sup>-3</sup> ; [Crotonic acid] = 1.0 mol dm <sup>-3</sup> ; Temp. = 288 K						
[H <sup>+</sup> ]/mol dm <sup>-3</sup>	0.10	0.20	0.40	0.60	0.80	1.00
CrA	9.63	11.7	13.5	16.2	18.9	22.5

### 3.5 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 DEACC 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 and k<sub>2</sub> are recorded in table 5.

**Table 5:** Effect of solvent on the oxidation of crotonic acid by DEACC at 308 K

Solvents	K (dm <sup>-3</sup> mol <sup>-1</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )	Solvents	K (dm <sup>-3</sup> mol <sup>-1</sup> )	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )
Chloroform	6.31	38.9	Toluene	5.75	10.2
1,2-Dichloroethane	5.94	44.7	Acetophenone	6.14	43.7
Dichloromethane	5.82	35.5	THF	5.81	20.4
DMSO	5.70	108	t-Butylalcohol	5.55	15.1
Acetone	6.05	32.4	1,4-Dioxane	5.67	21.9
DMF	5.90	63.1	1,2-Dimethoxyethane	5.84	12.0
Butanone	5.48	25.1	CS <sub>2</sub>	6.22	8.03
Nitrobenzene	5.33	50.1	Acetic Acid	5.99	10.5
Benzene	6.12	12.6	Ethyl Acetate	6.17	13.8
Cyclohexane	6.00	1.86			

### 3.6 Reactive Oxidizing Species:

The observed acid-dependence of the reaction rate may be explained on the basis of a protonation of DEACC in a pre-equilibrium (7), with both the protonated and deprotonated forms being active oxidizing species.



### 3.7 Solvent Effect:

The rate constants,  $k_2$ , in eighteen solvents ( $\text{CS}_2$  was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (8) of Kamlet et al[18].

$$\log k_2 = A_0 + p\pi^* + b\beta + \alpha \quad (8)$$

In this equation,  $\pi^*$  represents the solvent polarity,  $\beta$  the hydrogen bond acceptor basicities and  $\alpha$  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  $\alpha$ . The results of correlation analyses in terms of equation (8), a biparametric equation involving  $\pi^*$  and  $\beta$ , and separately with  $\pi^*$  and  $\beta$  are given below as equations (9) - (12).

$$\log k_2 = -4.33 + 1.50 (\pm 0.18) \pi^* + 0.13 (\pm 0.15) \beta + 0.01 (\pm 0.14) \alpha \quad (9)$$

$$R^2 = 0.8610; \text{ sd} = 0.16; n = 18; \psi = 0.41$$

$$\log k_2 = -4.32 + 1.50 (\pm 0.16) \pi^* + 0.13 (\pm 0.13) \beta \quad (10)$$

$$R^2 = 0.8609; \text{ sd} = 0.16; n = 18; \psi = 0.32$$

$$\log k_2 = -4.35 + 1.54 (\pm 0.16) \pi^* \quad (11)$$

$$r^2 = 0.8522; \text{ sd} = 0.16; n = 18; \psi = 0.39$$

$$\log k_2 = -3.80 + 0.40 (\pm 0.33) \beta \quad (12)$$

$$r^2 = 0.0855; \text{ sd} = 0.39; n = 18; \psi = 0.98$$

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

Kamlet's[18] triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion[19] the correlation is not even satisfactory (cf. equation 9). The major contribution is of solvent polarity. It alone accounted for *ca.* 85% of the data. Both  $\beta$  and  $\alpha$  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 (13).

$$\log k_2 = aA + bB + C \quad (13)$$

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 (9), separately with A and B and with (A + B).

$$\log k_2 = 0.70 (\pm 0.06) A + 1.49 (\pm 0.04) B - 4.17 \quad (14)$$

$$R^2 = 0.9872; \text{ sd} = 0.05; n = 19; \psi = 0.12$$

$$\log k_2 = 0.49 (\pm 0.49) A - 3.01 \quad (15)$$

$$r^2 = 0.0546; \text{ sd} = 0.40; n = 19; \psi = 0.99$$

$$\log k_2 = 1.44 (\pm 0.13) B - 3.61 \quad (16)$$

$$r^2 = 0.8763; \text{ sd} = 0.39; n = 19; \psi = 0.36$$

$$\log k_2 = 1.23 \pm 0.11 (A + B) - 3.81 \quad (17)$$

$$r^2 = 0.8860; \text{ sd} = 0.14; n = 19; \psi = 0.35$$

The rates of oxidation of cinnamic acid in different solvents showed an excellent correlation in Swain's equation [cf. equation (13)] with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for *ca.* 87% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 88% 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 ( $r^2 = 0.5372$ ;  $\text{sd} = 0.28$ ;  $\psi = 0.70$ ).

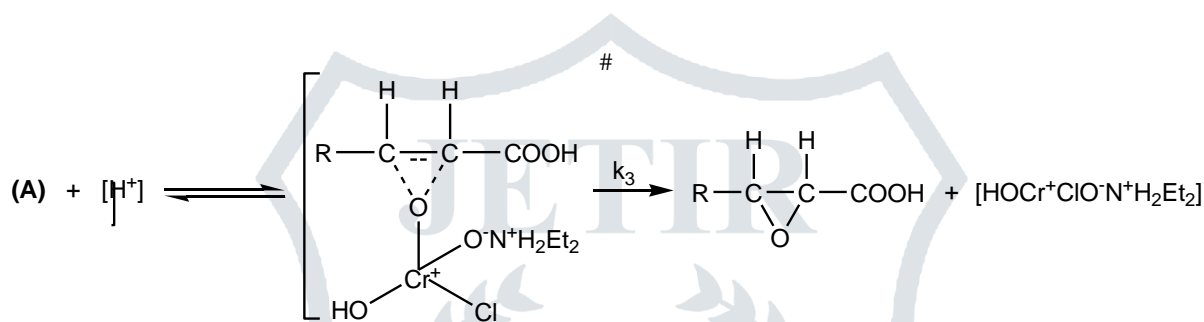
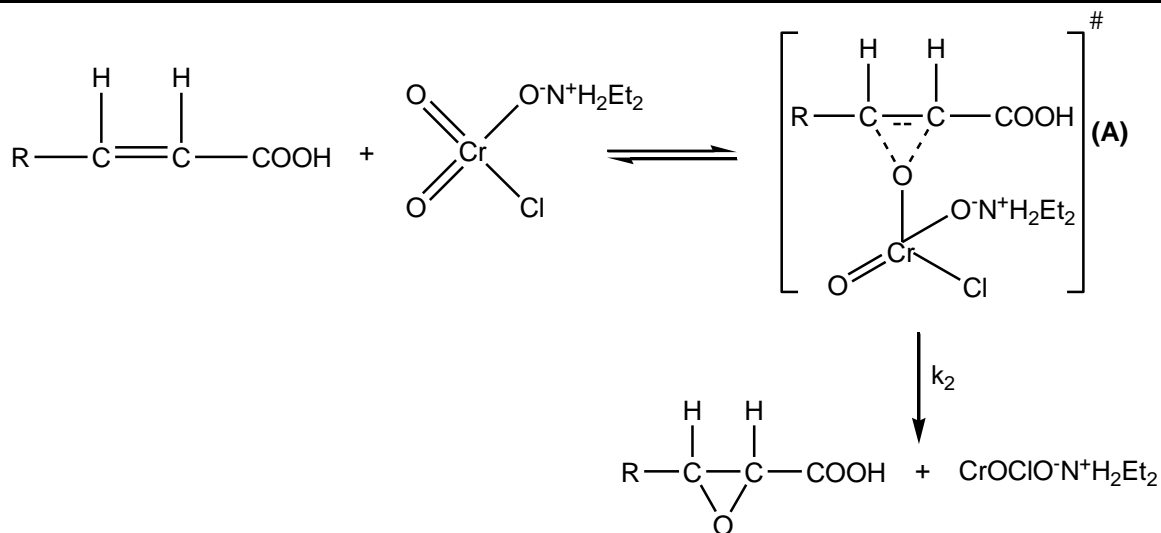
## 4. MECHANISM

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







## 5. CONCLUSION

Reaction is proposed to proceed on the basis of consideration of structure I of the unsaturated acids, because of observational evidences are in favour of structure I.

## 6. ACKNOWLEDGEMENTS

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## 7. REFERENCES

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