



## OXIDATION OF SOME UNSATURATED ACIDS BY QUINOLINIUM DICHROMATE: A KINETICS AND MECHANISTIC STUDY

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### ABSTRACT

The oxidation of maleic, fumaric, crotonic and cinnamic acids by quinolinium dichromate (QDC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding epoxide. The reaction is of first order with respect to QDC 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:  $k_{\text{obs}} = a + b [\text{H}^+]$ . 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.

### 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<sup>1-4</sup>. Quinolinium dichromate (QDC) is one such compound used for the oxidation of aliphatic primary and secondary alcohols<sup>5</sup>. 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<sup>6-10</sup>. Though the oxidation of alkenes by chromyl chloride and chromic acid has received much attention<sup>11,12</sup>, There seems to be no report available on the oxidation aspects using quinolinium dichromate (QDC). In continuation of our earlier work with halochromates, We have, therefore,

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undertaken an investigation of the oxidation of fumaric (FA), maleic (MA), crotonic (CrA) and cinnamic (CiA) acids by QDC in dimethylsulphoxide (DMSO) as a solvent. Mechanistic aspects are discussed.

## EXPERIMENTAL

### Materials

The unsaturated acids were commercial products and were used as supplied. QDC was prepared by the reported method<sup>5</sup> and its purity was ascertained by an iodometric method. Solvents were purified by the usual methods of purification<sup>13</sup>. 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 QDC. In a typical experiment, the unsaturated acid (0.2 mol) and QDC (4.76 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 recrystallization were 2.49 g (87%) and 2.50 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  $3.90 \pm 0.15$ .

### Kinetic measurements

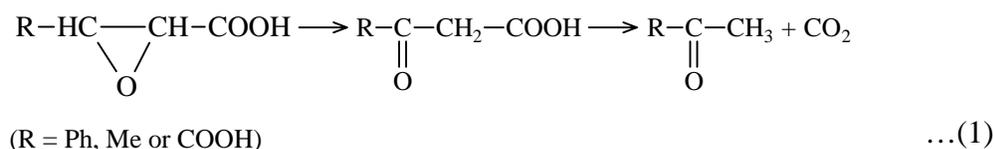
The pseudo-first order conditions, were attained by keeping an excess ( $\times 10$  or greater) of the reductant over QDC. The solvent was DMSO, unless specified otherwise. The reactions were followed at constant temperature ( $\pm 0.1$  K). The reactions were followed by monitoring the decrease in the concentration of QDC spectrophotometrically at 440 nm for at least three half-lives. The pseudo-first order rate constant,  $k_{\text{obs}}$ , was evaluated from the linear ( $r^2 > 0.995$ ) plots of  $\log [\text{QDC}]$  against time. The second order rate constant,  $k_2$ , was evaluated from the relation:  $k_2 = k_{\text{obs}}/[\text{reductant}]$ . All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

## RESULTS AND DISCUSSION

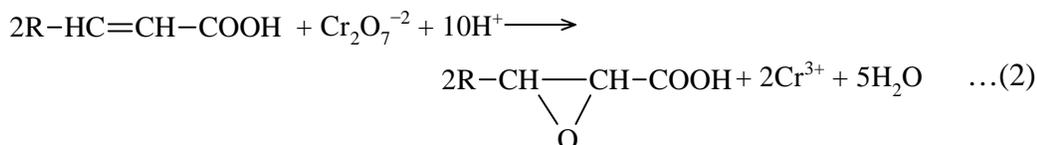
The rates and other experimental data were obtained for all the acids. Since the results are similar, only representative data are reproduced here.

### 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).

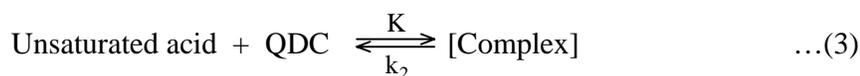


Epoxies are known to rearrange to ketones<sup>14</sup>.  $\beta$ -Ketoacids readily decarboxylate in acidic solutions<sup>15</sup>. Therefore, the overall oxidation process may be written as follows.



### Kinetic dependence

The reactions are of first order with respect to QDC (Fig. 1). Further, the pseudo-first order rate constant,  $k_{\text{obs}}$  is independent of the initial concentration of QDC. 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 (Fig. 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).



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

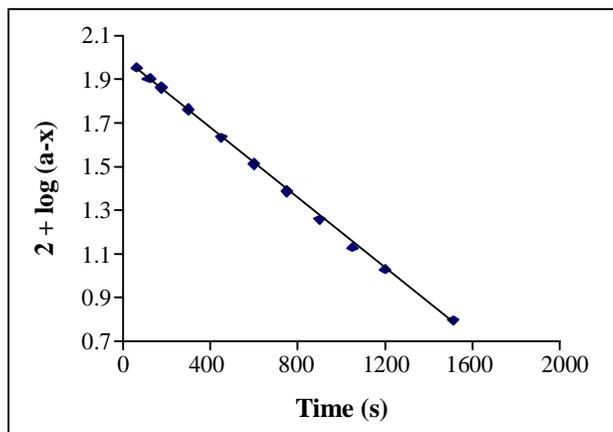
**Table 1: Rate constants for the oxidation of Crotonic acid by QDC at 288 K**

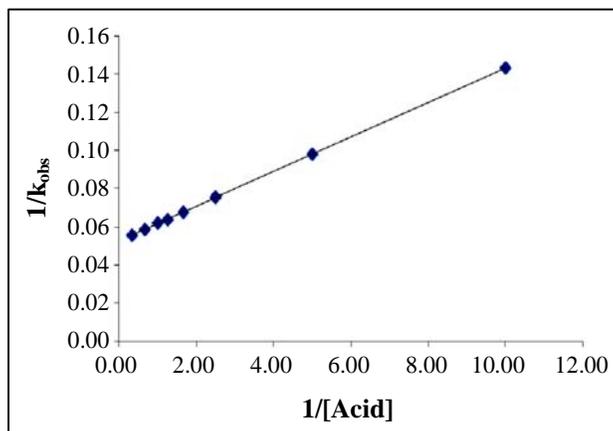
$10^3$ [QDC] (mol dm <sup>-3</sup> )	[CrA] (mol dm <sup>-3</sup> )	[TsOH] (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
1.00	0.10	0.00	6.98
1.00	0.20	0.00	10.2
1.00	0.40	0.00	13.2
1.00	0.60	0.00	14.7
1.00	0.80	0.00	15.6
1.00	1.00	0.00	16.1
1.00	1.50	0.00	17.0
1.00	3.00	0.00	17.9
2.00	0.40	0.00	13.5
4.00	0.40	0.00	12.6
6.00	0.40	0.00	13.8
8.00	0.40	0.00	13.0
1.00	0.20	0.00	11.7*

\* Contained 0.001 mol dm<sup>-3</sup> acrylonitrile

**Table 2: Dependence of the reaction rate on hydrogen-ion concentration**

[CrA] 0.10 mol dm <sup>-3</sup>	[QDC] 0.001 mol dm <sup>-3</sup>				Temp. 288 K	
[TsOH]/mol dm <sup>-3</sup>	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{\text{obs}}/\text{s}^{-1}$	8.22	9.45	11.7	14.4	16.2	19.8

**Fig. 1: Oxidation of crotonic acid by QDC: A typical kinetic run**



**Fig. 2: Oxidation of crotonic acid by QDC: A double reciprocal plot**

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 3 and 4).

### Test for free radicals

The oxidation of unsaturated acids, by QDC, 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  $0.05 \text{ mol dm}^{-3}$  of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

**Table 3: Rate constants for the decomposition of QDC–USA complexes and their activation parameters**

USA	$10^4 k_2 / (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$				$\Delta H^*$ (kJ mol <sup>-1</sup> )	$-\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
	288 K	298 K	308 K	318 K			
FA	4.95	8.64	15.3	26.1	$39.8 \pm 0.5$	$170 \pm 2$	$90.4 \pm 0.4$
CrA	18.9	33.3	56.7	95.4	$38.5 \pm 0.2$	$164 \pm 1$	$87.1 \pm 0.2$
MA	15.3	26.1	45.9	76.5	$38.5 \pm 0.5$	$165 \pm 2$	$87.7 \pm 0.4$
CiA	108	163	252	387	$30.0 \pm 0.7$	$179 \pm 2$	$83.2 \pm 0.5$

**Table 4: Formation constants for the decomposition of QDC–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	5.70	4.79	3.87	15.9 ± 0.8	31 ± 3	6.75 ± 0.6
CrA	5.85	4.96	4.06	3.17	17.9 ± 0.9	39 ± 3	6.40 ± 0.7
MA	6.12	5.22	4.35	3.44	17.0 ± 0.8	36 ± 2	6.54 ± 0.6
CiA	5.76	4.88	3.98	3.08	18.3 ± 0.9	41 ± 3	6.36 ± 0.8

**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 1). The hydrogen ion dependence has the following form as equation (6). The values of a and b, for the oxidation of crotonic acid are  $6.98 \pm 0.32 \times 10^{-4} \text{ s}^{-1}$  and  $12.5 \pm 0.53 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $r^2 = 0.9929$ ).

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

**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 QDC 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  $k_2$  are recorded in Table 3.

The rate constants,  $k_2$ , in eighteen solvents (CS<sub>2</sub> was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (7) of Kamlet et al.<sup>16</sup>

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \dots(7)$$

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 (7), a biparametric equation involving  $\pi^*$  and  $\beta$ , and separately with  $\pi^*$  and  $\beta$  are given below as equations (8) - (11).

$$\log k_2 = -3.78 + 1.70 (\pm 0.20) \pi^* + 0.19 (\pm 0.17) \beta + 0.02 (\pm 0.16) \alpha \quad \dots(8)$$

$$R^2 = 0.8636; \quad sd = 0.19; \quad n = 18; \quad \psi = 0.40$$

$$\log k_2 = -3.78 + 1.71 (\pm 0.19) \pi^* + 0.18 (\pm 0.15) \beta \quad \dots(9)$$

$$R^2 = 0.8634; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.39$$

$$\log k_2 = -3.75 + 1.76 (\pm 0.18) \pi^* \quad \dots(10)$$

$$r^2 = 0.8508; \quad sd = 0.18; \quad n = 18; \quad \psi = 0.40$$

$$\log k_2 = -2.78 + 0.49 (\pm 0.37) \beta \quad \dots(11)$$

$$r^2 = 0.0966; \quad sd = 0.45; \quad n = 18; \quad \psi = 0.98$$

Here  $n$  is the number of data points and  $\psi$  is the Exner's statistical parameter<sup>17</sup>.

Kamlet's<sup>16</sup> triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion<sup>17</sup> the correlation is not even satisfactory (cf. equation 8). 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<sup>18</sup> of cation- and anion-solvating concept of the solvents also (12).

$$\log k_2 = aA + bB + C \quad \dots(12)$$

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 (12), separately with  $A$  and  $B$  and with  $(A + B)$ .

$$\log k_2 = 0.84 (\pm 0.05) A + 1.76 (\pm 0.04) B - 4.01 \quad \dots(13)$$

$$R^2 = 0.9940; \quad sd = 0.04; \quad n = 19; \quad \psi = 0.08$$

$$\log k_2 = 0.59(\pm 0.58) A - 2.80 \quad \dots(14)$$

$$r^2 = 0.0375; \text{sd} = 0.47; n = 19; \psi = 0.99$$

$$\log k_2 = 1.70 (\pm 0.15) B - 3.73 \quad \dots(15)$$

$$r^2 = 0.8789; \text{sd} = 0.17; n = 19; \psi = 0.36$$

$$\log k_2 = 1.46 \pm 0.12 (A + B) - 3.98 \quad \dots(16)$$

$$r^2 = 0.8954; \text{sd} = 0.16; n = 19; \psi = 0.33$$

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.* 88% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 89% of the data. In view of the fact that solvent polarity is able to account for *ca.* 89% 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 ( $r^2 = 0.5451$ ;  $\text{sd} = 0.33$ ;  $\psi = 0.69$ ).

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

Solvents	K ( $\text{dm}^{-3} \text{mol}^{-1}$ )	$10^5 k_2$ ( $\text{s}^{-1}$ )	Solvents	K ( $\text{dm}^{-3} \text{mol}^{-1}$ )	$10^5 k_2$ ( $\text{s}^{-1}$ )
Chloroform	5.81	46.8	Toluene	5.27	12.0
1,2-Dichloroethane	4.90	51.3	Acetophenone	5.44	55.0
Dichloromethane	5.85	42.7	THF	6.11	22.4
DMSO	4.79	153	t-butylalcohol	5.60	18.2
Acetone	5.58	38.0	1,4-Dioxane	4.77	19.5
DMF	6.03	85.1	1,2-Dimethoxyethane	4.40	11.2
Butanone	5.25	27.5	CS <sub>2</sub>	4.71	5.13
Nitrobenzene	4.90	63.1	Acetic acid	5.90	9.77
Benzene	5.60	12.9	Ethyl acetate	5.29	17.0
Cyclohexane	6.12	1.41			

## Mechanism

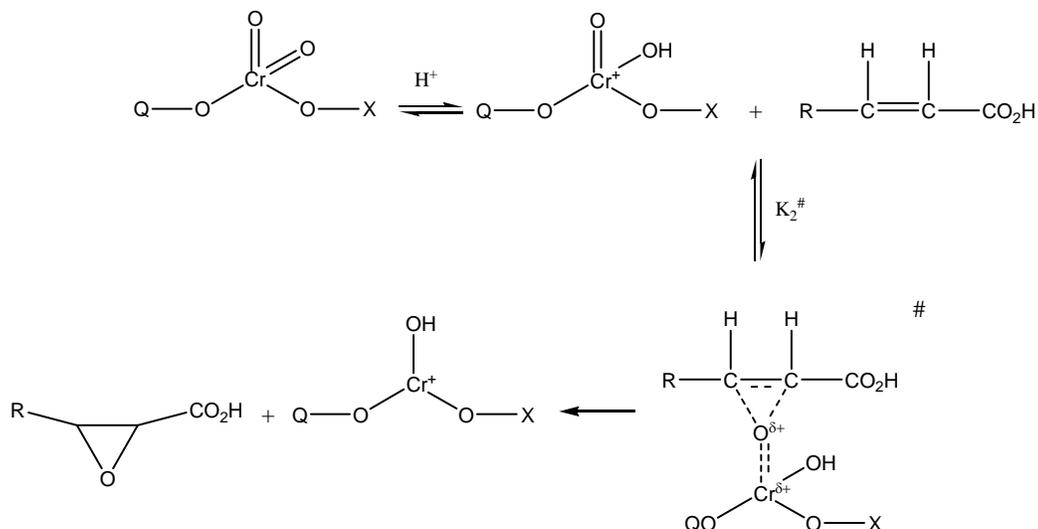
The reactions of alkenes with various Cr(VI) derivatives have been widely studied. The most extensively studied derivative is chromyl chloride. The results of the present study are comparable with those obtained with chromyl chloride.

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<sup>19</sup>. Therefore, an activated complex of type III is unlikely in view of the fact that the reactions of substituted styrenes<sup>20</sup> and alkenes<sup>21</sup> exhibit moderately large negative reaction constants (–1.99 and – 2.63, respectively).

In reactions involving fairly large degree of carbo-cationic character in the activated complex, reaction constant values of –3 to –5 have been observed<sup>22,23</sup>. In the oxidation of *trans*-monosubstituted cinnamic acid by acid borate, Reddy and Sundaram<sup>24</sup> 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<sup>19</sup> 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 3) showed that maleic acid is oxidized at a rate *ca.* 3 times that of fumaric acid. This militates against the formation of the activated complex II. The formation of a four-member cyclic activated complex is likely to be more vulnerable to steric factors. Sterically the attack of QDC 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-member cyclic activated complex (I) is less hindered in the oxidation of the *cis*-acid as compared to that in the *trans*-acid. However, the data against an involvement of the activated complex II is not conclusive. Freeman et al.<sup>11,20,21</sup> also have not been able show conclusively whether the activated complex had a three- or a four-member cyclic structure.





Scheme 1

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<sup>25</sup>, where the formation of a cabocationic 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**.

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