

# Periodic Research

## Studies on Kinetic and Thermodynamic Parameters of Oxidation of Unsaturated Acids by Benzimidazolium Fluorochromate in Dimethylsulphoxide



**Ammilal Rao**  
Assistant Professor,  
Dept. of Chemistry,  
University of Rajasthan,  
Jaipur, Rajasthan, India

### Abstract

The kinetics of oxidation of some unsaturated acids by benzimidazoliumfluorochromate (BIFC) has been studied in dimethylsulphoxide (DMSO) at different temperatures. The reaction is first order with respect to BIFC and the unsaturated acids. There is no free radical reaction. The rate of reaction is accelerated by hydrogen ions. The hydrogen-ion dependence has the form:  $k_{obs} = a + b [H^+]$ . The reaction has been operated at four different temperatures and the activation parameters were calculated. The reaction of these acids was done in nineteen different organic solvents. The solvent effect was examined by Kamlet's and Swain's multiparametric equations. Solvent effect specifies the importance of the cation-solvating power of the solvents. From the observed kinetic results an appropriate mechanism has been proposed.

**Keywords:** Kinetics, Oxidation, Unsaturated Acids, Mechanism.

### Introduction

In synthetic organic chemistry the selective oxidation of organic compounds in non aqueous conditions is a very important reaction. Many oxidants of Cr(VI) have been reported for the oxidation of selective organic compounds in non-aqueous condition<sup>1-5</sup>. Benzimidazoliumfluorochromate (BIFC) is a compound that used for the oxidation of aliphatic aldehydes<sup>6</sup>. Several halochromates have already been reported related to the kinetics and mechanistic aspects of the oxidation by Cr(VI) species<sup>7-17</sup>. In this paper I have reported investigation of the kinetics and thermodynamic parameters and mechanism of the oxidation of fumaric (FA), maleic (MA), crotonic (CrA) and cinnamic (CiA) acids by BIFC in dimethylsulphoxide (DMSO).

### Aim of the Study

Determination of kinetic parameters like rate laws, effect of catalysts, effect of temperature, effect of pH, solvent effect, kinetic isotope effect etc. and thermodynamic parameters like enthalpy, entropy, energy of reaction is the main objective of study. Formulation of suitable mechanism for the reaction on the basis of data obtained.

### Review of Literature

The oxidation of many organic compounds by QFC<sup>2</sup>, PFC<sup>3,9</sup>, QDC<sup>4</sup>, QBC<sup>5</sup>, MFC<sup>6</sup>, MCC<sup>11</sup>, IFC<sup>13</sup>, BPCC<sup>15</sup>, TPSD<sup>16</sup> and PBC<sup>17</sup> have been reported. There is no report on oxidation of unsaturated acids by BIFC. In continuation of earlier work I have undertaken an investigation on kinetic and thermodynamic aspects of this reaction.

### Materials and Methods

#### Materials

BIFC was prepared in the laboratory by the reported method<sup>6</sup> and iodometric method was to determine its purity. The unsaturated acids were commercially available and were used as supplied. Toluene-p-sulphonic acid (TsOH) was used as a source of hydrogen ions due to nature of the medium. Usual methods of purification<sup>18</sup> were used to purify the solvents.

#### Product Analysis

Analysis of product was carried out under kinetic conditions i.e. there was an excess of the reductant over BIFC. In the characteristic experiment, the unsaturated acid (0.2 mol) and BIFC (1.58 g, 0.01 mol) were dissolved in 100 mL of DMSO and were thus permitted to stand for ca.12 h to make certain the completion of the reaction. The solution was then treated with an excess (200 cm<sup>3</sup>) of a saturated solution of



Figure 1: Oxidation of crotonic acid by BIFC: A typical Kinetic Run

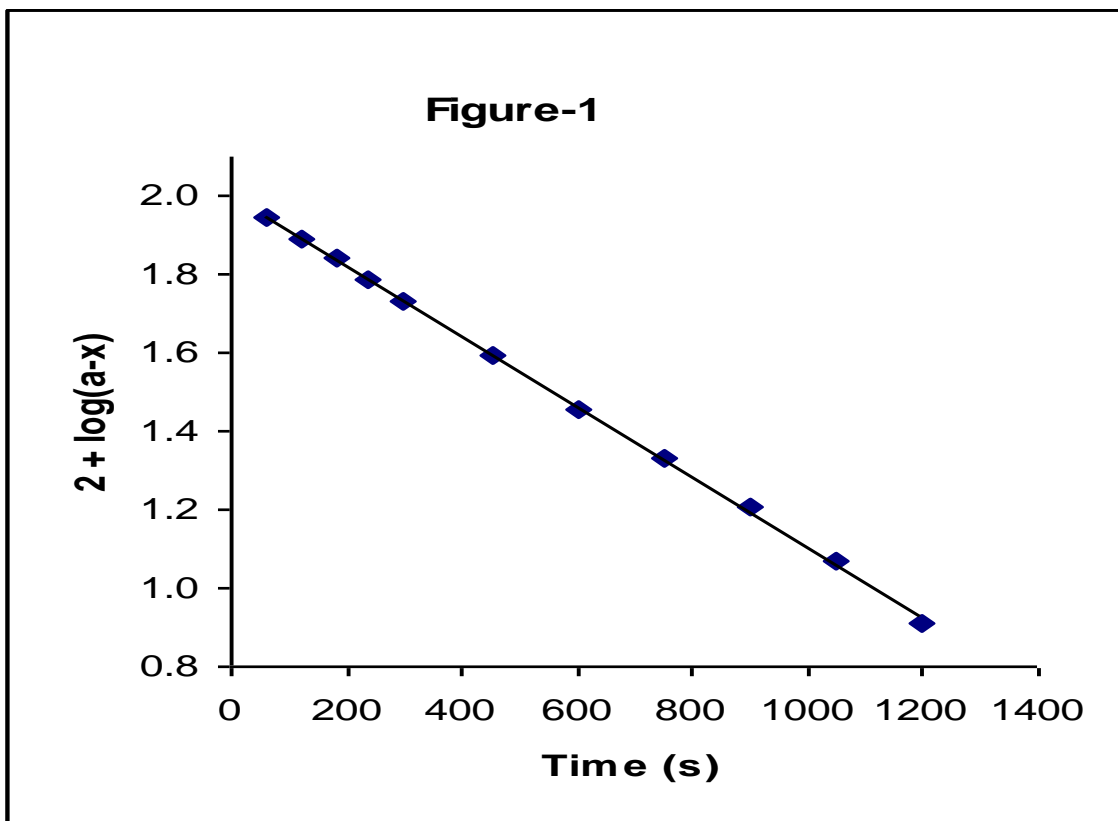
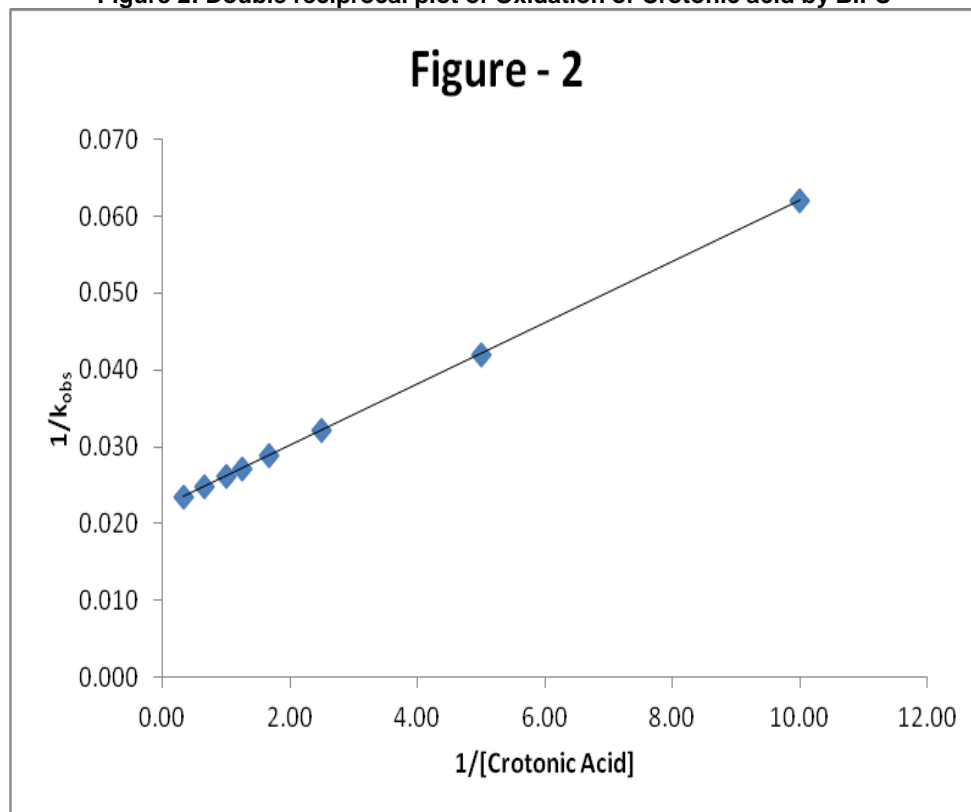


Figure 2: Double reciprocal plot of Oxidation of Crotonic acid by BIFC



**Table 1: Rate Constants for the Oxidation of Fumaric Acid by BIFC at 308 K**

$10^3$ [MFC] (mol dm <sup>-3</sup> )	[Fumaric acid] (mol dm <sup>-3</sup> )	[TsOH] (mol dm <sup>-3</sup> )	$10^4 k_{obs}$ (s <sup>-1</sup> )
1.00	0.10	0.00	5.99
1.00	0.20	0.00	9.29
1.00	0.40	0.00	12.8
1.00	0.60	0.00	14.7
1.00	0.80	0.00	15.8
1.00	1.00	0.00	16.6
1.00	1.50	0.00	17.8
1.00	3.00	0.00	19.1
2.00	0.40	0.00	13.5
4.00	0.40	0.00	12.6
6.00	0.40	0.00	14.4
8.00	0.40	0.00	13.2
1.00	0.10	0.10	7.02
1.00	0.10	0.20	8.10
1.00	0.10	0.40	10.2
1.00	0.10	0.60	11.7
1.00	0.10	0.80	14.4
1.00	0.10	1.00	16.2
1.00	0.20	0.00	8.10*

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

**Table 2: Formation constants of USA-BIFC complexes at different temperatures**

USA	K (dm <sup>3</sup> mol <sup>-1</sup> )			
	288 K	298 K	308 K	318 K
FA	5.66	4.84	4.08	3.24
CrA	6.40	5.62	4.76	3.96
MA	5.84	5.04	4.25	3.45
CiA	6.14	5.34	4.55	3.60

**Table 3: Thermodynamic parameters of USA-BIFC complexes**

USA	$-\Delta H$ (kJ mol <sup>-1</sup> )	$-\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G$ (kJ mol <sup>-1</sup> )
FA	16.8 ± 0.7	35 ± 3	6.35 ± 0.7
CrA	14.7 ± 0.5	27 ± 2	6.71 ± 0.5
MA	15.9 ± 0.6	31 ± 3	6.45 ± 0.5
CiA	15.2 ± 0.4	29 ± 2	6.58 ± 0.5

**Table 4: Rate constants for the decomposition of USA-BIFC complexes at different temperatures**

USA	$10^4 k_2$ /(dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) at			
	288 K	298 K	308 K	318 K
FA	6.92	12.5	20.6	34.4
CrA	27.2	45.0	79.1	126
MA	21.4	37.7	63.8	108
CiA	153	234	369	576

**Table 5: Activation parameters for the decomposition of USA-BIFC complexes**

USA	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$-\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
FA	37.6 ± 0.4	175 ± 1	89.6 ± 0.4
CrA	36.8 ± 0.6	166 ± 2	86.4 ± 0.5
MA	38.4 ± 0.3	164 ± 1	86.8 ± 0.2
CiA	31.4 ± 0.4	172 ± 2	82.4 ± 0.4

### Test for free radicals

The oxidation of unsaturated acids, by BIFC, in an atmosphere of nitrogen failed to stimulate the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate of reaction (Table 1). We further confirm the absence of free radicals in the reaction pathway, the reaction is carried out in the presence of 0.05 mol dm<sup>-3</sup> of 2,6-di-*t*-butyl-4-methylphenol (butylatedhydroxytoluene or

BHT). It is observed that BHT is recovered unchanged, almost quantitatively.

### Effect of Acidity

Due to non-aqueous nature of the solvent, *p*-toluene sulphonic acid (TsOH) is used as a source of hydrogen ions (Table 1). It is observed that the reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence taking the form as equation (6):

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

The least square value of a, b and coefficient of correlation (r) are recorded in the Table 6.

**Table 6: Statistical Data of the Analysis of Hydrogen- Ion Dependence of the Rate of Oxidation of Unsaturated Acids by BIFC**

USA	$10^4 a$ ( $s^{-1}$ )	$10^4 b$ ( $dm^3 mol^{-1} s^{-1}$ )	r	Temp (K)
FA	$5.99 \pm 0.18$	$10.2 \pm 0.32$	0.9980	308
CrA	$16.3 \pm 1.51$	$25.7 \pm 2.50$	0.9815	298
MA	$8.05 \pm 0.04$	$13.6 \pm 0.04$	0.9999	288
CiA	$5.79 \pm 0.05$	$10.0 \pm 0.10$	0.9997	288

### Effect of Solvents

The rates of the oxidation of the unsaturated acids by BIFC were obtained in nineteen different organic solvents. The solubility of reagents and reaction of BIFC with primary and secondary alcohols

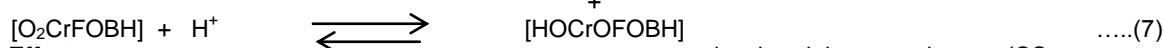
limited the choice of solvents. There was no reaction with the chosen solvents. Kinetics was similar in all the solvents. The values of K and  $k_2$  are recorded in Table 7.

**Table 7: Effect of solvents on the oxidation of crotonic acid by BIFC at 308 K**

Solvents	K ( $dm^{-3} mol^{-1}$ )	$10^3 k_2$ ( $s^{-1}$ )
Chloroform	6.31	22.4
1,2-Dichloroethane	5.86	30.3
Dichloromethane	5.37	23.5
DMSO	4.79	79.3
Acetone	5.14	21.4
DMF	5.53	41.7
Butanone	5.34	18.3
Nitrobenzene	5.63	33.8
Benzene	6.02	7.92
Cyclohexane	5.31	0.76
Toluene	5.24	6.47
Acetophenone	5.74	35.5
THF	4.38	11.3
t-Butyl alcohol	5.86	8.92
1,4-Dioxane	4.48	13.5
1,2-Dimethoxyethane	6.10	7.07
CS <sub>2</sub>	5.55	3.47
Acetic acid	5.65	5.24
Ethyl acetate	5.46	10.2

### Reactive Oxidizing Species

The effect of hydrogen ion concentration on the rate of reaction may be explained on the basis of



### Solvent Effect

Linear solvation energy relationship (8) of Kamlet et al.<sup>19</sup> was utilised for correlation of rate

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

In this equation,  $\pi^*$  represents the solvent polarity,  $\beta$  the hydrogen bond acceptor basicity and  $\alpha$  is the hydrogen bond donor acidity.  $A_0$  is the intercept term. Here out of the 18 solvents, 12 have a value of

$$\log k_2 = -4.01 + 1.69 (\pm 0.18) \pi^* + 0.18 (\pm 0.15) \beta + 0.08 (\pm 0.14) \alpha \quad \dots(9)$$

$$R^2 = 0.8821; \text{sd} = 0.17; n = 18; \psi = 0.39$$

$$\log k_2 = -4.03 + 1.72 (\pm 0.17) \pi^* + 0.15 (\pm 0.14) \beta \quad \dots(10)$$

$$R^2 = 0.8798; \text{sd} = 0.17; n = 18; \psi = 0.37$$

$$\log k_2 = -3.99 + 1.76 (\pm 0.17) \pi^* \quad \dots(11)$$

$$r^2 = 0.8708; \text{sd} = 0.17; n = 18; \psi = 0.37$$

$$\log k_2 = -3.02 + 0.46 (\pm 0.37) \beta \quad \dots(12)$$

$$r^2 = 0.0877; \text{sd} = 0.44; n = 18; \psi = 0.98$$

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

Kamlet's<sup>19</sup> triparametric equation explains ca. 88% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not

a protonation of BIFC in a pre-equilibrium (7), with both the protonated and deprotonated forms being reactive oxidizing species.

constants,  $k_2$ , in eighteen solvents (CS<sub>2</sub> was not considered, as the complete range of solvent parameters was not available).

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).

even satisfactory (cf. equation 9). The major contribution is of solvent polarity. It alone accounted for ca. 87% of the data. Both b and a play relatively minor role.

The data on the solvent effect were analyzed in terms of Swain's equation<sup>20</sup> of cation and anion

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

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

$$\log k_2 = 0.57 (\pm 0.08) A + 1.55 (\pm 0.06) B - 4.02 \quad \dots(14)$$

$$R^2 = 0.9769; \text{sd} = 0.07; n = 19; \psi = 0.16$$

$$\log k_2 = 0.35 (\pm 0.52) A - 2.96 \quad \dots(15)$$

$$r^2 = 0.0268; \text{sd} = 0.42; n = 19; \psi = 1.04$$

$$\log k_2 = 1.50 (\pm 0.12) B - 3.84 \quad \dots(16)$$

$$r^2 = 0.9072; \text{sd} = 0.31; n = 19; \psi = 0.31$$

$$\log k_2 = 1.22 \pm 0.13 (A+B) - 3.99 \quad \dots(17)$$

$$r^2 = 0.8308; \text{sd} = 0.17; n = 19; \psi = 0.42$$

The rates of oxidation of cinnamic acid in different solvents showed a very good correlation in Swain's equation [cf. equation (14)] 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 bad. The solvent polarity, represented by (A + B), also accounted for ca. 83% of the data. In view of the fact that solvent polarity is able to account for ca. 83% 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.

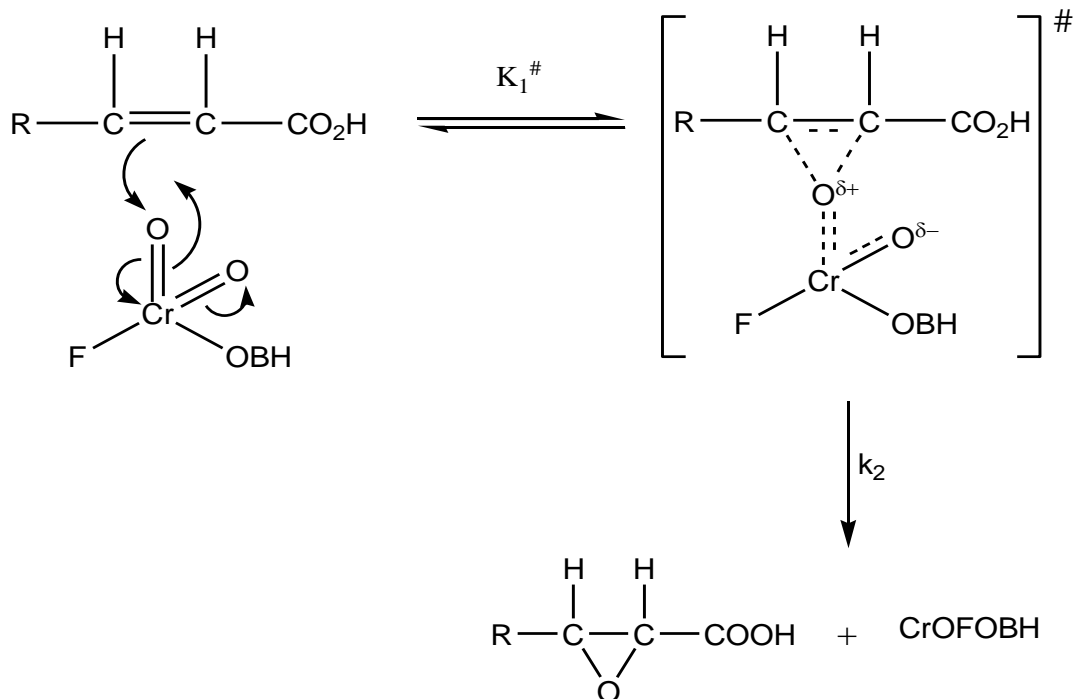
#### Mechanism

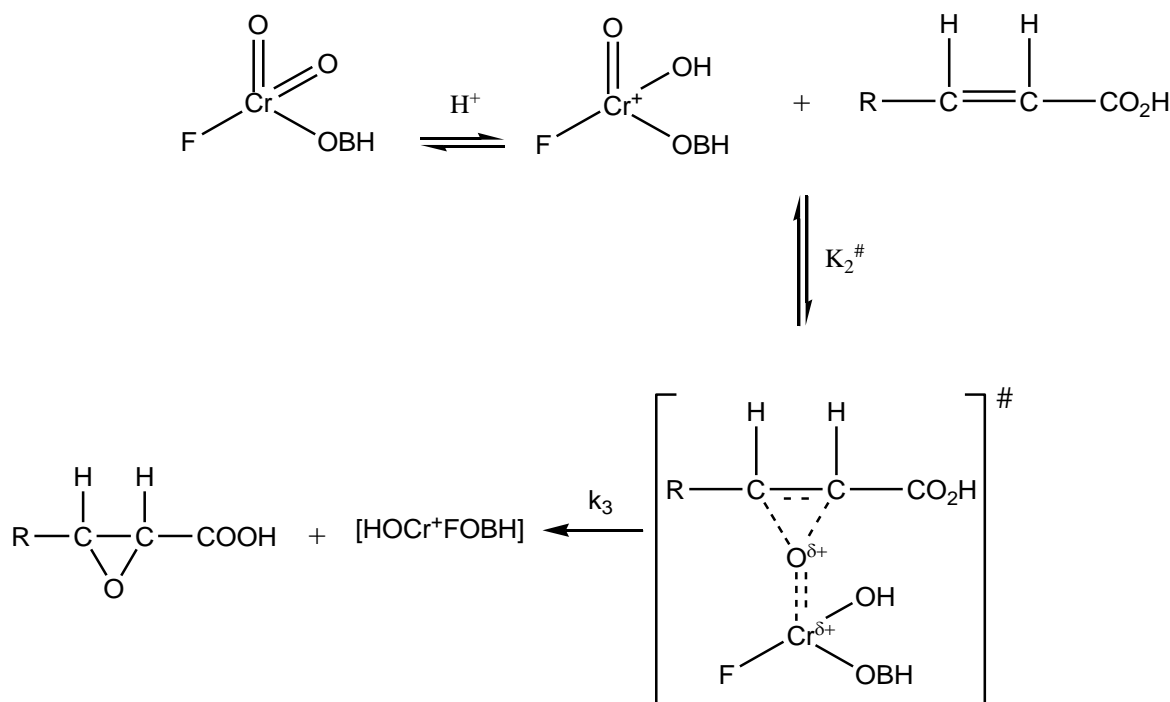
The low values of the enthalpies of activation show that bond-cleavage is not extensive in the formation of the activated complex. The formation of a rigid cyclic activated complex is indicated by the more negative values of the entropies of activation. The

solvating concept of the solvents also (13).

the solvent polarity. The rates in different solvents were analysed in terms of equation (13), separately with A and B and with (A + B).

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>9</sup>, where the formation of a carbocationic activated complex has been postulated, the value of b is 1.73. On the basis of the above experimental observations we propose/postulate the following composite scheme (Scheme - 1) for the present reaction.





Scheme - 1

**Conclusion**

Main product of the oxidation of unsaturated acids by BIFC is the corresponding epoxides. Reaction is found first order with respect to BIFC. The rate of reaction rise with increase in the concentration of hydrogen ions. There is no free radical reaction. Reaction occurs via formation of the activated complex.

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**Endnotes**

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