# OXIDATION OF DIOLS BY MORPHOLINIUM FLUOROCHROMATE: A KINETIC AND MECHANISTIC STUDY

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## ABSTRACT

The kinetics of oxidation of diols by morpholinium fluorochromate (MFC) has been studied in dimethyl sulfoxide (DMSO). Corresponding hydroxy carbonyl compounds are the main product of oxidation. The reaction is first order in MFC and follows Michaelis-Menten type of kinetics with respect to diols. The reaction is catalyzed by $H^+$ ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. Oxidation of deuterated ethylene glycol showed substantial primary kinetic isotopic effect ($k_H / k_D = 5.750$ at 298 K). Thermodynamic parameters like enthalpy, entropy and free energy of activation are discussed and validity of the isokinetic relationships also established. We have used nineteen different organic solvents for carrying out our analysis. Taft and Swain's multiparametric equations have been used for the solvent effect analysis. In our experiments rate constants have showed excellent correlation with Taft's $\sum\sigma^*$ values along with negative values for the reaction constant $\rho^*$. A suitable mechanistic pathway for the chromate ester formation has also been suggested.

**Keywords:** Diols, Morpholinium fluorochromate, kinetics, mechanism, oxidation, kinetic isotope effect, hydroxy aldehyde.

## 1. INTRODUCTION

Oxidation of hydroxyl compounds to the corresponding carbonyl compounds is a very important process in the synthetic organic chemistry. Several chromium (VI) derivatives have so far been reported to bring about this change [1, 2]. Chromium (VI) is a versatile oxidant, but is a mild and non-selective oxidant. To improve its selectivity, many organic halochromates have been used as lenient and selective oxidizing agents [3-5]. Literature studies have revealed that oxidation of diols can take place in two different ways. Some oxidants oxidize diols via glycol bond fission, resulting in the carbonyl compound [6, 7], while others oxidize the corresponding hydroxy carbonyl compound [8, 9]. Furthermore, it was observed that various Cr (VI) complexes undergo different kinetic and mechanistic processes for the oxidation of diols [10, 11]. Morpholinium fluorochromate (MFC) is an oxidant that has been previously used for the oxidation of different aliphatic alcohols [12, 13]. In this research article, we have described the kinetics of the oxidation of some diols by MFC, using dimethylsulfoxide (DMSO) as solvent. We have given emphasis on the structure-reactivity correlation. The mechanistic ways by which the oxidation of diols has taken place has also been suggested.

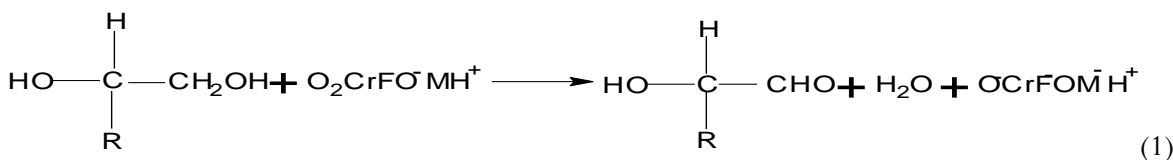## 2. EXPERIMENTAL

### 2.1. Material

MFC was prepared by the reported method [12] and its purity was checked by the iodometric method. All the diols were distilled under reduced pressure before using. Deuterated diols were prepared by the known method and isotopic purity of the diols was ascertained by taking their NMR spectrum which was around 90-91±5%. P-Toluene sulfonic acid (TsOH) was used as the hydrogen ions source due to its aqueous nature. TsOH is a strong acid and in polar medium such as DMSO, it gets completely ionized. Purification of solvents was done by simple methods [14].
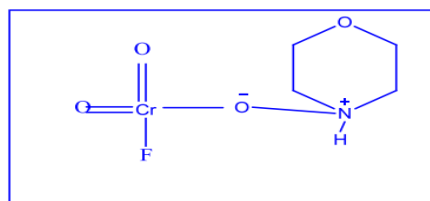


Structure of Morpholinium Fluorochromate

## 2.2. Product Analysis

Quantitative product analysis for the formation of hydroxy carbonyl compounds in relation to the oxidation of the diols was done under dynamic conditions. In a simple experiment diol (0.1 mol) and MFC (0.01 mol) were mixed in a 100 ml DMSO solution and 1.0 mol $dm^{-3}$ TsOH was added for the supply of $H^+$. The mixture was allowed to stand for overnight in a dark place for the completion of the reaction. A saturated solution of 250 ml of 2,4-dinitrophenyl hydrazine in 2 mol $dm^{-3}$ HCl (200 $cm^{-3}$) was made, mixed with the above solution and was allowed to cool in the refrigerator for 12h. The reaction mixture was now filtered, the solvent was taken out and the precipitated 2,4-dinitrophenylhydrazine (DNP) was collected on the filter paper, dried and was recrystallized with ethanol. All the DNP derivatives were found to be analogous. Melting point of DNP derivatives were compared with the literature values to identify the product. The yield of the individual DNP derivatives after recrystallization was around 86-91%.

## 2.3. Kinetic Measurements

Reactions were carried out under pseudo-first-order conditions by keeping an excess (×15 or greater) of substrate over MFC. The solvent used was DMSO. A constant temperature (±0.1 K) was maintained throughout our reaction. A decrease in the concentration of MFC at 356 nm for up to 85% of the reaction was observed. The linear least-squares plot of log [MFC] against time was used to evaluate the pseudo-first-order rate constant, $k_{obs}$. Equivalent kinetic runs showed that the rate constants were reproducible to within ±3%. In correlation analysis, we have used coefficient of determination ($R^2$ or $r^2$), standard deviation (SD) and Exner's parameter, $\psi$, as appraise of the excellence.
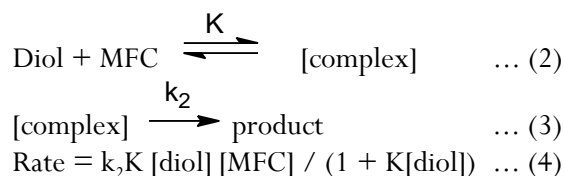
## 3. RESULTS

The rates and other experimental data were acquired for all the diols under study. Since the results are similar, only representative data are reproduced here. When oxidation of different diols was carried out by MFC, corresponding hydroxy carbonyl compounds were formed. The overall reaction can be written as eqn. 1 (here M = morpholine).



$$(1)$$

Here (R) is H, $CH_3$, $C_2H_5$ and $C_3H_7$ for different vicinal diols. In the case of 2,3-Butane diol instead of hydroxy aldehydes, we get corresponding ketones. MFC undergoes a two-electron change. Similar findings were observed with both pyridinium chlorochromate [15] and pyridinium fluorochromate [16]. The oxidation state was found to be 4 in the spent chromium species, which was verified by determining its IR, ESR and magnetic susceptibility [16, 17].

## 3.1. Induced Polymerization Test

Acrylonitrile and the substrate were kept in a conical flask and the vessel was flushed with nitrogen for about 30 min. A solution of MFC was also flushed with nitrogen. An aliquot of the oxidant solution was added to the solution of the substrate. Nitrogen was steadily passed through the reaction mixture. Each experiment was accompanied by a blank control. The oxidation of diols, in an atmosphere of nitrogen failed to induce polymerization of acrylonitrile. Further there was no effect of insertion of acrylonitrile on the rate of the reaction.

## 3.2. Rate Laws

Reaction was found to be of 1st order relative to MFC. Michaelis-Menten type of kinetics was followed by the oxidation of diols by MFC. A graph was plotted between log $k_{obs}$ versus log [diol], which was found to be linear with an intercept on the rate ordinate. The overall mechanism can be given as in Eqn. (2) and (3) and the rate law in Eqn. (4).

$$\text{Diol} + \text{MFC} \xrightleftharpoons{K} [\text{complex}] \quad \dots (2)$$

$$[\text{complex}] \xrightarrow{k_2} \text{product} \quad \dots (3)$$

$$\text{Rate} = k_2 K [\text{diol}] [\text{MFC}] / (1 + K[\text{diol}]) \dots (4)$$

The rate of reaction was found to be linearly increasing with an increase in the diols concentration. Table 1 and Fig. 1 represent a typical kinetic run and Figure 2 represents order of reaction.

**Table 1: Rate constants for the oxidation of diols by MFC at 308 K**

| [DIOL] (mol dm$^{-3}$) | $10^3$ [MFC] (mol dm$^{-3}$) | $10^3$ [H$^+$] (mol dm$^{-3}$) | Ethanediol $10^5 k_{obs}/s^{-1}$ | Propane-1,2-diol $10^5 k_{obs}/s^{-1}$ | Propane-1,3-diol $10^5 k_{obs}/s^{-1}$ | Butane-1,3-diol $10^5 k_{obs}/s^{-1}$ |
|---|---|---|---|---|---|---|
| 0.1 | 1.0 | 1.0 | 2.14 | 2.71 | 2.92 | 4.10 |
| 0.2 | 1.0 | 1.0 | 4.32 | 6.24 | 6.46 | 10.1 |
| 0.3 | 1.0 | 1.0 | 8.40 | 11.8 | 13.9 | 20.0 |
| 0.5 | 1.0 | 1.0 | 13.8 | 24.3 | 28.4 | 54.3 |
| 0.8 | 0.5 | 1.0 | 16.1 | 32.7 | 44.3 | 129 |
| 1.0 | 1.0 | 1.0 | 29.4 | 98.5 | 114 | 206 |
| 0.8 | 0.5 | 1.0 | 16.8 | 33.9 | 42.9 | 137 |
| 0.8 | 0.8 | 1.0 | 15.9 | 29.8 | 45.0 | 122 |
| 0.8 | 2.0 | 1.0 | 16.6 | 31.2 | 44.1 | 130 |
| 0.8 | 3.0 | 1.0 | 16.8 | 32.0 | 42.9 | 142 |
| 0.8 | 5.0 | 1.0 | 18.0 | 38.3 | 44.0 | 132 |
| 1.0 | 1.0 | 1.0 | 29.9[a] | 78.3[a] | 133[a] | 218[a] |
| 1.0 | 1.0 | 1.0 | 29.2[b] | 84.2[b] | 142[b] | 224[b] |

[a] & [b] *contained 0.001 and 0.005 mol dm$^{-3}$ acrylonitrile respectively*
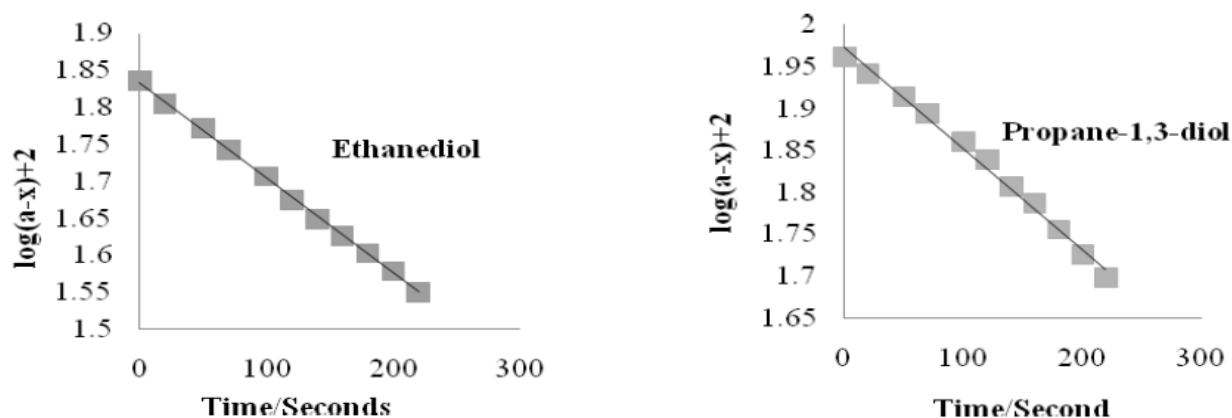


**Fig.1: Oxidation of diols by MFC: A typical kinetic run**
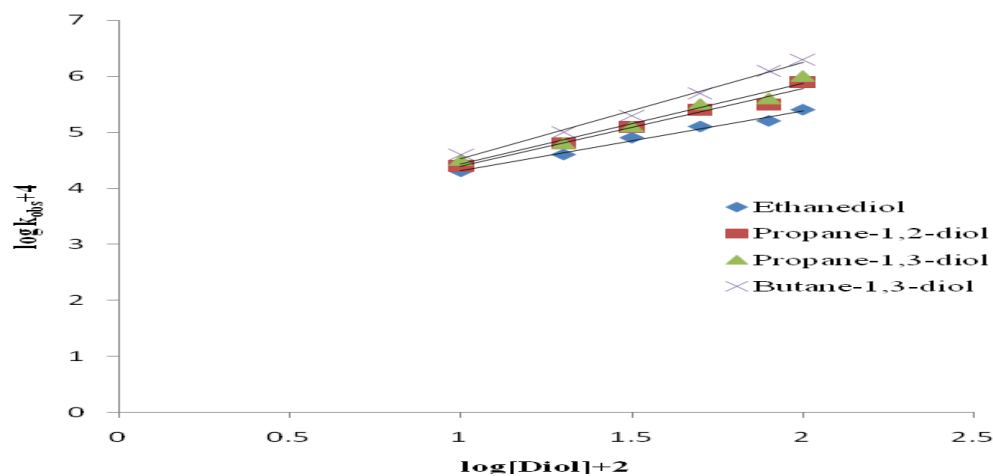


**Fig. 2: Order plot for the oxidation of diols by MFC at 308 K**

### 3.3. Effect of Hydrogen-Ion

Hydrogen ions are used to catalyze the reaction. The hydrogen ion dependence can be expressed by the form as: $k_{obs} = a + b [H^+]$ (*cf.* Table 2 & Figure 3).

### 3.4. Effect of Temperature

The calculation for the rate constants and activation parameters for the reactions were done for the oxidation of diols at 4 different temperatures between 298K - 328K (Table 3). The log k values at different temperatures are linearly related to inverse of the absolute temperature in all the cases (Fig. 4). This verifies the validity of Arrhenius equation for all the cases.

**Table 2: Dependence of rate constant on the $H^+$ concentration for the oxidation of diols by MFC**

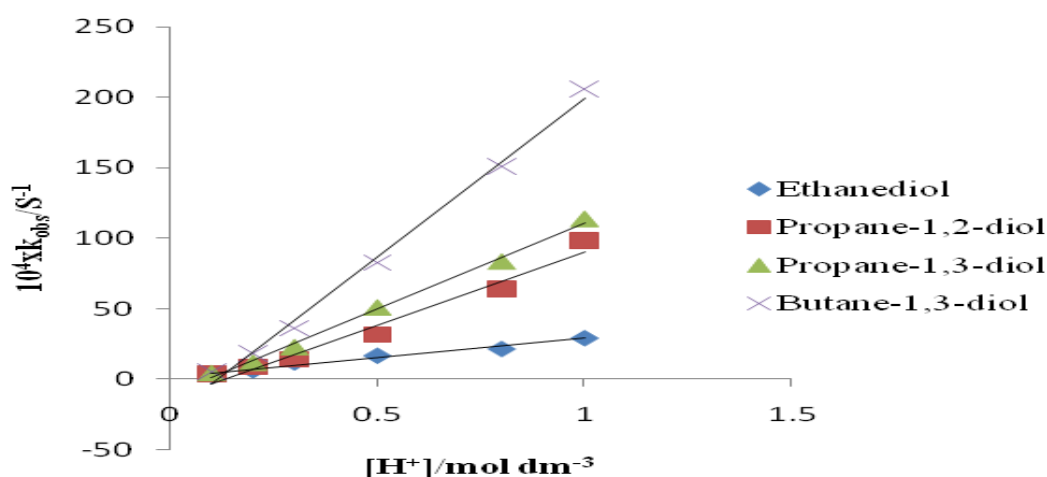| [Diol] 1.0 mol dm$^{-3}$ | [MFC] 0.001 mol dm$^{-3}$ | | Temperature 308 K | | | |
|---|---|---|---|---|---|---|
| $[H^+]$ / (mol dm$^{-3}$) | 0.1 | 0.2 | 0.3 | 0.5 | 0.8 | 1.0 |
| Ethanediol / ($10^5 k_{obs}/s^{-1}$) | 2.97 | 6.42 | 12.2 | 16.9 | 21.7 | 29.4 |
| Propane-1,2-diol / ($10^5 k_{obs}/s^{-1}$) | 3.21 | 8.24 | 13.8 | 31.2 | 63.8 | 98.5 |
| Propane-1,3-diol / ($10^5 k_{obs}/s^{-1}$) | 4.37 | 11.7 | 22.8 | 51.0 | 83.7 | 114 |
| Butane-1,3-diol / ($10^5 k_{obs}/s^{-1}$) | 5.28 | 18.5 | 36.2 | 82.7 | 151 | 206 |



**Fig. 3: Effect of hydrogen ion on the oxidation of diols by MFC**
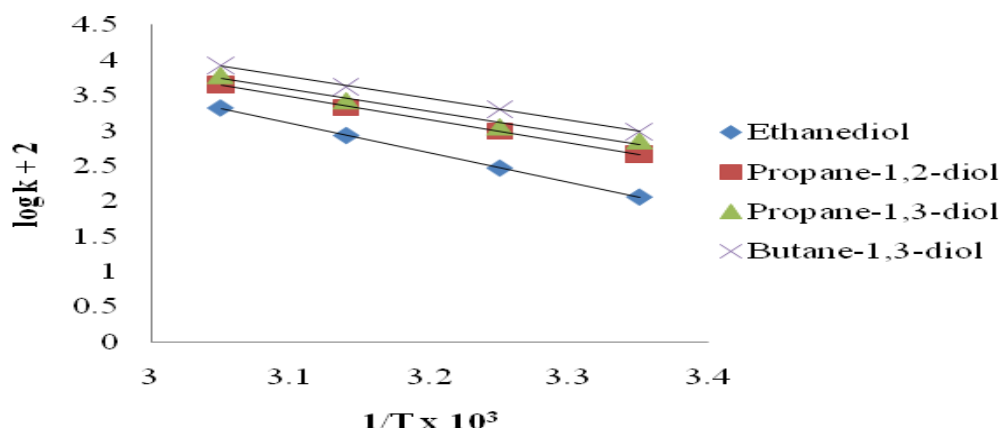


**Fig. 4: Effect of temperature on the oxidation of diols by MFC**

## 3.5. Kinetic Isotope Effect

The oxidation of DED i.e. $[1,1,2,2-^2H_4]$ ethanediol and others were studied to determine the significance of cleavage of $\alpha$-C-H bond of ethanediol and others in the rate determination step. The results are reported in the Table 3. They clearly show significant primary kinetic isotope effects ($k_H/k_D = 5.750$ at 298 K).

## 3.6. Isokinetic Relationship

Exner's method [18] was applied to test the isokinetic relationship for this reaction. The correlation was tested and found to be fit for it. Exner plot was linear ($r^2 = 0.9977$), for log values between 298 K and 328 K for diols. The value of isokinetic temperature determined by Exner's method is $1010\pm60$ K. The current values of isokinetic temperature of the views were of more physical significance. However, the linear isokinetic relationship suggests that all diols are oxidized in the same manner and follow same mechanistic pathways. (Fig. 5).

## 3.7. Solvent Effect

Oxidation of different diols by MFC has been studied in nineteen different organic solvents. Due to solubility of MFC and its reaction with primary and secondary alcohols, the choice of solvent selection is limited. All the diols have shown similar kinetics for the oxidation, in different solvents. The values for the rate constant k, are recorded in the Table 4 (Fig. 6).

**Table 3: Rate constants obtained for the oxidation of diols by MFC at different temperatures**

| DIOL | $10^4k/mol^{-1}dm^3s^{-1}$ | | | | $\Delta H^*$ | $\Delta S^*$ | $\Delta G^*$ |
|---|---|---|---|---|---|---|---|
| | 298 | 308 | 318 | 328 | (kJ mol$^{-1}$) | (J mol$^{-1}$ K$^{-1}$) | (kJ mol$^{-1}$) |
| Ethane-diol | 1.15 | 2.94 | 8.48 | 21.1 | 76.9$\pm$1.3 | -14$\pm$4 | 72.8$\pm$1.0 |
| Propane-1,2-diol | 4.61 | 9.85 | 21.2 | 45.4 | 59.4$\pm$0.8 | -34$\pm$2 | 69.3$\pm$0.6 |
| Butane-2,3-diol | 21.9 | 44.3 | 101 | 198 | 57.8$\pm$1.2 | -26$\pm$3 | 65.4$\pm$0.9 |
| Butane-1,2-diol | 5.65 | 10.1 | 25 | 58.6 | 61.7$\pm$3.5 | -25$\pm$1 | 69.0$\pm$2.7 |
| Propane-1,3-diol | 7.28 | 11.4 | 26.7 | 62.4 | 56.5$\pm$4.5 | -41$\pm$1 | 68.4$\pm$3.5 |
| Butane-1,3-diol | 9.7 | 20.6 | 43 | 85 | 56.4$\pm$0.1 | -38$\pm$1 | 67.4$\pm$0.1 |
| Butane-1,4-diol | 13.4 | 26.1 | 51 | 109 | 53.9$\pm$1.6 | -43$\pm$5 | 66.7$\pm$1.2 |
| Pentane-1,5-diol | 15.9 | 33.7 | 65 | 125 | 53.1$\pm$0.3 | -44$\pm$1 | 66.2$\pm$0.2 |
| 3-Methoxy-Butane-1-ol | 20.4 | 39.9 | 71 | 133 | 47.9$\pm$0.6 | -60$\pm$2 | 65.6$\pm$0.5 |
| DED* | 0.20 | 0.55 | 1.65 | 4.26 | 80.9$\pm$1.0 | -12$\pm$3 | 77.1$\pm$0.8 |
| $k_H/k_D$ | 5.75 | 5.34 | 5.14 | 4.95 | | | |

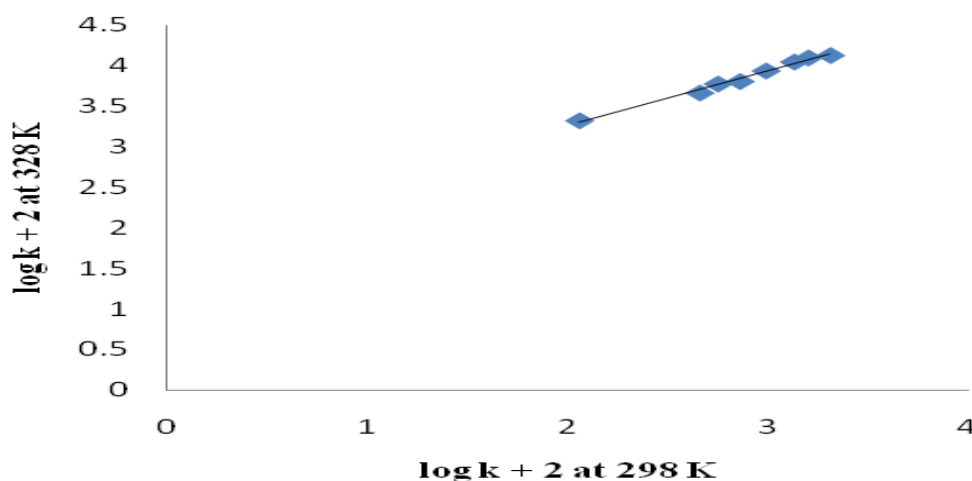*$[1,1,2,2-^2H_4]$ ethane-1,2-diol



**Fig. 5: Oxidation of diols by MFC: Exner's Isokinetic Relationship**

**Table 4: Rate constants for the oxidation of Ethanediol by MFC in different solvents at 308 K**

| Solvent | $10^4 k(\text{mol}^{-4}\text{dm}^{12}\text{s}^{-1})$ | Solvent | $10^4 k(\text{mol}^{-4}\text{dm}^{12}\text{s}^{-1})$ |
|---|---|---|---|
| Chloroform | 6.21 | Toluene | 2.01 |
| 1,2-Dichloromethane | 8.5 | Acetophenone | 13.8 |
| Dichloromethane | 7.8 | Tetrahydrofuran | 3.94 |
| DMSO | 2.94 | Tert-butyl alcohol | 2.46 |
| Acetone | 7.9 | Dioxane | 4.76 |
| DMF | 15.7 | 1,2-Dimethoxyethane | 1.68 |
| Butanone | 5.64 | Acetic acid | 1.1 |
| Nitrobenzene | 11.6 | Ethyl acetate | 2.99 |
| Benzene | 3.2 | Carbon disulfide | 0.84 |
| Cyclohexane | 0.12 | | |
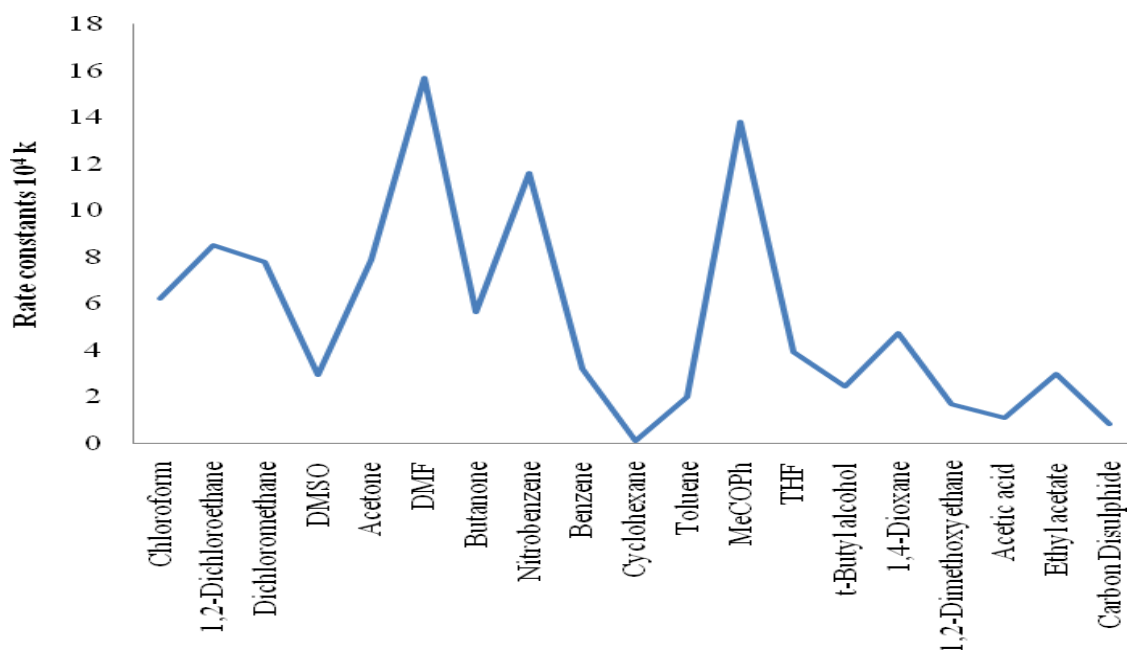


**Fig. 6: Oxidation of diols by MFC: Effect of Solvents**

## 4. DISCUSSION

The values of rate constant k, in 18 solvents ($CS_2$ was not studied, because the complete range of the solvent parameters is not available) were correlated in terms of linear solvation energy relationship of Kamlet *et al* [19].

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

Theanalyses in terms of equation (5), a two-parameter equation involving $\pi^*$ and $\beta$, and separately with $\pi^*$ and $\beta$ gave the following results. Here *n* is the number of data points.

$$\log k = -5.69 + 1.58 \pm 0.19 \pi^* - 0.25 \pm 0.14 \alpha + 0.29 \pm 0.15\beta \qquad \dots(6)$$

$R^2 = 0.8722$, sd = 0.18, n = 18, $\psi = 0.41$

$$\log k = -5.75 + 1.68 \pm 0.20 \pi^* + 0.09 \pm 0.15\beta \dots(7)$$

$R^2 = 0.8230$, sd = 0.19, n = 18, $\psi = 0.44$

$$\log k = -5.73 + 1.69 \pm 0.21 \pi^* \qquad \dots(8)$$

$r^2 = 0.8110$, sd = 0.20, n = 18, $\psi = 0.43$

$$\log k = -4.68 + 0.39 \pm 0.36 \beta \qquad \dots(9)$$

$r^2 = 0.0569$, sd = 0.43, n = 18, $\psi = 0.99$

The results showed that *ca.* 85% of data on the solvent effect can be explained by the equation (3). According to Exner's criterion, however, the correlation is poor. The major contribution is from the solvent polarity term, $\pi^*$. Both $\alpha$ and $\beta$ plays relatively insignificant roles. There is no significant collinearity between $\pi^*$ and $\beta$ for the eighteen solvents ($r^2 = 0.0477$, sd = 0.24).

The data on solvent effects were also analyzed with

Swain's equation [20] of cation and anion solvating concept of solvent.

$$\log k = aA + bB + C \qquad \dots (10)$$

Where A denotes the anion-solvating power of the solvent and B denotes the cation-solvating power; C is the intercept form and (A + B) is postulated to be indicative of solvent polarity. (a & b are stoichiometric coefficients). The rates in the various solvents were analyzed in term of Eqn. (10)

$$\log k = 0.53 \pm 0.02 \, A + 1.68 \pm 0.02 \, B - 5.83 \quad \dots (11)$$
$r^2 = 0.9981$, SD = 0.02, n = 19, $\psi$ = 0.03
$$\log k = 0.21 \pm 0.51 \, A - 4.79 \qquad \dots (12)$$
$r^2 = 0.0059$, SD = 0.42, n = 19, $\psi$ = 1.06
$$\log k = 1.60 \pm 0.08 \, B - 5.69 \qquad \dots (13)$$
$r^2 = 0.9791$, SD = 0.07, n = 19, $\psi$ = 0.19
$$\log k = 1.23 \pm 0.15 \, (A+B) - 5.75 \qquad \dots (14)$$
$r^2 = 0.7682$, SD = 0.21, n = 19, $\psi$ = 0.43

The oxidation rate in various solvents showed excellent correlation with the Swain's equationas cation solvating power played an important role. However, the role of anion-solvating powerwas found to be negligible. An attempt was made to correlate the data with the relative permeability of the solvents. The plot of log k against the inverse of relative permeability is not linear ($r^2$ = 0.6414). Thus, we can say that our reaction does not follow Kamlet's equation. In previous studies with MFC, it has been observed that the correlation analysis of solvent effects in terms of Kamlet's equation does not show good result. The correlation with Swain's equation is excellent and the main contribution to the solvent effect is to illustrate the solvent strength.

## 4.1. Correlation analysis of reactivity

Taft [21] has developed a LFER (linear free energy relationship) to correlate the structure and reactivity for the aliphatic system.

$$\log k = \rho^* \sigma^* + \log k_0 \qquad \dots (15)$$

For diols, the equation was modified as,

$$\log k = \rho^* \sum \sigma^* + \log k_0 \qquad \dots (16)$$

Here, $\sum \sigma^*$ represents the sum of the constants of the substituents in the two alcoholic carbons of the vicinal diols. In the present reaction, the oxidation rate of the four vicinal diols showed an excellent correlation with the negative reaction constants with the Taft's $\sum \sigma^*$ value. Although the number of compounds was small for the correlation analysis, the results can be used qualitatively. The negative polarity of the reaction constant determines the presence of an electron-

deficient center in the rate-determining step, resulting in an increase in the rate of the reaction with an increase in the electron donating power of the alkyl group. (*cf.* Fig. 7)

**Table 5: Correlation of rates of oxidation of diols in terms of Taft's equation**

| Tempera-ture/K | ρ* | R² | SD | ψ |
|---|---|---|---|---|
| 298 | -1.19±0.01 | 0.9998 | 0.01 | 0.015 |
| 308 | -1.11±0.02 | 0.9999 | 0.01 | 0.012 |
| 318 | -1.07±0.01 | 0.9998 | 0.01 | 0.014 |
| 328 | -1.02±0.02 | 0.9999 | 0.01 | 0.014 |

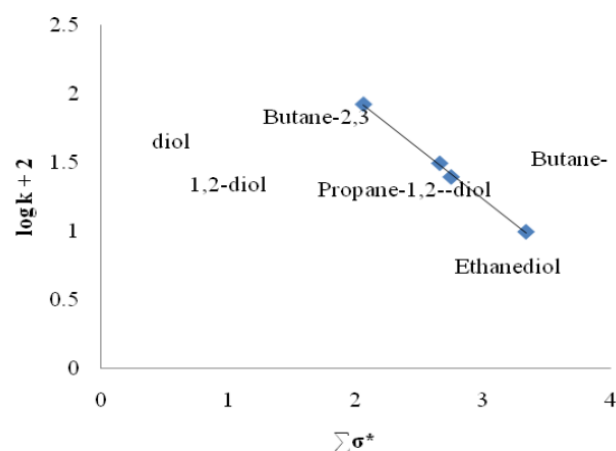*No. of data points = 4*



**Fig. 7: Oxidation of diols by MFC: Taft's Plot at 298 K mechanism**

The breaking of $\alpha$-C-H bond in the rate-determining step showed a significant kinetic isotopic effect exhibited by the reaction. The negative value of the polar reaction constant clearly indicates that transition state involves an electro-positive carbon center. Therefore, it is suggested that the hydride-ion transfer from the diol to the MFC takes place. The hydride-ion transfer mechanism can also be assisted by the greater role of the cation-solvation power of the solvents. Transfer of hydride ion might occur through a cyclic process via a chromate ester formation or by an acyclic bimolecular process. Studies of the dependence of kinetic isotopic effects on the temperature done by Kwart and Nickel [22] have shown that it can be beneficially used to detect this problem. The data of ethanediol and deuterated ethanediol, fitted with the expression $K_H / K_D = A_H / A_D \exp (E_a / RT)$, shows a direct correlation with the properties of a

symmetric transition state, in which the entropies of the reactivity of $K_H/K_D$ -related C-H bonds and C-D bonds ($\approx$4.5 kJ / mol) are equal to the zero-point energy difference, and the corresponding entropies of the corresponding reactions are approximately [23,24]. Similar phenomena have also been distinguished in the study of diols oxidation by QFC [11] and PBC [12]. Boardwell [25] provides strong evidence against hydrogen transfer, one-stage biomolecular processes, and even in the present study, it is clear that hydrogen transfer does not occur from the acyclic biomolecular

process. The only real symmetric processes involving linear hydrogen transfer are inherently sigmatropic rearrangements which are characterized by the transfer of hydrogen to the cyclic transition state [26].

Scheme (1) represents formation and protonation of chromate ester in the fast pre-equilibrium phase, which is the rate determining step followed by the decomposition of chromate ester. This scheme (1) accounts for all our observed results. (Scheme 2) represents rapid reversal protonation of chromate ester (A), which decreases the protonated ester faster than A.



**Scheme 1**



**Scheme 2**
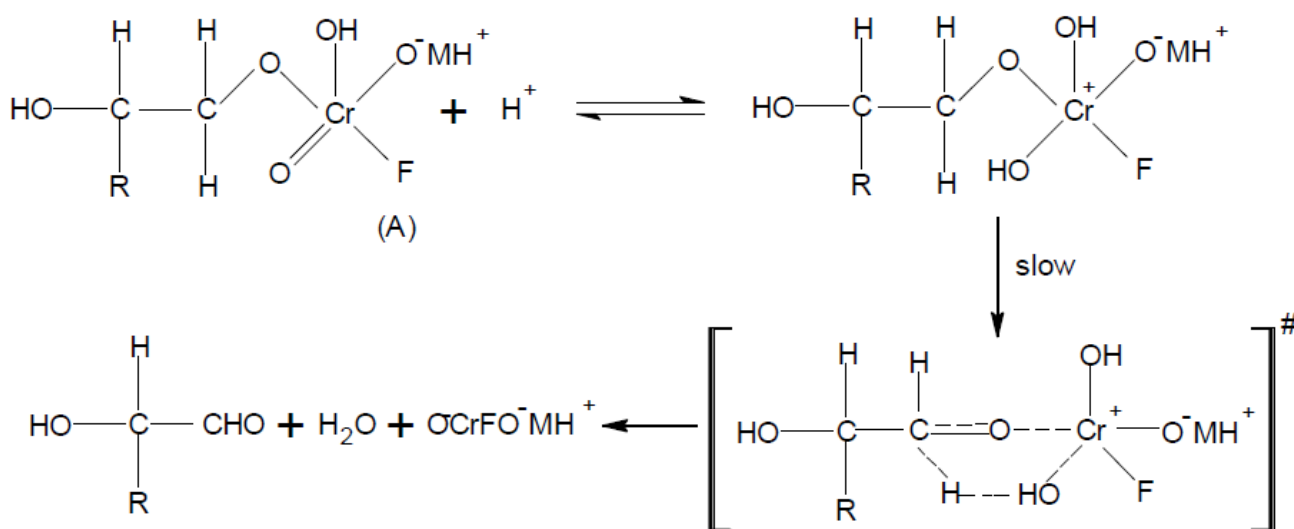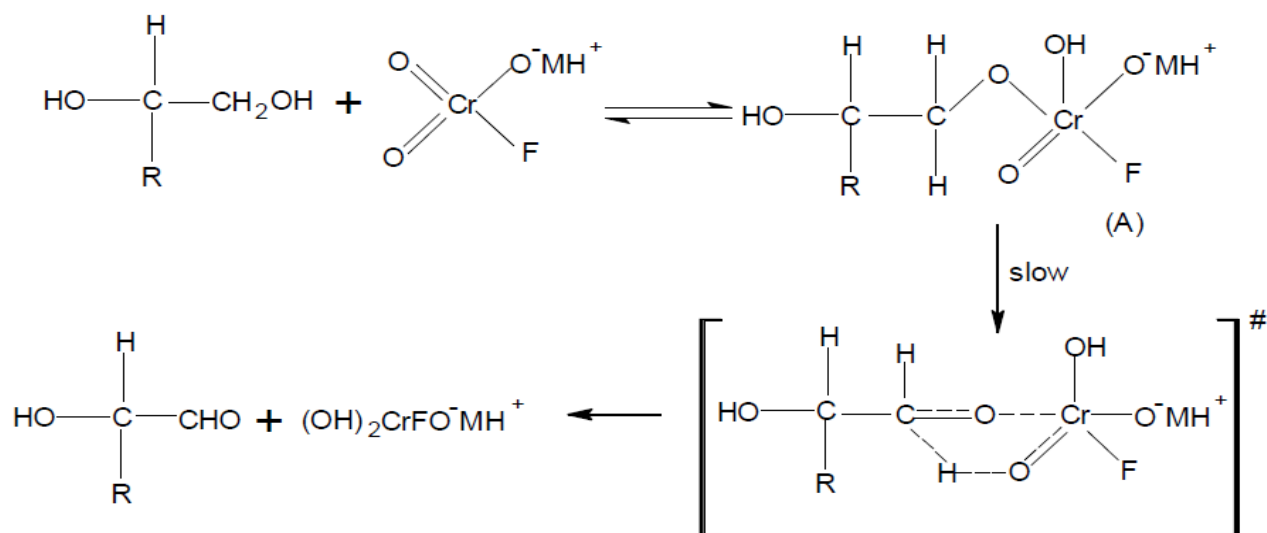
Here R is -H, -CH$_3$, -C$_2$H$_5$, -C$_3$H$_7$etc.

## 5. ACKNOWLEDGEMENTS

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