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Research Article

DIFFERENT α-HYDROXY ACIDS OXIDATION BY MORPHOLINIUM FLUOROCHROMATE: A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

The oxidation of different α-hydroxy acids by a selective and mild oxidizing agent Morpholinium Fluorochromate (MFC) in DMSO leads to the formation of corresponding oxoacids. The reaction was found to be of first order each in MFC. The reaction followed Michaelis-Menten type of kinetics with respect to the hydroxy acids. Polymerization of acrylonitrile showed no effect on the rate of the reaction. Primary kinetic isotope effect (k_H/k_D= 6.83 at 25ºC) was observed due to the oxidation of α-deuteriated mandelic acid. The solvent isotope effect was not observed. The reaction was catalyzed by the hydrogen ions. The hydrogen ion dependence has the following form: k_{obs}= a + b [H^+].Reaction was analysed by using Kamlet's and Swain's multiparametric equations. We have tried to propose a suitable mechanism for the reaction.

Keywords: *Correlation Analysis, Halo chromates, MFC, Kinetics, Mechanism, Oxidation*

INTRODUCTION

α-Hydroxy acids are the class of organic compounds in which a hydroxyl group and a carboxylic group is present. Some of the important members are glycolic acid obtained from sugarcane, lactic acid obtained from milk, malic acid obtained from apple, citric acid obtained from citrus fruits like lemon and orange), tartaric acid obtained from grape wine and mandelic acid obtained from bitter almonds. These AHA (alpha hydroxy acids) and their derivatives have a wide application in various fields like biological, vital, cosmetic and organic synthesis. These are very important in the organic synthesis of aldehydes via oxidative cleavage of bonds. Many research work on kinetic study of catalytic oxidation of glycolic acids by PMS (Maheshwari et al),oxidation of glycolic acid by hexamethylenetetramine-Bromine in glacial acetic acid medium (Tinsay et al), oxidation of hydroxy butyric acid salts by Ditelluratocuprate (III) in alkaline medium (Shan et al),induced electron transfer reaction in Pentaammine cobalt(III) complexes by QDC (Anandaratchagan *et al., 2011*), Qx.BC (Chandrasekaran and Subramani, 2012) and oxidation of some alpha hydroxy acids by TEAFC (Subash *et al.*, 2015), TEACC (Swami *et al.*, 2010) as well as by PDC (*Amed et al 2012*), oxidation of hydroxy acids by PFC, cobalt bounded and unbounded oxidation by 4-(DMA)PDC (Pownsamy *et al.,* 2015) has been reported. But still less work has been done in non-aqueous solvent. So, it is important to study kinetic and mechanistic aspects of these compounds in non-aqueous solvents for more detailing and characterization of these compounds.

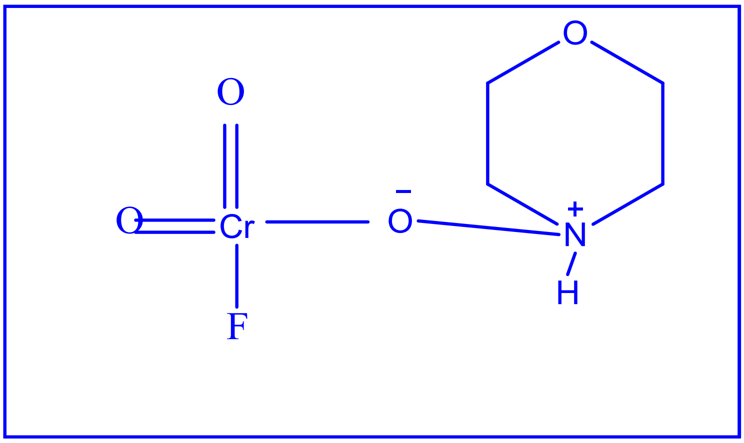
Hexavalent form of Chromium has been proved to be very effective reagent capable of oxidizing many oxidizable functional group . A lot of research has been done and many mild and selective oxidising agents have been prepared so far the oxidation of many of the organic compounds (Zeng & Hiran *et al.*, 2002). Many Cr (VI) compounds with heterocyclic bases like PCC (Corey and Boger, 1978), BpCC (Anbarasu and Selvi, 2013), Tetrachloro Aurate (III) (Sengupta *et al.,* 1999), N-Chlorosuccinamide, QBC (Saraswat *et al*, 2002), N-Bromonicotinamide (Pushpalatha, 2015), QCC (Nirayan *et al.,* 2003), MCC (Malani *et al.*, 2008), BTEAFC (Alhaji *et al.*, 2016), IFC (Pandurangan *et al.*, 1996), IDC (Sekar, 2003), MFC (Alangi *et al.*, 2011) have been developed to improve the selectivity of oxidation of organic compounds. The mildness and selectiveness of MFC was demonstrated effectively in oxidation of aryl alcohols on silica gel (Alangi *et al* 2011), primary alcohols (Vyas *et al.,* 2015), secondary alcohols (Purohit & Mishra *et al.,* 2016). and substituted benzaldehydes(Purohit & Mishra *et al.*, 2017). The oxidation of αhydroxy acids by MFC is not been reported so far. Therefore, in this paper we have presented the kinetics and mechanistic studies of the oxidation of some α-hydroxy acids by MFC in DMSO. And have evaluated the kinetic parameters as well as done correlation analysis.

MATERIALS AND METHODS

Chemicals

We have used all the α-hydroxy acids of A.R. Grade (E Merck, Germany). We have prepared Morpholinium Fluoro Chromate by the known reported methods (Alangi ***et al*** ¨ 2011) and we have checked its purity by an iodometric method. earlier (Vogel, 1956) The preparation of different α hydroxy acid like glycolic acid(GA), malic acid(MA), lactic acid (LA),mandelic acid(MLA) and some of the substituted mandelic acid have been described earlier(Kemp and Waters, 1964) and α-Deuteriated mandelic acid (PhCD (OH)COOH or DMA) was prepared by the method reported by Kemp and Water(Kemp and Water, 1964).The purity of MFC was found to be 95±5% by NMR spectra . PTS or p-Toluene Sulfonic Acid) was used as source of hydrogen ions due to non-aqueous condition of the solvent. Solvent purity was checked by the usual reported methods (Perrin ***et al.,*** 1988).

MORPHOLINIUM FLUOROCHROMATE



Instruments

We have used UV-Vis spectrophotometer model (AIMIL India model MK2) for caring out our experiments . λ_{max} 352 nm was selected as MFC showed (absorbance) λmax at 352 nm. Thermostat water bath was used for maintaining constant temperature conditions and other common laboratory equipment's were also used during the investigations.

Kinetic Experiments

By taking a large excess (*15 times or more) of hydroxy acids over MFC pseudo first order constants were achieved. We used DMSO as non-aqueous solvent. We kept the temperature constant to 303 (±0.1) 303K). The decrease in the MFC concentration were observed by monitoring spectrophotometrically at 352nm for up to 80% of the reaction. A graph was plotted between of log [MFC] against time and pseudo-first order rate constant k_1 was evaluated from linear least square from the graph. The second order rate constant k_2 was obtained from relation $k_2=k_1/$ [HA].All experiments were carried out in the absence of PTS except those where effect of H^+ concentration was studied.

Product Analysis

The product analysis was carried out under kinetic conditions i.e. with an excess of α-hydroxy acids was taken over MFC and made up to 50 ml in DMSO and kept in the dark for approximately 24hrs to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2mol/dm^3HCl and kept for 24 hours in a refrigerator. The precipitate of 2, 4-dinitrophenylhydrazone (DNP) was first filtered then dried and weighed. It was recrystallized from ethanol and weighed again. The weights of the DNP before and after recrystallization were determined. The DNP was found identical (m.p. and mixed m.p.) with the DNP of α hydroxy acids. The oxidation state of chromium in the product which was an oxo acid, in a completely reduced reaction mixtures was determined by an iodometric method and was 3.92 ±12.

RESULT AND DISCUSSION

The oxidation of different alpha hydroxy acids like glycolic acid, malic acid, lactic acid and mandelic acid were carried out by MFC in the DMSO at 30ºC, under pseudo first order conditions.For all the hydroxy acids rate and other experimental data's were obtained. . Since the results were similar, only representative data are reproduced here. The results obtained are discussed in the following paragraphs.

Stoichiometric Studies

The stoichiometric studies of the oxidation of different α-hydroxy acids by MFC were carried out with the excess of oxidant i.e. MFC. The unreacted concentration of Cr (VI) was determined iodometrically after nine half-lives when reaction was near to completion. The [H^+] and ionic strength was maintained at 30 ± 0.2 ºC. The difference in concentration of oxidant [MFC] was measured and then stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The amount of reduced chromium (VI) was also calculated from the decrease in the absorbance spectrophotometrically. Product analysis and stoichiometric results determination indicates overall reaction could be written as below (1).

$$\mathrm{ArCH(OH)COOH + O_2CrFO^-M^+H + H^+ \rightarrow ArCOCOOH + H_2O + OCrFO^-M^+H} \qquad \textbf{(1)}$$

It is clear from the above equation that MFC undergoes a two electron change. This is in compliance with the earlier observations with PCC (Corey and Boger 1978) and other halochromates.

Order of Reaction

The overall reaction is first order with respect to MFC as it is evident by getting a straight line plot between log [MFC] versus time. The pseudo first order rate constant is independent on initial concentration of oxidant i.e. MFC. Table 1 represents a typical kinetic run. The reaction with respect to the hydroxy acid also follow first order kinetics. A graph between log k_1 and log [AHA] was found to be linear (Fig:1).

Table 1: Kinetic data for oxidation of alpha hydroxy acid by MFC

10^3[MFC] (mol/dm^3)	**10^2[HA] (mol/dm^3)**	**PTS (mol/dm^3)**	**10^5 k_1(s^{-1})**			
			GLYCOLIC ACID	MANDELIC ACID	LACTIC ACID	MALIC ACID
0.10	1.0	0.10	10.4	20.6	31.7	35.7
0.10	1.5	0.10	15.9	28.1	45.2	47.8
0.10	2.0	0.10	23.2	37.6	52.2	53.1
0.10	2.5	0.10	29.4	48.7	59.3	67.9
0.10	3.0	0.10	33.5	70.4	78.0	144.5
0.10	1.0	0.10	21.8	24.5	30.4	35.5
0.10	1.0	0.15	29.3	38.2	47.8	50.2
0.10	1.0	0.20	34.7	50.0	60.3	75.6
0.10	1.0	0.25	36.0	65.6	82.1	96.8
0.10	1.0	0.30	45.0	79.5	96.5	102.6
0.10	2.0	0.10	37.7	43.2	75.6	81.4
0.15	2.0	0.15	37.3	43.2	76.5	85.4
0.20	2.0	0.20	30.6	47.1	78.9	92.6
0.25	2.0	0.25	37.1	48.4	77.0	85.5
0.30	2.0	0.30	38.8	48.6	74.3	86.2
0.10	2.0	0.10	37.0	43.0	75.4	81.2

- **Contained 0.001M acrylonitrile**

Effect of Acrylonitrile for Free Radicals

The polymerization of acrylonitrile was not observed in the oxidation of α-hydroxy acids by MFC Further, an addition of acrylonitrile had no effect on the rate (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol/l of 2, 6-di-t-butyl-4-methylphenol (Butylated Hydroxy Toluene or BHT). In the reaction BHT was recovered unchanged, almost same amount. Therefore it was confirmed that there was no free formation during this reaction.

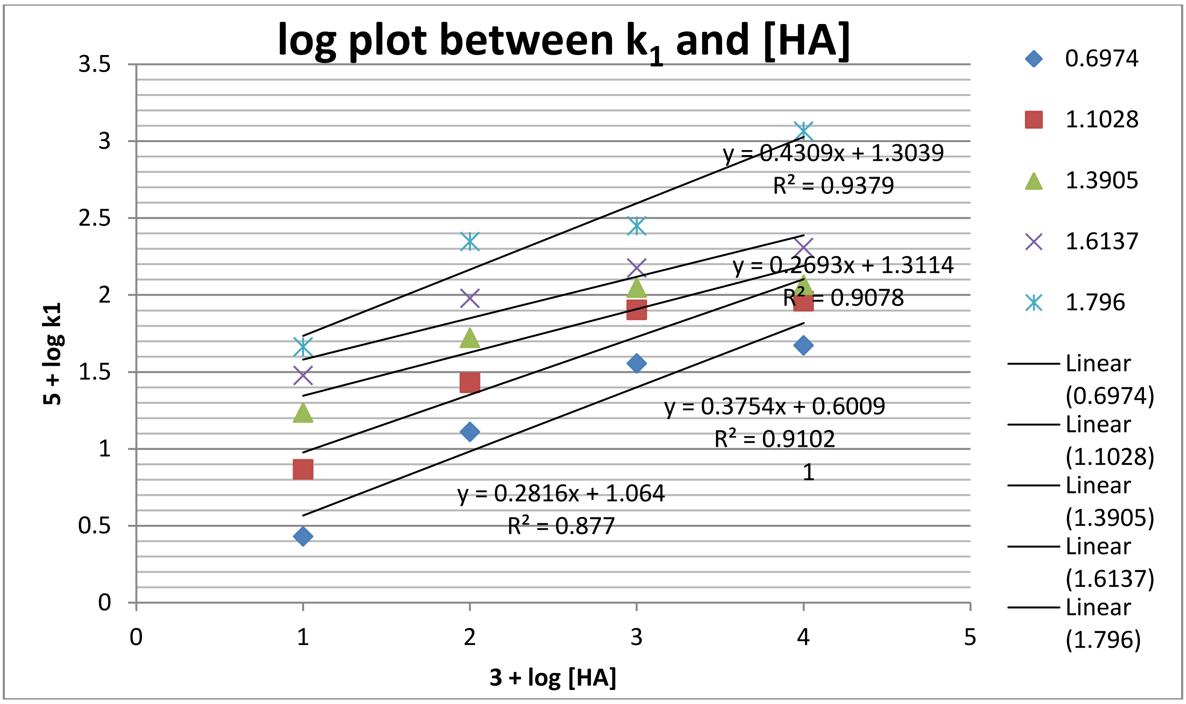


Figure 1: log plot between log k_1 and concentration of α-hydroxy acids

Effect of Catalyst

p-Toluene Sulfonic acid (TsOH) was used as a source of hydrogen ions due to non-aqueous conditions.The H^+ dependence has the following form as shown in the equation (2).

$k_{obs} = a + b [H^+]$ **(2)**

The values of a and b, for p-methyl mandelic acid, are 7.12±0.18 × 10^{-4} s^{-1} and 12.7±0.54 × 10^{-4} lit^3/mol/s respectively (r^2=0.9987). **Table 2** represents the effect of H^+ concentration of P-Mandelic acid by MFC.

Effect of Temperature

Effect of temperature on the rate was studied and rate constant were calculated at different temperatures. Similarly activation parameters were also calculated for the oxidation of different α-hydroxy acids by MFC as shown in the **(Table 3**). The log k_2 at different temperatures shows negative slope with respect to temperature in all the cases (Figure 2). The Arrhenius equation is therefore, valid for this reaction.

The correlation analysis between activation enthalpies and entropies of the oxidation of different α hydroxy acids and some substituted mandelic acid **(Table 4)** aren't very good, but are satisfactory (r^2 = 0.8826). Exner's[31] plot between log k at 25ºC and at 40ºC was found to be linear (r^2 =0.9991). The isokinetic temperature were evaluated from the Exner's plot and the value was found to be 933 ± 192ºC. The linear isokinetic correlation showed that all the hydroxy acids were oxidized by the same mechanism and the changes in the rate were due to changes in both the enthalpy and entropy of activation.

Table 2: Effect of hydrogen ion concentration on the oxidation of p-methylmandelic acid by MFC.

[MFC]=0.001 mol/dm^3 [HA]=0.01 mol/dm^3 Temperature=35 ºC

[H$^+$]	**0.01**	**0.20**	**0.40**	**0.60**	**0.80**	**1.00**
$10^4 k_{obs} s^{-1}$	**36.4**	**42.4**	**54.6**	**62.5**	**76.8**	**88.6**

Table 3: Activation parameters and second order rate constant for the oxidation of different alpha hydroxy acids by MFC in DMSO.

α-HYDROXY ACID	**10^4 k_2 (dm^3/mol/ s)**				**ΔH* (KJ/mol)**	**ΔS* (J/mol/K)**	**ΔG* (KJ/mol)**
	25ºC	30ºC	35ºC	40ºC			
GLYCOLIC ACID	10.462	21.56	32.10	45.02	50.6±0.6	-89±20.57	77.04±0.1
LACTIC ACID	21.79	32.15	43.56	50.32	44.20±3.4	-100±11.2	73.88±2.2
MALIC ACID	35.65	41.02	51.65	56.32	39.26±1.6	-114±5.5	73.20±1.3
MANDELIC ACID	20.613	30.45	41.85	52.41	41.92±3.6	-104±11.2	72.78±0.4
DEUTERIO-MANDELIC ACID	3.015	4.52	5.96	7.97	40.3±0.7	-108±24.1	76.1±1.2
K_H/k_D	6.83	6.73	7.02	6.57			

Table 4: Activation parameters and second order rate constant for the oxidation of some substituted mandelic acid by MFC in DMSO.

Substrate	**10^4 k_2 (dm^3/mol/ s)**				**ΔH* (KJ/mol)**	**ΔS* (J/mol/K)**	**ΔG* (KJ/mol)**
	25ºC	30ºC	35ºC	40ºC			
H	11.7	29.2	72.9	171	65.5±O.4	-74±12.1	87.4±0.3
p-Me	25.6	62.3	165	355	63.4±0.2	-95±25.1	85.7±0.1
P-OMe	50.6	126	299	636	62.0±0.3	-98±24.1	83.9±0.3
p-F	11.2	29.7	74.4	171	66.8±0.2	-90±15.3	87.4±0.2
p-Cl	7.03	18.8	47.9	112	67.4±0.3	-91±27.1	88.6±0.2
p-NO_2	0.55	1.54	4.23	11.3	74.1±0.4	-90±18.4	94.7±0.6
p-CF_3	1.61	4.42	11.9	27.3	69.2±0.3	-97±13.2	93.1±0.4
p-COOMe	2.18	5.87	15.8	36.7	69.5±0.2	-84±20.4	91.4±0.5
p-Br	6.94	18.9	46.4	108	67.2±0.1	-82±18.6	88.6±0.2
p-NHAr	24.4	62.4	144	324	63.3±0.2	-76±24.2	85.7±0.1
p-CN	0.97	2.70	7.23	18.9	71.2±0.1	-83±16.5	93.4±0.2
p-SMe	29.2	72.7	171	387	62.2±0.26	-96±14.9	85.3±0.1
p-NMe_2	216	516	1149	2345	59.1±0.3	-86±23.8	80.4±0.2

Kinetic Isotopic Effect

Kinetic isotopic effect is change in the rate observed when C-H is replaced by C-D and it tells us about C-H bond cleavage.

KIE = K_{H}/K_{D}

To make sure that cleavage of the C-H bond takes place in the rate determining step, the oxidation of α–Deuterio-mandelic acid (DMA) was studied. A substantial primary kinetic isotopic effect was observed as shown by the results **(Table 4).** The value of $k_H/\ k_D$ was found to be 6.83 at 25°C which is a primary kinetic isotopic effect.

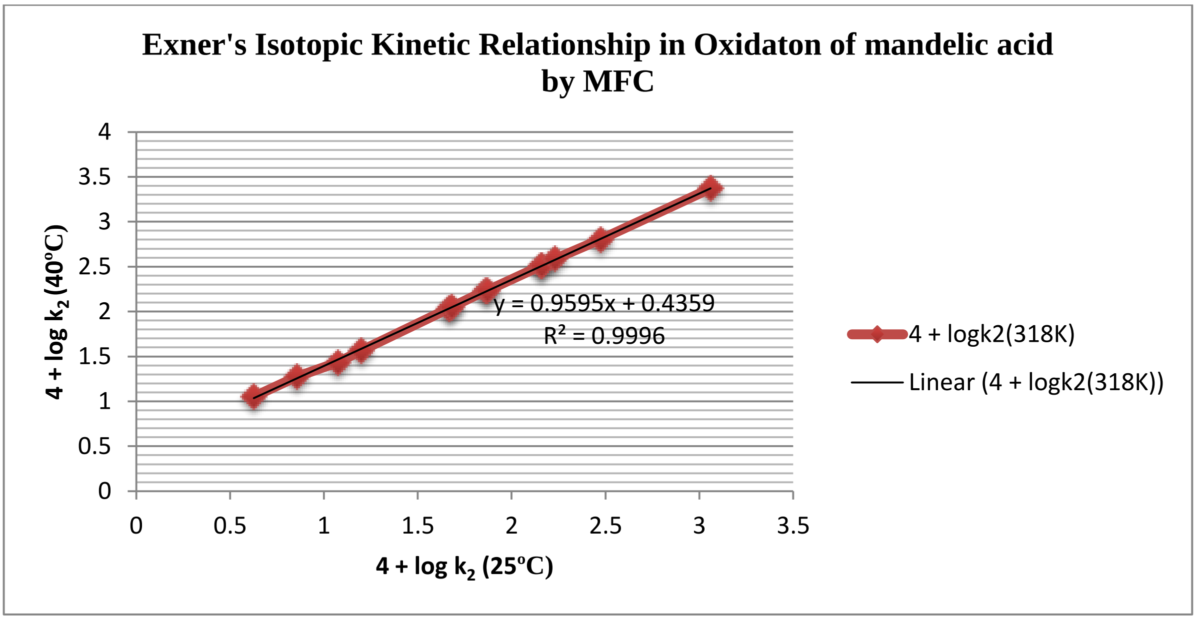


Figure 2: Exner's plot between 4 + log k_2(40°C) versus 4 + log k_2(35°C) temperature for Mandelic Acid.

Effect of Solvent

The oxidation of mandelic acid was carried out by MFC determined in 18 different organic solvents. Due to the limited solubility of MFC, there was no noticeable reaction with the solvent. Similar kinetics was observed in all the solvents. The values of k_2 at 30°C are recorded in Table 5 represents the values of k_2 at 30°C.

Table 5: Effect of solvent on the oxidation of mandelic acid by MFC at 30°C.

SOLVENT	10^4 k_2 (dm^3/mol/s)	SOLVENT	10^4 k_2 (dm^3/mol/s)
Chloroform	23.4	Toluene	9.58
1,2-Dichloroethane	27.85	Acetophenone	33.5
Dichloromethane	30.32	Tetrahydrofuran	16.45
Dimethyl sulfoxide	72.42	t-Butyl alcohol	12.12
Acetone	25.13	1,4-Dioxane	14.14
DMF	46.65	1,2-dimethoxyethane	8.09
Butanone	19.48	Ethyl acetate	13.1
Nitrobenzene	35.12	Carbon disulfide	6.14
Benzene	10.10	Acetic acid	6.01

Solvent Effect

The rate constants k_2, in eighteen solvents, were correlated in terms of linear solvation energy relationship of (Kamlet *et al.*, 1983.) CS_2 was not considered as the complete range of solvent parameters was not available,

$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha$ (3)

In this equation, π* represents the solvent polarity is represented by π*, the hydrogen bond acceptor basicitieAs MFC is not soluble in most of the solvents out of the 18 solvents, 12 have a value of zero for α. The results of correlation analysis in terms of equation (3), a parametric equation involving π* and β, and separately with π* and β are given below-

$\log k_2 = - 4.56 + (1.38 \pm 0.18)\, \pi^* + (0.13 \pm 0.18)\beta - (0.17 \pm 0.13)\alpha$ (4)
$R^2 = 0.8540$; sd = 0.12; n = 18; $\Psi = 0.47$
$\log k_2 = - 4.34 + (1.32 \pm 0.18)\, \pi^* + (0.18 \pm 0.12)\, \beta$ (5)
$R^2 = 0.8740$; sd = 0.12; n = 18; $\Psi = 0.49$
$\log k_2 = - 4.44 + (1.42 \pm 0.18)\, \pi^*$ (6)
$r^2 = 0.8740$; sd = 0.15; n = 18; $\Psi = 0.43$
$\log k_2 = - 2.34 + (1.32 \pm 0.18)\, \beta$ (7)
$r^2 = 0.0740$; sd = 0.38; n = 18; $\Psi = 0.99$
Here n is the number of data points and ψ is Exner's statistical parameter (Exner, 1964).

Kamlet's (Kamlet *et al.,* 1983) triparametric equation explained about 86 % of the effect of solvent on the oxidation. However, by Exner's criterion the correlation was not found to be satisfactory [cf. (4)]. The major contribution is the solvent polarity. Approximately. 85% of the data was because of solvent polarity. Both the β and α parameters plays relative minor role.
The data on the solvent effect were also analysed in terms of Swain's equation (Swain *et al.,* 1983) of cation- and anion- solvating concept of the solvents (equation 8).
$\log k_2 = aA + bB + C$ (8)
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 (8), separately with A and B and with (A+ B).
$\log k_2 = (0.45 \pm 0.04)\, A + (1.42 \pm 0.03)\, B - 4.17$ (9)
$R^2 = 0.9928$; sd = 0.03; n = 18; $\Psi = 0.09$
$\log k_2 = 0.26\, (\pm 0.48)\, A - 3.86$ (10)
$r^2 = 0.0159$; sd = 0.38; n = 18; $\Psi = 1.03$
$\log k_2 = 1.37\, (\pm 0.08)\, B - 4.32$ (11)
$r^2 = 0.9406$; sd = 0.09; n =18; $\Psi = 0.27$
$\log k_2 = 1.10 \pm 0.13\, (A + B) - 4.19$ (12)
$r^2 = 0.8156$; sd = 0.17; n = 18; $\Psi = 0.42$

The rate of oxidation of mandelic acid in different solvents exhibits an excellent correlation with Swain's equation (Swain *et al.,* 1983) (cf. equation 8) with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for nearly. 97% of the data. The anion-solvating power correlation was very poor. Here (A + B), as solvent polarity accounted for nearly 84% of the data, an attempt was made to correlate the rate with the relative effect of the solvent. But plot of $\log k_2$ against the inverse of the relative permittivity was not linear ($r^2 = 0.5428$; sd = 0.26; Ψ = 0.77).

Correlation Analysis of Reactivity

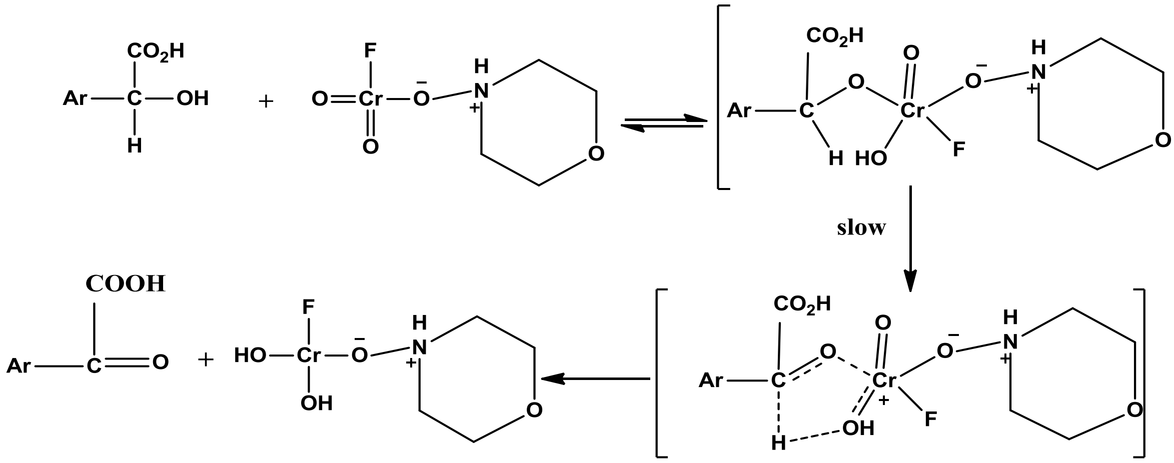
The effect of structure on reactivity of α hydroxy acids has long been correlated in terms of the Hammett equation or with dual substituent- parameter equations. The reaction rates did not yield very significant correlation. But the rate of oxidation of substituted mandelic acid correlated well with Brown's σ^+ equation. The large negative reaction constant and correlation with σ^+ values (Kwart and Slutsky**,** 1972) indicate an electron deficient carbon reaction centre (carbocationic) in the transition state (Table5).

Table 5: Effect of temperature on the reaction constant for the oxidation of hydroxy acid by MFC

Temperature(°C)	$-\rho^+$	r^2	sd	ψ
20 °C	2.08±0.01	0.99612	0.005	0.01
30 °C	1.86±0.02	0.980093	0.025	0.03
40 °C	1.84±0.01	0.981856	0.004	0.01
50 °C	1.80±0.01	0.994467	0.001	0.02

SCHEME 1 ACID-INDEPENDENT PATH

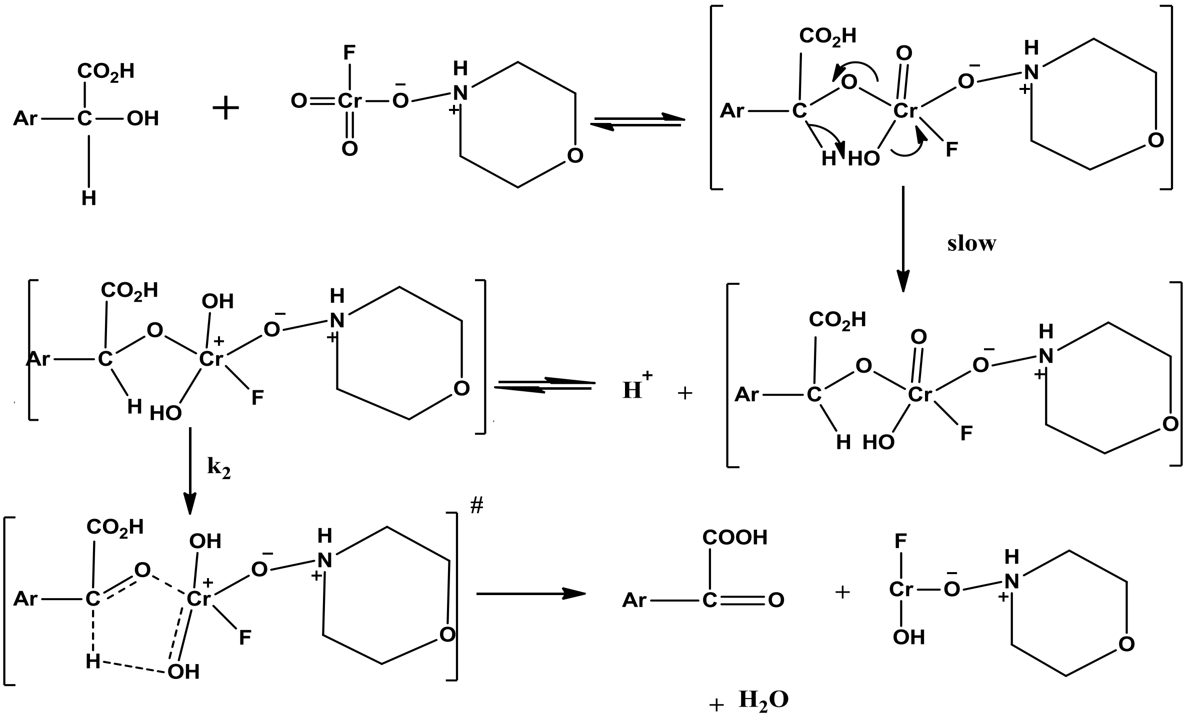
MECHANISM 1



CHROMATE ESTER

SCHEME 2 ACID-DEPENDENT PATH

MECHANISM 2



Mechanism

Due to the absence of the effect of added acrylonitrile on the reaction rate ,. the possibility of a one – electron oxidation, leading to the formation of free radicals was ruled out The presence of a considerable kinetic isotope effect in the oxidation of mandelic acid confirms the cleavage of the α-C-H bond in the rate-determining step. The large negative value of reaction constant (-1.86 at 30ºC) points to a highly electron deficient carbon centre in the transition state.

The transition state thus has a highly electron deficient carbon centre, supported by the solvent effect. Cation-solvating power of the solvents plays a great role in the formation of a carbocationic transition state. Therefore, the correlation analysis of the effect of substituent and solvents on the oxidation of mandelic acid supports the mechanism involving a hydride-ion transfer through a cyclic chromate ester.

(Kwart and Slutsky , 1972) have shown that a study of dependence of the kinetic isotopic effect on the temperature can be applied to resolve this problem. The data for protio- and deuterio-mandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$ shows a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference(Ea) for $k_{H/}k_D$ is equal to the zero-point energy difference for respective C-H and C-D bonds(≈6.83 kJ/mol) and frequency factors and entropies of activation of the respective reactions are nearly equal. Bordwell (Bordwell, 1970) and Littler (Littler *et al.*, 1971) have documented evidence against the occurrence of concerted one-step biomolecular processes by hydrogen transfer takes place in a cyclic manner. Involving six electrons and, formation of chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1 and 2). The observed negative entropy of activation also supports a polar transition state.

Just like the oxidation of α hydroxy acid by PFC and QCC, MFC also exhibits similar Michaelis-Menten kinetics with respect to hydroxy acids. The rate laws, H^+ dependence and kinetic isotope effect are similar to both the above cases. The reaction is proposed to proceeds through a hydride – ion transfer via chromate ester in the rate determining step (Scheme I). Hydride ion transfer is also supported by cation – solvating power of the solvents. Both protonated and deprotonated forms of MFC are reactive oxidizing species. The two schemes of the mechanisms are shown below.

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