



KINETICS AND MECHANISM OF THE OXIDATION OF SOME α -HYDROXY ACIDS BY IMIDAZOLIUM FLUOROCHROMATE

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ABSTRACT

The oxidation of glycollic, lactic, malic and a few substituted mandelic acids by imidazolium fluorochromate (IFC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding oxoacids. The reaction is first order each in IFC. Michaelies-Menten type of kinetics is observed with respect to the hydroxy acids. Reaction failed to induce the polymerisation of acrylonitrile. The oxidation of α -deuteriomandelic acid shows the presence of a primary kinetic isotope effect ($k_H/k_D = 5.75$ at 298 K). The reaction does not exhibit the solvent isotope effect. The reaction is catalysed by the hydrogen ions. The hydrogen ion dependence has the form: $k_{\text{obs}} = a + b [\text{H}^+]$. Oxidation of p-methyl mandelic acid has been studied in 19 different organic solvents. The solvent effect has been analysed by using Kamlet's and Swain's multiparametric equations. A mechanism involving a hydride ion transfer via a chromate ester is proposed.

Key words: Kinetics, Oxidation, Imidazolium fluorochromate, α -Hydroxy acid.

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 reported¹⁻⁵. Imidazolium fluorochromate (IFC) is one such compound used for the oxidation of phenylic alcohols and oximes⁶. 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 reported⁷⁻¹⁰. α -Hydroxy acids may be oxidized either as alcohols, yielding corresponding oxoacids¹¹ or they may undergo oxidative decarboxylation to yield a ketone¹². There seems to be no report available on the

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oxidation aspects using imidazolium fluorochromate (IFC). In continuation of our earlier work with halochromates, we now report the kinetics and mechanism of oxidation of some hydroxy acids by IFC in DMSO as solvent. A suitable mechanism has also been proposed.

EXPERIMENTAL

Materials

The hydroxy acids were commercial products of the highest purity available and were used as such. The preparation and specification of the substituted mandelic acids have been described earlier¹³. IFC was prepared by reported method⁶ and its purity was checked by an iodometric method. α -Deuteriomandelic acid (PhCD(OH)COOH or DMA) was prepared by the method of Kemp and Waters¹⁴. Its isotopic purity, ascertained by NMR spectra, was $95 \pm 5\%$. Due to the non-aqueous nature of the solvent, toluene *p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by their usual methods.

Product analysis

Product analyses were carried out under kinetic conditions i.e., with an excess of the reductant over IFC. In a typical experiment, mandelic acid (7.6 g, 0.05 mol) and IFC (1.88 g, 0.01 mol) were dissolved in 100 mL of DMSO and was allowed to stand in dark for ≈ 24 h to ensure the completion of the reaction. It was then treated with an excess (250 mL) of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrozone (DNP) was filtered off, dried, weighed, recrystallised from ethanol and weighed again. The product was identical (mp and mixed mp) to an authentic sample of DNP of phenylglyoxylic acid. Similar experiments with the other hydroxy acids yielded the DNP of the corresponding oxoacids in 78 to 88% yields, after recrystallization. The oxidation state of chromium in completely reduced reaction mixtures, as determined by an iodometric method, was 3.90 ± 0.15 .

Kinetic measurements

The pseudo-first order conditions were attained by keeping a large excess ($\times 15$ or greater) of the hydroxy acid over IFC. The temperature was kept constant to ± 0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of IFC spectrophotometrically at 352 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constants, k_{obs} , were computed from the linear least square plots of $\log [\text{IFC}]$ versus time. Duplicate kinetic runs showed that the rates were reproducible within $\pm 3\%$. The second order rate constants, k_2 , were calculated from the relation : $k_2 =$

$k_{\text{obs}}/[\text{hydroxy acid}]$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

RESULTS AND DISCUSSION

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

Stoichiometry

The oxidation of hydroxy acids resulted in the formation of the corresponding oxoacids. Product analysis and stoichiometric determinations indicated that the overall reaction could be written as (1).



IFC undergoes a two-electron change. This is according to the earlier observations with other halochromates^{15,16}.

Kinetics dependence

The reactions are of first order with respect to IFC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of IFC. 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 $1/[\text{Hydroxy acid}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate (Fig. 1). Thus, Michaelis-Menten type kinetics are observed with respect to the hydroxyl acid. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).



$$\text{Rate} = k_2 K [\text{HA}] [\text{IFC}] / (1 + K [\text{HA}]) \quad \dots(4)$$

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). Fig. 2 depict a typical kinetic run.

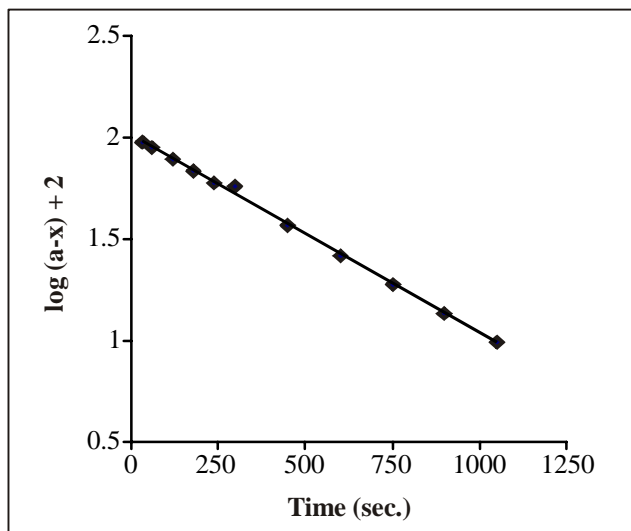


Fig. 1: Oxidation of Mandelic acids by IFC: A typical kinetic run

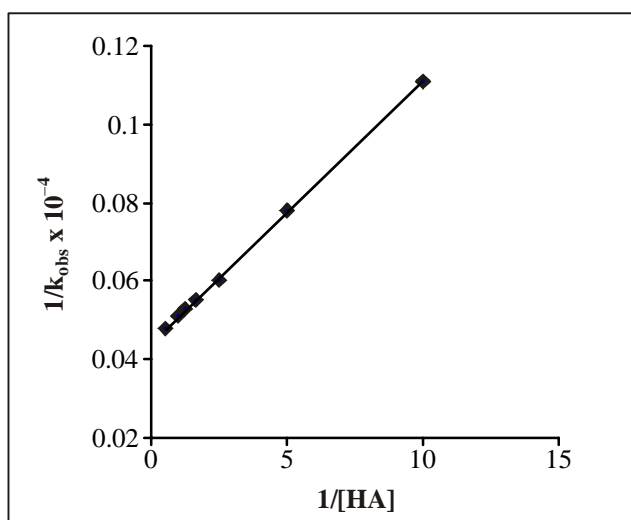


Fig. 2: $1/k_{obs}$ vs $1/[HA]$: A double reciprocal plot

Induced polymerisation of acrylonitrile

The oxidation of hydroxy acids, by IFC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (Table 1).

Table 1: Rate constants for the oxidation of mandelic acid by IFC at 288 K

10^3 [IFC] (mol dm ⁻³)	[HA] (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)
1.00	0.10	9.00
1.00	0.20	12.8
1.00	0.40	16.4
1.00	0.60	18.0
1.00	0.80	18.9
1.00	1.00	19.6
1.00	2.00	20.9
2.00	0.20	11.2
4.00	0.20	13.3
6.00	0.20	11.0
8.00	0.20	14.7
1.00	0.40	17.1*

* contained 0.001 mol dm⁻³ acrylonitrile

Effect of hydrogen ions

The reaction is catalysed by hydrogen ions. p-Toluene sulphonic acid (TsOH) was used as the source of hydrogen ions. The hydrogen ion dependence has the form $k_{\text{obs}} = a + b [\text{H}^+]$ (Table 2). The values of a and b, for p-methyl mandelic acid, are $2.00 \pm 0.03 \times 10^{-3} \text{ s}^{-1}$ and $3.79 \pm 0.05 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively ($r^2 = 0.9994$).

Table 2: Effect of hydrogen ion concentration on the oxidation of mandelic acid by IFC

[IFC] = 0.001 mol dm ⁻³ ;	[HA] = 0.10 mol dm ⁻³ ;				Temp. = 288 K	
[H ⁺]	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{\text{obs}}/\text{s}^{-1}$	10.5	12.6	15.6	18.9	22.5	25.2

Kinetic isotope effect

To ascertain the importance of the cleavage of the C-H bond in the rate-determining step, the oxidation of α -deuteriomandelic acid (DMA) was studied. Results showed the

presence of a substantial primary kinetic isotope effect (Table 4). The value of k_H/k_D is 5.75 at 298 K.

Effect of solvents

The rate of oxidation of mandelic acid was determined in nineteen different organic solvents. The choice of the solvents was limited by the solubility of IFC and reaction with primary and secondary alcohols. There was no noticeable reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of formation constants K and decomposition constants of the complex, k_2 are recorded in Table 5.

A satisfactory linear correlation ($r^2 = 0.9720$; $\psi = 0.18$; $sd = 1.38$; $Temp. = 965 \pm 10$) between the values the activation enthalpies and entropies of the oxidation of the nine aliphatic alcohols indicated the operation of compensation effect in this reaction¹⁷. The reaction also exhibited an excellent isokinetic effect, as determined by Exner's criterion¹⁸. An Exner's plot between $\log k_2$ at 288K and at 318 K was linear ($r = 0.9989$; $sd = 0.09$; $\psi = 0.05$; slope = 0.8678 ± 0.0088) (Fig. 3). The value of isokinetic temperature is 954 ± 26 K. The linear isokinetic correlation implies that all the hydroxyl acids are oxidized by the same mechanism and the changes in rate are governed by the changes in both; the enthalpy and entropy of the activation.

Table 3: Formation constants for the decomposition of IFC–hydroxy acid complexes and thermodynamic parameters

R	K / (dm ³ mol ⁻¹)				-ΔH (kJ mol ⁻¹)	-ΔS (J mol ⁻¹ K ⁻¹)	-ΔG (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
H	7.47	6.67	5.81	5.04	12.5 ± 0.4	18 ± 1	7.16 ± 0.3
p-F	6.57	5.81	5.03	4.20	13.8 ± 0.6	24 ± 2	6.81 ± 0.5
p-Cl	7.11	6.25	5.41	4.59	11.9 ± 0.3	17 ± 1	7.03 ± 0.3
p-Br	5.85	4.95	4.11	3.27	17.2 ± 0.7	37 ± 2	6.41 ± 0.6
p-Me	6.62	5.72	4.90	4.08	14.7 ± 0.5	27 ± 1	6.79 ± 0.4
p-Pr ⁱ	7.38	6.66	5.82	5.06	12.1 ± 0.4	17 ± 1	7.15 ± 0.4
p-OMe	5.58	4.87	4.13	3.41	15.0 ± 0.6	29 ± 2	6.37 ± 0.5
m-Cl	6.39	5.58	4.78	3.95	14.6 ± 0.6	27 ± 2	6.72 ± 0.5
m-NO ₂	6.57	5.75	4.92	4.04	14.7 ± 0.7	27 ± 2	6.78 ± 0.5

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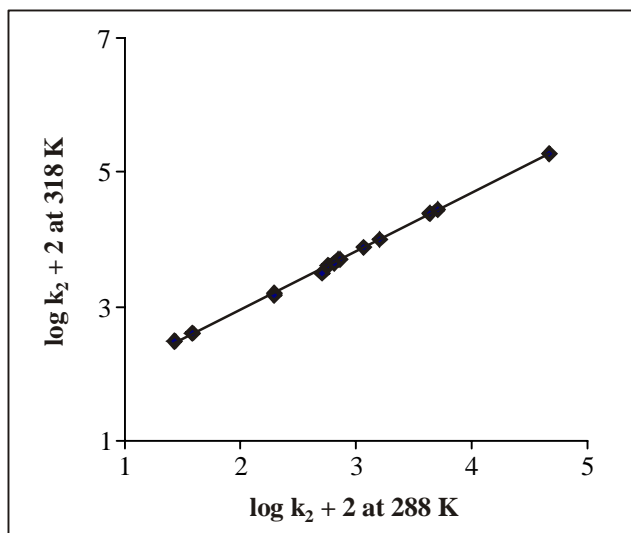
R	K/ (dm ³ mol ⁻¹)				-ΔH (kJ mol ⁻¹)	-ΔS (J mol ⁻¹ K ⁻¹)	-ΔG (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
p-NO ₂	5.94	5.09	4.25	3.44	16.3 ± 0.6	33 ± 2	6.45 ± 0.5
GA	6.39	5.64	4.92	4.15	13.4 ± 0.5	23 ± 2	6.75 ± 0.4
LA	7.56	6.81	6.03	5.31	11.5 ± 0.3	15 ± 1	7.22 ± 0.2
MLA	6.03	5.24	4.55	3.74	14.4 ± 0.6	27 ± 2	6.57 ± 0.5
DMA	5.31	4.57	3.85	3.09	16.1 ± 0.8	34 ± 2	6.21 ± 0.6

Table 4: Rate constants for the decomposition of IFC–hydroxyacid complexes and activation parameters

R	10 ⁴ k ₂ / (dm ³ mol ⁻¹ s ⁻¹)				ΔH* (kJ mol ⁻¹)	-ΔS* (J mol ⁻¹ K ⁻¹)	ΔG* (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
H	11.7	22.5	42.3	78.3	45.7 ± 0.7	143 ± 1	88.1 ± 0.3
p-F	16.2	30.6	56.7	99.9	43.7 ± 0.2	147 ± 1	87.3 ± 0.1
p-Cl	6.93	13.5	26.1	49.5	47.4 ± 0.5	141 ± 2	89.3 ± 0.3
p-Br	5.76	11.7	21.6	41.4	47.2 ± 0.5	143 ± 2	89.8 ± 0.4
p-Me	51.3	92.7	162	279	40.4 ± 0.2	149 ± 1	84.6 ± 0.2
p-Pr ⁱ	44.1	80.1	144	243	40.9 ± 0.2	148 ± 1	85.0 ± 0.2
p-OMe	477	783	1260	1980	33.6 ± 0.1	154 ± 1	79.3 ± 0.1
m-Cl	2.00	4.17	8.46	16.2	50.7 ± 0.2	140 ± 1	92.3 ± 0.1
m-NO ₂	0.39	0.88	1.90	4.14	57.3 ± 0.6	131 ± 2	96.1 ± 05
p-NO ₂	0.27	0.63	1.44	3.06	59.2 ± 0.3	127 ± 1	97.0 ± 0.2
GA	5.13	9.45	17.1	31.5	43.4 ± 0.7	158 ± 2	90.2 ± 0.5
LA	7.38	14.4	27.0	52.2	46.9 ± 0.6	142 ± 2	89.2 ± 0.5
MLA	6.48	12.6	22.5	43.2	45.2 ± 0.2	149 ± 3	89.6 ± 0.6
DMA	1.97	3.91	7.58	14.7	48.4 ± 0.5	148 ± 2	92.4 ± 0.4
k _H /k _D	5.94	5.75	5.58	5.33			

Table 5: Effect of solvents on the oxidation of *p*-methyl mandelic acid by IFC at 308 K

Solvents	K (dm ⁻³ mol ⁻¹)	10 ⁵ k ₂ (s ⁻¹)	Solvents	K (dm ⁻³ mol ⁻¹)	10 ⁵ k ₂ (s ⁻¹)
Chloroform	6.58	51.3	Toluene	4.27	12.0
1,2-Dichloroethane	5.94	64.6	Acetophenone	4.54	70.8
Dichloromethane	5.85	55.0	THF	5.37	22.4
DMSO	4.90	162	t-Butylalcohol	5.48	18.2
Acetone	4.38	41.7	1,4-Dioxane	4.39	25.7
DMF	5.55	77.6	1,2-Dimethoxyethane	5.13	13.2
Butanone	6.13	33.9	CS ₂	4.47	6.46
Nitrobenzene	5.14	63.1	Acetic acid	4.77	6.76
Benzene	6.39	14.8	Ethyl acetate	5.76	15.8
Cyclohexane	5.04	1.51			

**Fig. 3: Exner's isokinetic relationship in the oxidation of HA by IFC****Reactive oxidizing species**

The observed H⁺ dependence suggests that reaction follows two mechanistic pathways, one acid-independent and other acid-dependent. The acid catalysis may well be

attributed to a protonation of IFC to give a stronger oxidant and electrophile.



Solvent effect

The rate constants of oxidation, k_2 , in eighteen solvents (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 of Kamlet *et al.*¹⁹

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \dots(6)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α 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 α . The results of correlation analyses in terms of a biparametric equation involving π^* and β , and separately with π^* and β are given below [(7 - 10)].

$$\log k_2 = -4.28 + (1.68 \pm 0.23)\pi^* + (0.18 \pm 0.19)\beta - (0.16 \pm 0.18)\alpha \quad \dots(7)$$

$$R^2 = 0.8384; \text{sd} = 0.21; n = 18; \Psi = 0.44$$

$$\log k_2 = -4.24 + (1.74 \pm 0.21)\pi^* + (0.13 \pm 0.18)\beta \quad \dots(8)$$

$$R^2 = 0.8274; \text{sd} = 0.21; n = 18; \Psi = 0.44$$

$$\log k_2 = -4.27 + (1.77 \pm 0.21)\pi^* \quad \dots(9)$$

$$r^2 = 0.8210; \text{sd} = 0.20; n = 18; \Psi = 0.43$$

$$\log k_2 = -2.74 + (0.44 \pm 0.39)\beta \quad \dots(10)$$

$$r^2 = 0.0761; \text{sd} = 0.46; n = 18; \Psi = 0.99$$

Here n is the number of data points and Ψ is the Exner's statistical parameter²⁰.

Kamlet's¹⁹ triparametric equation explains *ca.* 88% of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 84% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's equation²¹ of cation- and anion-solvating concept of the solvents also (11).

$$\log k_2 = aA + bB + C \quad \dots(11)$$

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

$$\log k_2 = (0.62 \pm 0.05) A + (1.81 \pm 0.04) B - 4.05 \quad \dots(12)$$

$$R^2 = 0.9942; \text{sd} = 0.04; n = 19; \Psi = 0.08$$

$$\log k_2 = 0.36 (\pm 0.60) A - 2.71 \quad \dots(13)$$

$$r^2 = 0.0212; \text{sd} = 0.48; n = 19; \Psi = 1.01$$

$$\log k_2 = 1.76 (\pm 0.11) B - 4.21 \quad \dots(14)$$

$$r^2 = 0.9328; \text{sd} = 0.13; n = 19; \Psi = 0.27$$

$$\log k_2 = 1.42 \pm 0.15 (A + B) - 4.08 \quad \dots(15)$$

$$r^2 = 0.8341; \text{sd} = 0.20; n = 19; \Psi = 0.42$$

The rates of oxidation of *p*-methylmandelic acid in different solvents showed an excellent correlation in Swain's equation (cf. 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for *ca* 99% of the data. The correlation with the anion-solvating power was very poor. 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 the 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 ($r^2 = 0.5095$; $\text{sd} = 0.34$; $\Psi = 0.71$).

Table 6: Temperature dependence of the reaction constant

Temp./ K	288	298	308	318
ρ^*	-2.08 ± 0.01	-1.98 ± 0.02	-1.89 ± 0.01	-1.80 ± 0.02
r^2	0.9998	0.9989	0.9997	0.9999
sd	0.006	0.005	0.004	0.008

Correlation analysis of reactivity

The rate of oxidation of substituted mandelic acids correlated well with Brown's σ^+ values²², the reaction constant being negative (Table 5). The correlation with Hammett's σ values was not very significant. The large negative reaction constants and correlation with σ^+ values indicate a carbo-cationic reaction centre in the transition state.

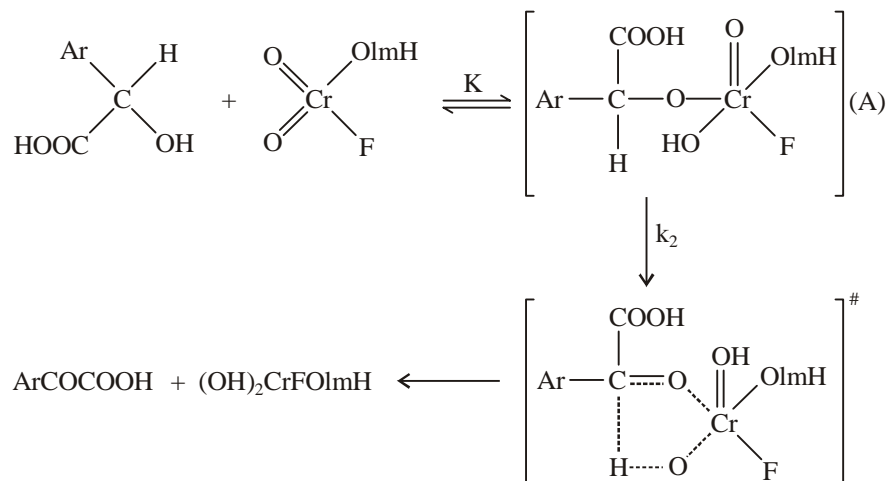
Mechanism

Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. The presence of a substantial kinetic isotope effect in the oxidation of mandelic acid²² confirms the cleavage of the α -C-H bond in the rate determining step. The large negative reaction constant together with the excellent correlation with Brown's σ^+ values²³ point to a highly electron-deficient carbon centre in the transition state. The transition state thus approaches a carbocation in character. This is supported by the solvent effect also. Greater role played by the cation-solvating power of the solvents supported the postulation of a carbocationic transition state. Therefore, the correlation analysis of substituent and solvent effects on the oxidation of mandelic acid supports the mechanism involving a hydride-ion transfer via a chromate ester.

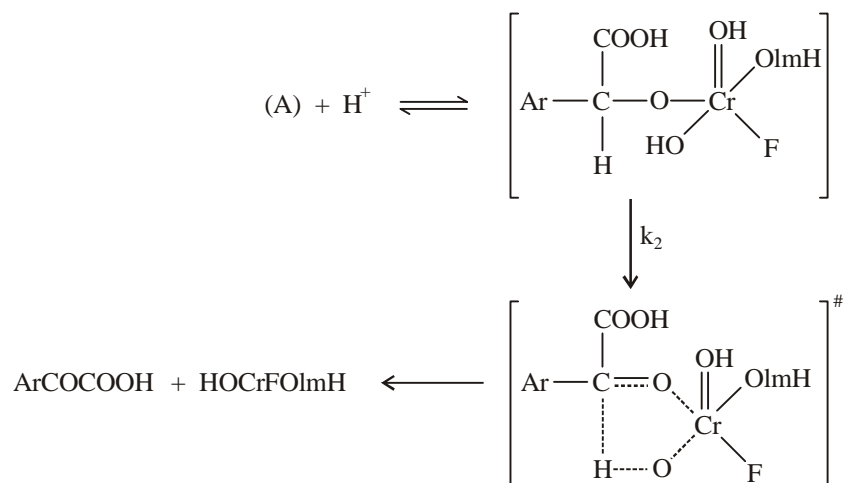
Kwart and Nickle²⁴ have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem. The data for protio- and deuteriomandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(E_a/RT)$ ^{25,26} show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (E_a) for k_H/k_D is equal to the zero-point energy difference for the respective C-H and C-D bonds (≈ 4.5 kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal.

Bordwell²⁷ has documented very cogent evidence against the occurrence of concerted one-step biomolecular processes by hydrogen transfer and it is evident that in the present studies also, the hydrogen transfer does not occur by an acyclic biomolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer²⁸. Littler²⁹ has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr (VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus, the overall mechanism is proposed to involve the formation of a 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**). The observed negative value of entropy of activation also supports a

polar transition state.



Scheme 1: Acid-independent path



Scheme 2: Acid-dependent path

The observed negative entropy of activation also supports it. As the charge separation takes place, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

It is of interest to compare the mode of oxidation of hydroxy acids by PCC³⁰, PFC³¹ MCC³² and IFC. The oxidation by PFC and IFC exhibited a similar kinetic picture i.e. Michaelis-Menten type kinetics with respect to hydroxy acids. While the oxidation by PCC

and MCC, showed a first order kinetics. The rate laws, hydrogen ion dependence and kinetic isotope effect are similar in both the cases. In the oxidations by PFC and IFC, excellent correlations were obtained in terms of Swain's equation with the cation solvating power of the solvents playing the major role. In all the three oxidations, the polar reactions are negative.

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