

# The Kinetics of Tripropylammonium Fluorochromate Oxidation of Mandelic Acids

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**ABSTRACT:** The oxidation of Mandelic Acids (MA) to the corresponding oxoacids with tripropylammonium fluorochromate (TriPAFC) in aqueous acetic acid has been studied. The reaction is first order with respect to [TriPAFC], [MA] and  $[H^+]$ . The oxidation of  $\alpha$ -deuteriomandelic acid shows the presence of a primary kinetic isotope effect ( $k_H/k_D = 5.54$  at 303 K). The reaction has been found to be catalyzed by  $H^+$  ions. The various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of the isokinetic relationship. The Exner plot showed that all the selected mandelic acids are oxidized by the same mechanism.

**KEYWORDS** Mandelic acid; Tripropylammonium fluorochromate; Hammett plot; Iso-kinetic temperature.

## INTRODUCTION

The kinetics of oxidation of organic compounds in non-aqueous and aquo-organic solvent media have revealed the important role of nonspecific and specific solvent effects on the reactivity [1]. The Hammett equation and its modified forms [2], all known as Linear Free Energy Relationships (LFER), have been found to be useful for correlating reaction rates and equilibrium constants for side chain reactions for *meta*- and *para*-substituted derivatives.

Hydroxy acids may be oxidized either as alcohols yielding corresponding oxoacids or may undergo decarboxylation to yield an aldehyde [3]. A perusal of literature showed that the kinetics and mechanism of the oxidation of  $\alpha$ -hydroxy acids by various oxidants such as benzyltrimethylammonium chlorobromate [4], ceric sulfate [5], quinolinium fluorochromate [6], 2,2'-bipyridinium chlorochromate [7], tetrabutylammonium tribromide [8], butyltriphenylphosphonium dichromate [9],

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benzyltriethylammonium chlorochromate [10], (bis(trifluoroacetoxy)iodo)benzene [11], tetraethylammonium chlorochromate [12] and quinolinium chlorochromate [13] have been reported.

Chromium(VI) based reagents are widely used in modern organic synthesis for the oxidation of a variety of compounds. Extensive work has led to the development of a good number of these oxidants such as tetramethylammonium fluorochromate [14], tributylammonium chlorochromate [15], trimethylammonium fluorochromate [16], isoquinolinium bromochromate [17], 4-benzylpyridinium fluorochromate [18], *N*-methylbenzyl ammonium fluorochromate (VI) [19], tetrahexylammonium chlorochromate [20], morpholinium chlorochromate [21] and tripropylammonium fluorochromate [22].

As a part of our continuing investigations on the oxidation of organic substrates by Cr(VI) [23-29], this paper reports the kinetic features of the oxidation of mandelic acids by TriPAFC in aqueous acetic acid medium. The objective of the present work includes a systematic study of the substituent and solvent effects on oxidation of a series of *para*-substituted mandelic acids, in the varying percentage of acetic acid-water, and the analysis of the data using linear free energy relationships with an aim to get better insight into the mechanism of mandelic acid oxidation.

## EXPERIMENTAL SECTION

### Materials

Tripropylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The mandelic acids used were with substituents H, *p*-OCH<sub>3</sub>, *p*-CH<sub>3</sub>, *p*-i-C<sub>3</sub>H<sub>7</sub>, *p*-F, *p*-Cl, and *p*-NO<sub>2</sub>. TriPAFC was prepared by reported method [22] and its purity is checked by an iodometric method. Acetic acid was purified by a standard method and the fraction distilling at 118 °C was collected.

### Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over TriPAFC. The progress of the reactions was followed by estimating the unreacted oxidant spectrophotometrically at 368 nm using UV-Vis spectrophotometer, Shimadzu UV-1800 model. The rate constants were determined by the least-squares method, from the linear plots ( $r > 0.96$ )

of log [TriPAFC] versus time. Replicate runs showed that the rate constants were reproducible to within  $\pm 3\%$ .

### Data Analysis

Correlation analysis was carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient ( $r$  in the case of simple linear regression and  $R$  in the case of multiple linear regressions) and Standard Deviation (SD).

### Product analysis

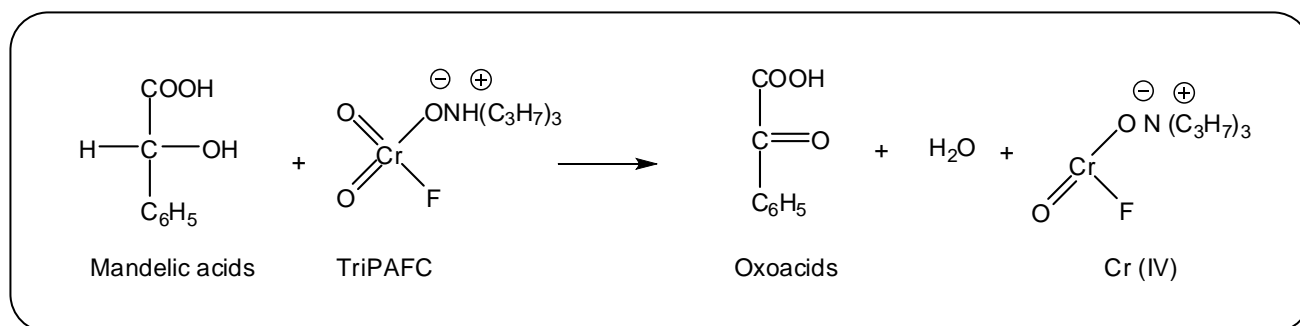
The formation of oxoacids as the product of the oxidation was confirmed by the following analysis. The quantitative estimation of oxoacids was carried out under kinetic conditions *i.e.* with an excess of the reductant over TriPAFC. In a typical experiment, mandelic acid (15.2 g, 0.1 mol), perchloric acid (0.24 mol) and TriPAFC (0.012 mol) were dissolved in an acetic acid-water mixture (50 % – 50%) and the solution was allowed standing in the dark for about 24 h to ensure completion of the reaction. The residue was treated with an excess (200 mL) of a saturated solution of 2,4-dinitro phenylhydrazine in 1 mol/dm<sup>3</sup> HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitro phenyl hydrozone (DNP) was filtered off, dried and recrystallized from ethanol. The product was identical (m.p. and mixed m.p.) to an authentic sample of the DNP of phenyl glyoxylic acid.

### Stoichiometric studies

To determine the stoichiometry, mandelic acids and TriPAFC were mixed in the ratio 1:2, 1:4, 1:6 and were allowed to react for 24 h at 303 K. The solvent composition 50% acetic acid – 50% water (*v/v*) and [H<sup>+</sup>] were maintained as in the corresponding rate measurements. The concentration of unreacted TriPAFC was determined.  $\Delta[\text{TriPAFC}]$  was calculated. The stoichiometry was calculated from the ratio between [MA] and [TriPAFC], showed that the stoichiometry is 1 :1 *i.e.* one mole of mandelic acids are oxidized per mole of TriPAFC.

## RESULTS AND DISCUSSION

Oxidation of the mandelic acids by TriPAFC results in the formation of the corresponding oxoacids as individual compounds. Analyses of product and stoichiometric determinations indicate the following overall reaction.



Scheme:

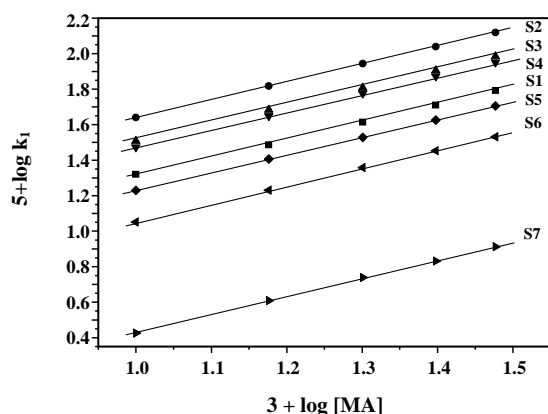


Fig. 1: Order plot for the substrate for the oxidation of MA (S1), *p*-OCH<sub>3</sub> (S2), *p*-CH<sub>3</sub> (S3), *p*-*i*-C<sub>3</sub>H<sub>7</sub> (S4), *p*-F (S5), *p*-Cl (S6) and *p*-NO<sub>2</sub> (S7) by TriPAFC at 303 K.

### Order of reaction

The kinetic studies were carried out under pseudo-first order conditions with the  $[\text{MA}] \gg [\text{TriPAFC}]$ . The first-order dependence of the reaction on TriPAFC is obvious from the linearity of the plots of  $\log [\text{TriPAFC}]$  versus time. Further, the pseudo-first-order rate constants,  $k_1$ , do not depend on the initial concentration of TriPAFC (Table 1). The rate of oxidation increased progressively on increasing the concentration of mandelic acids, indicating the first order dependence with the substrate. Linear plots of  $\log k_1$  vs.  $\log [\text{MA}]$  with the slopes (MA: slope = 1.03; *p*-OCH<sub>3</sub>: slope = 1.01; *p*-CH<sub>3</sub>: slope = 0.996; *p*-*i*-C<sub>3</sub>H<sub>7</sub>: slope = 1.04; *p*-F: slope = 0.994; *p*-Cl: slope = 1.06; *p*-NO<sub>2</sub>: slope = 1.03) demonstrate first order type kinetics on  $[\text{MA}]$  (Fig. 1). The  $k_1$  values at different  $[\text{MA}]$  are given in Table 1. The increase in  $[\text{HClO}_4]$  in the oxidation reaction increases the rate of the reaction and shows a direct first-order dependence on  $[\text{HClO}_4]$  (Table 1). A plot of  $\log k_1$  against  $\log [\text{H}^+]$  is linear with the slopes (MA: slope = 1.04; *p*-OCH<sub>3</sub>: slope = 0.992;

*p*-CH<sub>3</sub>: slope = 1.04; *p*-*i*-C<sub>3</sub>H<sub>7</sub>: slope = 0.995; *p*-F: slope = 1.04; *p*-Cl: slope = 0.991; *p*-NO<sub>2</sub>: slope = 0.988) (Fig. 2). The experimental data confirms the first order dependence on  $[\text{H}^+]$ .

### Test for free radicals

The oxidation of mandelic acids, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile had no effect on the rate of oxidation (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 dm<sup>-3</sup> of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

### Effect of MnSO<sub>4</sub>

Addition of Mn(II) (0.003 mol dm<sup>-3</sup>), in the form of MnSO<sub>4</sub>, retards the rate of the oxidation process (Table 1) indicating two-electron oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of anilines by Cr(VI) reagent. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV) reduces Cr(VI) to Cr(V) and the oxidation of mandelic acids by Cr(V) is fast [2].

### Kinetic isotope effect

To ascertain the importance of the cleavage of the  $\alpha$ -C-H bond in the rate-determining step, oxidation of  $\alpha$ -deuterio mandelic acid (DMA) was studied. Results showed the presence of a substantial primary kinetic isotope effect (Table 2).

### Effect of solvent polarity on reaction rate

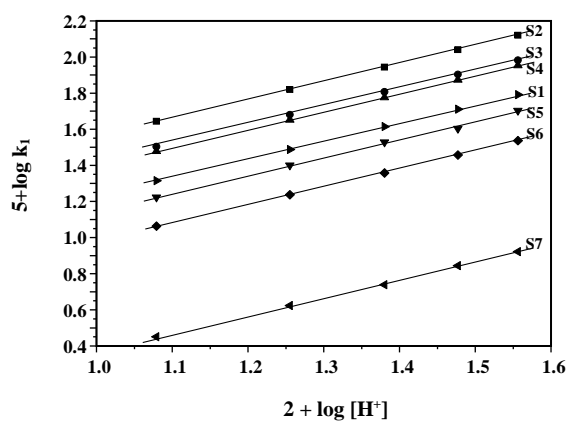
The effect from the solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 30% to 70% (Table 3). The plot of  $\log k_1$

**Table 1: Effect of variation of [S], [TriPAFC] and [H<sup>+</sup>] on the rate of reaction at 303 K<sup>a</sup>.**

(mol dm <sup>-3</sup> )			10 <sup>5</sup> k <sub>1</sub> (s <sup>-1</sup> )						
10 <sup>3</sup> [TriPAFC]	10 <sup>2</sup> [S]	[H <sup>+</sup> ]	MA	<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>p</i> - <i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
0.6	2.0	0.24	41.10	87.68	64.02	59.56	33.62	22.96	5.60
1.2	2.0	0.24	41.18	87.80	64.12	59.70	33.76	22.80	5.48
1.8	2.0	0.24	41.28	87.74	64.26	59.66	33.70	22.86	5.44
2.4	2.0	0.24	41.30	87.86	64.18	59.84	33.88	22.84	5.40
3.0	2.0	0.24	41.20	87.88	64.28	59.62	33.84	22.68	5.56
1.2	1.0	0.24	20.92	43.68	32.20	29.70	16.98	11.24	2.66
1.2	1.5	0.24	30.64	65.78	48.26	44.56	25.50	17.00	4.06
1.2	2.5	0.24	51.30	109.60	80.28	74.50	42.28	28.36	6.78
1.2	3.0	0.24	62.00	131.56	96.30	89.44	50.76	34.04	8.16
1.2	2.0	0.12	20.66	43.98	31.88	30.04	16.74	11.56	2.82
1.2	2.0	0.18	30.76	65.96	47.90	44.88	25.16	17.28	4.20
1.2	2.0	0.30	51.42	109.88	80.06	74.74	42.04	28.64	6.98
1.2	2.0	0.36	61.80	131.84	96.00	89.68	50.46	34.40	8.36
1.2	2.0	0.24	41.02 <sup>b</sup>	87.66 <sup>b</sup>	64.00 <sup>b</sup>	59.52 <sup>b</sup>	33.58 <sup>b</sup>	22.62 <sup>b</sup>	5.38 <sup>b</sup>
1.2	2.0	0.24	32.86 <sup>c</sup>	69.14 <sup>c</sup>	51.22 <sup>c</sup>	46.44 <sup>c</sup>	30.24 <sup>c</sup>	17.56 <sup>c</sup>	4.46 <sup>c</sup>

a) As determined by spectrophotometrically following the disappearance of Cr(VI) at 368 nm; Estimated from pseudo first order plots over 80% reaction. Solvent composition = 50% AcOH- 50% H<sub>2</sub>O (v/v);

b) Contained 0.005 mol dm<sup>-3</sup> acrylonitrile; c) Contained 0.003 mol dm<sup>-3</sup> MnSO<sub>4</sub>



**Fig. 2: Order plot for [H<sup>+</sup>] for the oxidation of MA (S1), *p*-OCH<sub>3</sub> (S2), *p*-CH<sub>3</sub> (S3), *p*-*i*-C<sub>3</sub>H<sub>7</sub> (S4), *p*-F (S5), *p*-Cl (S6) and *p*-NO<sub>2</sub> (S7) by TriPAFC at 303 K.**

versus 1/D (dielectric constant) is linear with positive slope suggesting the presence of either dipole-dipole or ion-dipole type of interaction between the oxidant and the substrate [30] (Fig. 3). The plot of log k<sub>1</sub> versus (D - 1) /

(2D + 1) is a curvature indicating the absence of dipole-dipole interaction in the rate determining step.

#### Structure-reactivity correlation

In order to study the effect of structure on reactivity, some *para*-substituted mandelic acids were subjected to oxidation kinetics by TriPAFC. It is interesting to note that the reactivity increases in the order

*p*-NO<sub>2</sub> < *p*-Cl < *p*-F < *p*-H < *p*-*i*-C<sub>3</sub>H<sub>7</sub> < *p*-CH<sub>3</sub> < *p*-OCH<sub>3</sub> for the substituents.

#### Activation parameters

The substrates mandelic acid and six *para*-substituted mandelic acids were subjected to oxidation kinetics by TriPAFC at four different temperatures viz., 298, 303, 308 and 313 K in 50% acetic acid – 50% water medium in presence of perchloric acid. The Arrhenius plot of log k<sub>2</sub> versus 1/T is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k<sub>2</sub> at 298, 303, 308 and

Table 2: Kinetic isotope effect on the oxidation of mandelic acid by TriPAFC.

Substrate	$10^5 \times k_1$ , (s <sup>-1</sup> )			
	298 K	303 K	308 K	313 K
MA	32.16	41.18	57.24	78.88
DMA	6.05	7.43	9.96	13.32
$k_H/k_D$	5.34	5.54	5.75	5.92

Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

$10^2[MA] = 2.0 \text{ mol/dm}^3$ ;  $10^3[\text{TriPAFC}] = 1.2 \text{ mol/dm}^3$ ;  $10[H^+] = 2.4 \text{ mol/dm}^3$

Table 3: Effect of varying solvent polarity on the rate of reaction for the oxidation of mandelic acids by TriPAFC at 303 K.

% AcOH-H <sub>2</sub> O (v/v)	D	$10^5 k_1$ (s <sup>-1</sup> )						
		MA	<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>p</i> -i-C <sub>3</sub> H <sub>7</sub>	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
30-70	72.0	31.58	71.00	51.08	47.86	26.80	18.24	4.40
40-60	63.3	36.60	77.62	57.28	53.70	29.86	20.42	4.94
50-50	56.0	41.18	87.80	64.12	59.70	33.76	22.80	5.48
60-40	45.5	53.08	107.10	79.06	72.40	42.18	28.18	6.82
70-30	38.5	66.72	132.12	97.72	90.16	51.88	34.28	8.32

$10^2[HA] = 2.0 \text{ mol/dm}^3$ ;  $10^3[\text{TriPAFC}] = 1.2 \text{ mol/dm}^3$ ;  $[H^+] = 0.24 \text{ mol/dm}^3$

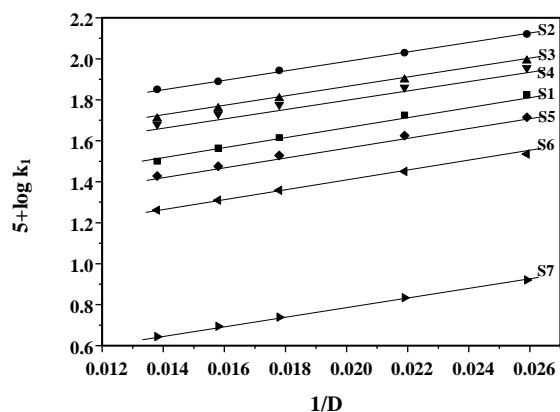


Fig. 3: Plot of  $1/D$  against  $\log k_1$  showing the effect of solvent polarity for the oxidation of MA (S1), *p*-OCH<sub>3</sub> (S2), *p*-CH<sub>3</sub> (S3), *p*-i-C<sub>3</sub>H<sub>7</sub> (S4), *p*-F (S5), *p*-Cl (S6) and *p*-NO<sub>2</sub> (S7) by TriPAFC at 303 K.

313 K using the Eyring relationship by the method of least square and presented in Table 4. The least square method gives the values and standard errors of enthalpy and entropy of activation respectively. Statistical analysis of the Eyring equation clearly confirms that the standard errors of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  correlate [31]. The entropy of activation is negative for all the mandelic acids.

### Isokinetic temperature

The linear relationship in Exner plots observed in the present study imply the validity of the isokinetic relationship [32]. The Exner plot of mandelic acids between  $\log k_2(T_2)$  and  $\log k_2(T_1)$  among the four experimental temperatures are presented in Fig. 4. The slope values of all the six possible correlations of mandelic acids and the calculated  $\beta$  values are listed in Table 5. The values of  $b$  are less than unity in all the plots. The isokinetic temperature values calculated for the six correlations are not differing very much from one another. The linear isokinetic correlation implies that all the *para*-substituted mandelic acids are oxidized by the same mechanism and the changes in the rate are governed by the changes in both the enthalpy and entropy of activation [33].

### Hammett Plot

A Hammett's plot for the oxidation of mandelic acid and six *para*-substituted mandelic acids by TriPAFC at various temperatures was found to be linear (Fig. 5). The value of the slope of the Hammett plot is known as reaction constant ( $\rho$ ). Reaction constant values at different temperatures are given in Table 6. According to Hammett,

**Table 4: Second order rate constants and activation parameters for the oxidation of mandelic acids by TriPAFC in aqueous acetic acid medium.**

Substrate	$10^3 k_2$ (dm <sup>3</sup> /mol s)				$E_a$ (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$-\Delta S^\ddagger$ (J/K mol)	$\Delta G^\ddagger$ (kJ/mol) (at 303 K)
	298 K	303 K	308 K	313 K				
MA	15.80	20.59	26.78	34.86	40.97	38.49±0.4	150.28±1.2	84.02±0.8
<i>p</i> -OCH <sub>3</sub>	35.10	43.90	54.85	68.56	34.66	32.17±0.4	164.83±1.2	82.11±0.8
<i>p</i> -CH <sub>3</sub>	25.25	32.06	40.72	51.68	37.15	34.66±0.4	159.28±1.2	82.92±0.8
<i>p</i> - <i>i</i> -C <sub>3</sub> H <sub>7</sub>	23.32	29.85	38.20	48.90	38.29	35.80±0.2	155.83±0.6	83.02±0.4
<i>p</i> -F	12.88	16.88	22.11	28.96	41.93	39.44±0.6	148.75±1.8	84.51±1.2
<i>p</i> -Cl	8.63	11.40	15.05	19.86	43.23	40.59±0.2	147.98±0.6	85.43±0.4
<i>p</i> -NO <sub>2</sub>	1.93	2.74	3.89	5.52	54.38	51.88±0.6	122.52±1.8	89.00±1.2

$10^2[HA] = 2.0 \text{ mol/dm}^3$ ;  $10^3[\text{TriPAFC}] = 1.2 \text{ mol/dm}^3$ ;  $[H^+] = 0.24 \text{ mol/dm}^3$   
Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

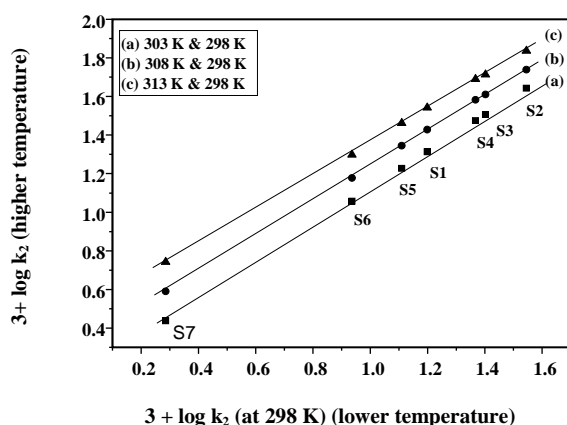
**Table 5: Results of Exner plots for oxidation of mandelic acids by TriPAFC in aqueous acetic acid medium.**

Correlation T <sub>2</sub> and T <sub>1</sub> (K)	Slope (b) <sup>c</sup>	Correlation coefficient	Iso-kinetic temperature (β, K)
303 and 298	0.958	0.993	491
308 and 298	0.915	0.997	482
313 and 298	0.873	0.990	478
308 and 303	0.955	0.998	473
313 and 303	0.912	0.995	475
313 and 308	0.954	0.990	472

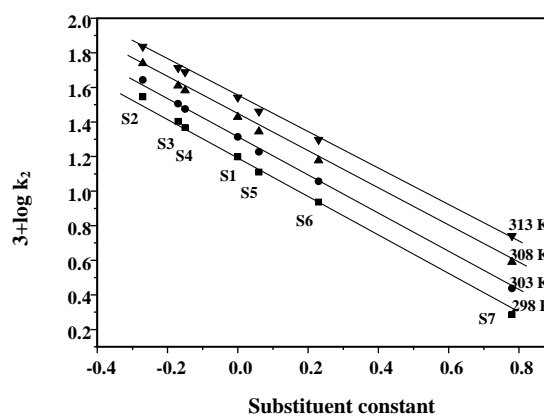
Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

$10^2[MA] = 2.0 \text{ mol/dm}^3$ ;  $10^3[\text{TriPAFC}] = 1.2 \text{ mol/dm}^3$ ;  $10[H^+] = 2.4 \text{ mol/dm}^3$

<sup>c</sup>The values were obtained by correlating log  $k_2$  (high temperature) with log  $k_2$  (low temperature) for the reactions of oxidations.



**Fig. 4: Exner's plot for the oxidation of MA (S1), *p*-OCH<sub>3</sub> (S2), *p*-CH<sub>3</sub> (S3), *p*-*i*-C<sub>3</sub>H<sub>7</sub> (S4), *p*-F (S5), *p*-Cl (S6) and *p*-NO<sub>2</sub> (S7) by TriPAFC at 303 K between 3 + log  $k_2$  (higher temperature) and 3 + log  $k_2$  (298 K) (lower temperature).**



**Fig. 5: Hammett plot for the oxidation of MA (S1), *p*-OCH<sub>3</sub> (S2), *p*-CH<sub>3</sub> (S3), *p*-*i*-C<sub>3</sub>H<sub>7</sub> (S4), *p*-F (S5), *p*-Cl (S6) and *p*-NO<sub>2</sub> (S7) by TriPAFC at 298 K, 303 K, 308 K and 313 K.**

**Table 6: Reaction constant values for the oxidation of mandelic acids by TriPAFC at different temperatures<sup>a</sup>.**

Temperature (K)	Reaction constant ( $\rho$ ) <sup>b</sup>	Correlation coefficient	Standard deviation
298	-1.1822±0.3	0.994	0.07
303	-1.1322±0.8	0.992	0.09
308	-1.0821±0.9	0.999	0.05
313	-1.0321±0.1	0.993	0.11

Solvent composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

$10^2[\text{MA}] = 2.0 \text{ mol/dm}^3$ ;  $10^3[\text{TriPAFC}] = 1.2 \text{ mol/dm}^3$ ;  $10[\text{H}^+] = 2.4 \text{ mol/dm}^3$

<sup>a</sup> $\sigma_p$  Values were taken from reported works [34].

<sup>b</sup>The values were obtained by correlating  $\log k_2$  with  $\sigma_p$  for the reactions of oxidations.

the reaction with positive  $\rho$  values are accelerated by electron withdrawal from a benzene ring, whereas those with negative  $\rho$  values are retarded by electron withdrawal from benzene ring [34]. In this oxidation reactions, the electron withdrawing groups decrease the rate and the electron donating groups increases the rate. These observations supporting the negative  $\rho$  values obtained from the Hammett plot.

### Mechanism

A hydrogen abstraction mechanism leading to the formation of free radicals may be discounted in view of the failure to induce polymerization of acrylonitrile [35] and the large values of the reaction constants. In most hydrogen abstraction reactions, the reaction constants have small magnitude [36]. The observed substantial kinetic isotope effect ( $k_H/k_D = 5.54$  at 303 K) suggests that the  $\alpha$ -C-H bond is cleaved in the rate-determining step. Correlation analysis of the substituent effect indicates the presence of a highly electron-deficient reaction center in the rate-determining step.

The fact that an excellent correlation is obtained with Hammett's  $\sigma$  values suggests that there is resonance interaction, in the transition state, between a developing positive center at the reaction site and the substituent. Thus, the transition state approaches a carbocationic in character. The mechanism is, however, supported by the observed negative entropy of activation for the conversion of the reactant molecules into the activated complex. As the process involves large charge separation in the transition state resulting in an increase in the total number of charges, the two ends become highly solvated. This results in immobilization of a large number of solvent molecules, reflected in the loss of entropy.

Therefore, a hydride ion transfer in the rate-determining step is suggested.

The hydride ion transfer may take place either by a cyclic process *via* an ester intermediate or by an acyclic one-step bimolecular process. Littler [37] has shown that a cyclic hydride transfer, in which the oxidation of alcohols by Cr(VI), involving six electrons and, being a Huckel-type system is an allowed process. Thus, a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step *via* a cyclic concerted symmetrical transition state leading to the product.

It is of interest to compare the results of oxidation of *a*-hydroxy acids by other oxidants containing Cr(VI). The oxidations of mandelic acid by two halochromates, *viz.* quinolinium fluorochromate (QFC) [6] and quinolinium chlorochromate (QCC) [13], are reported to involve an ester intermediate formation in the pre-equilibrium stage, which undergoes decomposition in the subsequent slow step *via* a cyclic, concerted and symmetrical transition state to give the corresponding oxoacid. The oxidations of mandelic acid by butyltriphenylphosphonium dichromate [9] also presented a similar kinetic picture. It seems that the mechanism of the oxidation of *a*-hydroxy acids depend on the nature of the oxidant.

Further, it is observed that oxidations of *a*-hydroxy acids by TriPAFC follow similar reaction path to that of alcohols [24], involving hydride-ion transfer from the substrate to the oxidant in the rate-determining step. A similar mechanism is also proposed for the oxidation of *a*-hydroxy acids by tetraethylammonium chlorochromate

(TEACC) [12]. The largely negative reaction constant together with the excellent correlation with Brown and Okamoto's  $\sigma^+$  values [38] points to a highly electron-deficient carbon center in the transition state.

## CONCLUSIONS

The oxidation of substituted mandelic acids with TriPAFC as an oxidant indicates the substituent reactivity follow the order  $p\text{-NO}_2 < p\text{-Cl} < p\text{-F} < p\text{-H} < p\text{-i-C}_3\text{H}_7 < p\text{-CH}_3 < p\text{-OCH}_3$ . The negative values of  $\Delta S^\ddagger$  provided support for the formation of a rigid activated complex and the Hammett's plot was found to be linear.

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