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## Kinetic studies on the oxidation of *dl*-mandelic acid by tripropylammonium fluorochromate in the presence of oxalic acid (A co-oxidation study)

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### ABSTRACT

The kinetics of oxidation of *dl*-mandelic acid (MA) by tripropylammonium fluorochromate (TriPAFC) was studied in aqueous acetic acid medium. The rate of reaction is first order with respect to TriPAFC, MA and  $[H^+]$  and the reaction is catalyzed by hydrogen ion. The reaction was studied in the presence of oxalic acid (OA). The oxidation leads to the formation of the phenyl glyoxalic acid. Various thermodynamic parameters have been determined at different acetic acid-water composition. A suitable mechanism has been proposed.

**Keywords:** kinetics, tripropylammonium fluorochromate, *dl*-mandelic acid, oxalic acid

### INTRODUCTION

The search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success based upon higher-valent transition metal oxo derivatives and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium and chromium have all proven to be capable of alcohol oxidation. In particular, there is continued interest in the development of new Cr(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. In recent years, significant improvements were achieved by the use of new oxidizing agents, such as tributylammonium chlorochromate [1], tetrabutylammonium fluorochromate [2], morpholinium chlorochromate [3], tetrahexylammonium bromochromate [4], triethylammonium chlorochromate [5], tetraethyl ammonium bromochromate [6], benzyltriethylammonium chlorochromate [7] and quinoxalinium dichromate [8].

Tripropylammonium fluorochromate is also one such oxidant developed recently [9 - 12]. It is a more efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

Among the different chelating agents [13–18] that promote Cr(VI) oxidation of different types of organic substrate, oxalic acid is quite important [19–22].

Extensive studies on the mechanism of oxidation of mandelic acid along with other hydroxy acids by several oxidants have been reported [23-30]. However, no detailed kinetic study of oxidation of *dl*-mandelic acid by TriPAFC in the absence and presence of oxalic acid have so far been attempted. Here we studied the kinetics of oxidation of *dl*-mandelic acid by TriPAFC in the absence and presence of oxalic acid. Mechanistic aspects are also discussed.

## MATERIALS AND METHODS

### Materials

Tripropylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Mandelic acid (SRL, AR) and oxalic acid (SRL, AR) were used after repeated crystallization from methanol. Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

### Kinetic measurements

The pseudo – first-order conditions were attained by maintaining a large excess ( x 15 or more) of mandelic acid over TriPAFC. The solvent was 50% acetic acid – 50% water (v/v), unless specified otherwise. The reactions were followed, at constant temperatures ( $\pm 0.01$  K), by monitoring the decrease in [TriPAFC] spectrophotometrically at 359 nm using UV–Vis spectrophotometer, Shimadzu UV-1800 model. The pseudo-first-order rate constant  $k_{obs}$ , was evaluated from the linear ( $r = 0.990$  to  $0.999$ ) plots of  $\log$  [TriPAFC] against time for up to 80% reaction. The second order rate constant  $k_2$ , was obtained from the relation  $k_2 = k_{obs} / [\text{MA}]$ .

### Product analysis

Product analysis was carried out under kinetic conditions *i.e* with excess of the mandelic acid over TriPAFC. In the present experiment, mandelic acid (15.2 g, 0.1 mol), perchloric acid (0.24 mol) and TriPAFC (0.012 mol) were dissolved in acetic acid – water mixture (50 % – 50%) and the solution was allowed to stand 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 hydrazone (DNP) was filtered off, dried and recrystallised from ethanol. The product was identical (mp and mixed mp) to an authentic sample of the DNP of phenyl glyoxylic acid.

## RESULTS AND DISCUSSION

Tripropylammonium fluorochromate is easily prepared as reported in the literature [10]. The oxidation of *dl*-mandelic acid by TriPAFC has been conducted in 50% acetic acid and 50% water medium at 303 K, under pseudo first order conditions in the absence and presence of oxalic acid and the result obtained were discussed in the following paragraphs.

### Order of the reaction

The reactions are first order with respect to TriPAFC as evidenced by a linear plot of  $\log$  [TriPAFC] against time. The pseudo first-order rate constants do not depend on the initial concentration of TriPAFC (Table 1). This further confirms first-order dependence of rate on oxidant concentration. Reaction rates increase linearly with increase in the concentrations of the mandelic acid (Table 1). A plot of  $\log k_{obs}$  vs  $\log$  [MA] is linear with a slope = 1.03, indicating that the order with respect to mandelic acid is also one. The acid catalysed nature of this oxidation is confirmed by an increase in the rate on the addition of H<sup>+</sup>. The plot of  $\log k_{obs}$  versus  $\log$  [H<sup>+</sup>] is a straight line with the slope of 1.09. Therefore, order with respect to H<sup>+</sup> is one. TriPAFC may become protonated in the presence of acid and the protonated TriPAFC may function as an effective oxidant.

### Induced Polymerization of Acrylonitrile

The possibility of radical formation and its involvement in the reaction has been ruled out as the addition of acrylonitrile in the reaction mixture developed no turbidity and hence the reaction rates was not affected even the [acrylonitrile] was at  $1.0 \times 10^{-3}$  to  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> (Table 2). Thus, a one – electron oxidation giving rise to free radicals is unlikely.

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

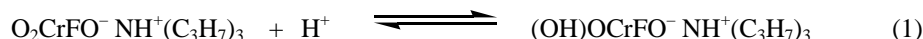
The addition of Mn(II), in the form of MnSO<sub>4</sub> retards the rate of oxidation. This indicates the involvement of Cr(IV) intermediate in the oxidation of MA by Cr(VI) reagent and confirms the two electron transfer process in the reaction. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV) reduces Cr(VI) to Cr(V) and the oxidation of MA by Cr(V) is fast. The decrease in the rate of Cr(VI) reduction on the addition of Mn(II) has been attributed to the removal of Cr(IV) by reaction with Mn(II) (Table 3).

### Effect of varying ionic strength of reaction rate

The ionic strength of the reaction medium is changed by the addition of anhydrous sodium perchlorate and the influence of ionic strength on the reaction rate has been studied. The values of the rate constants at different ionic strength of the reaction medium has no significant effect on the reaction rate (Table – 4).

**Effect of Acidity**

The reaction is catalyzed by hydrogen ions (Table 1). The acid-catalysis may well be attributed to a protonation of TriPAFC to give a stronger oxidant and electrophile.



The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC [31] and PFC [32].

**Effect of varying Oxalic acid concentration**

The concentration of oxalic acid is varied in the range of  $0.0 \times 10^{-3}$  to  $10.0 \times 10^{-3}$  mol dm<sup>-3</sup> at constant [TriPAFC], [MA] and [H<sup>+</sup>] at 303 K and the rates were measured (Table 5). We observed that the rate increases linearly with increasing oxalic acid concentration.

**Effect of solvent polarity on reaction rate**

The oxidation of mandelic acid has been studied in the binary mixture of acetic acid and water as the solvent medium. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table 4. The effect from solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 30% to 70%. The pseudo-first-order rate constants were estimated for the oxidation of mandelic acid, with TriPAFC in the presence of perchloric acid at a constant ionic strength. The reaction rate increases markedly with the increase in the proportion of acetic acid in the medium (Table 6). When the acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. The plot of log  $k_1$  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 [33]. Amis (1967) holds the view that in an ion-dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium [34].

**Thermodynamic parameters**

The kinetics of oxidation of mandelic acid was studied at four different temperatures *viz.*, 298, 303, 308 and 313 K at various percentage of acetic acid-water medium. The kinetics of oxidation of mandelic acid was also studied in the presence of oxalic acid. The second order rate constants were calculated (Table 6). The Arrhenius plot of log  $k_2$  versus 1/T is found to be linear. This shows that Arrhenius Equation is valid for this oxidation [35 – 37]. The enthalpy of activation, entropy of activation and free energy of activation were calculated from  $k_2$  at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 6. The entropy of activation is negative for mandelic acid in the absence and presence of oxalic acid.

Table – 1 Effect of variation of [MA], [TriPAFC] and [H<sup>+</sup>] on the rate of the reaction at 303 K<sup>a,b</sup>

$10^3[\text{TriPAFC}]$ (mol dm <sup>-3</sup> )	$10^2[\text{MA}]$ (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	$10^5 k_1$ (s <sup>-1</sup> )
0.6	2.0	0.24	41.12
1.2	2.0	0.24	41.18
1.8	2.0	0.24	41.28
2.4	2.0	0.24	41.30
3.0	2.0	0.24	41.20
1.2	1.0	0.24	20.24
1.2	1.5	0.24	30.64
1.2	2.5	0.24	51.30
1.2	3.0	0.24	62.00
1.2	2.0	0.12	20.66
1.2	2.0	0.18	30.76
1.2	2.0	0.30	51.42
1.2	2.0	0.36	61.80

<sup>a</sup>As determined by spectrophotometrically following the disappearance of Cr(VI) at 359 nm; the error quoted in  $k$  values is the 95% confidence limit of 'Student  $t$  test'.

<sup>b</sup>Estimated from pseudo first order plots over 80% reaction.  
Solvent Composition = 50% AcOH - 50% H<sub>2</sub>O (v/v)

**Table - 2 Rate constants for the oxidation of mandelic acid by TriPAFC in aqueous acetic acid medium in the presence of acrylonitrile (AN) at 303 K<sup>a</sup>**

$10^3$ [AN] (mol dm <sup>-3</sup> )	$10^5 k_t$ (s <sup>-1</sup> )
0.0	41.18
1.0	41.06
2.0	41.06
3.0	41.22
4.0	41.14
5.0	41.28

$10^2$ [MA] = 2.0 mol dm<sup>-3</sup>;  $10^3$ [TriPAFC] = 1.2 mol dm<sup>-3</sup>;  $10$  [H<sup>+</sup>] = 2.4 mol dm<sup>-3</sup>;  
Solvent composition : 50% Acetic acid – 50% Water (v / v)

**Table - 3 Rate constants for the oxidation of mandelic acid by TriPAFC in aqueous acetic acid medium in the presence of MnSO<sub>4</sub> at 303 K<sup>a</sup>**

$10^3$ [MnSO <sub>4</sub> ] (mol dm <sup>-3</sup> )	$10^5 k_t$ (s <sup>-1</sup> )
0.0	41.18
1.0	38.11
2.0	35.82
3.0	33.74
4.0	31.74
5.0	30.08

$10^2$ [MA] = 2.0 mol dm<sup>-3</sup>;  $10^3$ [TriPAFC] = 1.2 mol dm<sup>-3</sup>;  $10$  [H<sup>+</sup>] = 2.4 mol dm<sup>-3</sup>;  
Solvent composition : 50% Acetic acid – 50% Water (v / v)

**Table - 4 Effect of ionic strength the oxidation of mandelic acid by TriPAFC in aqueous acetic acid medium**

$10^2$ [NaClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	$10^5 k_t$ (s <sup>-1</sup> )
0.0	41.18
1.0	41.04
2.0	41.11
3.0	41.26
4.0	41.34
5.0	41.15

$10^2$ [MA] = 2.0 mol dm<sup>-3</sup>;  $10^3$ [TriPAFC] = 1.2 mol dm<sup>-3</sup>;  $10$  [H<sup>+</sup>] = 2.4 mol dm<sup>-3</sup>;  
Solvent composition: 50% Acetic acid – 50% Water (v / v)

**Table - 5 Rate constants for the oxidation of mandelic acid by TriPAFC in aqueous acetic acid medium in the presence of Oxalic acid at 303 K<sup>a</sup>**

$10^3$ [OA] (mol dm <sup>-3</sup> )	$10^5 k_t$ (s <sup>-1</sup> )
0.0	41.18
2.0	49.08
4.0	56.96
6.0	65.06
8.0	72.94
10.0	79.88

$10^2$ [MA] = 2.0 mol dm<sup>-3</sup>;  $10^3$ [TriPAFC] = 1.2 mol dm<sup>-3</sup>;  $10$  [H<sup>+</sup>] = 2.4 mol dm<sup>-3</sup>;  
Solvent composition: 50% Acetic acid – 50% Water (v / v)

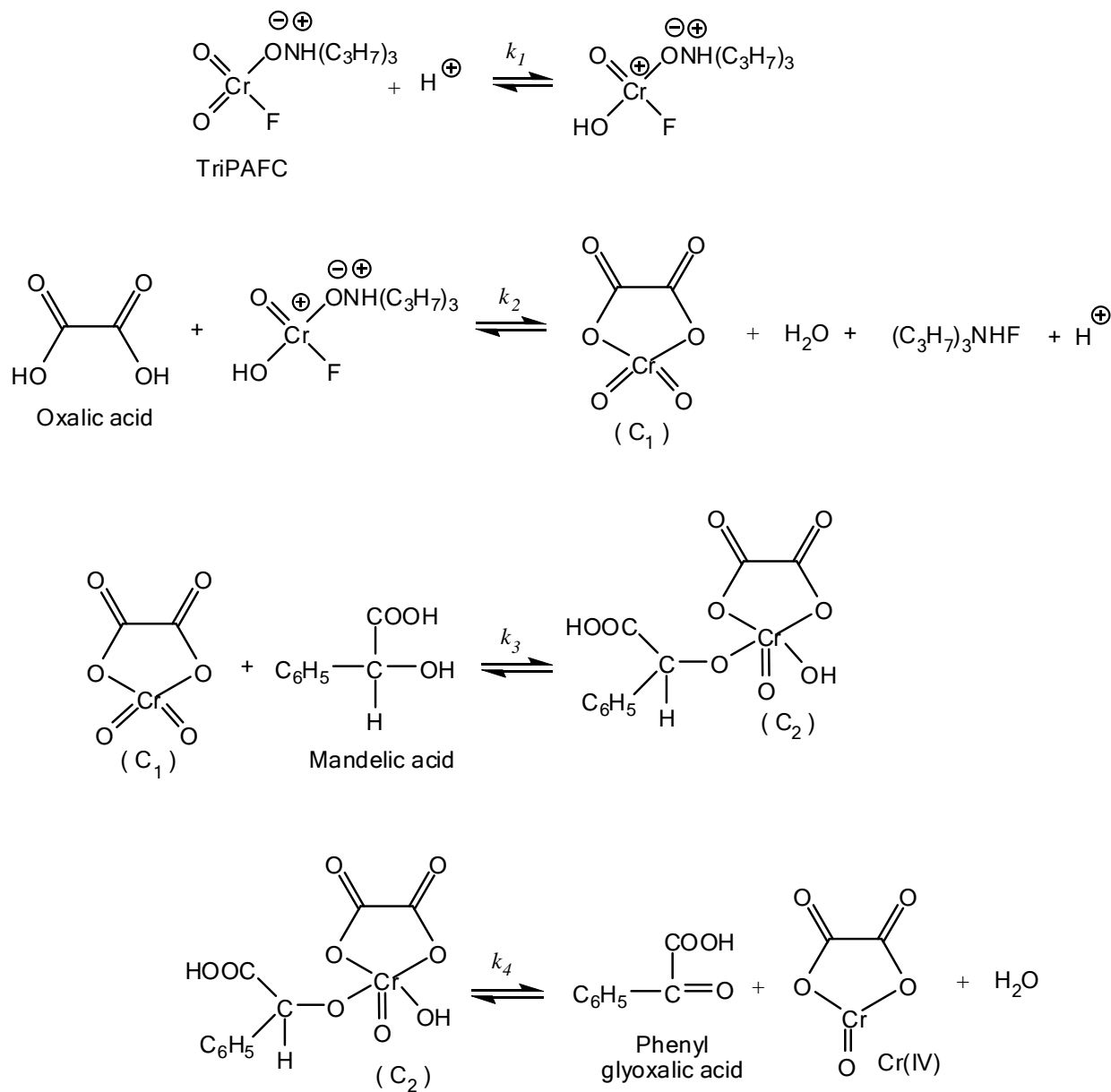
**Table – 6 Second order rate constants and activation parameters for the oxidation of dl-Mandelic acid by TriPAFC at various percentage of acetic acid-water medium in the presence and absence of Oxalic acid**

%AcOH - H <sub>2</sub> O (v/v)	$10^3 k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				$E_a$ (kJmol <sup>-1</sup> )	$-\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJmol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJmol <sup>-1</sup> ) (at 303 K)
	298 K	303 K	308 K	313 K				
No Catalyst								
30-70	12.33	15.79	21.60	29.44	45.37	138.22	42.89	84.77
40-60	14.29	18.30	25.47	34.69	46.34	133.44	43.81	84.24
50-50	16.08	20.59	28.62	39.44	46.91	131.13	44.23	83.96
60-40	20.02	28.34	34.83	48.11	44.04	138.41	41.35	83.29
70-30	25.21	33.59	42.49	59.63	43.27	137.82	40.40	82.16
Oxalic acid								
30-70	16.80	22.11	28.33	37.33	40.97	149.70	38.29	83.65
40-60	20.44	27.00	33.67	44.94	40.02	151.43	37.52	83.40
50-50	25.01	32.53	40.66	54.33	39.44	152.00	36.76	82.82
60-40	28.56	37.20	45.60	61.43	38.67	153.91	36.18	82.81
70-30	35.33	46.49	56.02	77.04	39.06	150.85	36.34	82.10

$10^2$ [MA] = 2.0 mol dm<sup>-3</sup>;  $10^3$ [TriPAFC] = 1.2 mol dm<sup>-3</sup>;  $10$  [H<sup>+</sup>] = 2.4 mol dm<sup>-3</sup>;  $10^3$  [OA] = 6.0 mol dm<sup>-3</sup>

**Reaction mechanism for TriPAFC oxidation of *dl*-mandelic acid in the presence of OA**

The findings with oxalic acid can be explained by considering the reaction mechanism outlined in Scheme - 1. Oxalic acid readily form complex ( $C_1$ ) with Cr(VI) [22]. In the next step, the complex reacts with the substrate to form a ternary complex ( $C_2$ ). This ternary complex ( $C_2$ ) undergoes redox decomposition by two electron transfer within the cyclic transition state in a rate-determining step involving simultaneous rupture of C–C and C–H bonds to give a phenyl glyoxalic acid and the Cr(IV)-OA complexes.



Scheme 1 Mechanism of oxidation of mandelic acid by TriPAFC in the presence of Oxalic acid

**CONCLUSION**

The kinetics of oxidation of mandelic acid has been investigated in aqueous acetic acid medium by spectrophotometrically at 303 K in the absence and presence of OA. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation. The oxidation of mandelic acid has been conducted at four different temperatures at various percentage of acetic acid-water medium in the absence and presence of OA. The lowering of dielectric constant of reaction medium increases the reaction rate significantly.

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