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## Kinetics and mechanism of oxidation of some $\alpha$ -hydroxy acids by triethylammonium fluorochromate in presence of picolinic acid catalyst in aqueous acetic acid media

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### ABSTRACT

We have described the catalytic activity of picolinic acid (PA) for the oxidation of some  $\alpha$ -hydroxy acids like glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) by triethylammonium fluorochromate (TriEAFc) in aqueous acetic acid medium. The oxidation leads to the formation of the corresponding oxo acids. The reaction is first order with respect to TriEAFc, hydroxy acids and  $[H^+]$  and the reaction is catalyzed by hydrogen ions. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. The reaction rates were determined at different temperatures and the activation parameters computed. A suitable mechanism has been proposed.

**Keywords:** picolinic acid, hydroxy acids, triethylammonium fluorochromate, kinetics

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### INTRODUCTION

Picolinic acid acts as a chelating agent of elements such as chromium, zinc, manganese, copper, iron, and molybdenum in the body. It is involved in phenylalanine, tryptophan, and alkaloids production, and for the quantitative detection of calcium. This forms a complex with zinc, may facilitate the passage of zinc through the gastrointestinal wall and into the circulatory system. During the past decades, picolinic acid was found to have a number of biological functions. Commercially picolinic acid is used as an intermediate to produce pharmaceuticals (especially local anesthetics) and metal salts for the application of nutritional supplements. Picolinic acid chromium salt, a dietary supplement, may be used to study its potential as a modulator of glucose uptake and the activity of insulin. Picolinic acid also has protective and therapeutic effects against tumor through activation and subsequent enhancement of macrophages-mediated cytotoxicity, and induces production of tumor-related proteins [1].

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizable functional group. A number of new Cr (VI) containing compounds, with heterocyclic bases have been studied in recent years for the oxidation of various organic substrates [2-9].

Triethylammonium fluorochromate [10-12] is also one such oxidant developed recently. 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. In this paper, we describe the kinetics and mechanism of the oxidation of glycolic, malic, lactic and mandelic acids by TriE AFC in aqueous acetic acid medium.

Among the different chelating agents [13-15] that promote Cr(VI) oxidation of different types of organic substrate, picolinic acid, 2,2'-bipyridine, and 1,10-phenanthroline are quite important [16-19].

The kinetics and mechanism of oxidation of hydroxy acids by various oxidants have been reported [20-28]. However, no detailed kinetic study of oxidation of hydroxy acids in the presence of picolinic acid by TriE AFC, a Cr(VI) reagent has so far been attempted. Hence we have studied the kinetics of oxidation of some  $\alpha$ -hydroxy acids like glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) in the presence of picolinic acid by TriE AFC and evaluated various thermodynamic parameters. A detailed mechanism involving a hydride-ion transfer in the rate determining step is discussed.

## MATERIALS AND METHODS

### Materials

Triethylamine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). The hydroxy acids used were glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA). Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected.

### Preparation of triethylammonium fluorochromate

Triethylammonium fluorochromate has been prepared from triethylamine, 40% hydrofluoric acid and chromium trioxide as reported in the literature [10].

### Kinetic measurements

The pseudo – first-order conditions were attained by maintaining a large excess (  $\times 15$  or more) of hydroxy acids over TriE AFC. 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 [TriE AFC] spectrophotometrically at 362 nm using UV-Vis spectrophotometer, Shimadzu UV-1800 model. The pseudo-first-order rate constant  $k_1$ , was evaluated from the linear ( $r = 0.990$  to  $0.999$ ) plots of  $\log [\text{TriE AFC}]$  against time for up to 80% reaction. The second order rate constant  $k_2$ , was obtained from the relation  $k_2 = k_1 / [\text{HA}]$ .

### Product analysis

Product analysis was carried out under kinetic conditions *i.e* with excess of the reductant over TriE AFC. In a typical experiment, mandelic acid (15.2 g, 0.1 mol), perchloric acid (0.28 mol) and TriE AFC (0.01 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  $\text{dm}^{-3}$  HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitro phenyl hydrozone (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.

### Stoichiometric studies

The stoichiometric studies for the oxidation of hydroxy acids by TriE AFC were carried out with oxidant in excess. The solvent composition 50% acetic acid – 50% water ( $v/v$ ) and  $[\text{H}^+]$  were maintained as in the corresponding rate measurements. The temperature was maintained at 303 K. The hydroxy acids and TriE AFC were mixed in the ratio 1:4, 1:5, 1:6 and were allowed to react for 24 h at 303 K. The concentration of unreacted TriE AFC was determined.  $\Delta[\text{TriE AFC}]$  was calculated. The stoichiometry was calculated from the ratio between  $[\text{HA}]$  and  $[\text{TriE AFC}]$ .

Stoichiometric analysis showed that the following overall reaction.



## RESULTS AND DISCUSSION

The oxidation of some  $\alpha$ -hydroxy acids like glycolic acid, malic acid, lactic acid and mandelic acid by TriE AFC have been conducted in 50% acetic acid and 50% water medium at 303 K, under pseudo first order conditions. The result obtained were discussed in the following paragraphs.

**Effect of varying the concentration of picolinic acid**

The concentration of picolinic 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 [TriE AFC], [HA] and [H<sup>+</sup>] at 303 K and the rates were measured (Table 1). We observed that the rate increases linearly with increasing picolinic acid concentration.

**Table - 1** Rate constants for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by by TriE AFC in aqueous acetic acid medium in the presence of picolinic acid at 303 K

10 <sup>3</sup> [PA] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>t</sub> (s <sup>-1</sup> )			
	GA	MLA	LA	MA
0.0	21.48	26.88	32.14	54.22
2.0	24.82	30.60	36.28	61.32
4.0	28.18	34.42	40.60	68.56
6.0	31.66	38.70	45.22	75.90
8.0	34.72	42.60	49.32	82.94
10.0	38.14	46.44	53.40	90.12

<sup>a</sup>As determined by a spectrophotometric technique following the disappearance of oxidant

10<sup>2</sup>[HA] = 2.0 mol dm<sup>-3</sup>; 10<sup>3</sup>[TriE AFC] = 1.0 mol dm<sup>-3</sup>; [H<sup>+</sup>] = 0.28 mol dm<sup>-3</sup>

Solvent composition: 50% Acetic acid – 50% Water (v/v)

<sup>b</sup>Estimated from pseudo-first order plots over 80% reaction

**Effect of acrylonitrile and MnSO<sub>4</sub>**

The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals (Table – 2). However, the addition of Mn(II) (0.003 mol dm<sup>-3</sup>), 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 hydroxy acids by Cr(VI) reagent and confirms the two electron transfer process in the reaction.

**Table - 2** Rate constants for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by TriE AFC in aqueous acetic acid medium in the presence of picolinic acid catalyst at 303 K<sup>a,b</sup>

10 <sup>3</sup> [TriE AFC] (mol dm <sup>-3</sup> )	10 <sup>2</sup> [HA] (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] (mol dm <sup>-3</sup> )	10 <sup>5</sup> k <sub>t</sub> (s <sup>-1</sup> )			
			GA	MLA	LA	MA
0.4	2.0	0.28	31.58	38.62	45.12	75.86
1.0	2.0	0.28	31.66	38.70	45.22	75.90
1.6	2.0	0.28	31.72	38.68	45.18	75.94
2.2	2.0	0.28	31.60	38.84	45.30	75.98
2.8	2.0	0.28	31.54	38.76	45.08	75.82
1.0	1.0	0.28	185.60	19.16	22.50	37.76
1.0	1.5	0.28	23.56	28.88	33.80	56.78
1.0	2.5	0.28	39.42	48.18	56.46	94.70
1.0	3.0	0.28	47.36	57.90	67.70	113.68
1.0	2.0	0.16	18.26	22.34	25.98	43.40
1.0	2.0	0.22	24.98	30.62	35.74	59.63
1.0	2.0	0.34	38.68	47.12	55.08	92.10
1.0	2.0	0.40	45.40	55.46	64.80	108.50
1.0	2.0	0.28	31.54 <sup>c</sup>	38.78 <sup>c</sup>	45.28 <sup>c</sup>	75.88 <sup>c</sup>
1.0	2.0	0.28	24.68 <sup>d</sup>	31.04 <sup>d</sup>	36.28 <sup>d</sup>	59.20 <sup>d</sup>

<sup>a</sup>As determined by a spectrophotometric technique following the disappearance of oxidant

10<sup>2</sup>[HA] = 2.0 mol dm<sup>-3</sup>; 10<sup>3</sup>[TriE AFC] = 1.0 mol dm<sup>-3</sup>; [H<sup>+</sup>] = 0.28 mol dm<sup>-3</sup>; 10<sup>3</sup>[PA] = 6.0 mol dm<sup>-3</sup>

Solvent composition : 50% Acetic acid – 50% Water (v/v)

<sup>b</sup>Estimated from pseudo-first order plots over 80% reaction

<sup>c</sup>Contained 0.001 mol dm<sup>-3</sup> acrylonitrile; <sup>d</sup>In the presence of 0.003 mol dm<sup>-3</sup> Mn(II).

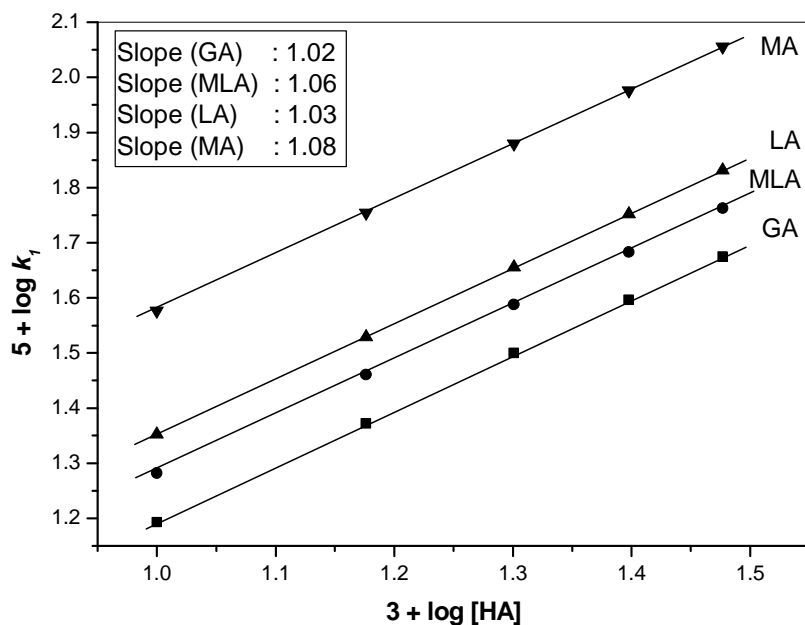


Fig 1. Showing the order plot of glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) in the presence of picolinic acid catalyst

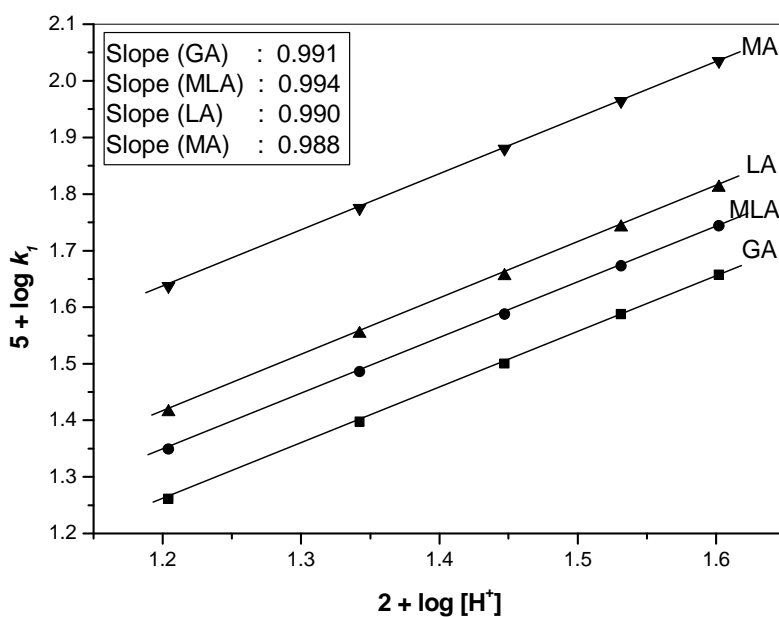


Fig 2. Showing the order plot of  $[H^+]$  for the oxidation of glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) in the presence of picolinic acid catalyst

**Order of the reaction**

The concentration of TriEAFC was varied in the range of  $0.4 \times 10^{-3}$  to  $2.8 \times 10^{-3}$  mol dm<sup>-3</sup> at constant [HA], [H<sup>+</sup>] at 303 K and the rates were measured (Table 2). The near constancy in the value of  $k_1$  irrespective of the concentration confirms the first order dependence on TriEAFC.

The rate of oxidation increased progressively on increasing the concentration of hydroxy acids (Table 2). The plot of  $\log k_1$  versus  $\log [HA]$  gave unit slope for GA, MLA, LA and MA respectively (Fig. 1). Under pseudo-first-order conditions, the plot of  $k_1$  versus [HA] is linear passing through origin. These results confirm the first-order nature of the reaction with respect to [HA].

Perchloric acid has been used as a source of H<sup>+</sup> in reaction medium. The acid catalysed nature of this oxidation is confirmed by an increase in the rate on the addition of [H<sup>+</sup>] (Table 2). The plot of  $\log k_1$  versus  $\log [H^+]$  is a straight line with unit slope for GA, MLA, LA and MA respectively. Therefore, order with respect to [H<sup>+</sup>] is one for GA, MLA, LA and MA respectively. TriEAFC may become protonated in the presence of acid and the protonated TriEAFC may function as an effective oxidant.

**Effect of solvent polarity on reaction rate**

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 hydroxy acids, with TriEAFC in the presence of perchloric acid at a constant ionic strength. The reaction rate is increases markedly with the increase in the proportion of acetic acid in the medium (Table 3). 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 [29, 30] (Fig. 3). Positive slope of  $\log k_1$  versus  $1/D$  plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step.

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 [31].

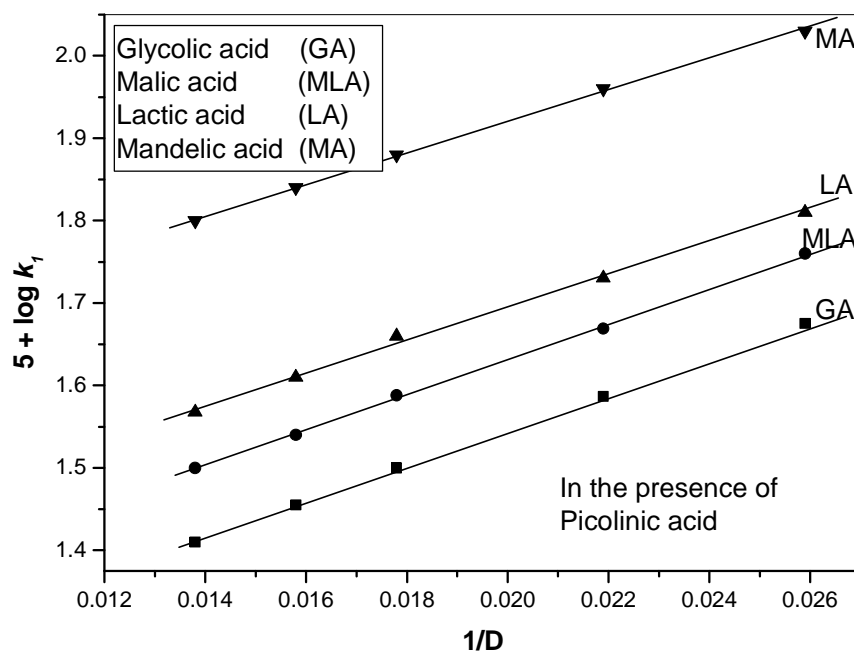


Fig 3. Plot of  $1/D$  against  $\log k_1$  showing effect of solvent polarity in the presence of picolinic acid catalyst

Table – 3 Pseudo-first order rate constants for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by TriEAFc at various percentage of acetic acid-water medium in the presence of picolinic acid catalyst at 303 K

% AcOH - H <sub>2</sub> O (v/v)	Dielectric constant	10 <sup>3</sup> k <sub>1</sub> (s <sup>-1</sup> )			
		GA	MLA	LA	MA
30-70	72.0	25.70	31.62	36.94	63.08
40-60	63.3	28.51	34.67	40.69	69.18
50-50	56.0	31.66	38.70	45.22	75.90
60-40	45.5	38.60	46.76	54.26	91.00
70-30	38.5	47.32	57.54	65.10	107.40

$$10^2[\text{HA}] = 2.0 \text{ mol dm}^{-3}; 10^3[\text{TriEAFc}] = 1.0 \text{ mol dm}^{-3}; [\text{H}^+] = 0.28 \text{ mol dm}^{-3}; 10^3[\text{PA}] = 6.0 \text{ mol dm}^{-3}$$

### Thermodynamic parameters

The kinetics of oxidation of hydroxy acids was studied at four different temperatures *viz.*, 298, 303, 308 and 313 K. The second order rate constants were calculated (Table 4). The Arrhenius plot of log  $k_2$  versus 1/T is found to be linear. 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 4. The entropy of activation is negative for hydroxy acids.

Table – 4 Second order rate constants and activation parameters for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by TriEAFc in acetic acid-water medium in the presence of picolinic acid catalyst

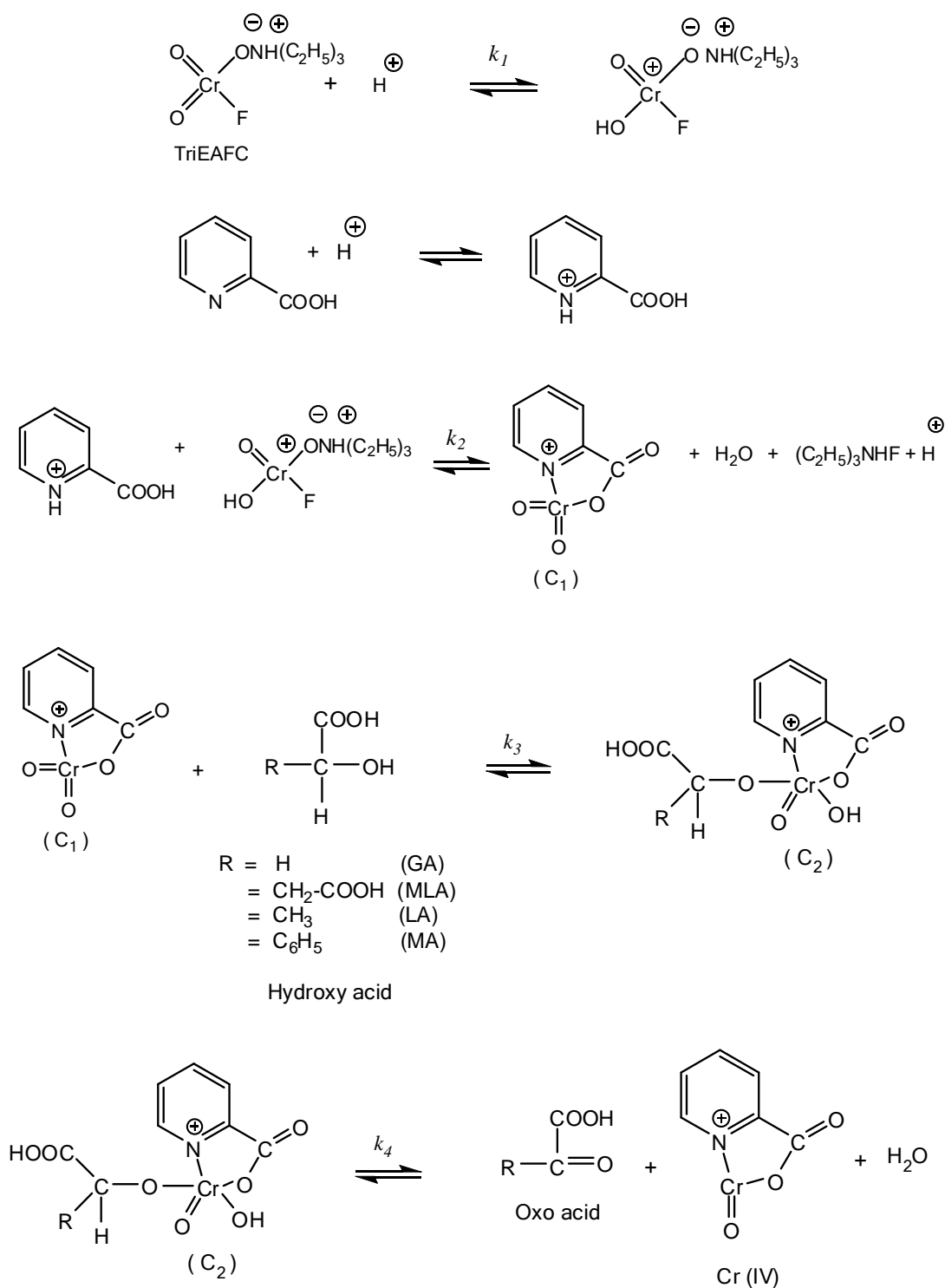
% AcOH - H <sub>2</sub> O (v/v)	10 <sup>3</sup> k <sub>2</sub> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				E <sub>a</sub> (kJ mol <sup>-1</sup> )	-ΔS <sup>#</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )	ΔH <sup>#</sup> (kJ mol <sup>-1</sup> )	ΔG <sup>#</sup> (kJ mol <sup>-1</sup> ) (at 303 K)
	298 K	303 K	308 K	313 K				
GA	11.55	15.83	21.70	29.72	49.02	125.96±1.2	46.34±0.4	84.50±0.8
MLA	14.28	19.35	26.25	35.70	47.48	129.42±1.8	44.80±0.6	84.02±1.2
LA	16.87	22.61	30.30	40.60	45.56	134.58±0.6	42.88±0.2	83.65±0.4
MA	29.20	37.95	49.33	64.10	40.78	146.07±1.5	38.10±0.5	82.35±1.0

$$10^2[\text{HA}] = 2.0 \text{ mol dm}^{-3}; 10^3[\text{TriEAFc}] = 1.0 \text{ mol dm}^{-3}; [\text{H}^+] = 0.28 \text{ mol dm}^{-3}; 10^3[\text{PA}] = 6.0 \text{ mol dm}^{-3}$$

### Mechanism for TriEAFc oxidation of α-hydroxy acid in the presence of picolinic acid

From the product analysis, DNP was confirmed. Hence, it shows that under the experimental conditions employed in the present study, hydroxy acids were oxidized to the corresponding oxo acids. 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. In this oxidation, the cleavage of the α-C-H bond takes place in the rate-determining step. Therefore, a hydride-ion transfer in the rate determining step is suggested. Positive slope of log  $k_1$  versus 1/D plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step.

The findings with picolinic acid can be explained by considering the reaction mechanism outlined in Scheme-1. It is believed that the catalytic activity of complexing agent such as picolinic acid depends on their ability to stabilize intermediate chromium valence states [32]. TEAFCH<sup>+</sup> reacts with picolinic acid to form a binary complex (C<sub>1</sub>). In the next step, the binary complex (C<sub>1</sub>) reacts with the substrate to form a ternary complex (C<sub>2</sub>). This ternary complex (C<sub>2</sub>) 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 oxo acid and the Cr(IV)-PA complexes. The negative entropy of activation in conjunction with other kinetic observations supports the mechanism outlined in Scheme-1.



Scheme 1 Mechanism of picolinic acid catalysed oxidation of hydroxy acids by TriEAFC

## CONCLUSION

The kinetics of oxidation of hydroxy acids has been investigated in aqueous acetic acid medium in the presence of perchloric acid by spectrophotometrically at 303 K. The oxidation of hydroxy acids by TriEAFC is first order each

with respect to the hydroxy acids, TriEAFc and hydrogen ion. The oxidation is catalysed by picolinic acid. The lowering of dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation. The order of reactivity is GA < MLA < LA < MA in the presence of picolinic acid. The reaction rate is higher in LA than in GA due to the inductive effect. Enhanced reactivity in MA may be due to the stabilization of the intermediate formed through resonance.

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