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Oxidation of 4-oxo-4-phenyl butanoic acid by tripropylammonium fluoro chromate in the presence of picolinic acid – A kinetic and mechanistic study

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ABSTRACT

The oxidation of 4-oxo-4-phenyl butanoic acid (4-oxo acid) by tripropylammonium fluorochromate (TriPAFC) resulted in the formation of benzoic acid. The catalytic activity of picolinic acid (PA) has been studied in 50% acetic acid – 50 % water medium. The reaction is first order each in [TriPAFC], [4-oxo acid] and [H^+]. The reaction rates were determined at different temperatures and the activation parameters computed. From the results, a suitable mechanism has been proposed.

Keywords: 4-oxo acid; kinetics; tripropylammonium fluorochromate; picolinic acid

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INTRODUCTION

In 4-oxo acids, the carbonyl and the carboxyl groups are separated by two carbon atoms and so they possess the characteristics of both compounds without the direct influence of the other group. Many of the 4–oxoacids and their esters possess fungicidal, bactericidal and anti–inflammatory activities [1]. Kinetics and mechanism of oxidation of 4-oxo acids by different oxidants like permanganate [2], pyridinium fluorochromate [3], *N*-bromosuccinimide [4], *N*-chlorosaccharin [5], *N*-bromosaccharin [6], *N*-chlorobenzamide [7] and *N*-bromoacetamide [8] have been the subject of study by various workers.

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidiasable 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 [9-16].

Tripropylammonium fluorochromate is also one such oxidant developed recently [17-20]. 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 [21-24] that promote Cr(VI) oxidation of different types of organic substrate, picolinic acid, 2,2'-bipyridine, and 1,10-phenanthroline are quite important [25–28].

As a part of our continuing investigations on the oxidation of organic substrates by Cr(VI) [29, 30], this paper reports the kinetic features of the oxidation of 4-oxo-4-phenyl butanoic acid by TriPAFC in the presence of picolinic acid. Mechanistic aspects are also discussed.

MATERIALS AND METHODS

Materials

Tripropyl amine and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected. Perchloric acid is used as the source of hydrogen ion.

Preparation of Tripropylammonium fluorochromate

Tripropylammonium fluorochromate is easily prepared as follows: Chromium (VI) oxide (15.0 g, 0.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrofluoric acid (11.3 mL, 0.225 mol) was added with stirring at 0 °C. To the resultant orange solution, tripropylammine (28.3 mL, 0.150 mol) was added drop wise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 x 60 ml) and dried in vacuum for 2 h at room temperature [18].

Tripropyl amine Tripropylammonium fluorochromate (1)

The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The Cr (VI) content may be easily determined iodometrically.

Preparation of 4–oxo–4–phenyl butanic acid

The 4–oxo–4–phenyl butanic acid is synthesized by the Friedel–Craft's reaction between succinic anhydride and benzene in the presence of anhydrous aluminium chloride [2].

Kinetic measurements

The pseudo – first-order conditions were attained by maintaining a large excess (x 15 or more) of 4-oxo acid over TriPAFC. The reactions were followed, at constant temperatures (± 0.01 K), by monitoring the decrease in [TriPAFC] spectrophotometrically at 364 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.

RESULTS AND DISCUSSION

Product study was made under mineral acid catalysed condition in 4–oxo–4–phenyl butanic acid. The product was obtained which had melting point of 121 °C. The product was dissolved in benzene and a careful TLC analysis was done with benzoic acid and 4–oxo–4–phenyl butanoic acid as references. Only one spot corresponding to benzoic acid was obtained. The stoichiometric studies for the oxidation of 4-oxo acid by TriPAFC were carried out with oxidant in excess. The stoichiometric studies showed that 1 mol of TriPAFC reacts with 1 mol of 4–oxo–4–phenyl butanic acid.

Kinetic study for the oxidation of 4-oxo-4-phenyl butanoic acid by TriPAFC has been conducted in 50% acetic acid – 50 % water medium at 303 K in the presence of picolinic acid under pseudo-first order conditions and the results obtained were discussed here.

Effect of varying the concentrtation of picolinic acid

The concentration of picolinic acid is varied in the range of 0.0 x 10^{-3} to 8.0 x 10^{-3} mol dm^{-1} at constant [TriPAFC], [4-Oxo acid] and [H^+] at 303 K and the rates were measured (Table 1). We observed that the rate increases linearly with increasing picolinic acid concentration.

Effect of varying TriPAFC concentration

The concentration of TriPAFC was varied in the range of 0.6 x 10^{-3} to 2.6 x 10^{-3} mol dm^{-1} at constant [4-Oxo acid], [H^+] at 303 K and the rates were measured (Table 1). The near constancy in the value of k_{obs} irrespective of the concentration confirms the first order dependence on TriPAFC.

Effect of varying 4-Oxo acid concentration

The concentration of 4-Oxo acid is varied in the range of 1.2 x 10^{-2} to 2.8 x 10^{-2} mol dm^{-1} at 303 K and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of 4-Oxo acid. The plot of log k_{obs} *versus* log [4-Oxo acid] gave the slope of 1.02. Under pseudo-first-order conditions, the plot of k_{obs} *versus* [4-Oxo acid] is linear passing through origin. These results confirm the first-order nature of the reaction with respect to [4-Oxo acid].

Effect of varying perchloric acid concentration

Perchloric acid has been used as a source of H^+ in reaction medium. The concentration of H^+ was varied in the range 0.1 to 0.42 mol dm^{-1} keeping all other reactant concentration as constant at 303 K and the rates were measured (Table 1). The acid catalysed nature of this oxidation is confirmed by an increase in the rate on the addition of H^+. The plot of log k_{obs} *versus* log [H^+] is a straight line with the slope of 1.01. Therefore, order with respect to H^+ is one. TriPAFC may become protonated in the presence of acid and the protonated TriPAFC may function as an effective oxidant.

Table - 1 Rate constants for the oxidation of 4-oxo-4-phenyl butanoic acid by TriPAFC in aqueous acetic acid medium in the presence of picolinic acid at 303 K[a,b]

10^3[TriPAFC] (mol dm^{-3})	10^2[4-Oxo] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^3 [PA] (mol dm^{-3})	10^4 k_1 (s^{-1})
1.1	2.0	0.26	0.0	12.26
1.1	2.0	0.26	2.0	12.66
1.1	2.0	0.26	4.0	13.18
1.1	2.0	0.26	6.0	14.70
1.1	2.0	0.26	8.0	15.58
0.6	2.0	0.26	6.0	14.62
1.6	2.0	0.26	6.0	14.76
2.1	2.0	0.26	6.0	14.72
2.6	2.0	0.26	6.0	14.78
1.1	1.2	0.26	6.0	8.70
1.1	1.6	0.26	6.0	11.66
1.1	2.4	0.26	6.0	17.78
1.1	2.8	0.26	6.0	20.58
1.1	2.0	0.10	6.0	5.52
1.1	2.0	0.18	6.0	10.28
1.1	2.0	0.34	6.0	19.10
1.1	2.0	0.42	6.0	23.74
1.1	2.0	0.26	6.0	14.67[c]
1.1	2.0	0.26	6.0	12.72[d]

[a] *As determined by a spectrophotometric technique following the disappearance of oxidant*
10^2[4-Oxo acid] = 2.0 mol dm^{-3}; 10^3[TriPAFC] = 1.1 mol dm^{-3}; [H^+] = 0.26 mol dm^{-3}
Solvent composition : 50% Acetic acid – 50% Water (v / v)
[b] *Estimated from pseudo-first order plots over 80% reaction*
[c] *Contained 0.001 mol dm^{-3} acrylonitrile.*
[d] *In the presence of 0.003 mol dm^{-3} Mn(II).*

Effect of acrylonitrile and $MnSO_4$

The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals (Table – 1). However, the addition of Mn(II) (0.003 mol dm^{-}3), in the form of $MnSO_4$ 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. 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 hydroxy acids by Cr(V) is fast [31]. 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) [32].

Effect of solvent polarity on reaction rate

The oxidation of 4-oxo-4-phenyl butanoic acid in the presence of picolinic acid has been studied in the binary mixture of acetic acid and water as the solvent medium. For the oxidation of 4-oxo-4-phenyl butanoic acid, the reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table 2. 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, 34] (Fig. 1).

Table – 2 Pseudo-first order rate constants for the oxidation of 4-oxo-4-phenyl butanoic acid by TriPAFC at various percentage of acetic acid-water medium in the presence of picolinic acid at various temperatures

%AcOH - H_2O (*v/v*)	Dielectric constant	$10^4 k_1$ (s^{-1}) 298 K	303 K	308 K	313 K
30-70	72.0	8.32	11.66	16.32	22.68
40-60	63.3	9.18	13.00	18.50	25.60
50-50	56.0	10.42	14.70	20.40	28.60
60-40	45.5	11.72	17.06	24.40	33.60
70-30	38.5	13.92	19.30	27.30	37.86

10^2[4-oxo] = 2.0 mol dm^{-}; 10^3[TriPAFC] = 1.1 mol dm^{-3}; 10^3 [PA] = 6.0 mol dm^{-3}; 10 [H^+] = 2.6 mol dm^{-3}

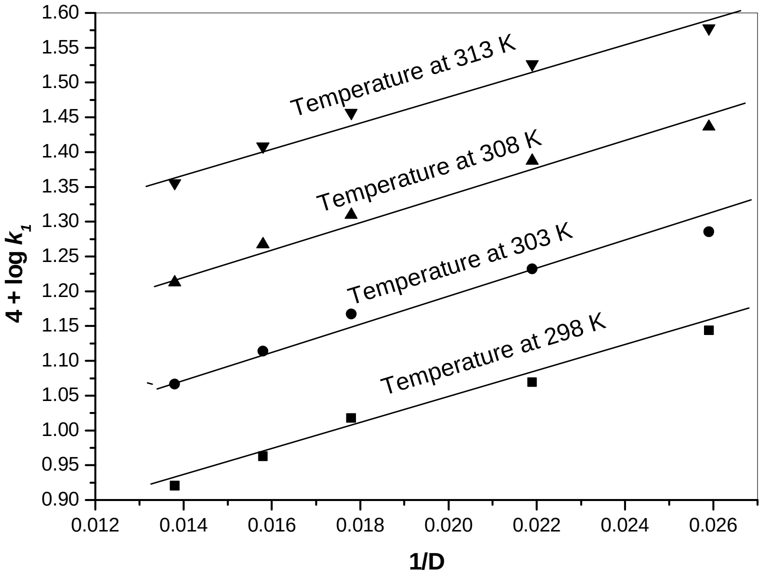


Figure 1 Plot of 1 / D against log k_1 showing effect of solvent polarity at various temperatures in the presence of picolinic acid

Rate of enolisation by bromination method

It has been reported earlier in the case of oxidation of keto compounds that the oxidation proceeds *via* enolisation of the keto compounds. The rate of enolisation of keto compound is faster than the rate of oxidation. The reactive species of the substrate may be determined by enolisation, which is an acid as well as base catalysed reaction and proceeds by a concerted or push–pull mechanism. The rate of enolisation was determined by bromination method for the system under investigation.

The order of bromination reaction with respect to the 4-oxo-4-phenyl butanoic acid, bromine and H^+ has been determined. These data indicate that the bromination of the 4-oxo-4-phenyl butanoic acid is first order each with respect to the substrate and H^+ ion but zero order with respect to bromine.

Thermodynamic parameters

The kinetics of oxidation of 4-oxo acid in the presence of picolinic is studied at four different temperatures viz., 298, 303, 308 and 313 K at various percentage of acetic acid-water medium. The second order rate constants were calculated (Table 3). 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 3.

Table – 3 Second order rate constants and activation parameters for the oxidation of 4-oxo-4-phenyl butanoic acid by TriPAFC at various percentage of acetic acid-water medium in the presence of picolinic acid

%AcOH - H_2O (*v/v*)	10^2k_2 ($dm^3mol^{-1}s^{-1}$)				E_a (kJ mol^{-1})	$-\Delta S^\#$ (J K^{-1} mol^{-1})	$\Delta H^\#$ (kJ mol^{-1})	$\Delta G^\#$ (kJ mol^{-1}) (at 303 K)
	298 K	303 K	308 K	313 K				
30-70	4.16	5.83	8.16	11.34	52.08	105.28±1.2	49.58±0.4	81.48±0.8
40-60	4.59	6.50	9.25	12.80	53.41	099.92±0.6	50.73±0.2	81.00±0.4
50-50	5.21	7.35	10.20	14.30	52.26	102.79±1.2	49.97±0.4	81.12±0.8
60-40	5.86	8.53	12.20	16.80	54.75	093.41±1.8	50.08±0.6	80.38±1.2
70-30	6.96	9.65	13.65	18.93	51.88	101.83±1.8	49.20±0.6	80.05±1.2

10^2[4-oxo] = 2.0 mol dm^- ; 10^3[TriPAFC] = 1.1 mol dm^{-3}; 10^3 [PA] = 6.0 mol dm^{-3} ; 10 [H^+] = 2.6 mol dm^{-3}

Isokinetic relationship

The reaction is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship.

$$\Delta H^\# = \Delta H^o + \beta \Delta S^\# \qquad (2)$$

The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. Exner suggested a method of testing the validity of isokinetic relationship [35]. The isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to Eq (3).

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \qquad (3)$$

The linear relationship in Exner plot at 4 + log k_2 (298 K) and 4 + log k_2 (308 K) observed in the present study imply the validity of the isokinetic relationship (Fig. 2). Isokinetic temperature obtained is 649 ±4 K. The linear isokinetic correlation implies that 4-oxo acid at various percentage of solvent composition is oxidized by the same mechanism and the changes in the rate are governed by the changes in both the enthalpy and entropy of activation [36].

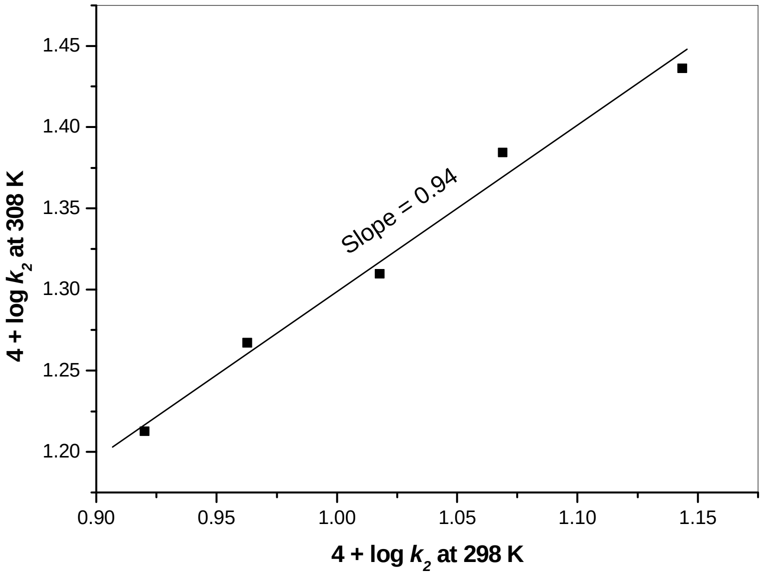
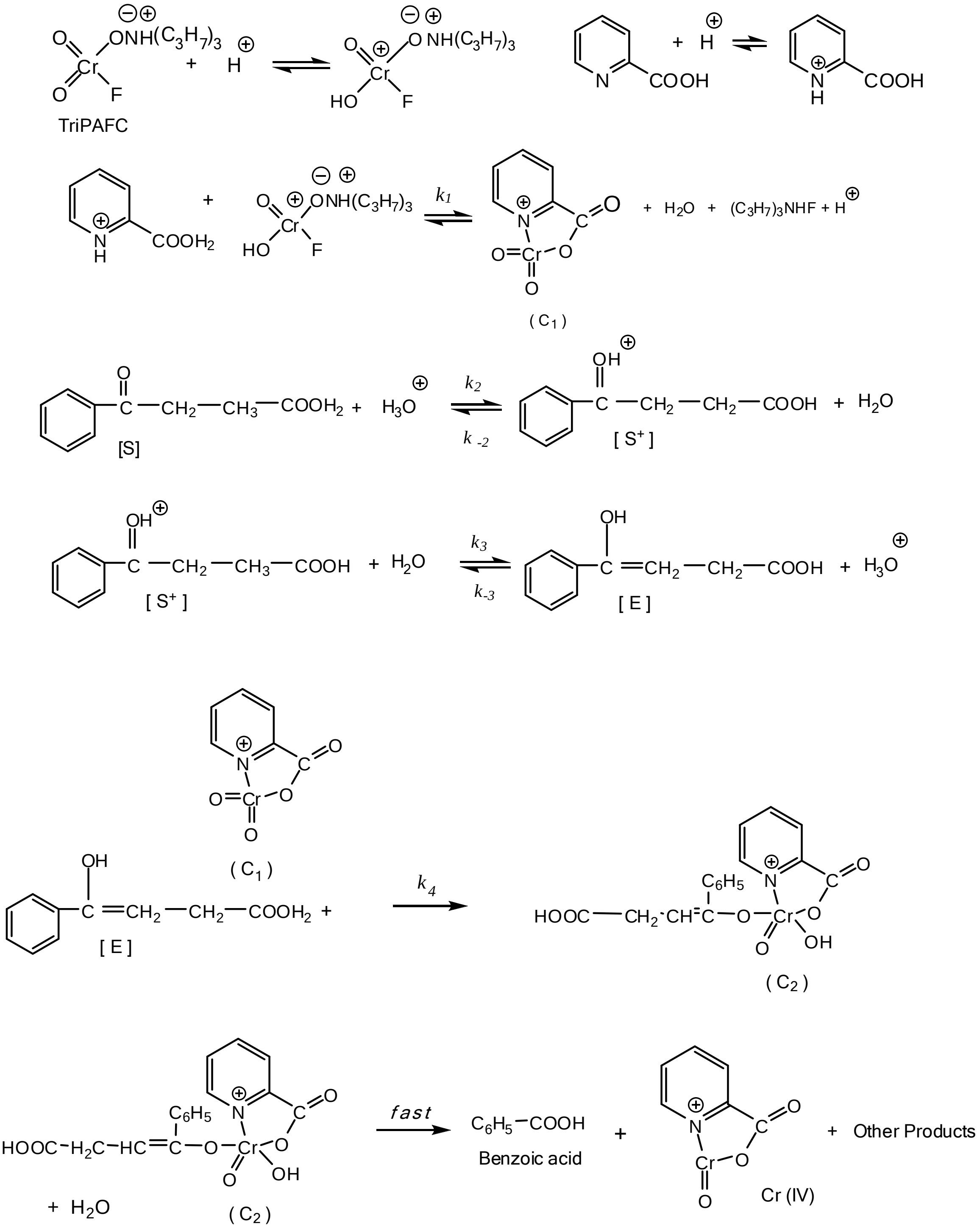


Figure 2 Exner plot at 4 + log k_2 (298 K) and 4 + log k_2 (308 K) for the oxidation of 4-Oxo acid by TriPAFC in the presence of picolinic acid at various percentage of acetic acid-water medium

Mechanism of oxidation

A probable mechanism for the oxidation of 4-oxo-4-phenyl butanoic acid in the presence of picolinic acid by TriPAFC has been proposed based on the experimental results and in analogy with the oxidation of oxo compounds with the other oxidants. The results obtained in the kinetic study are briefly summarized below: The reaction is first order each with respect to the 4-oxo-4-phenyl butanoic acid, TriPAFC and H^+ ion. The linear increase in the reaction rate with the increase in $[H^+]$ ion is attributed to the formation of protonated TriPAFC *i.e.*, TriPAFCH$^+$ and to the enolisation of the 4-oxo-4-phenyl butanoic acid. The formation of TriPAFCH$^+$ ion and the enolisation of the 4-oxo-4-phenyl butanoic acid are facilitated at lower dielectric constant of the medium. The rate of enolisation is found to be greater than the rate of oxidation. The course of oxidation does not involve any free radical intermediate. It is believed that the catalytic activity of complexing agent such as picolinic acid depends on their ability to stabilize intermediate chromium valence states [37]. Picolinic acid readily form complex (C_1) with Cr(VI). 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 benzoic acid and the Cr(IV)-PA complexes. Considering these facts and findings a suitable mechanism has been proposed for the oxidation (Scheme–1).



Scheme 1 Mechanism of oxidation of 4-Oxo acid by TriPAFC in the presence of picolinic acid

CONCLUSION

The kinetics of oxidation of 4-Oxo acid by TriPAFC was studied in 50% acetic acid – 50% water (*v/v*) at 303 K. The reaction is first order each in [TriPAFC], [4-oxo acid] and $[H^+]$. The rate of enolisation was determined by bromination method for the system under investigation. The stoichiometry study showed that 1 mol of TriPAFC reacts with 1 mol of 4–oxo–4–phenyl butanic acid. The reaction is catalysed by picolinic acid. The Cr(VI)-PA complex is believed to be the probable electrophile in the catalyzed oxidation. Using the Eyring relationship the enthalpy of activation, entropy of activation and free energy of activation were calculated.

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