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RESEARCH ARTICLE

Kinetics and Mechanism of Oxidation of some *α* - Hydroxy Acids by Tripropylammonium Fluorochromate in Aqueous Acetic Acid Medium

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Abstract: The oxidation of some *α*-hydroxy acids like glycolic, lactic and mandelic acids by tripropylammonium fluorochromate (TriPAFC) have been studied in aqueous acetic acid medium. The oxidation leads to the formation of the corresponding oxo acids. The reaction is first order with respect to TriPAFC, hydroxy acids and $[H^+]$ and the reaction is catalyzed by hydrogen ions. The reaction has been studied in different percentage of acetic acid-water mixture. A suitable mechanism has been proposed.

Keywords: Tripropylammonium fluorochromate, Hydroxy acids, Kinetics, Oxidation

Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds[1]. Cr(VI) as chromate or dichromate is highly soluble in water and is reported to be highly toxic[2]. Hence, 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. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists.

In recent years, some new Cr(VI) based reagents like tetraethyl ammonium bromochromate[3], benzimidazolium fluorochromate[4], triethylammonium chlorochromate[5], imidazolium fluorochromate[6], tetrahexylammonium fluorochromate[7] and tributylammonium chlorochromate[8] were proposed.

Tripropylammonium fluorochromate[9,10] 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, lactic and mandelic acids by TriPAFC in aqueous acetic acid medium.

The kinetics and mechanism of oxidation of hydroxy acids by various oxidants have been reported[11-19]. However, no detailed kinetic study of oxidation of hydroxy acids by TriPAFC, a Cr(VI) reagent has so far been attempted. This prompted us to undertake the present investigation. The present work reports the kinetics of oxidation of α-hydroxy acids by TriPAFC and evaluates the reaction constants. Mechanistic aspects are also discussed.

Experimental

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

Preparation of tripropylammonium fluorochromate

Tripropylammonium fluorochromate has been prepared from tripropylamine, 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 (×15 or more) of hydroxy acids over TriPAFC. The solvent was 50% acetic acid -50% water (v/v), unless specified otherwise. The reactions were followed, at constant temperatures (±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 $k_2 = k_{obs}$ / [HA].

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

Product analysis was carried out under kinetic conditions *i.e.,* with excess of the reductant over TriPAFC. In a typical experiment, mandelic acid (15.2 g, 0.l mol), perchloric acid (0.24 mol) and TriPAFC (0.012 mol) were dissolved in acetic acid – water mixture (50%- 50%) and the solution was allows 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^{-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 TriPAFC were carried out with oxidant in excess. The solvent composition 50% acetic acid -50% water (v/v) and $[H^+]$ were maintained as in the corresponding rate measurements. The temperature was maintained at 303 K. The hydroxy acids and TriPAFC 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 TriPAFC was determined. Δ[TriPAFC] was calculated. The stoichiometry was calculated from the ratio between [HA] and [TriPAFC].

Stoichiometric analysis showed that the following overall reaction.

$$RCH(OH)COOH + O_2CrFO^-NH^+(C_3H_7)_3 \longrightarrow RCOCOOH + H_2O + OCrFO^- NH^+(C_3H_7)_3 \quad (1)$$

Results and Discussion

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

Effect of varying TriPAFC concentration

The concentration of TriPAFC was varied in the range of $0.6x10^{-3}$ to $3.0x10^{-3}$ mol dm^{-1} at constant [HA], [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 hydroxy acids concentration

The concentration of the substrates GA, LA, MA were varied in the range of $1.0x10^{-2}$ to $3.0x10^{-2}$ 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 hydroxy acids. The plot of log k_{obs} *versus* log [HA] gave the slope of 1.01, 1.08 and 1.03 respectively for GA, LA and MA respectively (Figure 1). Under pseudo-first-order conditions, the plot of of k_{obs} *versus* [HA] is linear passing through origin. These results confirm the first-order nature of the reaction with respect to [HA].

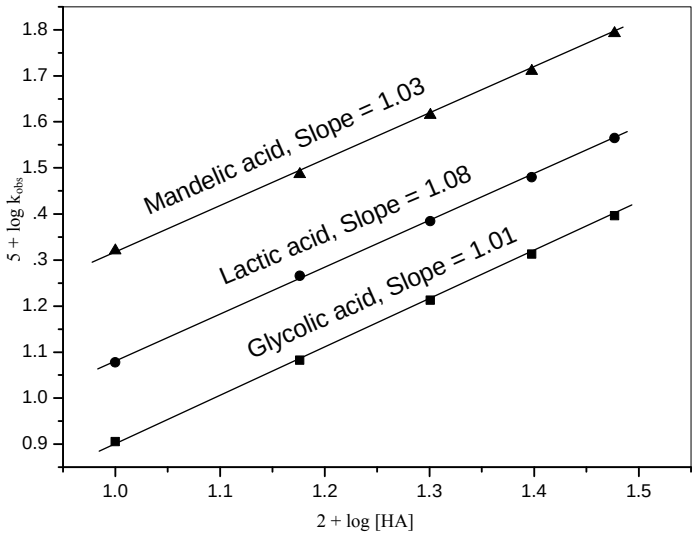


Figure 1. Order plot of HA for the oxidation of hydroxy acids by TriPAFC

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 0.12 to 0.36 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 1.04, 1.07 and 1.09 respectively for GA,

LA and MA respectively. Therefore, order with respect to H^+ is one for GA, LA and MA respectively. TriPAFC may become protonated in the presence of acid and the protonated TriPAFC may function as an effective oxidant.

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[20]. 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[21] with Mn(II).

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.

$$O_2CrFO^- NH^+(C_3H_7)_3 + H^+ \rightleftharpoons (OH)OCrFO^- NH^+(C_3H_7)_3 \quad (2)$$

The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC[22] and PFC[23].

Table 1. Effect of variation of [HA], [TriPAFC] and [H^+] on the rate of the reaction at 303 K[a,b]

10^3[TriPAFC], mol dm^{-3}	10^2[HA], mol dm^{-3}	[H^+], mol dm^{-3}	10^5 k_1, s^{-1}		
			GA	LA	MA
0.6	2.0	0.24	16.18	24.28	41.12
1.2	2.0	0.24	16.32	24.22	41.18
1.8	2.0	0.24	16.22	24.10	41.28
2.4	2.0	0.24	16.42	24.18	41.30
3.0	2.0	0.24	16.30	24.30	41.20
1.2	1.0	0.24	8.04	11.96	20.42
1.2	1.5	0.24	12.56	18.44	30.64
1.2	2.5	0.24	26.26	30.18	51.30
1.2	3.0	0.24	24.88	36.72	62.00
1.2	2.0	0.12	8.22	12.06	20.66
1.2	2.0	0.18	12.20	18.30	30.76
1.2	2.0	0.30	20.16	30.32	51.42
1.2	2.0	0.36	24.22	30.16	61.80
1.2	2.0	0.24	16.14	24.16	41.06[c]
1.2	2.0	0.24	13.82	20.32	33.74[d]

[a]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'. [b]Estimated from pseudo first order plots over 80% reaction. Solvent Composition = 50% AcOH - 50% H_2O (v/v) [c]Contained 0.001 mol dm^{-3} acrylonitrile. [d]In the presence of 0.003 mol dm^{-3} Mn(II)

Kinetic isotope effect

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

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

Substrate	$10^5 \times k_1$, s^{-1}			
	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_2O (v/v) 10^2[MA] = 2.0 mol dm^{-3}; 10^3[TriPAFC] = 1.2 mol dm^{-3}; 10 [H^+] = 2.4 mol dm^{-3}

Effect of solvent polarity on reaction rate

The oxidation of α-hydroxy acid has been studied in the binary mixture of acetic acid and water as the solvent medium. For the oxidation of all hydroxy acids, the reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table 3.

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 TriPAFC 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). When the acid content increases in the medium, the acidity of the medium is increased whereas the dielectric constant of the medium is decreased. These two effects cause the rate of the oxidation to increase markedly. The enhancement of the reaction rate with an increase in the amount of acetic acid generally may be attributed to two factors, *viz*, (i) the increase in acidity occurring at constant [H^+], and (ii) the decrease in the dielectric constant with an increase in the acetic acid content.

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[24,25] (Figure 2). Plot of log k_1 *versus* (D – 1) / (2D+ 1) is a curvature indicating the absence of dipole – dipole interaction in the rate determining step. 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[26]. Due to the polar nature of the solvent, transition state is stabilized, *i.e.,* the polar solvent molecules surround the transition state and result in less disproportion.

Table 3. Effect of varying solvent polarity on the rate of reaction at 303 K

%Acetic acid-Water (v/v)	Dielectric constant	1 / D	$10^5 k_1$, s^{-1}		
			GA	LA	MA
30-70	72.0	0.0138	12.52	18.10	31.58
40-60	63.3	0.0158	14.44	21.56	36.60
50-50	56.0	0.0178	16.32	24.22	41.18
60-40	45.5	0.0219	20.30	32.00	53.08
70-30	38.5	0.0259	26.12	40.36	66.72

10^2[HA] = 2.0 mol dm^- ; 10^3[TriPAFC] = 1.2 mol dm^{-3}; 10 [H^+] = 2.4 mol dm^{-3}

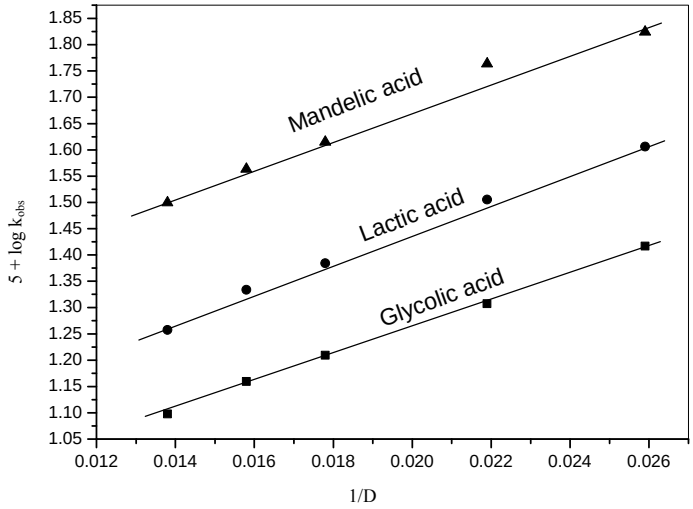


Figure 2. Plot of 1 / D against log k_{obs} showing effect of solvent polarity

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. Activation parameters and second order rate constants for the oxidation of hydroxy acids by TriPAFC in aqueous acetic acid medium

Substrate	$10^3 k_2$, $dm^3 mol^{-1} s^{-1}$				E_a	$\Delta H^{\#}$	$-\Delta S^{\#}$ JK^{-1}	$\Delta G^{\#}$ $kJmol^{-1}$,
	298 K	303 K	308 K	313 K	$kJmol^{-1}$	$kJmol^{-1}$	mol^{-1}	at 303 K
GA	6.08	8.16	11.21	15.22	47.60	44.35	138.64	86.35
LA	9.04	12.11	15.80	20.45	42.12	39.44	151.26	85.27
MA	16.08	20.59	28.62	39.44	46.72	44.23	131.25	84.00

Solvent Composition = 50% AcOH -50% H_2O (v/v) 10^2 [HA] = 2.0 mol dm^{-3}; 10^3 [TriPAFC] = 1.2 mol dm^{-3}; 10 $[H^+]$ = 2.4 mol dm^{-3}

Isokinetic relationship

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

$$\Delta H^{\#} = \Delta H^{o} + \beta \Delta S^{\#} \quad (3)$$

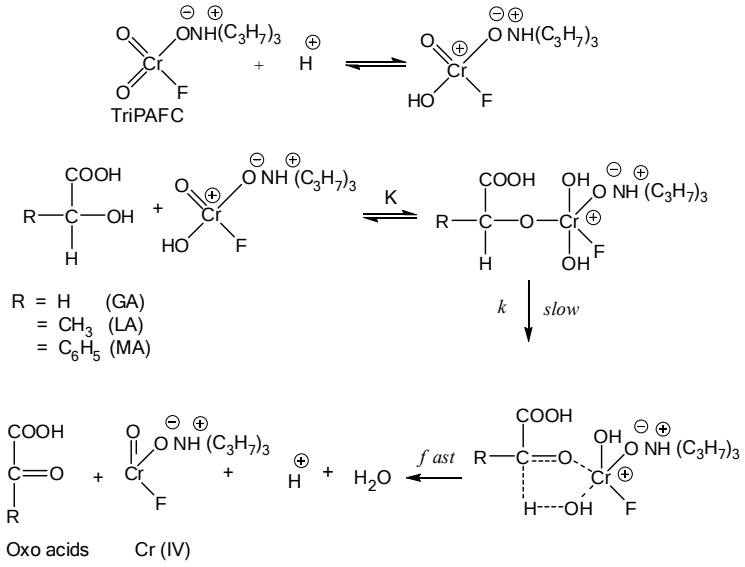
The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature, the variation of substituent has no influence on the free energy of activation. Exner[27] suggested a method of testing the validity of isokinetic relationship. 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 (4).

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \quad (4)$$

The linear relationship in Exner plots[28,29] at 4 + log k_2 (303 K) and 4 + log k_2 (308 K) observed in the present study imply the validity of the isokinetic relationship. Isokinetic temperature obtained is 418±12 K. The linear isokinetic correlation implies that GA, LA and MA 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[30].

Mechanism of oxidation

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. Based on the above kinetic observations the following mechanism is proposed for the reaction. 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 DMA confirms the cleavage of the α–C–H bond 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 negative entropy of activation in conjunction with other experimental data supports the mechanism outlined in (Scheme 1).



Scheme 1. Mechanism of oxidation of hydroxy acids by TriPAFC

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 TriPAFC is first order each with respect to the hydroxy acids, TriPAFC and hydrogen ion. The oxidation is catalysed by perchloric 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 < LA < MA. 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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