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Der Pharmacia Lettre, 2015, 7 (11):100-106 (http://scholarsresearchlibrary.com/archive.html)



Studies on the kinetics of triethylammonium fluorochromate oxidation of some α -hydroxy acids in acetic acid-water medium

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ABSTRACT

The oxidation of some α -hydroxy acids like glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) by triethylammonium fluorochromate (TriEAFC) 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 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. Various thermodynamic parameters have been determined. A suitable mechanism has been proposed.

Keywords: triethylammonium 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.

A number of new Cr(VI) containing compounds like tetraethyl ammonium bromochromate [3], benzimidazolium fluorochromate [4], triethylammonium chlorochromate [5], tripropylammonium fluorochromate [6], tetrahexylammonium fluorochromate [7], tributylammonium chlorochromate [8] and quinoxalinium dichromate [9] were proposed.

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 TriEAFC in aqueous acetic acid medium.

The kinetics and mechanism of oxidation of hydroxy acids by various oxidants have been reported [13-21]. However, no detailed kinetic study of oxidation of hydroxy acids by TriEAFC, a Cr(VI) reagent has so far been attempted. Hence we have studied the kinetics of oxidation of some α -hydroxy acids like glycolic acid (GA), malic acid (MLA), lactic acid (LA) and mandelic acid (MA) by TriEAFC 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 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 (x 15 or more) of hydroxy acids over TriEAFC. The solvent was 50% acetic acid-50% water (ν/ν), unless specified otherwise. The reactions were followed, at constant temperatures (± 0.01 K), by monitoring the decrease in [TriEAFC] 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 [TriEAFC] against time for up to 80% reaction. The second order rate constant k_2 , was obtained from the relation $k_2 = k_1 / [HA]$.

Product analysis

Product analysis was carried out under kinetic conditions *i.e* with excess of the reductant over TriEAFC. In a typical experiment, mandelic acid (15.2 g, 0.1 mol), perchloric acid (0.28 mol) and TriEAFC (0.01 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 TriEAFC were carried out with oxidant in excess. The solvent composition 50% acetic acid – 50% water (ν/ν) and [H⁺] were maintained as in the corresponding rate measurements. The temperature was maintained at 303 K. The hydroxy acids and TriEAFC 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 TriEAFC was determined. Δ [TriEAFC] was calculated. The stoichiometry was calculated from the ratio between [HA] and [TriEAFC].

Stoichiometric analysis showed that the following overall reaction. $RCH(OH)COOH + O_2CrFO^-NH^+(C_2H_5)_3 \longrightarrow RCOCOOH + H_2O + OCrFO^-NH^+(C_2H_5)_3$ (1)

RESULTS AND DISCUSSION

The oxidation of some α -hydroxy acids like glycolic acid, malic acid, lactic acid and mandelic acid by TriEAFC 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.

Order of the reaction

The reactions are first order with respect to TriEAFC as evidenced by a linear plot of log [TriEAFC] against time. The pseudo first-order rate constants do not depend on the initial concentration of TriEAFC (Table 1). This further confirms first-order dependence of rate on oxidant concentration.

The rate of oxidation increased progressively on increasing the concentration of hydroxy acids (Table 1). The plot of log k_1 versus log [HA] gave the slope of 1.026, 1.032, 0.990 and 0.982 respectively for GA, MLA, LA and MA respectively (Fig. 1). Under pseudo-first-order conditions, the plot of 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^+ in reaction medium. The acid catalysed nature of this oxidation is confirmed by an increase in the rate on the addition of $[H^+]$ (Table 1). The plot of log k_1 versus log $[H^+]$ is a straight line with the slope of 0.994, 0.989, 0.993 and 0.996 respectively for GA, MLA, LA and MA respectively. Therefore, order with respect to $[H^+]$ 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 acrylonitrile and MnSO₄

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.

10 ³ [TriEAFC]	$10^{2}[HA]$	$[H^+]$	$10^5 k_l \ (s^{-1})$			
(mol dm ⁻³)	(mol dm^{-3})	(mol dm^{-3})	GA	MLA	LA	MA
0.4	2.0	0.28	21.38	26.84	32.04	54.16
1.0	2.0	0.28	21.48	26.88	32.14	54.22
1.6	2.0	0.28	21.44	26.94	34.10	54.32
2.2	2.0	0.28	21.50	26.76	34.06	54.10
2.8	2.0	0.28	21.42	26.80	34.22	54.26
1.0	1.0	0.28	10.70	13.22	15.88	27.00
1.0	1.5	0.28	16.02	20.08	23.92	40.48
1.0	2.5	0.28	27.60	33.60	40.04	67.66
1.0	3.0	0.28	31.96	40.20	48.06	81.18
1.0	2.0	0.16	12.40	15.50	18.52	31.12
1.0	2.0	0.22	16.98	21.26	25.40	42.78
1.0	2.0	0.34	26.20	32.80	39.16	65.98
1.0	2.0	0.40	30.84	38.52	46.08	77.62
1.0	2.0	0.28	21.34 ^c	26.78 ^c	32.12 ^c	54.14 ^c
1.0	2.0	0.28	16.88 ^d	21.44 ^d	25.68 ^d	44.78 ^d

Table - 1 Rate constants for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by TriEAFC in aqueous acetic acid medium at 303 K^{a,b}

^aAs determined by a spectrophotometric technique following the disappearance of oxidant

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

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

^bEstimated from pseudo-first order plots over 80% reaction

^cContained 0.001 mol dm⁻³ acrylonitrile; ^dIn the presence of 0.003 mol dm⁻³ Mn(II).



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



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)

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 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 [22, 23] (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.

Table – 2	Pseudo-first order rate constants for the oxidation of glycolic acid, malic acid, lactic acid and mandelic acid by TriEAFC a	t
	various percentage of acetic acid-water medium at 303 K	

	Dielectric	$10^5 k_l (s^{-1})$					
% ACOH - H ₂ O ($%$)	constant	GA	MLA	LA	MA		
30-70	72.0	16.60	21.40	25.70	42.20		
40-60	63.3	18.90	23.46	28.66	47.10		
50-50	56.0	21.48	26.88	32.14	54.22		
60-40	45.5	27.40	33.00	39.12	66.55		
70-30	38.5	33.88	40.74	47.86	83.16		

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

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 [24]. 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.



Fig 3. Plot of 1 / D against log k_1 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 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. The entropy of activation is negative for hydroxy acids.

 Table – 3 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

%AcOH - H ₂ O (v/v)	$10^{3}k_{2} (\mathrm{dm^{3}mol^{-1}s^{-1}})$			Б	۸ ۲ #	۸ LI#	$\Delta G^{\#}$	
	298 K	303 K	308 K	313 K	$(kJ mol^{-1})$	$(J K^{-1} mol^{-1})$	$(kJ mol^{-1})$	(kJ mol ⁻¹) (at 303 K)
GA	7.50	10.74	15.32	21.94	55.52	107.58±1.8	53.04±0.6	85.64±1.2
MLA	9.61	13.44	18.84	26.33	52.27	116.58 ± 1.8	49.59±0.6	84.91±1.2
LA	11.66	16.07	21.86	30.30	49.39	124.82 ± 2.1	46.91±0.7	84.73±1.4
MA	20.30	27.11	36.02	47.94	44.61	136.31±1.2	41.93±0.4	83.23±0.8

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

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. 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 negative entropy of activation in conjunction with other kinetic observations supports the mechanism outlined in (Scheme-1).





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 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 < MLA < 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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