Oxidation of lactic acid by pyridinium fluorochromate: A kinetic and mechanistic study

S. Zaheer Ahmed[1], S. Syed Shafi[2] and S. Sheik Mansoor[3*]

[1]*Department of Chemistry, Islamiah College, Vaniyambadi, India*
[2]*Department of Chemistry, Thiruvalluvar University, Vellore, India*
[3]*Department of Chemistry, C. Abdul Hakeem College, Melvisharam, India*

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ABSTRACT

The kinetics and mechanism of the oxidation of lactic acid (LA) by pyridinium fluorochromate (PFC) has been studied by spectrophotometric method in 50% acetic acid – 50% water (v/v) medium in a temperature range of 298 K- 313 K. Under the conditions of the pseudo-first order, the reaction follows first order with respect to [LA], [H^+] and [PFC]. The reaction is catalysed by perchloric acid. There is no salt effect. The rate increases with increase in the percentage of acetic acid and the plot of log k_{obs} versus 1/D is linear with a positive slope indicating the positive ion – dipole nature of the reaction. Activation parameters have been evaluated. Based on the experimental results, a probable reaction mechanism of oxidation was proposed.

Keywords: Kinetics, Oxidation, lactic acid, pyridinium fluorochromate.
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INTRODUCTION

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. However, these two oxidation states are characterized by markedly different physical/chemical behavior and toxicity. Cr(III) is readily precipitated or absorbed on a variety of inorganic and organic surfaces at near neutral pH [1,2]. Cr(III), as an essential trace metal nutrient, also improves lipid profile and glucose tolerance by increasing the level of high density lipoprotein cholesterol and decreasing total serum cholesterol [3]. In contrast, the hexavalent form is of prime concern because of its high toxicity. Cr(VI) usually occurs as the highly soluble anion. The main sources of chromium pollution are mining, leather tanning, cement industries, electro plating, production of steel and other metal alloys, photographic material, and corrosive paints [4-6]. The hexavalent form of chromium has been demonstrated to be associated with the toxic parameters and classified as human carcinogen and mutagen [7]. Breathing high levels of hexavalent chromium can damage and irritate nose, lungs, stomach, and intestine [8-10]. At present, there have been some researches regarding this type of reaction system [11-12], while thorough research is essential for understanding its role in the oxidation of some organic compounds. The objectives of this research were to evaluate the kinetics of chromate reduction by lactic acid and investigate their redox mechanisms.

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidiasable functional group [13]. A number of new chromium(VI) containing compounds, with heterocyclic bases, like pyridinium chlorochromate(PCC [14], pyridinium bromochromate (PBC) [15], quinoliium chlorochromate (QCC) [16], benzimidazolium fluorochromate (BIFC) [17], quinolinium bromochromate (QBC) [18], imidazolium fluorochromate (IFC) [19], pyridinium fluorochromate (PFC) [20], tributylammonium chlorochromate (TriBACC) [21], tripropylammonium fluorochromate (TriPAFC) [22] quinolinium fluorochromate (QFC) [23] and imidazoliun dichromate (IDC) [24] have been developed to improve the selectivity of oxidation of organic compounds. The kinetics and mechanism of oxidation of hydroxy acids by various oxidants have been reported [25-33]. However, the kinetics of oxidation of lactic acid by PFC, a Cr(VI) reagent has not yet been

studied. This prompted us to undertake the present investigation. The present work reports the kinetics of oxidation of lactic acid by PFC and evaluates the rate constants. Mechanistic aspects are also discussed.

Lactic acid is a carboxylic acid with the chemical formula $C_3H_6O_3$. It has a hydroxy group adjacent to the carboxyl group, making it an alpha hydroxyl acids. Lactic acid is also known as milk acid. It is a chemical compound that plays a role in various biochemical processes and was first isolated in 1780 by the Swedish Chemist Carl Wilhelm Scheele.

In animals, L-lactate is constantly produced from pyruate *via* the enzyme lactate dehydrogenase (LDH) in a process of fermentation during normal metabolism and exercise. It does not increase in concentration until the rate of lactate production exceeds the rate of lactate removal, which is governed by a number of factors, including mono carboxylate transporters, concentration and isoform of LDH, and oxidative capacity of tissues. The concentration of blood lactate is usually 1–2 mmol/L at rest, but can rise to over 20 mmol/L during intense exertion.

In industry, lactic acid fermentation is performed by lactic acid bacteria. These bacteria can also grow in the mouth; the acid they produce is responsible for the tooth decay known as caries. [34-35].

In medicine, lactate is one of the main components of lactated Ringer's solution and Hartmann's solution. These intravenous fluids consist of sodium and potassium cations along with lactate and chloride anions in solution with distilled water, generally in concentrations isotonic with human blood. It is most commonly used for fluid resuscitation after blood loss due to trauma, surgery, or burn injury

Although glucose is usually assumed to be the main energy source for living tissues, there are some indications that it is lactate, and not glucose, that is preferentially metabolized by neurons in the brain of several mammals species (the notable ones being mice, rats, and humans) [36-37]. According to the lactate-shuttling hypothesis, glial cells are responsible for transforming glucose into lactate, and for providing lactate to the neurons [38-39]. Because of this local metabolic activity of glial cells, the extracellular fluid immediately surrounding neurons strongly differs in composition from the blood or cerebro-spinal fluid, being much richer with lactate, as it was found in microdialysis studies [36].

The role of lactate for brain metabolism seems to be even more important at early stages of development (prenatal and early postnatal), with lactate at these stages having higher concentrations in body liquids, and being utilized by the brain even more preferentially over glucose [36].

The oxidation product of lactic acid is pyruvic acid. Pyruvic acid ($CH_3COCOOH$) is an organic acid, a ketone, as well as the simplest of the alpha-keto acids. The carboxylate (COOH) ion (anion) of pyruvic acid, CH_3COCOO^-, is known as pyruvate, and is a key intersection in several metabolic pathways. Pyruvate is an important chemical compound in biochemistry. It is the output of the anaerobic metabolism of glucose known as glycolysis. It supplies energy to living cells through the citric acid cycle (also known as the Krebs cycle) when oxygen is present (aerobic respiration), and alternatively ferments to produce lactate when oxygen is lacking (fermentation).

Literature survey reveals that no report is available on the kinetics of oxidation of lactic acid by PFC. In this article, the kinetics and mechanism of oxidation of lactic acid by PFC is reported, with the view to understand the mechanism of this biologically important hydroxy acid because it may reveal the mechanism of lactic acid metabolism.

MATERIALS AND METHODS

Materials
Lactic acid (99%, s.d. fine), pyridine (99%, Merck, India), CrO_3 (99%, Merck, India), hydrofluoric acid (47%, Merck, India) were used as supplied and their stock solutions were prepared in double distilled (first time from alkaline $KMnO_4$), deionized and CO_2 free water. Acetic acid was purified by standard method and the fraction distilling at 118°C was collected.

Preparation of Pyridinium fluorochromate
Pyridinium fluorochromate has been prepared from Pyridine, 47 % hydrofluoric acid and chromium trioxide in the molar ratio   1: 1.3: 1 at 0°C. PFC is obtained as yellow orange crystals. It is non-hygroscopic, light insensitive on storage [20]. The purity of PFC was checked by the iodometric method.

Kinetic measurements

All kinetic measurements were carried out on a Spectrophotometer. The progress of the reaction was followed at 363 nm by monitoring the changes in absorbance of remaining Cr(VI). All measurements were made at 303 K. The required [LA], [HClO$_4$], and [NaClO$_4$] were premixed in a reaction vessel, thermostated in an oil bath, and PFC solution (thermally equilibrated) was then added prior to the absorbance measurements. Under pseudo-first-order conditions of lactic acid, the plots of log A *versus* time (A is absorbance intensity) were linear up to 80% completion of the reaction with an average of linear regression coefficients, $r \geq 0.994$.

Product identification

Product analysis was carried out under kinetic conditions *i.e* with excess of the reductant over PFC. In a typical experiment, lactic acid (0.l mol), perchloric acid (0.1 mol) and PFC (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 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 pyruvic acid.

Stoichiometric studies

The stoichiometric studies for the oxidation of lactic acid by PFC 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 lactic acid and PFC 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 PFC was determined. Δ[PFC] was calculated. The stoichiometry was calculated from the ratio between [LA] and [PFC].

Stoichiometric analysis showed that the following overall reaction.

$$CH_3CH(OH)COOH + O_2CrFO^-PyH^+ + H^+ \longrightarrow CH_3COCOOH + H_2O + OCrFO^-PyH^+ \qquad (1)$$

RESULTS AND DISCUSSION

Effect of varying PFC concentration

The concentration of PFC was varied in the range of 0.6 x 10^{-3} to 1.4 x 10^{-3} mol dm^{-1} at constant [LA], [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 PFC.

Effect of varying LA concentration

The concentration of the substrate, LA were varied in the range of 1.0 x 10^{-2} to 3.0 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 hydroxy acids. The plot of log k_1 *versus* log [LA] gave the slope of 1.05 (r = 0.997). Under pseudo-first-order conditions, the plot of 1/k_1 versus 1/[LA] were linear with a negligible intercept indicating that the intermediate formed in a slow step got consumed in a subsequent fast step.

Effect of varying perchloric acid concentration

Perchloric acid has been used as a source of H$^+$ in reaction medium. The concentration of perchloric acid was varied in the range 0.06 to 0.14 mol dm^{-3} keeping all other reactant concentration as constant at 303 K and the rates were measured (Table-1). The acid catalyzed nature of this oxidation is confirmed by an increase in the rate on the addition of perchloric acid. The plot of log k_1 versus log [H$^+$] is a straight line (R^2 = 0.993) with a slope of 1.06. Therefore, order with respect to H$^+$ is one. PFC may become protonated in the presence of acid. The protonated PFC may function as an effective oxidant similar to that of chromium trioxide oxidation [40,41]. Protonated PFC is likely to be a better electrophile and a better oxidant compared to a neutral one. The effects of the dielectric constant of the medium and the ionic strength indicate the reaction to be of ion–dipole type. Thus in the reaction mechanism the protonated PFC species behaves as a dipole.

Effect of Acidity

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

$$O_2CrFO^-PyH^+ + H^+ \rightleftharpoons (OH)OCr^+FO^-PyH^+ \qquad (2)$$
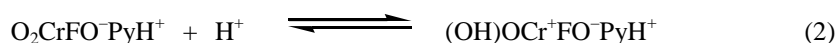
The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC [42] and PFC [43].

Induced Polymerization of Acrylonitrile

Vinyl monomers like acrylonitrile are added to the reaction mixture under nitrogen atmosphere to find out whether the reaction under investigation involves the formation of free radicals as the reaction intermediates . In the present study, freshly distilled acrylonitrile free from inhibitor is added to the reaction mixture containing 0.1 M perchloric acid. After the completion of the reaction, the reaction mixture is diluted with methanol to observe the formation of polymer. It is observed that the oxidation reaction does not induce the polymerization (Table – 2). Thus, a one – electron oxidation giving rise to free radicals is unlikely.

### 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 – 3) .

Effect of solvent polarity on reaction rate

The oxidation of lactic acid has been studied in the binary mixture of acetic acid and water as the solvent medium. For the oxidation of lactic 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–4. 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 [44,45].

Thermodynamic parameters

The reactions were studied in the temperature range from 298 to 313 K to calculate the rate constants and various thermodynamic parameters (Table – 5). A plot of log k_1 versus 1/T (inverse of absolute temperature) is a straight line with negative slope. This shows that Arrhenius Equation is valid for this oxidation [46 – 48]. The large negative value of entropy of activation $\Delta S^{\#}$ suggests slow bimolecular reaction in the rate determining step and that the rate-determining transition state is less disorderly than the reactants, i.e., a rigid transition state by an associative process [49]. This transition state complex is unstable and the chromate ester bond breaks to form the product. According to Pearson also the large negative entropy value obtained in the present study, suggests that the solvent molecules are strongly oriented or 'frozen' around the ions thereby resulting in the loss of entropy and accounts for the lowering of rate coefficient values with increase in the polarity of the medium [50].

Scheme – 1 Mechanism of oxidation of Lactic acid by PFC
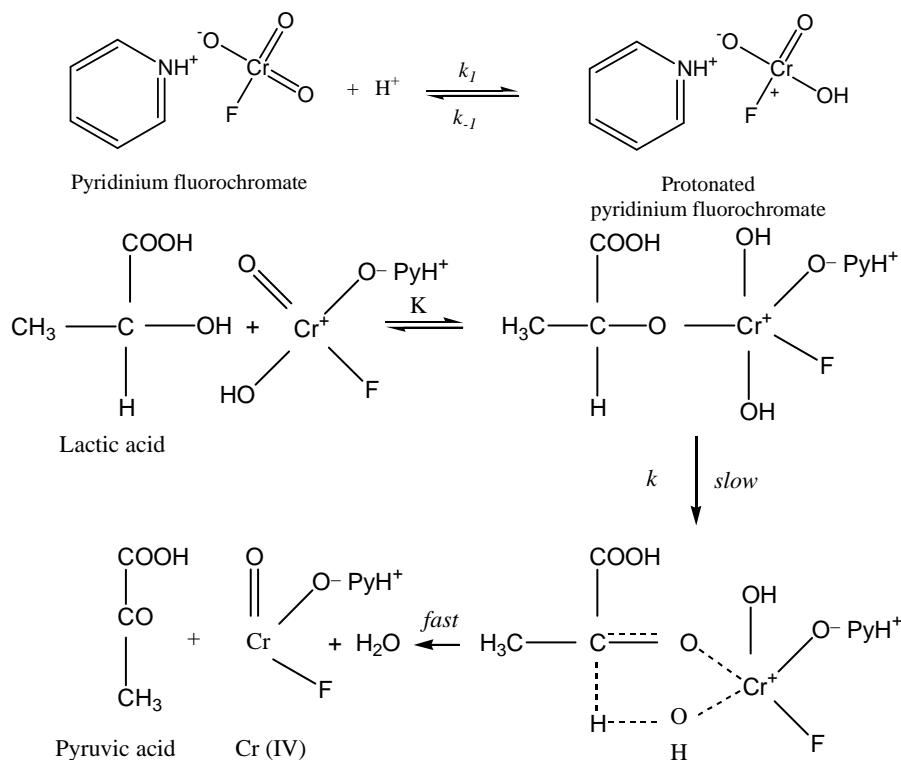
Mechanism of oxidation

From the product analysis, DNP was confirmed. Hence, it shows that under the experimental conditions employed in the present study, lactic acid is oxidized to pyruvic acid. 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. Therefore, a hydride-ion transfer in the rate determining step is suggested. Based on the above kinetic observations the following mechanism is proposed for the reaction (Scheme-1).

Table -1 Effect of variation of [LA], [PFC] and [H$^+$] on the rate of the reaction at 303 K.

Solvent composition = 50% AcOH - 50% H$_2$O (v/v)

10^3 [PFC] (mol dm^{-3})	10^2 [LA] (mol dm^{-3})	10 [H$^+$] (mol dm^{-3})	10^5 k_1 (s^{-1})
0.6	2.0	0.1	13.00
0.8	2.0	0.1	13.30
1.0	2.0	0.1	13.50
1.2	2.0	0.1	13.60
1.4	2.0	0.1	13.50
1.0	1.0	0.1	6.80
1.0	1.5	0.1	10.29
1.0	2.5	0.1	17.35
1.0	3.0	0.1	20.90
1.0	2.0	0.06	7.92
1.0	2.0	0.08	10.40
1.0	2.0	0.12	15.96
1.0	2.0	0.14	18.90

Table – 2 Effect of acrylonitrile (AN) on the oxidation of Lactic acid by PFC at 303 K

10^2[LA] = 2.0 mol dm^{-3} ; 10^3[PFC] = 1.0 mol dm^{-3} ; 10 [H$^+$] = 1.0 mol dm^{-3}
Solvent composition = 50% AcOH - 50% H$_2$O (v/v)

10^3 [AN] (mol dm^{-3})	10^5 k_1 (s^{-1})
0.0	13.50
1.0	13.48
2.0	13.44
3.0	13.36
4.0	13.40
5.0	13.52

Table – 3 Effect of ionic strength on the oxidation of Lactic acid by PFC at 303 K

10^2[LA] = 2.0 mol dm^{-3} ; 10^3[PFC] = 1.0 mol dm^{-3} ; 10 [H$^+$] = 1.0 mol dm^{-3}
Solvent composition = 50% AcOH - 50% H$_2$O (v/v)

10^2 [NaClO$_4$] (mol dm^{-3})	10^5 k_1 (s^{-1})
0.0	13.50
1.0	13.36
2.0	13.38
3.0	13.44
4.0	13.56
5.0	13.32

Table – 4   Effect of varying solvent polarity on the rate of reaction at 303 K
$10^2[LA] = 2.0\ mol\ dm^{-3}$; $10^3[PFC] = 1.0\ mol\ dm^{-3}$; $10\ [H^+] = 1.0\ mol\ dm^{-3}$

% Acetic acid – Water (v/v)	Dielectric constant	1 / D	$10^5\ k_1$ (s^{-1})
30 – 70	72.0	0.0138	10.80
40 – 60	63.3	0.0158	12.20
50 – 50	56.0	0.0178	13.50
60 – 40	45.5	0.0219	16.40
70 – 30	38.5	0.0259	19.52

Table –5 Activation parameters and second order rate constant for the oxidation of lactic acid by PFC in aqueous acetic acid medium
$10^2[LA] = 2.0\ mol\ dm^{-3}$; $10^3[PFC] = 1.0\ mol\ dm^{-3}$; $10\ [H^+] = 1.0\ mol\ dm^{-3}$
Solvent composition = 50% AcOH - 50% H_2O (v/v)

Substrate	$10^3\ k_2$ (dm^{3}mol^{-1}s^{-1})				E_a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol	$\Delta G^{\#}$ kJ mol^{-1} at 303 K
	298 K	303 K	308 K	313 K				
LA	5.40	6.75	8.72	11.60	38.30	36.95	164.46	86.78

CONCLUSION

The kinetics of oxidation of lactic acids has been investigated in aqueous acetic acid medium in the presence of perchloric acid by spectrophotometrically at 303 K. The oxidation of lactic acids by pyridinium fluorochromate is first order each with respect to the LA, PFC and hydrogen ion. The oxidation is catalysed by mineral acid. The lowering of dielectric constant of reaction medium increases the reaction rate significantly. The ionic strength of the reaction medium does not affect the rate of the oxidation. The reaction does not shows the polymerization, which indicates the absence of free radical intermediate in the oxidation. A suitable mechanism is proposed involving the hydride - ion transfer in the rate determining step.

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