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Kinetics of Oxidation of α - Amino acids by Tripropylammonium fluorochromate(TriPAFC) in Acid medium

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Abstract: Kinetics of oxidation of a typical amino acids namely Glycine and Leucine by Tripropylammonium fluorochromate (TriPAFC) has been studied in sulphuric acid medium at 25 ^{o}C. The rate shows second order dependence on [TriPAFC] and first order dependence on three [amino acids], which tends to second order dependence on $[H^{+}]$ = 0.1mol dm^{-3}. The reaction is almost independent of other effects, like chloride, sulphate ions. Effect of ionic strength and dielectric constant of medium has also been studied. The reaction has been studied at different temperatures and a mechanism conforming to the kinetic observations is suggested.
Keywords: Kinetics, Oxidation, amino acids, TriPAFC.

Introduction:

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of variety of organic compounds. Chromium compounds especially Cr(VI) reagents have been versatile reagents and capable of oxidizing almost all the oxidisible organic functional moieties[1] The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

A number of new chromium(VI) containing compounds like pyrazinium chlorochromate[2], benzyltrimethylammonium chlrochromate[3], triethylammonium chlrochromate[4], morpholinium chlrochromate[5,6] 4-(dimethylamino)pyridinium chlrochromate[7], quinolinium flurochromate[8], quilnolinium bromochromate[9], quilnolinium dichromate[10], tributylammonium chlorochromate[11], tripropylammonium fluorochromate[12], and isoquinolinium bromochromate[13] have been used to study the kinetics and mechanism of various organic compounds.

Most of the studies on α-anino acid oxidations by Mn(VII)[14-18], Cr(VI)[19] and hydrogen peroxide[20,21] deal with the analysis of intermediates have been made to understand the mechanisum. Persulphate[22-24] and chloramine-T[25] oxidation of glycine, DL- α- alanine and α-valine were recently reported. In this paper the results on the kinetics of oxidation of glycine and luecine by TriPAFC in H_2SO_4 medium are reported and a probable mechanism is suggested.

Experimental

Material and Methods:

TriPAFC was prepared in accordance to the procedure reported earlier[26]. An aqueous solution of the compound was prepared, standardized iodometrically and stored in brown bottle to prevent its photochemical degradation. Amino acids (Aldrich) were of accepted grades of purity and were used without further purification. All other reagents were of analytical grade. The ionic strength of the system was maintained at a constant high value using concentrated solution of $NaClO_4$. Solutions of amino acids were prepared in doubly distilled water and these solutions were employed for kinetic studies. The reaction was carried out in glass stoppered pyrex boiling tube (1.5" x 7"). Kinetics of reaction was followed in the temperature range 30-60°C. For this purpose Colora Ultra thermostat (West German) was used. The temperature could be regulated with an accuracy of ±0.1°C.

Kinetic procedure:

In a typical experiment, appropriate amount of the substrate, acid and water were taken in a reaction vessel and thermostated at desired temperature (30-60°C) for thermal equilibrium. A measured amount of oxidant solution (TriPAFC) thermostated at same temperature was rapidly added to the mixture in the reaction vessel.

The progress of the reaction was monitored by iodometric determination of unreacted oxidant (TriPAFC) in a measured aliquot of the reaction mixture at different intervals of time. This was done by pipeting 5ml aliquot of the reaction mixture at regular intervals and run into conical flask containing quenching mixture (Ice cold mixture of 10ml of 10%KI, 10ml of 2N H_2SO_4 and 50ml of ice cold water).

The liberated iodine was then titrated against standard sodium thiosulphate solution, using starch as internal indicator near the end point. The course of the reaction was followed for two half lives. The titer at t = 0 gives the value of 'a'. The titer at any instant of time denotes (a-x). Plot of log (a-x) (log [oxidant]) vs time or log Vo/v vs time were made. The values of pseudo first order rate constant k^1 obtained were reproducible within ± 3%. Regression analyses of the experimental data to obtain regression co-efficient 'r' were carried out using CASIO fx-100s (VPAM) Scientific calculator.

Stoichiometry:

Reaction mixture containing different composition of TriPAFC and aminoacids, at constant $[H_2SO_4]$ ($2x10^{-2}$mol dm^{-3}) were equilibrated with occasional shaking at 25°C for 24 hours. Excess of TriPAFC was estimated by iodometric titration against sodium thiosulphate solution. It showed that one mole of TriPAFC consumed per mole of amino acid.

Results:

The kinetics of oxidation of glycine and leucine by tripropylammonium fluorochromate in sulphuric acid medium has been investigated at several initial concentrations of reactions. In the presence of excess [amino acid] at fixed $[H_2SO_4]$, plots log[TriPAFC] vs time were linear **(Table-1,fig.1)** indicating a second order dependence of rate on [TriPAFC]. The pseudo first order rate constants k are calculated from the plots and are given in **Table -2.**

At constant [TriPAFC], $[H_2SO_4]$ and temperature the rate increased with increase of [amino acid] and a plot of log k vs log[amino acid] is linear with slope indicating first order dependence on [amino acid] (**Table -3).**

$$R\text{-}CHNH_2COOH + [FCrO_3]^-N^+H(C_3H_7)_3 + H_2O \longrightarrow R\text{-}CHO + CO_2 + NH_3 + {}^+NH(C_3H_7)_3OH^- + CrO_2HF$$

Where, R = H for Glycine and $–CH_2\text{-}CH(CH_3)–CH_3$ for Leucine.

Scheme -1

TABLE – 1: Rate of amino acids oxidation by TriPAFC (Representative run)
[AA] = 2 x10^{-2}mol dm^{-3}; [TriPAFC] = 2 x10^{-3}mol dm^{-3}; [H_2SO_4] = 0.1mol dm^{-3}, Tempr. = 303K

	Glycine		Leucine	
Time min)	%T	2+ Log(OD)	%T	2 + Log(OD)
0	23.1	1.39	13.9	1.93
5	24.5	1.35	16.0	1.90
10	25.9	1.26	19.5	1.85
15	27.3	1.17	22.9	1.80
20	28.5	1.07	27.3	1.75
25	29.9	0.99	29.9	1.72
30	31.3	0.91	32.7	1.68
	k = 1.604x$10^{-5}$$sec^{-1}$ r 0.9966		k = 1.883x$10^{-5}$$sec^{-1}$ r 0.9971	

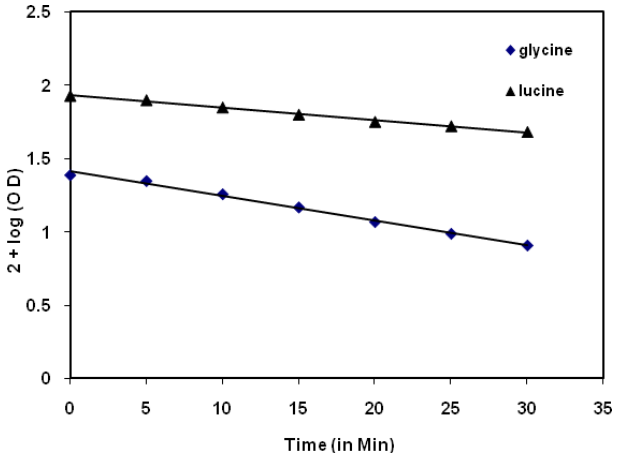


Figure. 1

TABLE –2: Effect of varying [TriPAFC] on the rate of oxidation of amino acids
[AA] = 2 x10^{-2}mol dm^{-3},[H_2SO_4] = 0.1mol dm^{-3}; Tempr. = 303K

	10^5 k sec^{-1}	
10^3 [TriPAFC] mol dm^{-3}	Glycine	Leucine
1.6	1.406	1.704
1.8	1.498	1.799
2.0	1.604	1.883
2.2	1.669	1.973
2.4	1.744	2.057

TABLE – 3: Effect of varying [AA] on the rate of oxidation by TriPAFC
[TriPAFC] = 2 x10^{-3}mol dm^{-3} ; [H_2SO_4] = 0.1mol dm^{-3}, Tempr. = 303K

	10^5 k sec^{-1}	
10^2[AA]mol dm^{-3}	Glycine	Leucine
0.5	0.821	0.987
1.0	1.236	1.420
1.5	1.410	1.720
2.0	1.604	1.883
2.5	1.699	2.079
3.0	1.771	2.204
3.5	1.848	2.346

Effect of H_2SO_4 on reaction rate: The reaction rate was studied as a function of the concentration of sulphuric acid. The rate increased with increase in [H_2SO_4] and a plot of log k vs log[H^+] was linear with a slope value two, indicating second order on [H^+] (**Table-4).**

Effect of ionic strength on reaction rate: Ionic strength of the reaction mixture was varied by adding $NaClO_4$ (0.01- 1.0mol dm^{-3}), which had no effect on rate (**Table -5).**

Effect of Cl^- and SO_4^{2-} ions on reaction rate: The addition of Cl^- and SO_4^{2-} ions in the form of NaCl and Na_2SO_4 (0.01 to 1.0mol/dm^3) to reaction mixture has no effect on the rate (**Table –6).**

TABLE – 4: Effect of [H^+] on the rate of oxidation of amino acids
[TriPAFC] = 2 x10^{-3}mol dm^{-3} ; [AA] = 2 x10^{-2}mol dm^{-3}, Tempr. = 303K

	10^5 k sec^{-1}	
[H^+]mol dm^{-3}	Glycine	Leucine
0.04	1.346	1.409
0.07	1.537	1.580
0.10	1.604	1.883
0.13	1.888	2.050
0.16	2.084	2.283

TABLE – 5: Effect of ionic strength on the rate for the oxidation of amino acids
[AA] = 2 x10^{-2}mol dm^{-3}; [TriPAFC] = 2 x10^{-3}mol dm^{-3}; [H_2SO_4] = 0.1mol dm^{-3};
Tempr. = 303K

	10^5 k sec^{-1}	
[ClO_4^-]mol/dm^3	Glycine	Leucine
0.00	1.604	1.883
0.01	1.610	1.882
0.25	1.602	1.885
0.5	1.601	1.879
0.75	1.612	1.899
1.0	1.602	1.884

TABLE –6: Effect of [Cl^-] and [SO_4^{2-}] on the rate for the oxidation of amino acids
[AA] = 2 x10^{-2}mol dm^{-3}; [TriPAFC] = 2 x10^{-3}mol dm^{-3}; [H_2SO_4] = 0.1mol dm^{-3};
Tempr.= 303K

	10^5 k sec^{-1}	
[Cl^-]mol/dm^3	Glycine	Leucine
0.00	1.604	1.883
0.01	1.612	1.879
0.25	1.602	1.890
0.5	1.602	1.879
0.75	1.612	1.897
1.0	1.606	1.885
[SO_4^{2-}]mol/dm^3		
0.0	1.604	1.883
0.01	1.610	1.882
0 .25	1.602	1.885
0.5	1.601	1.879
0.75	1.612	1.799
1.0	1.602	1.884

Effect of varying dielectric constant of solvent: The solvent composition of the medium was varied by adding methanol (0 - 40% v/v) to the reaction mixture. The rate increased with increase in proportion of methanol content in glycine, valine and lucine. Plots of log k vs 1/D were linear with positive slopes for glycine, valine and lucine (**Table-7, fig .2).** Measurement of rate constants were done both in presence and absence of amino acids with TriPAFC and the rate constants were taken for the calculation of effective k, although the rate of oxidation of methanol in presence of AA is negligible under the present conditions employed. But alcohols undergo oxidation to yield aldehydes with TriPAFC at reflux temperature for 1-2 hours.

Effect of Temperature: The reaction was studied at different temperatures (298 – 313K) and the value of k' were determined from the first order plots. The Arrhenius plots of log k vs 1/T were found to be linear (**Table –8, Fig.3).** The activation energies (Ea) were calculated from the slope of the plots. From this value, the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and the frequency factor (logA) were evaluated (**Table -9).**

TABLE –7: Effect of dielectric constant (D) of solvent on the rate reaction for the Oxidation of amino acids
[AA] = 2 x10^{-2}mol dm^{-3}; [TriPAFC] = 2 x10^{-3}mol dm^{-3}; [H_2SO_4] = 0.1mol dm^{-3};
Tempr.= 303K

			10^5 k sec^{-1}	
MeOH(% in v/v)	D	10^2/D	Glycine	Leucine
00	76.73	1.30	1.604	1.883
10	72.37	1.38	1.822	2.140
20	67.48	1.48	2.038	2.380
30	62.71	1.60	2.250	2.640
40	58.06	1.72	2.520	2.903

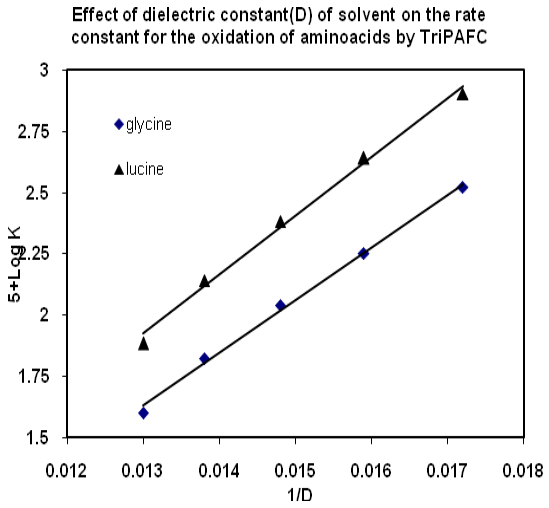


Figure. 2

TABLE –8: Effect of varying Temperature on the rate reaction for the oxidation of amino acids
[AA] = 2 x10^{-2}mol dm^{-3}; [TriPAFC] = 2 x10^{-3}mol dm^{-3}; [H_2SO_4] = 0.1mol dm^{-3}

	10^5 k sec^{-1}		
T(K)	10^3/T	Glycine	Leucine
298	3.355	1.604	1.883
303	3.300	1.795	2.142
308	3.246	2.000	2.364
313	3.194	2.152	2.579

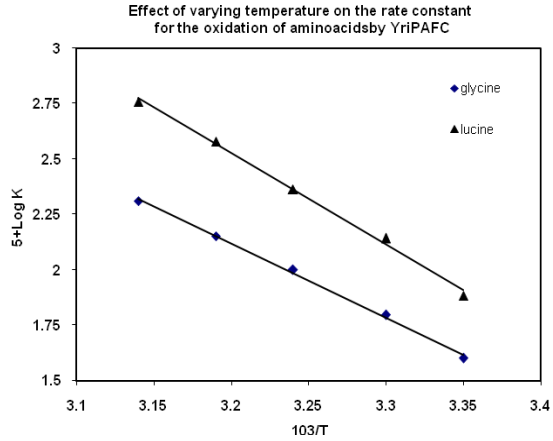


Figure. 3

TABLE –9: Activation parameters for oxidation of amino acids by TriPAFC in H_2SO_4 medium

Thermodynamic Parameters	Glycine	Leucine
Ea KJ mol^{-1}	65.40	80.41
$\Delta H^{\#}$ KJ mol^{-1}	62.86	77.87
$\Delta S^{\#}$ JK^{-1} mol^{-1}	-104.27	-50.03
$\Delta G^{\#}$ KJ mol^{-1}	94.75	93.18
Log A	7.79	10.62

Test for free radicals: Addition of reaction mixture to aqueous acrylamide monomer solutions did not initialize polymerization, showing the absence of free radical species.

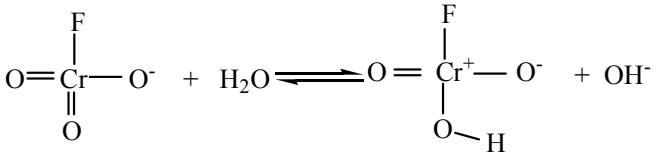
Product Analysis:

After the reaction was completed, the reaction products were extracted with ether and subjected to column chromatography on silica gel (60-200 mesh) using gradient elution (dichloromethane to chloroform). Aldehydes were analyzed qualitatively by gas chromatography. The retention values of formaldehyde, and 3 - methylbutanal are 6.0 and 28.9 respectively, which are identical with authentic samples. Ammonia and CO_2 were detected by the conventional tests.

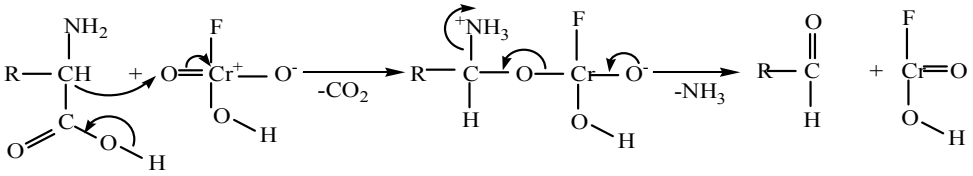
Conclusion:

The sequence of oxidation of α–amino acids by TriPAFC in sulphuric acid medium is as shown in the Scheme- 2. The TriPAFC in acid medium gets protonated and the protonated TriPAFC is difficult to visualize which is similar to benzimidazolim fluorochromate. But participation of protonated chromium (VI) oxidation is well known[27]. The 'k' values representative run clearly indicate that the rate of oxidation depends on hydrophobicity of amino acids. Less hydrophobic amino acids tend to undergo easy oxidation with TriPAFC compare to the more hydrophobic amino acids(see k values in Table -1). Based on the available literature the following mechanism is proposed for the oxidation of amino acids by TriPAFC[28,29]. In the first step flurochromate gets protaonated. The protonated flurochromate brings out the decarboxylation of amino acid followed by deamination resulting in the formation of aldehyde and Cr(IV).

i)



ii)



iii)

$$^{+}NH(C_3H_7)_3 + OH^- \rightleftharpoons NH(C_3H_7)_3OH$$

Where, R = H for Glycine and $–CH_2-CH(CH_3)–CH_3$ for Leucine

Scheme -2

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