Kinetics and Thermodynamics of Mandelic Acid Oxidation By Tripropylammonium Halochromates(X=F,Cl) In Micellar Medium

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ABSTRACT : Two new Versatile reagent *Tripropylammonium Fluorochromate(TriPAFC)* and Tripropylammonium Chlorochromate(TriPACC) has been employed for the oxidation of Mandelic acid. Rate of the réaction is catalysed by surfactant Sodium LaurylEther Sulphate(SLES). The Oxidation has been studied spectrophotometrically at room température in perchloric acid medium. Rate of TriPAFC and TriPACC oxidation of Mandelic acid has been followed under pseudo-first order condition. Rate constants were calculated by the integrated rate equation. The graph of logk versus time was linear and the slope is near to unity, rate constant calculated from graph also agreed with experimental value shows the first order rate dépendance on Mandelic acid. Product formed in this oxidation of Mandelic acid was analysed, polymerization test were carried to confirm that the reaction follows ionic mechanism and stoichiometric data has been accounted. Temperature of the substrate is varried and from the rate constant value, Thermodynamic parameters like Activation energy, Enthalpy change, Entropy change and change in Gibb's free energy is calculated using Arrhenius and Evrings plot. All the kinetic runs were repeated and the rate constants were reproducible within ±2% range.

Keywords : Mandelic acid, oxidation, perchloric acid, Sodium LaurylEther Sulphate, Temperature

I. Introduction

Chromium compounds have been widely used in aqueous and non- aqueous medium for the oxidation of a variety of organic compounds ^[1-3]. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents capable of oxidizing almost all the oxidizable organic functional groups. The study of both very slow and very fast reactions can pose severe Experimental problems. The development of newer Cr(VI) reagents for the oxidation of organic substrates continues to be of interest.

The new reagent Tripropylammonium Fluorochromate(TriPAFC) and Tripropylammonium Chlorochromate (TriPACC) prepared is highly soluble in water, it is economic, stable, non-hygroscopic and easy to prepare in good yield (97%). It is reported to be highly toxic; there is a continued interest in this reagent for the selective and effective oxidation of the substrate under mild conditions. A number of new Cr (VI) reagents like Tripropylammonium fluorochromate^[14], Pyridinium fluorochromate^[15], Tetrabutylammonium chlorochromate^[16] and tetraethyl ammonium chlorochromate^[17] has been used to study the kinetics and mechanism of various organic compounds.

Rate of the reaction is determined at room temperature by spectrophotometrically. Oxidation of Mandelic acid is done in perchloric acid medium in presence of micelle SLES. Due to distribution of the substrate between aqueous and micelles phases, the rate of the reaction of the substrate are different. Basically, the rate effects can be attributed to electrostatic and hydrophobic interaction between the substrate and the surfactant aggregate and in some cases to change in structure of the surrounding water, on simple electrostatic consideration.

Rate is increased by increase in concentration of substrate, Perchloric acid and micelle. Decrease in Absorbance from 373nm for TriPAFC and 370.5nm for TriPACC is observed. Rate of the reaction also been determined at four different temperatures from 303K to 318K for Mandelic acid by keeping other reagents constant at constant temperature. Temperature is maintained using constant temperature bath. Activation parameters were calculated from the graph by plotting log (k_2) versus (1/T) for Arrhenius plot is linear with negative slope.

II. Materials And Methods

All the chemicals used are of Analytical grade. DL-Mandelic acid, 60% A.R.Perchloric acid were commercial products (E.Merck Ltd, Mumbai, India) and directly used.Tripropylamine, Sodium LaurylEther Sulphate (SLES) was purchased from SD fine chemicals, India. Double Distilled water was used as solvent. Perchloric acid was standardized using standard sodium carbonate (Merck, India) solution with methyl orange as Indicator.

2.1. Kinetic methods and Rate Measurements

Elico UV-Visible (FL244) Spectrophotometer has been used to study the oxidation of Mandelic acid by TriPAFC and TriPACC in presence of Micellar catalyst. The solution of temperature pre-equilibrated. The rate measurement was carried out on $30 \pm 0.2^{\circ}$ C in 100% aqueous medium. The Temperature was controlled by electrically operated thermostat. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5ml in each kinetic run. The reactions were carried out under pseudo-first order conditions, keeping the substrate concentration always in excess. The pseudo-first order rate constant of each kinetic run was evaluated from the slope of the linear plot of log (a-x) versus time, according to the first order rate equation by the method of least square.

 $\bar{k} = (2.303/t) \log (a/(a-x)) ----- (1)$

 $k_1 = 2.303$ x slope expressed in sec⁻¹ where k_1 is the pseudo-first order rate constant, 't' is the time in sec. and 'a' and (a-x) denote the initial concentration and concentration at time 't' respectively of oxidant.

2.3. Thermodynamic methods

Time is a variable in kinetics but not in thermodynamics; rates dealt with in the latter are with respect to temperature, pressure, etc., but not with respect to time; equilibrium is a time independent state. Thermodynamic parameters such as Activation Energy, Frequency factor, Enthalpy of Activation, Entropy of Activation and free energy of Activation has been calculated at four different temperatures from the equations given below. From Arrhenius Equation the speed of the chemical reaction increases exponentially with temperature.

 $k = A.exp [-E_a/RT]$ ------ (2)

 $Log A = log k_2 + [E_a/2.303RT] ----- (3)$

The equation is in accordance with empirical fact that for most of reactions plot of $3 + \log k$ versus 10^3 / T is a Arrhenius plot which gives a straight line and slope is $-E_a$ /2.303R, E_a calculated in this way is called Arrhenius activation energy. Intercept gives the value of log A.

 $\begin{array}{l} \Delta H = E_a - RT - \dots (4) \\ \Delta S = 2.303 \ R \ (logA - log \ exp \ [k_BT/h]) & - \dots (5) \\ \Delta G = \Delta H - T\Delta S & - \dots (6) \end{array}$

Two oxidants TriPAFC and TriPACC were synthesized by the given procedure

2.4. Preparation of Tripropylammonium Fluorochromate TriPAFC, (C₃H₇)₃NH [CrO₃F]

Tripropylammonium Fluorochromate TriPAFC by the reported procedure ^[15] Chromium (VI) oxide (10g, 10 mmol) and 9.0 mL (20 mmol) 40 % hydrofluoric acid were added to 20 mL of water in a 100 mL polyethylene beaker with stirring at 0°C. To the resultant orange solution, Triproylamine (14ml, 20mmol) was added drop wise and stirring was continued over a period of half an hour. The precipitated solid was isolated by filtration and washed with petroleum ether and dried under vacuum for 2 hours. Yield: 45.8(98%); mp 142°C.IR spectral data shows peak at 904,647,949 cm⁻¹.Electronic absorption occurs at 22321 cm⁻¹. UV/Visible and¹H-NMR and ¹⁹F-NMR was all consistent with the TriPAFC structure. The pH of 0.01 M solution of TriPAFC in water was 3.3. Purity of the oxidant was checked by Iodimetric procedure.

2.5. Preparation of Tripropylammonium Chlorochromate TriPACC, (C₃H₇)₃NH [CrO₃Cl]

Tripropylammonium Chlorochromate TriPACC by the reported procedure ^[16]

Chromium (VI) oxide (10g, 10m mol) and 2.5 mL (15 mmol) 40 % hydrofluoric acid were added to 20 mL of water in a 100 mL polyethylene beaker with stirring at 0°C. To the resultant orange solution, Triproylamine (15ml, 15mmol) was added drop wise and stirring was continued over a period of half an hour. The precipitated solid was isolated by filtration and washed with petroleum ether and dried under vacuum for 2 hours. Yield: 45.8(95%); mp 135°C.IR spectral data shows peak at 901, 432, 949 cm⁻¹.Electronic absorption occurs at 22123 cm⁻¹. UV/Visible and¹H-NMR and ¹³C-NMR was all consistent with the TriPAFC structure. The pH of 0.01 M solution TriPACC in water was 2.9. Purity of the oxidant was checked by Iodimetric procedure

2.6. Product Analysis

The carbonyl compound formed during the oxidation of Mandelic acid by both TriPAFC and TriPACC was analyzed by the following general procedure. The reaction mixture, after 9 half lives was neutralized to pH = 6.0 by the addition of saturated KHCO₃ solution and the resultant solution are filtered off. The filtrate was extracted with diethyl ether several times and the ether extracts were made up to known volume. The amount of Benzaldehyde formed was determined by measuring the absorbance at 280nm. Benzaldehyde formed was analyzed as 2, 4-dinitrophenyl-hydrazone derivative (b.pt-178°C).

2.6. Stoichiometry and polymerization test

The stoichiometric studies for the oxidation of Mandelic acid by both TriPAFC and TriPACC in the presence of micelle SLES were carried out at 30 ± 0.2 °C. The Stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. Polymerization test with acrylonitrile was carried out to check the formation of intermediate radicals during the oxidation of Mandelic acid by both TriPAFC and TriPACC in perchloric acid medium.

III. Result And Discussion

The kinetics of both TriPAFC and TriPACC oxidation of Mandelic acid at room temperature 30 ± 0.2 °C in perchloric acid medium in presence of micelles is attempted.

3.1. Rate Dependence on varying TRIPAFC and TRIPACC concentration

The rate of TriPAFC and TriPACC oxidation of Mandelic acid has been followed under pseudo first order condition by keeping excess of the Mandelic acid concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of log k versus time was linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows first order dependence. The rate of **TriPAFC** was given in Table – 1, Fig.1and rate of **TriPACC was given in** Table – 2 and Fig.2. All the kinetic runs were repeated and the rate constants were reproducible within $\pm 2\%$ range. Concentration of TriPAFC and TriPACC varied at $1.0x10^{-2}$, $2.0x10^{-2}$, $3.0x10^{-2}$, $4.0x10^{-2}$ mol dm⁻³, keeping other concentrations of Mandelic acid, perchloric acid and temperature constant.

-d[Mandelic acid] / dt = k_1 [Mandelic acid] ------ (11)



[Mandelic acid] = 4.0×10^{-1} mol dm ⁻ [SLES] = 1.0×10^{-1} mol dm ⁻				
Time(Sec)	(a – x) mol dm ⁻³	$10^3 k_1 s^{-1}$		
60	0.5846	3.78		
120	0.572	3.7		
180	0.559	3.7		
240	0.5465	3.76		
300	0.5339	3.78		
360	0.523	3.72		
420	0.51	3.79		
480	0.4986	3.78		
540	0.4886	3.7		
600	0.4768	3.78		
660	0.4658	3.79		
Experimental value		3.76		
Graphical value		3.839		



Fig.1: Pseudo first order plot of logk versus time rate dependence for TriPAFC

		TABLE – 2			
$[TriPACC] = 4.0x10^{-2} \text{ mol dm}^{-3}$ $[HClO_4] = 4.0x10^{-2} \text{ mol dm}^{-3}$					
[Mandelic acid]	$= 4.0 \times 10^{-1} \text{ mol dm}^{-3} \text{ [SLES]} =$	$1.0 \times 10^{-3} \text{ mol dm}^{-3}$			
Time(Sec)	$(a - x) \mod dm^{-3}$	$10^4 k_1 s^{-1}$			
60	0.662	1.984			
120	0.602	1.978			
180	0.544	1.980			
240	0.491	1.989			
300	0.431	1.971			
360	0.371	1.989			
420	0.311	1.982			
480	0.245	1.975			
540	0.172	1.977			
600	0.099	1.974			
Experimental value 1.979					
Graphical value		1.980			





On increasing the concentration of Mandelic acid at 1.0×10^{-1} to 4.0×10^{-1} mol dm⁻³ and by keeping other constituents constants, the rate increases proportionately. The plot of 4+logk versus 2+ log [Mandelic acid] is a linear with slope nearness to Unity shows the first order rate dependence of Mandelic acid. The rate is compared for the both the absence and presence of micelle. The rate of **TriPAFC** was given in Table – 3, Fig.3and rate of **TriPACC was given in** Table – 4 and Fig.4.





3.3. Rate Dependence on varying Perchloric acid concentration

On varying the concentration of Perchloric acid at 1.0×10^{-2} to 4.0×10^{-2} mol dm⁻³ and by keeping other constituents constants, the rate was found to be nearly constant. The plot of 4+logk versus 2+log[Perchloric acid] is a linear with slope nearness to Unity shows the Pseudo first order rate dependence of Perchloric acid.

The rate is measured in presence of micelle. It was shown in Table-5 and Fig.5.

 $Rate = k_{obs}[Cr (VI)][HClO_4] \quad ----- (12)$

[TriPAFC and TriPACC] = 4.0×10^{-2} mol dm ⁻³	[Mandelic acid] = 4.0×10^{-1} mol dm ⁻³
$[Temperature] = 30 + 0.2^{\circ}C$	$[SLES] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$

Liomporatai	$c_{\rm J} = 50 \pm 0.2$ c	<i>,</i>	[DLLD] = 1.0	mor uni
Perchloric acid	TriPAFC		TriPACC	
	$10^4 k_1 s^{-1}$	$10^{2} k_{2} mol^{-1} dm^{3} s^{-1}$	$10^4 k_1 s^{-1}$	$10^{2} k_{2} mol^{-1} dm^{3} s^{-1}$
0.1	0.802	0.802	0.975	0.975
0.2	1.611	0.806	1.946	0.973
0.3	2.421	0.807	2.929	0.976
0.4	3 189	0 797	3 889	0.972



Fig .5: Pseudo first order plot of rate dependence of HClO₄

3.4. Rate Dependence on varying Micellar concentration

On varying the concentration of micelle Sodium LaurylEther Sulphate (SLES) at 0.0001, 0.0052, 0.001 and 0.005 mol dm⁻³ shows a progressive increase in the rate. A plot of logk versus 3+[SLES] gives sigmoidal curve with CMC value $(1.1\pm0.6)\times10^{-3}$. Comparison of rate is given in Table-6 and Fig.6 below

TABLE – 6

 $[TriPAFC and TriPACC] = 4.0x10^{-2} mol dm^{-3}$ [Temperature] = 30 ± 0.2°C [HClO₄] = 4.0x10^{-1} mol dm^{-3}

remperator	50 <u>-</u> 0. <u></u> 0		[110104]	monto morum
ISI ESI	TriPAFC		TriPACC	
mol dm ⁻³	$10^4 k_1$	$10^{2} k_{2} dm^{3}$	$10^4 k_1$	$10^{2} k_{2} dm^{3}$
0.0001	0.124	1.441	1.756	2.102
0.0005	1.222	1.470	1.926	2.110
0.001	1.444	1.444	2.106	2.109
0.005	1.602	1.455	2.216	2.110
0.01	1.621	1.451	2.226	2.111





3.5. Thermodynamic parameters

Oxidation of Mandelic acid by TriPAFC and TriPACC was carried out at four different temperatures keeping all reactant concentrations constant. The rate constant calculated is given in the Table-7 and Table-8. The Arrhenius plot of **logk2 Vs 10^3/T** is given in Fig.7. Arrhenius parameters at 313K for the oxidation of Mandelic acid by TriPAFC and TriPACC is given in Table-9.

TABLE	-7

 $[TriPAFC] = 4.0x10^{-2} \text{ mol dm}^{-3}$ [Mandelic acid] = $4.0x10^{-1} \text{ mol dm}^{-3}$ [HClO₄] = $4.0x10^{-2} \text{ mol dm}^{-3}$

$[\text{HCIO}_4] = 4.0 \times 10^{-110}$ mol dm					
Temperature(K)	$10^4 k_1 s^{-1}$	10 ³ k ₂ mol ⁻¹ dm ³ s ⁻¹			
303	2.413	7.963			
308	2.834	9.201			
313	3.233	10.33			
318	3.657	11.50			



 $[TriPACC] = 4.0x10^{-2} \text{ mol dm}^{-3}$ [Mandelic acid] = $4.0x10^{-1} \text{ mol dm}^{-3}$ [HClO₄] = $4.0x10^{-2} \text{ mol dm}^{-3}$

[
Temperature(K)	$10^4 k_1 s^{-1}$	10 ³ k ₂ mol ⁻¹ dm ³ s ⁻¹
303	5.032	16.607
308	5.676	18.428
313	6.252	19.974
318	6.846	21.528



Fig.7: Arrhenius plot of log k Vs [1/T] to calculate thermodynamic parameters TABLE-9

Arrhenius parameters at 313K for the oxidation of Mandelic acid b	y]	TriPAFC	and	TriPA	VCC
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Arrhenius parameters	[TriPAFC]	[TriPACC]
Ea KJmol ⁻¹	18.902	19.042
ΔH KJmol ⁻¹	16.299	16.44
$-\Delta S J K^{-1} mol^{-1}$	186.9	190.04
∆G KJmol ⁻¹	74.8	75.91
Log A	3.664	3.973

3.6. Polymerisation test and Stoichiometry

To a solution of 0.1 mol dm⁻³ of Mandelic acid in perchloric acid medium, a few drops of acrylonitrile was added and shaken well. To this 5 ml of 0.01 mol dm⁻³ solution of oxidant in aqueous medium and stirred well and kept under nitrogen atmosphere in a thermostat for one hour. No polymer formation was observed which indicates the absence of radical formation as an intermediate during the course of the reaction. The estimation of unreacted oxidant TriPAFC and TriPACC indicated that one mole of the oxidant was consumed by 0.65 mole of the Mandelic acid (1.00: 0.65) ratio.

IV. Conclusion

The Mandelic acid oxidation by two new reagents TriPAFC and TriPACC has been investigated in perchloric acid medium at room temperature. The oxidation of Mandelic acid is first order with respect to each TriPAFC and TriPACC, perchloric acid. This oxidation is catalysed by anionic micelle Sodium Lauryl Ether sulphate (SLES). On varying the concentration of substrate, perchloric acid shows a progressive increase in the reaction rate with slope is near to unity. Effect of variation of TriPAFC and TriPACC on Mandelic acid has no progress of increase on rate. Variation of Micellar concentration shows a progress of increase in the rate and a plot gives sigmoidal curve. Rate of oxidation of Mandelic acid and perchloric acid for TriPAFC is faster than TriPAFC Polymerization test shows no intermediate is formed during the course of the reaction. Stoichiometry data shows that one mole of the oxidant was consumed by 0.65 mole of the Mandelic acid. Thermodynamic parameters are calculated at four different temperatures, Arrhenius plots were given.

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