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Kinetics of Mandelic Acid Oxidation by Tri Butyl Ammonium Chloro Chromate in presence of micelles

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Abstract : *A new Versatile reagent TriButylAmmonium ChloroChromate(TriBACC) has been employed for the oxidation of Mandelic acid in perchloric acid medium. Rate of the réaction is catalysed by surfactants namely Benzalkonium chloride(BKC) and Sodium LaurylEther Sulphate(SLES). The Oxidation has been studied spectrophotometrically at room temperature.Rate of TriBACC 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, Polymerisation test were carried out using Acrylonitrile and stoichiometric data has been evaluated.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.All the kinetic runs were repeated and the rate constants were reproducible within ±2% range.*
Keywords : *Benzalkonium chloride, Kinetics, Mandelic acid, Oxidation, Thermodynamic parameters.*

I. Introduction

In the past decades Cr (VI) reagents has been proved to be a versatile reagents for the oxidation of most organic functional groups[1]. On the Development of new Cr (VI) reagents Majority of the kinetic investigations has been conducted for the reactions occurring on convenient time scale. The study of both very slow and very fast reactions can pose severe Experimental problems. Advanced computational methods of theoretical chemistry and powerful computers are being applied for the predicting of rate of the chemical reactions[2,3].

The new reagent TriButylAmmonium Chlorochromate (TriBACC) 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[4], Pyridinium fluorochromate[5], Tetrabutylammonium chlorochromate[6] and tetraethyl ammonium chlorochromate[7] 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 micelles (BKC and 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 375nm for TriBACC is observed. Rate of the reaction also been determined at four different temperatures from 303K to 318K for Mandelic acid by keeping other reagents at constant temperature. Temperature is maintained using constant temperature bath. Activation parameters were calculated from the graph by plotting log (k/T) versus (1/T) is a linear.

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.Tributylamine, Sodium LaurylEther Sulphate (SLES) and Benzalkonium chloride were Purchased from SD fine chemicals, India.Double Distilled water were 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 TriBACC in presence of micellar catalyst. The solution of temperature pre-equilibrated. The rate measurement were carried out on 30 ± 0.2° 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.

$k = (2.303/t)*\log (a/ (a-x))$ ----- (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.

$k = A.\exp [-E_a/RT]$ ------ (1)

$\text{Log } A = \log k_2 + [E_a/2.303RT]$ ------ (2)

The equation is in accordance with empirical fact that for most of reactions plot of $3 + \log k_2$ 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.

$\Delta H = E_a – RT$ ----- (3)

$\Delta S = 2.303 R (\log A – \log \exp [k_BT/h])$ ----- (4)

$\Delta G = \Delta H - T\Delta S$ ------ (5)

2.4. Preparation of TriButylAmmonium Chlorochromate (TriBACC) $(C_4H_9)_3NH[CrO_3Cl]$

TriButylAmmonium Chlorochromate (TriBACC) by the reported procedure [8]

Chromium (VI) oxide (15g, 0.15mol) and 6M Hydrochloric acid (25ml, 0.3mol) was added and stirred at 0°C. To the resultant orange solution, Tributylamine (71.29ml, 0.3mol) 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 165°C.IR spectral data is 913,432,970 cm^{-1}. UV/Visible and^{1}H-NMR was all consistent with the TriBACC structure. Electronic absorption at 22026 cm^{-1}^{1}H-NMR (500 MHz, CD_3CN): o = 1.2 (*t*, 3H), *o* = 1.6 (*m*, 4H), *o* = 2.7 (*t*, 2H), *o* = 7.5 ppm (*s*, 1H).Purity of the oxidant is tested using iodimetric procedure.

2.5. Product Analysis

The carbonyl compound formed during the oxidation of Mandelic acid by TriBACC 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 $KHCO_3$ 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 the Product 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 TriBACC in the presence of micelle 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 byTriBACC in perchloric acid medium.

III. Result and Discussion

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

3.1. Dependence of rate on varying TriBACC concentration

The rate of TriBACC 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. It was given in Table – 1 and fig.1. All the kinetic runs were repeated and the rate constants were reproducible within ± 2%

range. Concentration of TriBACC varied at $1.0\text{x}10^{-2}$, $2.0\text{x}10^{-2}$, $3.0\text{x}10^{-2}$, $4.0\text{x}10^{-2}$ mol dm^{-3}, keeping other concentrations of Mandelic acid, perchloric acid and temperature constant.

$-d[\text{Mandelic acid}] / dt = k_1 [\text{Mandelic acid}]$ ------- (10)

TABLE – 1

$[\text{TriBACC}] = 4.0\text{x}10^{-2}$ mol dm^{-3} $[HClO_4] = 4.0\text{x}10^{-2}$ mol dm^{-3}

$[\text{Mandelic acid}] = 4.0\text{x}10^{-1}$ mol dm^{-3} $[\text{Micelle}] = 1.0\text{x}10^{-3}$ mol dm^{-3}

Time(Sec)	**(a – x) mol dm^{-3}**	**$10^3 k_1$ s^{-1}**
60	2.5499	2.79
120	2.1578	2.78
180	1.7997	2.86
240	1.5671	2.73
300	1.3100	2.77
360	1.1212	2.75
420	0.9339	2.79
480	0.8144	2.73
540	0.6955	2.72
600	0.5902	2.72
Experimental value		2.76
Graphical value		2.781

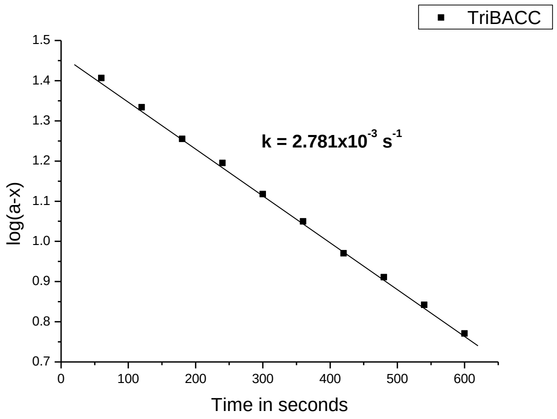

Fig.1: Pseudo first order plot of logk versus time rate dependence for TriBACC

3.2. Dependence of rate on varying Mandelic acid concentration

On increasing the concentration of Mandelic acid at $1.0\text{x}10^{-1}$ to $4.0\text{x}10^{-1}$ mol $\text{dm}^{-3}$and by keeping other constituents constants, the rate increases proportionately. The plot of 4+logk versus 2+ logs [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. It was shown in Table-2 and Fig.2.

TABLE – 2

$[\text{TriBACC}] = 4.0\text{x}10^{-2}$ mol dm^{-3} $[HClO_4] = 4.0\text{x}10^{-2}$ mol dm^{-3}

[Temperature] = 30 ± 0.2°C $[\text{Micelle}] = 1.0\text{x}10^{-3}$ mol dm^{-3}

Mandelic acid	**$10^4 k_1$ s^{-1}**	**$10^2 k_2$ mol^{-1} dm^3 s^{-1}**	**BKC**		**SLES**	
			$10^4 k_1$ 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}**
1.0	2.14	2.14	2.44	2.44	2.85	2.85
2.0	4.34	2.17	4.90	2.45	5.69	2.84
3.0	6.47	2.15	7.29	2.43	8.53	2.84
4.0	8.66	2.16	9.74	2.44	11.46	2.86

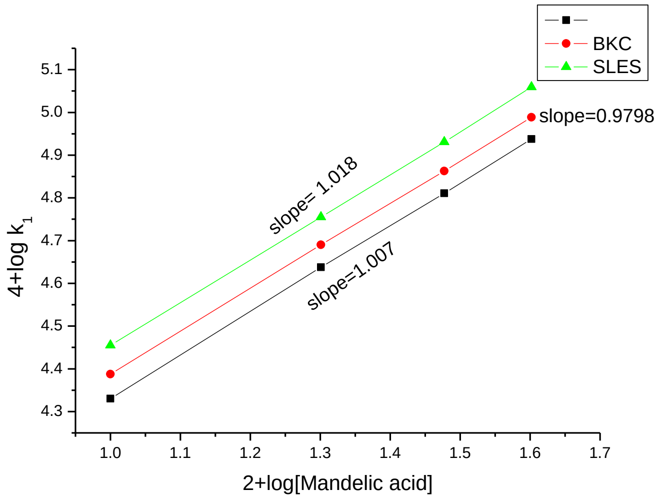

Fig.2: rate dependence of Mandelic acid in absence and presence of micelle

3.3. Dependence of rate on varying Perchloric acid concentration

On varying the concentration of Perchloric acid at $1.0x10^{-2}$ to $4.0x10^{-2}$ 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-3 and Fig.3.

Rate = k_{obs}[TriBACC][$HClO_4$] ------- (11)

TABLE – 3

[TriBACC] = $4.0x10^{-2}$ mol dm^{-3} [Mandelic acid] = $4.0x10^{-1}$ mol dm^{-3}

[Temperature] = 30 ± 0.2°C [Micelle] = $1.0x10^{-3}$ mol dm^{-3}

Perchloric acid	**BKC**		**SLES**	
	$10^4 k_1$ 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	0.758	7.58	0.682	6.82
0.2	1.504	7.52	1.359	6.80
0.3	2.262	7.54	2.068	6.89
0.4	3.113	7.78	2.714	6.79

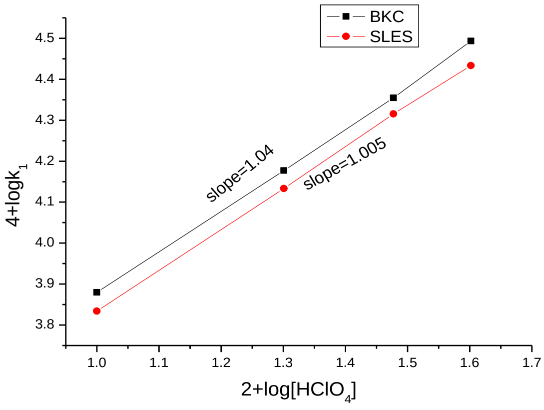

Fig .3: Pseudo first order plot of rate dependence of $HCLO_4$

3.4. Dependence of rate on varying Micellar concentration

On varying the concentration of micelle Benzalkonium chloride (BKC) and Sodium Lauryl Ether Sulphate (SLES) at 0.0052, 0.01, 0.015 and 0.03 mol dm^{-3} shows a progressive increase in the rate. A plot of logk versus 3+ [micelle] gives sigmoidal curve with CMC value (1.1±0.6) $x10^{-3}$.Comparision of rate is given below

TABLE – 4

[TriBACC] = 4.0×10^{-2} mol dm^{-3} [Mandelic acid] = 4.0×10^{-1} mol dm^{-3}
[Temperature] = 30 ± 0.2°C [$HClO_4$] = 4.0×10^{-2} mol dm^{-3}

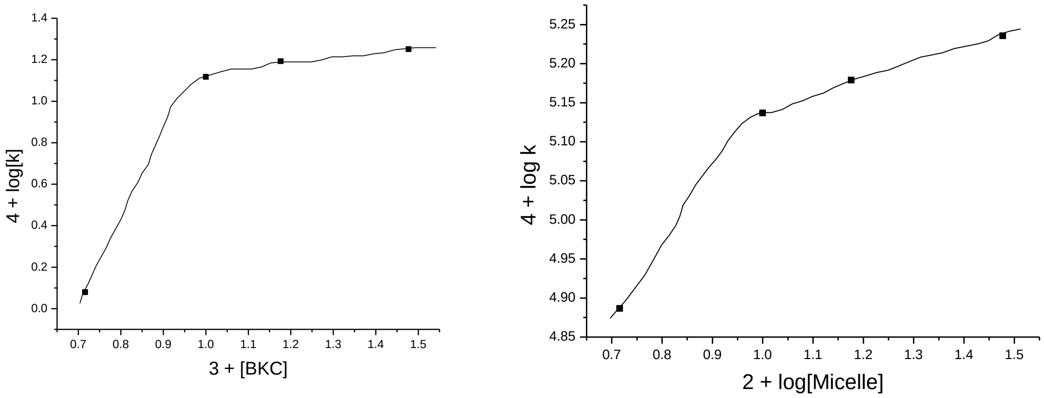

Fig .4: Rate dependence of micellar (BKC & SLES) variation

3.5. Thermodynamic parameters

Oxidation of Mandelic acid by TriBACC was carried out at four different temperatures keeping all reactant concentrations constant. The rate constant calculated is given in the Table-5.The Arrhenius plot of logk_2 Vs $10^3/T$ is given in Fig.5. Arrhenius parameters at 313K for the oxidation of Mandelic acid by TriBACC is given in Table-6

TABLE – 5

[TriBACC] = 4.0×10^{-2} mol dm^{-3} [Mandelic acid] = 4.0×10^{-1} mol dm^{-3}
[$HClO_4$] = 4.0×10^{-2} mol dm^{-3} [Micelle] = 1.0×10^{-3} mol dm^{-3}

Temperature(K)	**$10^4 k_1$ s^{-1}**	**$10^3 k_2$ mol^{-1} dm^3 s^{-1}**
303	2.14	7.06
308	2.44	7.92
313	2.72	8.69
318	3.07	9.65

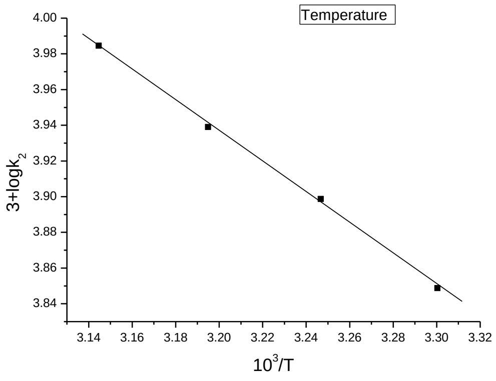

Fig.5: Arrhenius plot of log k_2 Vs [10^3/T] to calculate thermodynamic parameters

TABLE-6Arrhenius parameters at 313K for the oxidation of Mandelic acid by TriBACC

Arrhenius parameters	[Mandelic acid]
Ea KJmol^{-1}	19.065
ΔH KJmol^{-1}	16.463
-ΔS JK^{-1}mol^{-1}	191.2
ΔG KJmol^{-1}	76.3
Log A	4.12

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 TriBACC 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 new reagent TriBACC has been investigated in perchloric acid medium at room temperature. The oxidation of Mandelic acid is first order with respect to each TriBACC, perchloric acid. This oxidation is catalysed by cationic micelle-Benzalkonium chloride and 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. Variation of micellar concentration shows a progress of increase in the rate and a plot gives sigmoidal curve.

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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References

[1]. Patel S and Mishra B K, *Tetrahedron*, 2007, 63(21), 4367-4406

[2]. H.Diebler,M.Eigen,G.Ilgenfritz,G.Maass and R.Winkler,Pure Applied chemistry,20,93(1969)

[3]. G.Porter,"Fast Reactions and Primary Processes in chemical Kinetics", Noble symposium, Almquist and wiksell, Stockholm, 168(1968).

[4]. Shanthi S and Mansoor S S, *Chem Sci Trans*., 2015, 4(1), 213- 221.

[5]. Hiran B L, Khuntwal J, Malkani R K and Singh D, *Arab J Chem*., 2011.

[6]. Dharmaraja J, Krishnasamy K and Shanmugam M, *E-J Chem*., 2008, 5, 754-760.

[7]. Swami P, Yajurvedi D, Mishra P and Sharma P K, *Int J Chem Kinet*., 2010, 42(1), 50 –55.

[8]. Shahriare ghammamy and Mehdi Mazareey, J.Serb.chem.society(70(5) 687-693,2005.

[9]. Gould E S, and Taube H, J. Am chem. Soc. 86; 1964: 1318

[10]. Maqsood Ahmed Malik, Al-Nowaiser F M, Int J. Chem.Kinet. 42; 2010: 704-712.

[11]. Saleem Malik V, Vannamuthu I, Syed Shaffi S and Sheik Mansoor S, Chem Sci Trans., 2015, 4(2), 523-533.

[12]. S. Sheik Mansoor,V.Saleem Malik,K.Aswin, K.Logaiya, A.M. Hussain,J of Saudi chem.society,Sep -2012.

[13]. Kazem Mahanpour, Shahriare Ghammamy, Rahmattollah Rahimi,Asian J of chemistry, Vol. 21, No. 6 (2009), 4404-4408.

[14]. S.A. Chimatadar, M.S.Salunke, S.T.Nandibewoor, Indian J. Chem., 2006, 45A, 388.