KINETIC ANALYSIS OF OXIDATION OF α-HYDROXY ACIDS BY TETRAMETHYLAMMONIUM CHLOROCHROMATE IN MICELLES MEDIUM

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ABSTRACT

The oxidation of pentaamineCo(II)complexes of bounded and unbounded α-hydroxy acids by Tetramethylammonium Chlorochromate (TMACC) is studied at four different temperatures in micelles medium and the rate of the reaction is observed through UV-Visible spectrophotometer at 504 nm. Under constant solution conditions, the addition of micelles enhances the rate of the reaction. The kinetic and stoichiometric data are consistent with the appropriate mechanism.

Keywords: α-hydroxy Acids, Cobalt, Kinetics, Micelles, Oxidation, Stoichiometry, Tetramethylammonium Chlorochromate.

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INTRODUCTION

A literature survey reveals that no report is available on the kinetics of oxidation of α-hydroxy acids by TMACC. The present studies are aimed at determining induced electron transfer reactions in pentaammineCo(II)complexes of both bounded and unbounded α-hydroxy acids with TMACC in presence of micelles.[1-7] Primary aliphatic alcohols may be oxidized either as alcohols, yielding corresponding oxoacids or they may undergo oxidative decarboxylation to yield a ketone. Several studies on pyridinium fluorochromate[8], quinolinium fluorochromate[9], iso quinolinium dichromate[10], tetrahydropyranyl ethers[6], and tetraethylammonium chlorochromate[11] have been used to study the kinetics and mechanism of various organic compounds. TMACC is an orange powder, which is prepared by the dropwise addition of CrO_3 in a 6 N HCl solution of Tetramethylammonium Chlorochromate at room temperature. The micelles used in the present work are Sodium lauryl Ether Sulphate (NaLES), Benzethonium Chloride (BTCl), and Polysorbate 80. The bounded ligands like α-hydroxy acids, dicarboxylic acids, and α-amino acids, have a saturated fragment separating Co(II)from the site of initial reaction irradiation of this Co(II)complexes may involve reduction at the Co(II)center, and carbon-carbon fission.[12] To execute such a process, kinetic studies on the rates of disappearance of Co(II)coupled with rates of formation of Co(II) and organic products will be useful. This has formed part of the present work, along with the estimation of quantum yield in each case. A qualitative correlation between quantum yield and the electronic influence can also be attempted. The reaction has been evolved by the inner-sphere mechanism.

EXPERIMENTAL

Material and Methods

An orange powder (20.2g, 96% yield) TMACC is synthesized by the reported method[6], which gets decomposed at 210-212°C into dark brown material. The α-hydroxy acids such as mandelic acid, lactic acid, and malic acid are prepared as their perchlorates by the literature method.[13] Solvents like ethanol, methanol, ether, and perchloric acid were purified by ordinary methods. Product analysis is carried out to determine the yield of Co(II) determined to be nearly 100%. The micelles are purified by the procedure available in the literature.[14] The commercial samples of the micelles are being washed repeatedly with anhydrous ether and have been recrystallized several times from alcohol with the addition of anhydrous ether. All the chemicals used are E. Merck and BDH annular and conductivity water is used to prepare all solutions. The kinetics studies are carried out by allowing reactions in glass stopper corning glass vessels. From the reaction mixture 5ml of the solution is titrated against sodium thiosulphate using starch as an indicator. The rate of the reaction (-dc/dt) in each kinetic run is determined by the slope of the tangent drawn at a fixed concentration of Tetramethylammonium Chlorochromate. The rate measurements are carried out on 30 ± 0.2°C in100% aqueous medium for α-hydroxy acids. TMACC is also carried out at four different temperatures. The temperature is controlled by an electrically operated thermostat. According to literature[15] the presence of free radicals in the reaction is evaluated. Ionic strength is maintained by the addition of small quantities of $HClO_4$. The concentration of ionic strength and α-hydroxy acids are varied in the range $[0.1 – 0.4] \times 10^2$ mol dm^{-3}. The reaction is first order with respect to the α-hydroxy acids. The second-order plots are also made for comparable concentrations of α-hydroxy acids and micelles. The values reported are the averages of at least two runs.

RESULTS AND DISCUSSION

The rate and other experimental data for all the studies of α-hydroxy acids have been obtained. Since the results are similar, only representative data have been produced here.

Stoichiometric Studies[16, 17]

The stoichiometric analysis for the TMACC oxidation of pentaammineCo(II)complexes of α-hydroxy acids and unbounded ligand in the presence of micelles are carried out at 30 ± 0.2°C Table-1. The concentration of TMACC was determined both iodometrically and spectrophotometrically from the change in absorbance monitored at 504 nm. Δ[TMACC] is calculated after applying the due blank corrections for the decomposition of TMACC and aquation of Co(III) complex of α-hydroxy acids in the presence of micelles.

Table-1: Stoichiometric Data for TMACC Oxidation of Co(III) Bounded & Unbounded α -hydroxy Acids in the Presence of Micelles

10^3[Compound] mol dm^{-3}	10^2[TMACC]$_{Initial}$ mol dm^{-3}	10^2[TMACC]$_{final}$ mol dm^{-3}	$\Delta 10^3$[TMACC] mol dm^{-3}	[Compound: Δ[TMACC]
Mandelic acid	1.0		1.10	1.00: 1.10
1.0	2.0	0.89	2.01	1.00: 1.01
2.0	2.0	1.81	4.02	1.00: 1.03
4.0		1.62		
Lactic acid	1.0		1.02	1.00: 1.00
1.0	2.0	0.91	1.91	1.00: 0.99
2.0	2.0	1.82	4.01	1.00: 1.01
4.0		1.61		
Maleic acid	1.0		1.20	1.00: 1.21
1.0	2.0	0.89	2.21	1.00: 1.11
2.0	2.0	1.79	4.31	1.00: 1.08
4.0		1.58		
Mandelato	1.0		0.52	2.00: 1.01
1.0	2.0	0.98	1.11	2.00: 1.12
2.0	2.0	1.90	2.02	2.00: 1.01
4.0		1.98		
Lactato	1.0		0.50	2.00: 0.99

1.0	2.0	0.97	1.01	2.00: 1.01
2.0	2.0	1.91	2.01	2.00: 1.02
4.0		2.01		
Malato	1.0		0.51	2.00: 1.02
1.0	2.0	0.96	1.21	2.00: 1.23
2.0	2.0	1.89	2.01	2.00: 1.00
4.0		1.99		

TMACC= 0.09 mol dm^{-3}, [HClO$_4$] = 0.30 mol dm^{-3}, [Micelles] = 1.00 x 10^{-3} mol dm^{-3}, [(NH$_3$)$_5$ Co(III)-L]^2 = [0.1 – 0.4] x 10^2 mol dm^{-3} , Temperature = 30 ± 0.2°C.

A similar calculation about Δ[TMACC] is made for the unbound ligand also. The stoichiometry is calculated from the ratio between reacted [oxidant] and [substrate]. This value was then compared with the amount of Co(III), carbonyl compound, and Co(II)keto acid complex. The results suggested that for 1.0 mole of Co(II)complex, about 0.5 moles of TMACC is consumed, whereas with the unbound ligands for 1.0 mole of α-hydroxy acids about 1.0 mole of TMACC is consumed. Product and Stoichiometric analysis are carried out for the oxidation of complexes and free ligands in three different (Anionic, Cationic, and Neutral) micelles medium with increasing micelles concentration an increase in the rate is observed.

Effect of Ionic Strength
The kinetic analysis is studied at different ionic strengths, 0.1, 0.2, 0.3, and 0.4 using an appropriate mixture of α-hydroxy acids and perchloric acid. Ionic strength increases the rate of reaction. The rate constants are summarized in Table-2 and illustrated in Fig.-1.

Table-2: Kinetic Rate Data for Oxidation of α-hydroxy Acids in Perchloric Acid at Constant Ionic Strength

10^3 Substrate	[HClO$_4$]	10^{3}k$_1$ s^{-1}
Mandelic acid	0.1	2.470
	0.2	2.475
	0.3	2.480
	0.4	2.485
Lactic acid	0.1	3.750
	0.2	3.755
	0.3	3.760
	0.4	3.765
Malic acid	0.1	3.100
	0.2	3.105
	0.3	3.110
	0.4	3.115

TMACC= 0.09 mol dm^{-3}, [HClO$_4$] = 0.30 mol dm^{-3}, [α-hydroxy acids] = [0.1 - 0.4] x 10^2 mol dm^{-3} , Temperature = 30 ± 0.2°C.

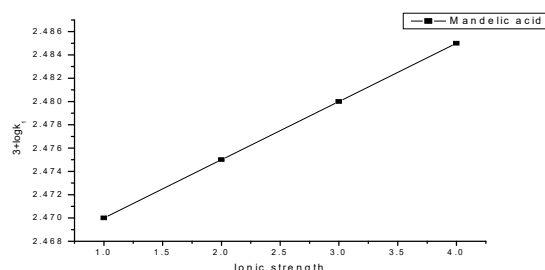Figure-1 clearly shows that an increase in the concentration of ionic strength of solvent increases the rate constant.

Fig.-1: Plot of 3+logk1 Versus Ionic Strength of α-hydroxy Acids in Perchloric Acid

Effect of Temperature[18]

The kinetics of oxidation of α-hydroxy acids by TMACC is carried out at four different temperatures (303 K, 308 K, 313 K & 318 K) keeping other experimental conditions constant. The second-order rate constants are calculated in Table -3. The Arrhenius plot of log k_2 versus 1/T is found to be linear. The enthalpy of activation, the entropy of activation, and the free energy of activation are calculated from k_2 at 303, 308, 313, and 318 K using the Arrhenius and Eyring plots. The thermodynamic parameters for the oxidation of lactic acid are found to be $\Delta H^{\#}$=55.59 ± 1.5 kJ/mol, $-\Delta S^{\#}$=130.58 ± 4.5 J/K/mol, and $\Delta G^{\#}$=91.97± 2.5 kJ/mol. Kinetics of oxidation of α-hydroxy acids by TMACC results in Arrhenius plot of log k_2 versus 1/T linear.

Table-3: Activation Parameters and Second Order Rate Constants for the Oxidation of α-hydroxy Acids by TMACC

Substrate	10^2 X $k_2$dm³/mol/sec				$\Delta H^{\#}$ (kJ/mol)	$-\Delta S^{\#}$ (J/K/mol)	$\Delta G^{\#}$ (kJ/mol)
Lactic acid	303 K	308 K	313 K	318 K			
	6.61	9.12	0.96	15.00	55.59 ± 1.5	130.58± 4.5	91.97± 2.5

Polymerization of Acrylonitrile

The oxidations of α-hydroxy acids by TMACC in an atmosphere of nitrogen fail to induce the polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile has no effect on the rate Table-5. The absorbance of free radicals could be confirmed in the reaction mechanism.

Dependence of Rate on Co(III) Complexes of Both Bounded & Unbounded α-hydroxy Acids in Micelles Medium[19,20]

The rate of Tetramethylammonium Chlorochromate oxidation of pentaamminecobalt(II)complexes of both bounded & unbounded α-hydroxy acids have been followed under pseudo-first order condition by keeping excess of the α-hydroxy acids concentration than the reagent. The rate constants are calculated by the integrated rate equation.[21-24] The graph of the logarithm of concentration versus time is linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows first-order dependence on [α-hydroxy acids] Table-4, (Fig.-2), $[(NH_3)_5 Co(III)-L]^2$ & [TMACC]. This is further substantiated by the study of changing the concentration of Co(III) complexes of both bounded & unbounded α-hydroxy acids from [0.1 to 0.4] X 10^2 mol dm⁻³ at a fixed concentration in micelles medium. The rate constants obtained for the different concentrations of α-hydroxy acids are nearly constant. Hence the rate of disappearance of Co(III) complexes of both bounded & unbounded α-hydroxy acids in this concentration range studied is given in Table-5 and 6.

$$-d[\text{α-hydroxy acids}] / dt = k_1[\text{α-hydroxy acids}] \qquad (1)$$
$$-d[(NH_3)_5Co(III)-L]^{2+}] / dt = k_1[(NH_3)_5Co(III)-L]^{2+}] \qquad (2)$$

All the kinetic runs were repeated and the rate constants were reproducible within ± 2% range.

Table-4: First Order Rate on TMACC Oxidation of Mandelic Acid

Time (s)	log(a-x) mol dm⁻³	$10^4 k_1$ (s⁻¹)
300	0.661	2.462
600	0.633	2.463
900	0.602	2.464
1200	0.575	2.479
1500	0.542	2.465
1800	0.515	2.460
2100	0.488	2.461
2400	0.459	2.462
2700	0.428	2.464
3000	0.402	2.460

TMACC= 0.09 mol dm⁻³, [HClO₄] = 0.30 mol dm⁻³, Temperature = 30 ± 0.2°C, L= Mandelic acid.
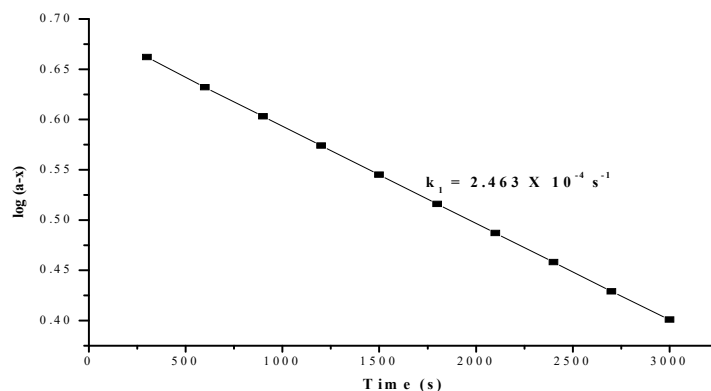
Fig.-2: First Order Dependence Plot

Table-5: First Order Rate on TMACC Oxidation of α-hydroxy Acids in Micellar Medium.

10^2[α-hydroxy acids] mol dm^{-3}	$10^4 k_1$ (s^{-1})	NaLES	BTCl	POLY SORBATE 80
		$10^4 k_1$(s^{-1})	$10^4 k_1$(s^{-1})	$10^4 k_1$(s^{-1})
Mandelic acid				
0.1	0.6105	2.2204	5.9901	6.7883
0.2	1.2211	4.4408	11.9802	13.5766
0.3	1.8316	6.6612	17.9703	20.3649
0.4	2.4421	8.8816	23.9604	27.1532
Lactic acid				
0.1	3.9422	10.5064	19.1800	20.5179
0.2	7.8840	21.0127	38.3600	41.0358
0.3	11.8261	31.5191	57.5400	61.5537
0.4	15.7684	42.0254	76.7201	82.0716
Malic acid				
0.1	1.5277	7.5778	8.4604	8.6550
0.2	3.0554	15.1555	16.9208	17.3101
0.3	4.5831	22.7332	25.3812	25.9650
0.4	6.1108	30.3110	33.8416	34.6201

TMACC= 0.09 mol dm^{-3}, [HClO$_4$] = 0.30 mol dm^{-3}, [α-hydroxy acids] = [0.1 – 0.4] x 10^2 mol dm^{-3}, [Micelles] = 1.00 x 10^{-3} mol dm^{-3}, Temperature = 30 ± 0.2°C.

Table-6: First Order Rate on TMACC Oxidation Pentaamminecobalt(II)Complexes of α-hydroxy Acids in Micellar Medium

10^2[(NH$_3$)$_5$Co(III) - L]mol dm^{-3}	$10^4 k_1$ (s^{-1})	NaLES	BTCl	POLY SORBATE 80
		$10^4 k_1$ (s^{-1})	$10^4 k_1$ (s^{-1})	$10^4 k_1$ (s^{-1})
Mandelato 0.1	0.9625	1.7224	2.0900	2.5617
0.2	1.9251	3.4448	4.1801	5.1234
0.3	2.8877	5.1672	6.2700	7.6851
0.4	3.8502	6.8896	8.3600	10.2468
Lactato 0.1	3.9151	4.9461	5.3160	6.2812
0.2	7.8314	9.8921	10.6320	12.5624
0.3	11.7471	14.8382	15.9480	18.8436
0.4	15.6628	19.7842	21.1264	25.1248

KINETIC ANALYSIS OF OXIDATION OF α-HYDROXY ACIDS   P. Rajkumar *et al.*

Malato	0.1	2.9817	3.1908	3.6962	5.9170
	0.2	5.9634	6.3816	7.3924	11.8340
	0.3	8.9451	9.5724	11.0886	17.7510
	0.4	11.9268	12.7632	14.7848	23.6681

TMACC= 0.09 mol dm^{-3}, [HClO$_4$] = 0.30 mol dm^{-3}, [Micelles] = 1.00 x 10^{-3} mol dm^{-3}, [(NH$_3$)$_5$ Co(III)- L]^2 = [0.1 – 0.4] x 10^2 mol dm^{-3}, Temperature = 30 ± 0.2°C.

Mechanism

TMACC oxidizes the OH center of both bounded and unbounded α-hydroxy acids at a rate comparable to that of the free ligand. There is 100% reduction at the Proton center, which forms a Tetramethylammonium Chlorochromate ester that can decompose in a slow step, and proceeds through C-C bond fission leading to the formation of carbonyl compounds with the evolution of carbon dioxide and H$_2$ gas. Considering these facts and findings with these results, the reaction schemes (scheme-1) & (scheme-2) have been proposed for the TMACC oxidation of pentaammineCo(II)complexes of α-hydroxy acids.
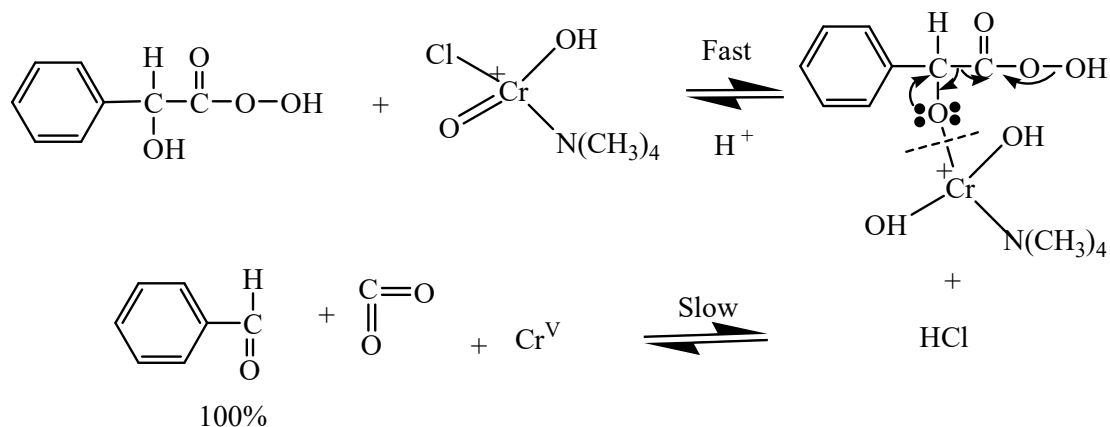
Scheme 1
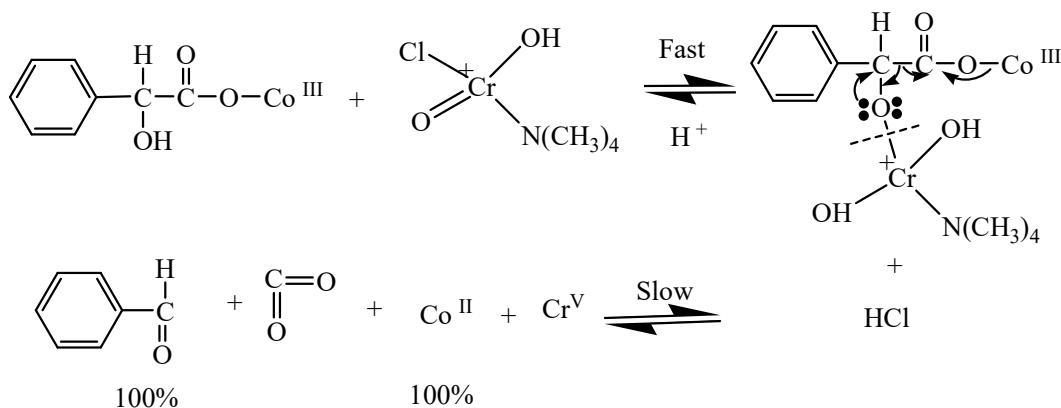
Scheme-2

CONCLUSION

A mechanism involving the one-electron transfer for the complex and two-electron transfers for the ligand is proposed. The 1.0 mole of Co(III) complexes of α-hydroxy acids consumes 0.5 moles of TMACC, whereas 1.0 mole of unbounded α-hydroxy acids consumes 1.0 mole of TMACC. It explains the synchronous C-C bond fission, decarboxylation, and electron transfer to the Co(III) center. The added micelles enhance the rate of oxidation of a reaction. Among three different micelles, Polysorbate 80 reacts faster than NaLES and BTCl. The results obtained (nearly 100% carbonyl compounds) with TMACC are very satisfactory and show the new reagent as a valuable addition to the existing oxidizing agents. The appropriate methodology has been adapted.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing / editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:
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