KINETIC STUDIES OF THE OXIDATION OF CINNAMYL ALCOHOL BY POTASSIUM SALTS IN ACIDIC MEDIUM

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ABSTRACT

Oxidation of alcohols to carbonyl compounds is an important industrial reaction.Several organic oxidizing agents have been used to oxidize alcohols but there are few reports of the use of inorganic oxidants.

This paper reports the kinetic,thermodynamic and mechanistic aspects of the oxidation of the primary unsaturated alcohol,Cinnamyl alcohol using the rarely used Potassium salts,$KBrO_3$,KIO_3 and KIO_4 in acidic medium.Cinnamyl alcohol,found in cinnamon leaves, is used in the preparation of perfumes and deodorants.The oxidation was studied under first order kinetic conditions ([oxidant] << [alc.]). The unreacted oxidant was estimated titrimetrically at regular intervals of time and the rate constant of oxidation(k) was determined from the linear plots of log(unreacted oxidant) vs. time.

The oxidation rate was determined at different temperatures and from the Arrhenius plots of log k vs.T^{-1},the thermodynamic activation were determined. Based on the experimental data obtained, suitable reaction mechanisms have been suggested for the oxidation of Cinnamyl alcohol.

Keywords: Oxidation, Cinnamyl alcohol, kinetics, Arrhenius plot, reaction mechanism,halic acids, thermodynamic activation parameters.

INTRODUCTION

The oxidation of alcohols has been widely reported[1,2].However the kinetic and thermodynamic aspects of the oxidation of perfumery alcohols have been rarely discussed.In our laboratory we have studied the kinetic,thermodynamic and mechanistic aspects of the oxidation of perfumery alcohols using a variety of organic and inorganic oxidizing agents[3-9].

This paper reports the kinetic and thermodynamic study of the oxidation of the unsaturated primary alcohol ,Cinnamyl alcohol using the Potassium salts, $KBrO_3$,KIO_3 and KIO_4 as oxidants in acidic medium.The effects of alcohol and salt concentrations and temperature on the oxidation rate of Cinnamyl alcohol have been studied.The thermodynamic activation parameters of the oxidation reaction have been determined from the variation of rate with temperature and interpreted in terms of the reaction mechanisms proposed.

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MATERIALS AND METHODS

Cinnamyl alcohol ($C_6H_5CH= CHCH_2OH$) was obtained from E.Merck,Germany and used as received. Analar Grade Potassium salts and other chemicals required for the kinetic study were obtained from S D Fine Chemicals Ltd.Mumbai.Double distilled water was used throughout for the kinetic study.

The oxidation of Cinnamyl alcohol was studied under first order kinetic conditions with respect to the inorganic oxidant.The alcohol and oxidant solutions were allowed to equilibrate in a previously adjusted thermostat (accuracy +/- 0.1^0C) for 15 minutes.Then the solutions were quickly mixed to initiate the reaction.The progress of the reaction was monitored at regular time intervals by iodometric titration of the unreacted oxidant.The rate constant (k) were determined from the first order plots of log(unreacted oxidant) vs.time.

The reaction was carried out in the temperature range308-318 K and from the Arrhenius plots of logk vs T^{-1},the energy of activation € and other thermodynamic activation parameters were evaluated.

RESULTS AND DISCUSSION

I.Effect of alcohol and oxidant concentrations of oxidation rate of Cinnamyl alcohol

Potassium salts oxidized Cinnamyl alcohol to Cinnamaldehyde in acidic medium.For all the inorganic oxidants used,the oxidation rate increased with [alc.] but decreased with [oxidant] (Table1).
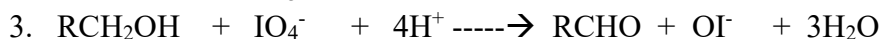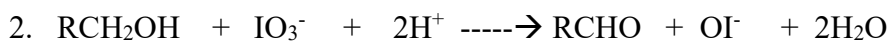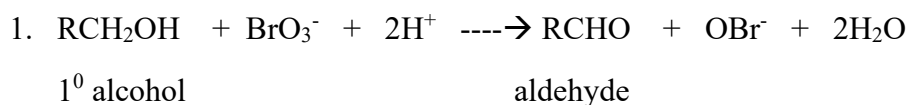
Table 1. Rate constant data of oxidation of Cinnamyl alcohol by Potassium salts in acidic medium

$[H_2SO_4]$ = 0.1 mol dm^{-3} Temperature = 303 K

[alc.]x 10^1 mol dm^{-3}	[oxidant]x 10^3 mol dm^{-3}	$KBrO_3$	KIO_3	KIO_4
		k x $10^2 s^{-1}$	k x $10^2 s^{-1}$	k x $10^2 s^{-1}$
0.25	5.00	1.32	1.07	0.81
0.50	5.00	1.33	1.09	0.82
0.63	5.00	1.37	1.11	0.85
0.75	5.00	1.41	1.16	0.90
0.88	5.00	1.47	1.21	0.96
1.00	5.00	1.60	1.34	1.00
1.00	2.50	1.55	1.29	1.04
1.00	5.00	1.55	1.30	1.05
1.00	10.00	1.46	1.21	0.95
1.00	15.00	1.38	1.14	0.89
1.00	20.00	1.36	1.11	0.85
1.00	25.00	1.32	1.07	0.81

Reaction Mechanism of Oxidation of Cinnamyl alcohol

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In acidic medium, $KBrO_3$, KIO_3 and KIO_4 form the corresponding halic acids $HBrO_3$, HIO_3 and HIO_4 respectively, which are strong acids and oxidizing agents[10-12].

1. $RCH_2OH + BrO_3^- + 2H^+ ----\rightarrow RCHO + OBr^- + 2H_2O$

   1^0 alcohol   aldehyde

2. $RCH_2OH + IO_3^- + 2H^+ -----\rightarrow RCHO + OI^- + 2H_2O$
3. $RCH_2OH + IO_4^- + 4H^+ -----\rightarrow RCHO + OI^- + 3H_2O$

The product of the oxidation reaction ie. Cinnamaldehyde was identified by 2,4 - dinitrophenyl hydrazine test and confirmed by TLC.

The oxidizing powers of the Potassium salts follow the sequence:

$KBrO_3 > KIO_3 > KIO_4$ (Table 1)
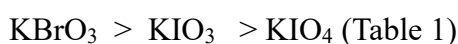
Analar Grade K_2SO_4 was used to study the effect of ionic strength (μ) on the oxidation rate of Cinnamyl alcohol in the range $\mu = 0.05-0.25$ mol dm^{-3}. For all the inorganic oxidants under study, the oxidation rates were found to be independent of ionic strength (μ) due to the involvement of a non- ionic species viz.alcohol in the reaction. This is in accordance with the Bronsted-Bjerrum equation,

$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$ where Z_A and Z_B are the valencies of the ions involved in the reaction. The graphs of $\log k$ vs $\sqrt{\mu}$ were found to be parallel to the $\sqrt{\mu}$ axis indicating that rate constant k is independent of ionic strength. This observation is borne out by the reaction mechanism proposed for the oxidation of Cinnamyl alcohol.

II Effect of Temperature on oxidation rate of Cinnamyl alcohol

The oxidation was carried out in the temperature range 308-318K and the thermodynamic activation parameters were calculated (Table2).

Table 2. Thermodynamic activation parameters for the oxidation of Cinnamyl alcohol by Potassium salts in acidic medium

[alc.]=0.1 mol dm^{-3} [Oxidant]=5 x 10^{-3} mol dm^{-3} [H_2SO_4] =0.1 mol dm^{-3}

Temp.(K)	$k \times 10^2$ s^{-1}	E kJ mol^{-1}	$K^* \times 10^{15}$	ΔG^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* kJ $K^{-1} mol^{=1}$
$KBrO_3$						
308	0.71	62.94	1.12	86.77	60.42	-0.0870
311	1.00	62.94	1.56	87.27	60.38	-0.0876
313	1.25	62.94	1.96	88.18	60.34	-0.0889
318	1.66	62.94	2.50	88.95	60.30	-0.0900
KIO_3						
308	0.97	45.22	1.51	87.40	42.66	-0.1477
311	1.26	45.22	1.96	87.53	42.64	-0.1431
313	1.53	45.22	2.35	87.68	42.62	-0.1439
318	1.91	45.22	2.88	88.53	42.58	-0.1445
KIO_4						

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308	0.46	81.80	0.73	87.82	79.28	-0.0282
311	0.75	81.80	1.17	88.06	79.23	-0.0287
313	1.02	81.80	1.56	88.73	79.19	-0.0305
318	1.40	81.80	2.11	89.35	79.15	-0.0321

Some of the important inferences from the thermodynamic study are :

1) K*,the equilibrium constant for the formation of the activated complex from the reactant molecules increases with temperature indicating that K*, like rate constant k, is a function of temperature.
2) The negative values of the entropy of activation,ΔS* indicate the curtailment of the rotational and vibrational motions of the reacting system due to the formation of a rigid activated complex and subsequent reorientation of the water molecules around the activated complex[13,14].
3) The constant values of ΔS* at all temperatures indicate that the site of oxidation of the alcohol ie.-OH bond remains the same at different temperatures.

CONCLUSIONS

Potassium salts $KBrO_3$,KIO_3 and KIO_4 were effectively used in acidic medium to oxidize Cinnamyl alcohol to Cinnamaldehyde.The oxidation rates increased with alcohol concentration but decreased with oxidant concentration.The reaction showed decrease in entropy of activation.Suitable reaction mechanisms have been proposed for the oxidation process.

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