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KINETIC STUDIES OF THE OXIDATION OF SECONDARY CYCLIC PERFUMERY ALCOHOLS USING $K_2S_2O_8$ IN ACIDIC MEDIUM

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ABSTRACT

This paper reports the kinetic studies of the oxidation of secondary cyclic perfumery alcohols, Borneol, Isoborneol and Menthol by Potassium persulphate under first-order kinetic conditions with respect to the oxidant. The progress of the oxidation was monitored by iodometric titration of the unreacted oxidant at regular time intervals. The reaction was found to be independent of ionic strength. From the variation of reaction rate with temperature, the thermodynamic activation parameters of the oxidation have been evaluated.

Keywords: secondary cyclic alcohols, Potassium persulphate, oxidation, first-order kinetics, ionic strength, steric effect.

INTRODUCTION

The oxidation of alcohols to carbonyl compounds has been reported.[1-3] We have studied the kinetics of oxidation of industrially important alcohols and phenols using a variety of organic and inorganic oxidants.[4-12]

This paper reports the kinetic and thermodynamic aspects of the oxidation of secondary cyclic perfumery alcohols, Borneol, Isoborneol and Menthol using $K_2S_2O_8$ in acidic medium. The effects of:

(1) alcohol and oxidant concentrations,
(2) ionic strength and
(3) the temperature on the oxidation rate has been studied. The observed sequence of oxidation rates of perfumery alcohols has been explained on the basis of their steric, isomeric and structural characteristics.

EXPERIMENTAL

The perfumery alcohols, procured from S.H. Kelkar & Co., Mumbai and Shaivi Industries, Lucknow, India were used after distillation. All other chemicals used were of the Analytical grade.

The oxidation was studied under first-order kinetic conditions with respect to the inorganic oxidant and the unreacted oxidant was estimated iodometrically. The first order rate constants were determined from the linear first order plots of log(a-x) versus time. K_2SO_4 was used to determine the effect of ionic strength ($\mu=5$ to 25×10^{-2} mol dm^{-3}) on the oxidation rate. The oxidation was carried out in the temperature range 303-318K and from the Arrhenius plots of log k versus 1/T, the energy of activation, E and other thermodynamic activation parameters were evaluated.

RESULTS AND DISCUSSION

The secondary alcohols were oxidized to the corresponding ketones by $K_2S_2O_8$ in acidic medium. The bicyclic alcohol, Borneol with –OH group in the endo position, was oxidized to camphor which on reduction gives the isomeric alcohol, Isoborneol. For all the alcohols studied, the oxidation rate increased with alcohol concentration but decreased with oxidant concentration (Table-1, Fig.-1).

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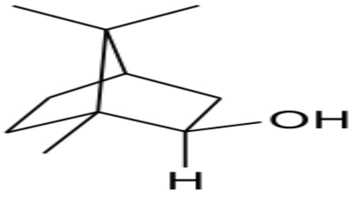
Reaction Mechanism of Oxidation of Secondary Alcohols

In acidic medium, $K_2S_2O_8$ forms $H_2S_2O_8$ which is a strong acid and strong oxidizing agent[13,14]. For secondary alcohols , the oxidation reaction can be shown as:

$$RR'CHOH + H_2S_2O_8 \rightarrow RR'C{=}O + 2H_2SO_4$$

The product of the reaction ie. ketone was identified by 2,4-dinitrophenyl hydrozone test and confirmed by TLC.

Sequence of oxidation rates of alcohols: Isoborneol > Borneol > Menthol (Table-1,Fig.-1)



Isoborneol

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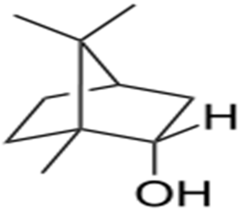

Borneol

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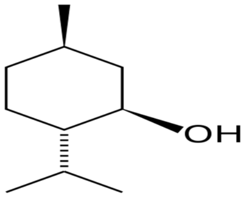

Menthol

The oxidation rates of the secondary alcohols are consistent with respect to their steric hindrance effects on the oxidation. Menthol has the most hindered α-hydrogen and hence is least susceptible to oxidation.

Table-1: Rate Constant Data for the Oxidation of Secondary Cyclic Alcohols by $K_2S_2O_8$ in Acidic Medium
$[H_2SO_4]$ = 1M Temperature =303K

[alc.]x 10^1 mol dm^{-3}	$[K_2SO_4]$x 10^3 mol dm^{-3}	Isoborneol k x 10^3 s^{-1}	Borneol k x 10^3 s^{-1}	Menthol k x 10^3 s^{-1}
1.00	2.50	2.53	6.40	1.20
1.00	5.00	2.21	6.36	1.13
1.00	10.00	1.91	6.08	0.62
1.00	15.00	1.87	5.73	0.60
1.00	20.00	1.70	5.11	0.55
1.00	25.00	1.66	5.07	0.51
0.25	5.00	2.72	1.89	0.74
0.50	5.00	4.28	1.98	0.81
0.63	5.00	5.30	2.10	1.04
0.75	5.00	6.20	2.40	1.11
0.88	5.00	6.40	2.70	1.13
1.00	5.00	6.84	2.79	1.15

Effect of Ionic Strength on Oxidation Rates of Secondary Alcohols

K_2SO_4 was used to study the effect of ionic strength on the oxidation rates in accordance with the Bronsted-Bjerrum equation in the range $\mu = 5$ to 25×10^{-3} mol dm^{-3}.

$$\text{Log } k = \log k_0 + 1.02\, Z_A Z_B \sqrt{\mu} \qquad (1)$$

The graphs of log k versus $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation reaction involves a nonionic species and hence is independent of ionic strength.

Effect of Temperature on Oxidation Rates of Secondary Alcohols

From the variation of oxidation rates of alcohols with temperature (303-318K) the thermodynamic activation parameters were evaluated (Table-3). The negative values of ΔS^* indicate a decrease in the degrees of freedom of the reacting system due to the formation of a transient activated complex[15] followed by reorientation of the solvent molecules around the activated complex[16].This results in the curtailment of the vibrational and rotational motions of the reacting molecules.

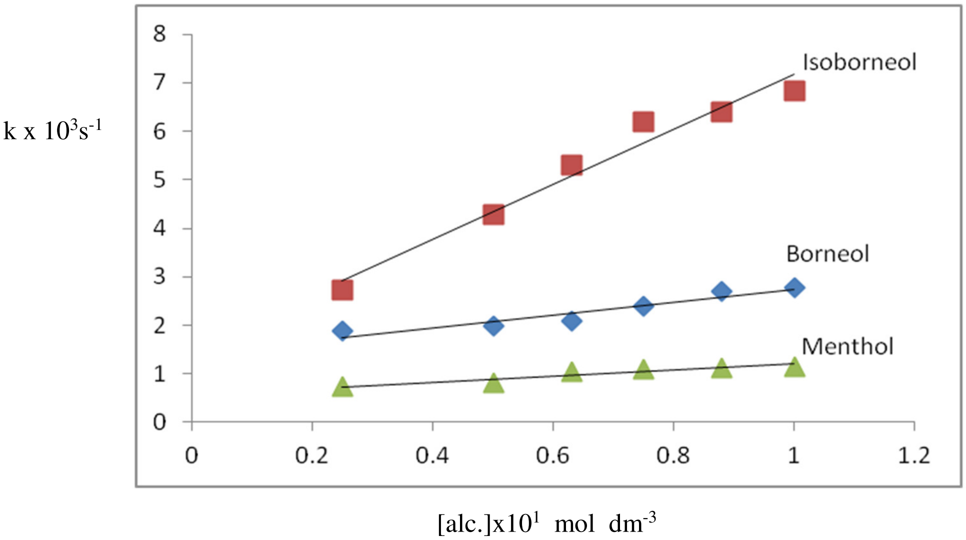

Fig.-1: Variation of the Rate Constant of Oxidation of Secondary Alcohols with [alc.]

Table-2: Effect of Ionic Strength on the Oxidation Rates of Secondary Cyclic Alcohols using $K_2S_2O_8$ as Oxidant in Acidic Medium

[alcohol] = 0.1M , [$K_2S_2O_8$] = 0.005M, [H_2SO_4]=0.5M, Temperature =303K

[K_2SO_4]	Isoborneol	Borneol	Menthol
μx10^2 mol dm^{-3}	k x 10^3 s^{-1}	k x 10^3 s^{-1}	k x 10^3 s^{-1}
5	0.90	3.22	0.50
10	0.94	4.93	0.60
15	0.99	4.49	1.04
20	0.99	4.51	1.20
25	0.94	3.29	0.78

Table-3: Thermodynamic Activation Parameters of the Oxidation of Secondary Cyclic Alcohols by $K_2S_2O_8$ in Acidic Medium

Temp.(K)	k x 10^3 s^{-1}	E kJ mol^{-1}	K* x 10^{16}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
Isoborneol						
303	2.40	26.81	3.79	24.29	89.46	-0.2153
308	2.72	26.81	4.24	24.24	90.67	-0.2150
313	3.29	26.81	5.05	24.20	91.66	-0.2151
318	3.92	26.81	5.91	24.16	92.72	-0.2150
Borneol						
303	0.74	10.92	3.54	8.40	89.63	-0.2682
308	0.78	10.92	3.76	8.36	90.97	-0.2680
313	0.85	10.92	4.09	8.32	92.21	-0.2680
318	0.90	10.91	4.31	8.28	93.56	-0.2681
Menthol						
303	0.23	28.23	0.37	25.71	95.36	-0.2290
308	0.25	28.23	0.40	25.66	96.74	-0.2300
313	0.30	28.23	0.46	25.62	97.90	-0.2302
318	0.39	28.23	0.59	25.58	98.81	-0.2300

CONCLUSION

1. The sequence of oxidation of the secondary cyclic perfumery alcohols is:
   Isoborneol > Borneol > Menthol.
2. The oxidation of the secondary cyclic alcohols is independent of ionic strength and is accompanied by a decrease in the entropy of activation.

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