#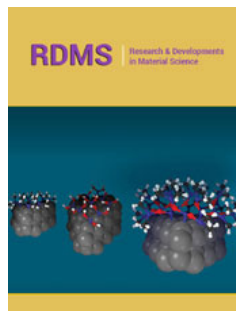 Kinetic Studies of the Oxidation of Primary Acyclic and Secondary Cyclic Perfumery alcohols using N- Bromosuccinimide in Alkaline Medium

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Abstract

India has a large perfumery industry and a worldwide market for perfumes, fragrances and cosmetic formulations. Many of these perfumery chemicals are extracted from Indian plants and hence the study of perfumery alcohols becomes relevant. The quantitative aspects of the oxidation of alcohols to the corresponding carbonyl compounds has been extensively reported. But literature survey shows relatively few reports of the kinetic and thermodynamic studies of oxidation of perfumery alcohols. This paper reports the kinetics of the controlled oxidation of 1) primary acyclic alcohols, Geraniol, Nerol and Citronellol and 2) secondary cyclic alcohols, Cyclopentanol and Cyclohexanol using N- Bromosuccinimde in alkaline medium. The oxidation was carried out under first order kinetic conditions with respect to the organic oxidant i.e. [oxidant] << alc.].

The effects of alcohol and oxidant concentrations, ionic strength and temperature on the rates of oxidation of alcohols has been studied. The thermodynamic activation parameters were determined from the change of oxidation rate of alcohol with temperature and interpreted in terms of the rection mechanism proposed for the oxidation.

Keywords: Primary acyclic alcohols; Secondary cyclic alcohols; Oxidation; N-Bromosuccinimide; Kinetics; Ionic strength; Thermodynamic activation parameters; Entropy of activation; Reaction mechanism

Introduction

The quantitative aspects of the oxidation of alcohols has been extensively reported [1-6] but there are few reports of the kinetic studies of oxidation of perfumery alcohols [7-10]. We have earlier reported the kinetics of oxidation of some industrially important alcohols using organic and inorganic oxidants [11-14].

This study deals with the first order kinetics of the controlled oxidation of primary acyclic alcohols, Geraniol, Nerol and Citronellol and secondary cyclic alcohols, Cyclopentanol and Cyclohexanol by N-Bromosuccinimide in alkaline medium. The effects of alcohol and oxidant concentrations, ionic strength and temperature on the oxidation rates of the alcohols under study have been studied. On the basis of the experimental data obtained suitable reaction mechanisms have been suggested for the oxidation of perfumery alcohols.

Materials and Methods

The perfumery alcohols were obtained from S H Kelkar & Co., Mumbai and used after distillation. Analytical Grade N-Bromosuccinimide and chemicals were used to study the oxidation of alcohols. The requisite solutions of alcohol and oxidant ([Oxidant] << [alc.]) were

allowed to equilibrate in a previously adjusted thermostat (accuracy +/- 0.1 °C) for about 15 minutes. After the temperature equilibrium was attained, the solutions were quickly mixed to initiate the reaction. Aliquots of the reaction mixture were withdrawn at regular time intervals during the course of the reaction, the reaction was arrested using ice and the unreacted oxidant was estimated iodometrically. The rate constants (k) were determined from the straight line graphs of log (unreacted oxidant) v/s time.

The effect of ionic strength on oxidation rate was determined by using Analytical Grade K_2SO_4 in dilute solution. From the effect of temperature on oxidation rate of alcohol, the thermodynamic activation parameters were evaluated and interpreted in terms of the reaction mechanism suggested for the oxidation.

Results and Discussion

The primary acyclic alcohols, Geraniol, Nerol and Citronellol were oxidized to the corresponding aldehydes by N-Bromosuccinimide [NBS] in alkaline medium.
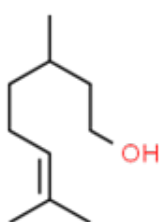
The rate constant data for oxidation of these primary acyclic alcohols is given in Table 1.

Table 1: Rate constant data for oxidation of primary acyclic alcohols by N-Bromosuccinimide in alkaline medium at 303K.

[NaOH] = 0.05mol dm^{-3}

| [alc.]x 10^1 mol dm^{-3}	[NBS] x 10^3 mol dm^{-3}	Nerol k x 10^2 s^{-1}	Geraniol k x 10^2s^{-1}	Citronellol k x 10^2s^{-1}
0.25	5.00	7.65	3.40	0.69
0.50	5.00	8.09	4.30	1.61
0.63	5.00	8.41	4.60	2.30
0.75	5.00	8.99	5.00	3.45
0.88	5.00	9.04	5.20	4.37
1.00	5.00	9.06	5.50	4.83
1.00	2.50	9.32	7.20	6.62
1.00	5.00	9.25	6.40	5.68
1.00	10.00	9.07	5.80	5.45
1.00	15.00	8.77	5.60	4.94
1.00	20.00	7.27	4.90	4.74
1.00	25.00	7.18	4.00	4.37

Citronellol

Geraniol

The oxidation rates of alcohols follow the sequence, Nerol > Geraniol > Citronellol which is consistent with regard to their steric hindrance effects on their oxidation (Table 1)
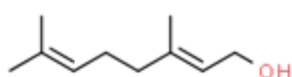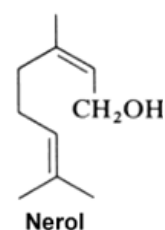
For all the primary acyclic alcohols studied, the oxidation rate increased with [alc.] but decreased with [NBS] (Table1).

Reaction mechanism of oxidation of primary acyclic alcohols by N-Bromosuccinimide in alkaline medium

In alkaline medium, the oxidation proceeds via the formation of a complex between the active species of the oxidant and the substrate followed by the decomposition of the complex in a slow rate determining step to yield the aldehyde.
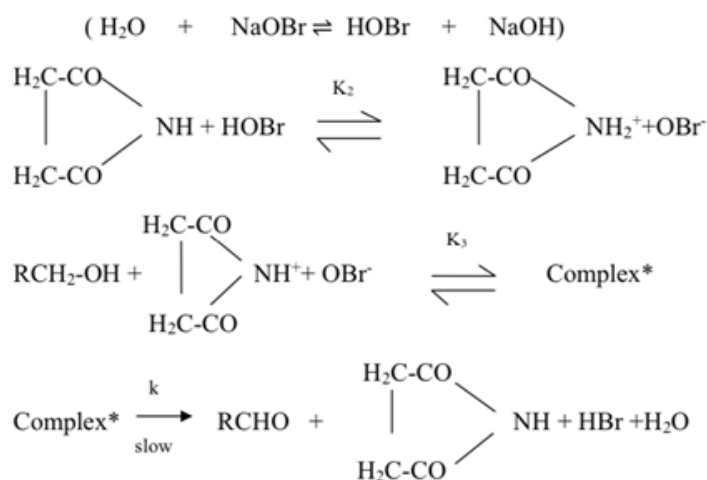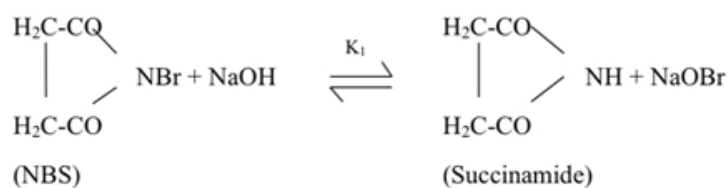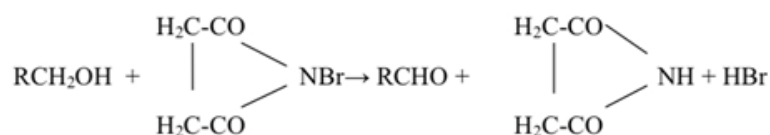
The unreacted oxidant (NBS) was estimated iodometrically, as

$$N\text{-Bromosuccinimide} + 2I^- + 2H^+ \rightarrow \text{Succinimide} + I_2 + HBr$$

The product of the oxidation reaction ie aldehyde was identified by

2,4–dinitrophenylhydrozone test and confirmed by TLC.
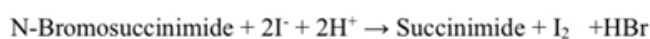
(In the case of a secondary alcohol RR'CHOH, the corresponding ketone, RR'C=O is produced).

Effect of ionic strength on the oxidation rates of primary acyclic alcohols by N-Bromosuccinimide in alkaline medium

Table 2: Effect of ionic strength on the rates of oxidation of primary acyclic alcohols by N-Bromosuccinimide in alkaline medium.

[alc.]=0.1mol dm^{-3} [NaOH]= 0.05mol dm^{-3} [NBS}=2.5x10^{-3}mol dm^{-3}

Temperature= 313K

μ mol dm^{-3}	$\mu^{1/2}$	$k \times 10^2$ s^{-1}		
		Nerol	Geraniol	Citronellol
0.00	0.00	9.68	4.82	7.19
0.05	0.22	9.31	4.37	6.49
0.10	0.32	9.24	3.44	5.79
0.15	0.39	9.06	2.29	5.60
0.20	0.45	8.77	1.60	4.90
0.25	0.50	7.17	0.68	4.00

Analar Grade K_2SO_4 was used in the range μ=0.05-0.25mol dm^{-3} to study the effect of ionic strength on oxidation rates of primary acyclic alcohols (Table 2).

The graphs of log k v/s $\mu^{1/2}$ were found to be straight lines parallel to the $\mu^{1/2}$ axis indicating that ionic strength has no effect on the oxidation rate of alcohols as borne out by the reaction mechanism suggested. This observation is in accordance with the Bjerrum-Bronsted equation, $\log k=\log k_0+1.02\ Z_A Z_B \mu^{1/2}$ where Z_A and Z_B are the valencies of the ions involved in the oxidation reaction.

Effect of temperature on the oxidation rates of primary acyclic alcohols by N-Bromosuccinimide in alkaline medium.

The reaction was carried out in the temperature range 303-318K and the rate constants were determined from the Arrhenius plots of logk v/s T^{-1}. From the variation of oxidation rate with temperature, the thermodynamic activation parameters were determined (Table 3) and interpreted in terms of the reaction mechanism proposed.

Table 3: Thermodynamic activation parameters of the oxidation of Primary acyclic alcohols by N-Bromosuccinimide in alkaline medium.

[alc.]= 0.1mol dm^{-3}, [NaOH]=0.05mol dm^{-3}, [NBS]= 2.5x10^{-3}mol dm^{-3}

Temp.(K)	k x10^{2}s^{-1}	E kJ mol^{-1}	K* x 10^{15}	ΔG* kJ mol^{-1}	ΔH* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
NEROL						
308	7.02	15.61	1.11	13.09	81.00	-0.2241
311	7.53	15.61	1.17	13.05	82.19	-0.2244
313	8.31	15.61	1.27	13.01	83.31	-0.2245
318	8.59	15.61	1.30	12.97	84.60	-0.2251
GERANIOL						
308	2.70	17.75	4.28	15.24	83.36	-0.2248
311	2.90	17.75	4.55	15.19	84.60	-0.2253
313	3.20	17.75	4.91	15.15	85.76	-0.2256
318	3.40	17.75	5.13	15.11	87.01	-0.2261
CITRONELLOL						
308	5.39	56.09	1.40	53.53	83.01	-0.0973
311	7.97	56.09	1.24	53.53	82.01	-0.0924
313	10.53	56.09	1.62	53.49	82.66	-0.0932
318	11.54	56.09	1.74	53.45	83.78	-0.0954

For all the alcohols studied, the oxidation rate increased with temperature. The negative values of entropy of activation (ΔS^*) indicate a decrease in the degrees of freedom due to the formation of a rigid activated complex during the course of the reaction. This results in the orientation of the solvent molecules around the activated complex and consequently the entropy of the reacting system [15,16].
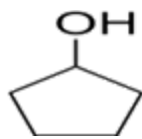
The secondary cyclic alcohols, Cyclopentanol and Cyclohexanol were oxidized to the corresponding ketones by N-Bromosuccinimide in alkaline medium.

Table 4 gives the rate constant data of these secondary cyclic alcohols.

Table 4: Rate constant data of the oxidation of secondary cyclic alcohols by N-Bromosuccinimide in alkaline medium at 303K.

[alc.] x 10^1 mol dm^{-3}	[NBS] x 10^3 mol dm^{-3}	Cyclopentanol k x 10^{2}s^{-1}	Cyclohexanol k x 10^{2}s^{-1}
0.25	5.00	0.92	0.92
0.50	5.00	2.30	1.38
0.63	5.00	3.00	2.53
0.75	5.00	3.68	3.22
0.88	5.00	4.14	3.68
1.00	5.00	5.06	5.29
1.00	2.50	5.92	5.52
1.00	5.00	4.83	4.37
1.00	10.00	4.37	2.76
1.00	15.00	3.91	2.53
1.00	20.00	3.00	2.30
1.00	25.00	1.84	1.61

The oxidation rates follow the sequence, Cyclopentanol > Cyclohexanol.

OH

Cyclopentanol

OH
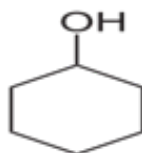
Cyclohexanol

5, 7 and 8 membered rings in cyclic alcohols are more reactive than 6 -membered rings as in Cyclohexanol [17-19]; (Table 4). 6-membered rings have least strain and hence are least susceptible to oxidation. For both cyclic alcohols under study, the oxidation rate is proportional to alcohol concentration but inversely proportional to NBS concentration (Table 4).

Effect of ionic strength on the oxidation rates of secondary cyclic alcohols using N-Bromosuccinimide in alkaline medium

Analytical grade K_2SO_4 was used in the range $\mu=0.05-0.25$mol dm^{-3} to study the effect of ionic strength on the rates of oxidation of secondary cyclic alcohols (Table 5). The graphs of logk v/s $\mu^{1/2}$ were found to be straight lines parallel to the $\mu^{1/2}$ axis indicating that the oxidation is independent of ionic strength.

Table 5: Effect of ionic strength on the oxidation of cyclic secondary alcohols by N-Bromosuccinimide in alkaline medium.

[alc.]=0.1mol dm^{-3}, [NaOH]=0.05mol dm^{-3}, [NBS]=2.5 $x10^{-3}$ mol dm^{-3}

Temperature=313K

μ mol dm^{-3}	$\mu^{1/2}$	Cyclopentanol k x $10^2 s^{-1}$	Cyclohexanol k x $10^2 s^{-1}$
0.00	0.00	3.81	2.99
0.05	0.22	3.91	2.99
0.10	0.32	3.92	3.08
0.15	0.39	4.14	3.22
0.20	0.45	4.33	3.45
0.25	0.50	4.47	3.67

Effect of temperature on oxidation rates of secondary cyclic alcohols by N-Bromosuccinimide in alkaline medium

Table 6: Thermodynamic activation parameters of the oxidation of secondary cyclic alcohols by N-Bromosuccinimide in alkaline medium.

[alc.]=0.1mol dm^{-2}, [NaOH]=0.05mol dm^{-3}, [NBS]= 2.5x10^{-3}mol dm^{-3}

Temp.(K)	k x $10^2 s^{-1}$	E kJ mol^{-1}	K* x 10^{15}	ΔG^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* kJ $K^{-1} mol^{-1}$
Cyclopentanol						
308	2.07	56.88	3.28	84.07	54.36	-0.0981
311	3.45	56.88	5.32	85.04	54.29	-0.0989
313	4.37	56.88	6.70	84.99	54.27	-0.0981
318	4.60	56.88	6.94	86.25	54.23	-0.1006
Cyclohexanol						
308	1.38	94.12	2.15	86.50	91.56	-0.0167
311	2.30	94.12	3.55	86.04	91.53	-0.0177
313	3.68	94.12	5.64	85.39	91.52	-0.0196
318	4.83	94.12	7.29	86.08	91.48	-0.0170

The oxidation of secondary cyclic alcohols, Cyclopentanol and Cyclohexanol was carried out in the temperature range 308-318K and from the change of oxidation rate with temperature, the thermodynamic activation parameters were determined (Table 6).

Conclusion

The oxidation rate increases with alcohol concentration but deceases with oxidant concentration for all the perfumery alcohols investigated.

Ionic strength has no effect on the rates of oxidation of the alcohols indicating the involvement of a non-ionic species (alcohol) in the oxidation process.

The oxidation is accompanied by decrease in entropy of activation due to the orientation of solvent molecules around the

rigid activated complex formed as an unstable intermediate during the reaction.

The constant values of entropy of activation at different temperatures for a given alcohol indicate that the site of oxidation i.e.-OH bond is the same at all temperatures.

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