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KINETIC AND THERMODYNAMIC STUDIES OF THE OXIDATION OF PERFUMERY ALCOHOLS USING POTASSIUM PERIODATE IN ACIDIC MEDIUM

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ABSTRACT

Oxidation is one of the most important industrial reactions as it yields useful products. Literature survey indicates the use of a variety of organic oxidants for the oxidation of alcohols to the corresponding carbonyl compounds but inorganic oxidants have rarely been used. The quantitative conversion of alcohols to aldehydes/ketones has been reported by several workers but there are relatively few reports about the kinetic and thermodynamic investigations of the oxidation of alcohols. We report herein the kinetics of the controlled oxidation of some perfumery and fragrance alcohols using potassium periodate (KIO_4) in acidic medium. The secondary cyclic alcohols, borneol, isoborneol and menthol are extensively used in the manufacture of perfumes and fragrances. Menthol is also used in medicine as a local anaesthetic and counter irritant. The aliphatic alcohols, 2-propanol, 2-butanol and 3-methyl-1-butanol are used as diluents in perfumery formulations. The oxidation was carried out under pseudo uni-molecular kinetic conditions with respect to the inorganic oxidant. The progress of the reaction was monitored by iodometric estimation of the oxidant at regular time intervals during the course of the reaction. For all the alcohols studied, it was found that the oxidation rate increased with alcohol concentration but decreased with oxidant concentration.

Keywords: cyclic alcohols, aliphatic alcohols, inorganic oxidant, kinetics, thermodynamic activation parameters, ionic strength, entropy of activation.

INTRODUCTION

Literature search reveals the kinetic and thermodynamic studies of various types of reactions including oxidation and reduction of compounds using a variety of experimental techniques.[1-8]
The quantitative aspects of the oxidation of alcohols using organic oxidising agents have been widely reported but there are few reports of the kinetic and thermodynamic studies of oxidation of alcohols. Further, inorganic salts have rarely been used for the oxidation of alcohols. We have reported the kinetics of oxidation of some industrially important alcohols using a variety of organic oxidants.[9-13] This paper deals with the kinetic and thermodynamic aspects of the oxidation of secondary alcohols, borneol, isoborneol and menthol; and aliphatic alcohols,2-propanol,2-butanol and 3-methyl-1-butanol,using potassium periodate in acidic medium. These alcohols are used in the manufacture of perfumes fragrances and cosmetics. Menthol, found in mint [*Mentha piperita(Lamiaceae)*] also finds use in medicine
The effects of alcohol and oxidant concentrations ,ionic strength and temperature(303-318K) on the rate of oxidation of alcohols have been studied in detail. The sequence of oxidation rates of the perfumery alcohols have been explained on the basis of their steric, structural and isomeric characteristics.

EXPERIMENTAL

The perfumery alcohols were procured from perfume manufacturers and purified by distillation before use in the kinetic experiments. All other chemicals and reagents used were of Analytical Grade. The oxidation of alcohols was studied under pseudo first order kinetic conditions with respect to the oxidant, KIO_4 which contains halogen in +7 oxidation state. Aliquots of the reaction mixture were withdrawn at

regular time intervals, the reaction was arrested using ice and the unreacted oxidant was estimated iodometrically.

The pseudo first order rate constants were determined from the linear plots of log (unreacted KIO_4) versus time. The effect of ionic strength on oxidation rate was studied using K_2SO_4 in the range, $\mu = 5$ to 25×10^{-2} mol dm^{-3}. From the Arrhenius plots of logk vs 1/T, the energy of activation and other thermodynamic activation parameters were determined and interpreted.

RESULTS AND DISCUSSION

The secondary alcohols were oxidised to the corresponding ketones by KIO_4 in acidic medium. The primary aliphatic alcohol, 3-methyl-1-butanol was oxidised to aldehyde.

Effect of alcohol and oxidant concentrations on oxidation rate
For all the perfumery alcohols investigated, the oxidation rate increased with alcohol concentration but decreased with oxidant concentration (Table-1, Figs.-1 and 2).
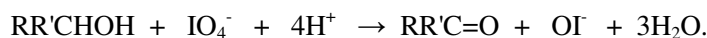
Reaction mechanism of oxidation of alcohols
In acidic medium, KIO_4 rapidly forms periodic acid, HIO_4 which is a strong acid and also a strong oxidising agent.[14,15] The oxidation of alcohol results in the formation of the hypohalite ion, OI^-.

For primary alcohols, the oxidation reaction can be shown as-

$$RCH_2OH + IO_4^- + 4H^+ \rightarrow RCHO + OI^- + 3H_2O.$$
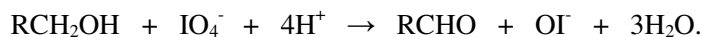
For secondary alcohols, the oxidation reaction can be shown as-

$$RR'CHOH + IO_4^- + 4H^+ \rightarrow RR'C=O + OI^- + 3H_2O.$$

The unreacted KIO_4 was estimated iodometrically. The product of the reaction i.e aldehyde/ketone was identified by 2,4-dinitrophenyl hydrazone test and confirmed by TLC.

Sequences of oxidation rates of alcohols:

(1) Secondary cyclic alcohols: Borneol > Isoborneol > Menthol (Table-1,Fig.-1).
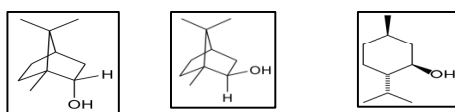
Borneol has the least hindered alpha hydrogen hence its oxidation is the fastest. Whereas menthol has the most hindered alpha hydrogen and hence it is least susceptible to oxidation.

(2) Aliphatic alcohols: 2-propanol > 2 -butanol > 3-methyl-1 butanol (Table-1,Fig.-2)

Table-1: Rate constant data for the oxidation of perfumery alcohols by KIO_4 in 0.1 M H_2SO_4 at temperature 303K

[alc.] X10^1 mol dm^{-3}	[KIO$_4$] X 10^3 mol dm^{-3}	k X 10^4 s^{-1}			k X 10^3 s^{-1}		
		Borneol	Isoborneol	Menthol	2-propanol	2-butanol	3-methyl-1-butanol
1.00	2.50	9.64	7.02	3.27	10.17	9.67	5.14
1.00	5.00	9.02	6.49	2.85	9.12	5.76	3.68
1.00	10.00	8.38	3.92	2.61	5.76	2.76	2.49

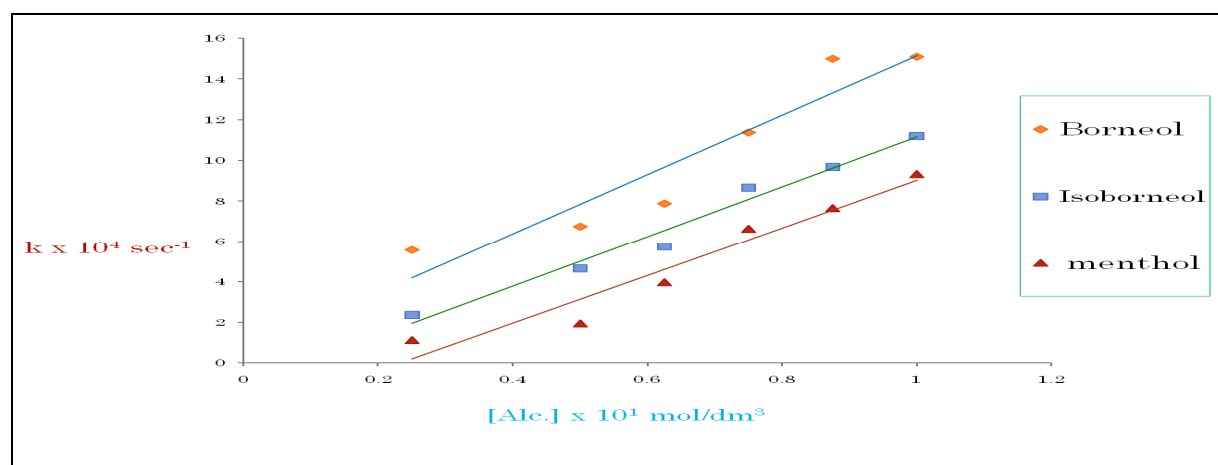| 1.00	15.00	7.27	3.75	2.60	5.14	2.53	0.37
1.00	20.00	6.49	3.59	2.42	4.93	2.07	0.30
1.00	25.00	5.26	3.07	2.37	2.74	1.52	0.29
0.25	5.00	5.62	2.35	1.11	3.68	3.22	1.22
0.50	5.00	6.85	2.60	1.93	4.95	3.69	1.36
0.63	5.00	8.85	4.72	3.96	5.76	4.15	1.68
0.75	5.00	9.92	9.12	6.63	7.14	4.84	2.63
0.88	5.00	9.99	9.36	7.65	8.68	7.37	3.45
1.00	5.00	12.24	10.24	9.12	9.12	5.76	3.68

Fig.-1: Variation of rate constant of oxidation of secondary cyclic alcohols with [Alc.]
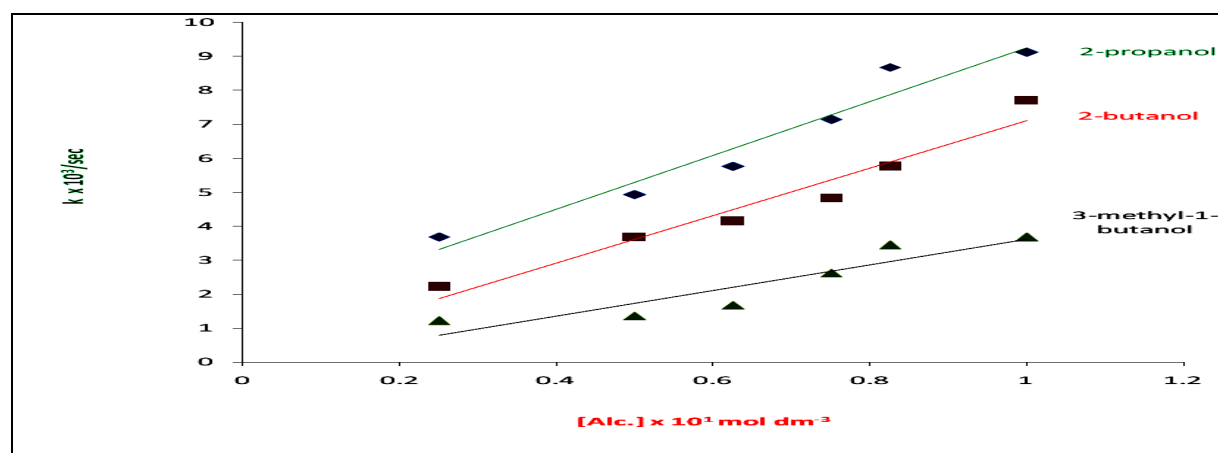

Fig.-2: Variation of rate constant of oxidation of aliphatic alcohols with [Alc.]

The oxidation rates are inversely proportional to the chain lengths of the aliphatic alcohols. The oxidation rates of alcohols were found to be independent of ionic strength as borne out by the reaction mechanism suggested for the oxidation of alcohols. The oxidation was studied in the temperature range 303-318K and from the temperature dependence of oxidation rate, the thermodynamic activation parameters were evaluated and correlated with the dynamics of the oxidation process. The sequences have been explained on the basis of steric hindrance, isomeric and structural features and chain length of the perfumery alcohols.

K_2SO_4 was used to determine the effect of ionic strength (μ) on the oxidation rate in accordance with the Bronsted-Bjerrum equation-

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

Effect of ionic strength on oxidation rate of alcohols

K_2SO_4 was used to study the effect of ionic strength on oxidation rate in the range, $\mu = 5$ to 25×10^{-2} mol dm^{-3} at 313K (Table-2). The graphs of log k vs $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rate is independent of ionic strength. This observation is supported by the reaction mechanism given.

Table-2: Effect of ionic strength on the oxidation rates of perfumery alcohols by KIO_4 in 0.1M H_2SO_4.[alc]=0.1 mol $dm^{-3,}$ [KIO_4] = 2.5×10^{-2} mol dm^{-3}, Temperature = 313K

$\mu \times 10^2$ mol dm^{-3}	$k \times 10^4 s^{-1}$			$k \times 10^3 s^{-1}$		
	Borneol	Isoborneol	Menthol	2-propanol	2-butanol	3-methyl-1-butanol
0	6.85	5.98	1.64	9.02	5.52	5.25
5	7.02	5.75	1.68	9.12	5.76	5.30
10	6.85	5.06	1.68	9.26	5.70	5.30
15	6.85	6.67	1.57	9.02	5.51	5.07
20	7.12	4.83	1.64	9.24	5.88	5.30
25	7.02	5.75	1.98	9.24	5.14	5.75

Effect of temperature on oxidation rates of perfumery alcohols

The oxidation was studied in the temperature range 303-318K and the thermodynamic activation parameters were evaluated (Table-3). For all the alcohols under study, the rate constants(k) increased with temperature and were inversely proportional to the energy of activation(E).

Table-3: Thermodynamic activation parameters of the oxidation of perfumery alcohols by KIO_4 in 0.1M H_2SO_4 at 303K

Alcohol	E kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	ΔS^* kJ K^{-1} mol^{-1}
Borneol	11.30	8.78	85.80	-0.2542
Isoborneol	11.72	9.20	86.06	-0.2537
Menthol	12.14	9.42	86.91	-0.2551
2-propanol	11.15	0.89	85.61	-0.2487
2-butanol	13.24	0.91	86.48	-0.2598
3-methyl-1-butanol	14.41	1.44	88.38	-0.2524

The negative values of entropy of activation (ΔS^*) indicate decrease in the degrees of freedom of the reaction system due to the formation of a rigid activated complex during the course of the reaction and reorientation of water molecules around the activated complex. This curtails the vibrational and rotational motions of the reacting molecules leading to decrease in entropy.[16,17] For all the alcohols under study, the entropy of activation were found to be constant at all temperatures indicating that the site of oxidation of alcohols is the same at all temperatures.

CONCLUSION

The oxidation rates of the perfumery alcohols follow the sequences:
(1) secondary cyclic alcohols : borneol > isoborneol > menthol,
(2) aliphatic alcohols : 2-propanol > 2-butanol > 3-methyl-1-butanol.
Ionic strength has no effect on the oxidation rates of the alcohols under investigation.

ACKNOWLEDGEMENTS

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