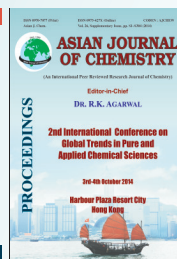


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A Comparative Study of Oxidation Rates of Some Industrially Important Alcohols Using Inorganic Salts

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A variety of organic oxidants have been used for the oxidation of alcohols to aldehydes/ketones under different experimental conditions. The quantitative aspects of the oxidation of alcohols have been exhaustively reported but there are few reports of the kinetic studies of the oxidations of alcohols. This paper describes the kinetics of the controlled oxidation of the secondary cyclic alcohols, borneol, isoborneol and menthol using the inorganic salts, KBrO_3 , KIO_3 and KIO_4 in acidic medium. The stereoisomers, borneol and isoborneol are used in the preparation of perfumes. Menthol also finds use in medicine as a local anaesthetic and counter irritant. The oxidation rates of the perfumery alcohols were determined using pseudo first order kinetics with respect to the oxidant *i.e.*, $[\text{alc.}] \gg [\text{ox.}]$. The progress of the reaction was continuously monitored by titrimetric estimation of the unreacted oxidant during the course of the reaction. The oxidation rates increased with $[\text{alc.}]$ but decreased with increasing $[\text{ox.}]$. K_2SO_4 was used to determine the influence of ionic strength on the rate of reaction. The oxidation rate of the alcohols was found to be independent of ionic strength as borne out by the reaction mechanism suggested. From the variation of oxidation rate with temperature the thermodynamic activation parameters were evaluated and explained in terms of the dynamics of the oxidation process. For all the inorganic oxidants used, the oxidation rates showed the same sequence: borneol > isoborneol > menthol. The sequence has been explained on the basis of steric hindrance, isomeric and structural features of the alcohols under investigation. Suitable reaction mechanisms have been given on the basis of the formation of the halic acids, HBrO_3 , HIO_3 and HIO_4 in acidic medium. Halic acids are strong acids as well as strong oxidizing agents.

Keywords: Cyclic alcohols, Inorganic salts, Controlled oxidation, Kinetics, Activation parameters, Steric hindrance.

INTRODUCTION

In our laboratory we have studied the kinetics of different types of alcohols using organic oxidants¹⁻⁴. This paper discusses the kinetic and thermodynamic aspects of the oxidation of the secondary cyclic alcohols, borneol, isoborneol and menthols using inorganic salts KBrO_3 , KIO_3 and KIO_4 as oxidizing agents in acidic medium. These alcohols are widely used in the preparation of perfumes and fragrances. From the effect of temperature on the oxidation rates of alcohols, the activation parameters have been determined and interpreted in terms of the dynamics of the oxidation process.

EXPERIMENTAL

The perfumery alcohols were procured from (1) S.H. Kelkar & Co. Ltd., Mumbai and (2) Shaivi Industries, Lucknow and purified by distillation. All the other chemicals and reagents used were of Analytical Grade. The controlled oxidation of the secondary alcohols to ketones was studied under pseudo

first order kinetic conditions with respect to the inorganic oxidants KBrO_3 and KIO_3 containing halogen in the +5 oxidation state and KIO_4 containing halogen in the +7 oxidation state. The progress of the oxidation reaction was monitored by the iodometric estimation of the inorganic oxidant at regular time intervals. The pseudo first order rate constants (*k*) were determined from the linear plots of $\log(a-x)$ vs. time. K_2SO_4 was used to study the effect of ionic strength (μ) on the oxidation rate in dilute solution in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$. The oxidation was studied in the temperature range 303-318 K and the activation parameters were evaluated.

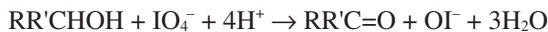
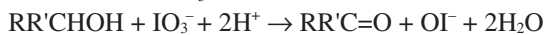
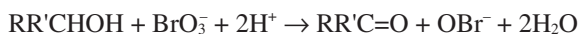
RESULTS AND DISCUSSION

The secondary cyclic alcohols, borneol, isoborneol and menthol were oxidized to the corresponding ketones by KBrO_3 / KIO_3 / KIO_4 in acidic medium.

Effect of alcohol and inorganic oxidant concentrations on oxidation rate of alcohols: For all the alcohols studied

the oxidation rate increased with alcohol concentration but decreased with oxidant concentration.

Reaction mechanism of oxidation of alcohols: In acidic medium, KBrO_3 , KIO_3 and KIO_4 rapidly form the corresponding halo acids *e.g.*, HBrO_3 , HIO_3 and HIO_4 which are strong acids and strong oxidizing agents^{5,6}. The oxidation of alcohols results in the formation of the corresponding hypohalite ions OBr^- or OI^- , respectively.



The unreacted inorganic oxidants were estimated iodometrically. The product of the reaction *i.e.*, ketone was identified by 2,4-dinitrophenylhydrazine test and TLC.

Sequence of oxidation rates of alcohols: For all the oxidants, the oxidation rates of alcohols followed the same sequence:



TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION
OF PERFUMERY ALCOHOLS IN 0.05
M H_2SO_4 TEMPERATURE = 303 K

[alc.] $\times 10^1$ mol dm^{-3}	[KBrO ₃] $\times 10^3$ mol dm^{-3}	Borneol ($k \times 10^3 \text{ s}^{-1}$)	Isoborneol ($k \times 10^3 \text{ s}^{-1}$)	Menthol ($k \times 10^3 \text{ s}^{-1}$)
(a) KBrO ₃ as oxidant				
1.00	2.50	12.90	10.91	10.17
1.00	5.00	10.24	9.58	9.35
1.00	10.00	9.64	9.46	7.62
1.00	15.00	9.02	8.94	7.72
1.00	20.00	8.38	9.34	6.91
1.00	25.00	7.27	7.66	6.08
0.25	5.00	7.62	6.54	5.76
0.50	5.00	8.85	7.62	6.45
0.63	5.00	9.26	8.68	7.62
0.75	5.00	9.92	9.12	8.23
0.88	5.00	9.99	9.36	8.86
1.00	5.00	12.24	10.24	9.12
(b) KIO ₃ as oxidant				
1.00	2.50	10.06	7.29	8.06
1.00	5.00	9.78	6.91	5.07
1.00	10.00	7.68	6.21	1.84
1.00	15.00	6.57	5.91	1.61
1.00	20.00	5.76	5.09	1.61
1.00	25.00	3.47	4.61	1.38
0.25	5.00	6.67	4.61	2.38
0.50	5.00	7.51	4.47	2.53
0.63	5.00	8.99	5.53	2.76
0.75	5.00	9.23	6.13	3.68
0.88	5.00	10.40	7.23	5.53
1.00	5.00	11.90	7.83	5.99
(c) KIO ₄ as oxidant				
1.00	2.50	0.96	0.70	0.33
1.00	5.00	0.90	0.65	0.29
1.00	10.00	0.84	0.39	0.26
1.00	15.00	0.73	0.38	0.26
1.00	20.00	0.65	0.36	0.24
1.00	25.00	0.53	0.31	0.24
0.25	5.00	0.56	0.24	0.11
0.50	5.00	0.69	0.26	0.19
0.63	5.00	0.89	0.47	0.40
0.75	5.00	0.99	0.91	0.66
0.88	5.00	1.00	0.94	0.77
1.00	5.00	1.22	1.02	0.91

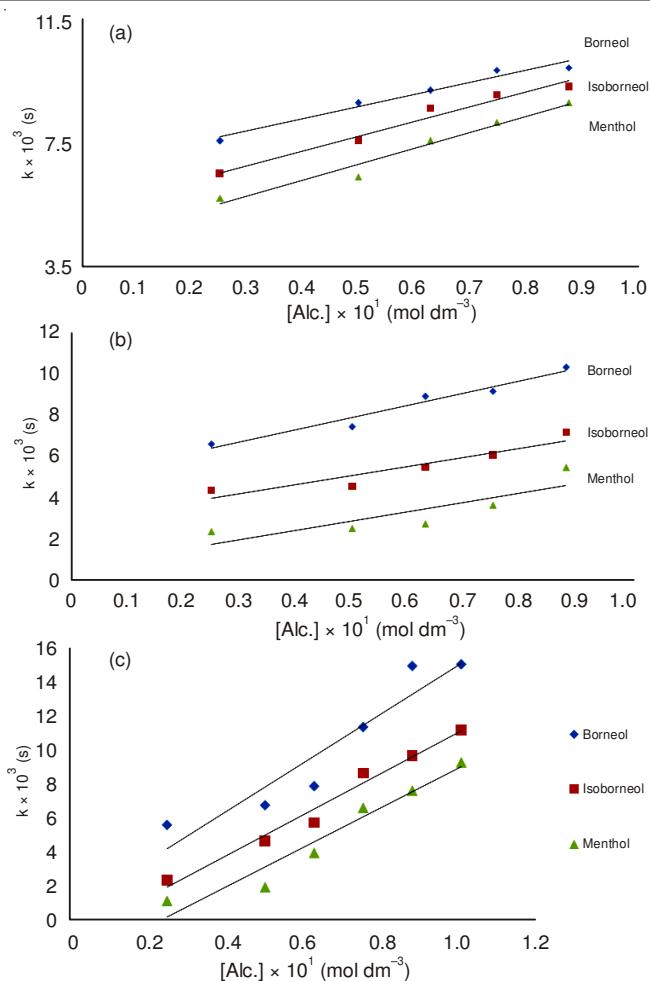


Fig. 1. (a) Variation of rate constant of oxidation of perfumery alcohols with [alc.] using KBrO_3 oxidant; (b) Variation of rate constant of oxidation of perfumery alcohols with [alc.] using KIO_3 oxidant; (c) Variation of rate constant of oxidation of perfumery alcohols with [alc.] using KIO_4 oxidant

Borneol has the least hindered α -hydrogen hence it is most vulnerable to oxidation and its oxidation is the fastest. Menthol has the most hindered α -hydrogen hence it undergoes slowest oxidation.

Sequence of efficiency of oxidants: For all the alcohols studied, the efficiency of the inorganic oxidants followed the same sequence *i.e.*,



Effect of ionic strength on oxidation rate of alcohols: The effect of ionic strength on oxidation rate of alcohols was studied by using K_2SO_4 in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$ (Tables 2a-c). The graph of $\log k$ vs. $\sqrt{\mu}$ was found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rate is independent of ionic strength.

Effect of temperature on oxidation rate of alcohols: From the variation of oxidation rate with temperature in the range 303-318 K, the thermodynamic activation parameters were evaluated (Tables 3a-c).

The important inferences from this thermodynamic study are:

(1) The oxidation rate of alcohols increases with temperature but is inversely proportional to the energy of activation (E).

TABLE-2
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES OF
PERFUMERY ALCOHOLS [alc.] = 0.1 M, [ox.] = 2.5×10^{-3} M,
[H₂SO₄] = 2.5×10^{-2} M. TEMPERATURE = 313 K

$\mu \times 10^2 \text{ mol dm}^{-3} (\text{K}_2\text{SO}_4)$	Borneol ($k \times 10^3 \text{ s}^{-1}$)	Isoborneol ($k \times 10^3 \text{ s}^{-1}$)	Menthol ($k \times 10^3 \text{ s}^{-1}$)
(a) KBrO ₃ as oxidant			
0.00	10.20	9.26	6.91
5.00	10.24	9.24	6.58
10.00	10.14	9.26	6.59
15.00	10.12	9.24	6.91
20.00	10.32	9.24	6.08
25.00	10.24	9.42	6.08
(b) KIO ₃ as oxidant			
0.00	7.82	5.52	2.76
5.00	7.84	5.51	2.84
10.00	7.12	5.52	2.76
15.00	7.25	5.03	2.84
20.00	7.68	5.67	2.69
25.00	7.68	5.67	2.81
(c) KIO ₄ as oxidant			
0.00	0.69	0.60	0.16
5.00	0.70	0.58	0.17
10.00	0.69	0.51	0.17
15.00	0.69	0.67	0.16
20.00	0.71	0.48	0.16
25.00	0.70	0.58	0.20

TABLE-3
THERMODYNAMIC ACTIVATION PARAMETERS
FOR THE OXIDATION OF PERFUMERY
ALCOHOLS IN 0.05 M H₂SO₄ AT 303 K

Alcohol	E (kJ mol ⁻¹)	K* \times 10 ¹⁶	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	ΔS^* (kJ K ⁻¹ mol ⁻¹)
(a) KBrO ₃ as oxidant					
Borneol	11.30	1.62	8.78	85.80	-0.2542
Isoborneol	11.72	1.46	9.20	86.06	-0.2537
Menthol	12.14	1.04	9.42	86.91	-0.2551
(b) KIO ₃ as oxidant					
Borneol	29.83	0.91	27.31	93.05	-0.2170
Isoborneol	33.52	0.87	31.00	93.16	-0.2205
Menthol	53.91	0.82	51.39	96.65	-0.1494
(c) KIO ₄ as oxidant					
Borneol	33.72	1.57	31.20	91.69	-0.1996
Isoborneol	21.83	1.46	19.31	91.90	-0.2396
Menthol	31.27	1.05	28.75	92.71	-0.2111

(2) The equilibrium constant (K^*) for the formation of activated complex from the reactant molecules also increases with temperature.

(3) For a given alcohol and oxidant, the energy of activation is constant at all temperature indicating that the site of oxidation of the alcohols is the same at all temperatures.

Negative values of ΔS^* indicate the reorientation of solvent molecules at the -OH bond of the rigid activated complex formed during the reaction. As a result, the vibrational and rotational motions of the reacting system are curtailed leading to decrease in the degrees of freedom.

Conclusion

For all the oxidants, KBrO₃, KIO₃ and KIO₄ the oxidation rates of alcohols follow the sequence:



Among the oxidants studied, KBrO₃ is the strongest oxidant and KIO₄ is the weakest. The oxidation rate is not affected by the ionic strength of the reacting solution.

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