



## A Kinetic Approach to the Oxidation of Some Perfumery Alcohols by *N*-Bromosuccinimide in Alkaline Medium

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The aliphatic alcohols, 2-propanol, 2-butanol and 3-methyl-1-butanol are extensively used as diluents in the manufacture of perfumes. Secondary alcohols, borneol, isoborneol and menthol are used in the preparation of fragrances, flavours and cosmetics. The pseudo first order kinetics of the oxidation of these alcohols has been studied using *N*-bromosuccinimide in alkaline medium as the oxidant. The progress of the reaction was monitored by iodometric titration of the unreacted oxidant at regular time intervals. The rate constants (*k*) of the oxidation reaction were determined from the straight lines plots of  $\log(a-x)$  versus time. The effects of (i) alcohol concentration (ii) oxidant concentration (iii) ionic strength (iv) temperature in the range 303-318 K on the oxidation rate has been studied in detail. It was observed that the reaction rate increases with [Alc] but decreases with oxidant concentration. The oxidation rate increases with ionic strength. From the effect of temperature on the reaction rate, the energy of activation and other thermodynamic activation parameters,  $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$  have been evaluated. Suitable reaction mechanism and rate laws have suggested for the oxidation process. The oxidation rates follow the sequence: (1) for aliphatic alcohols, 2-propanol > 2-butanol > 3-methyl-1-butanol, which has been explained on the basis of chain length. (2) for secondary alcohols borneol > isoborneol > menthol, which has been explained on the basis of structures, steric factors and isomeric characteristics of the alcohols under study.

**Key Words:** Perfumery alcohols, Oxidation, Reaction mechanism, Energy of activation, Entropy of activation.

### INTRODUCTION

*N*-Halosuccinimides with positive halogens have been used to oxidize a variety of substances in acidic medium<sup>1-4</sup>. But there are relatively few reports of the use of *N*-bromosuccinimide (NBS) as oxidizing agent in alkaline medium. In our laboratory we have studied the kinetic aspects of the oxidation of industrial alcohols including perfumery alcohols<sup>5,6</sup>. This paper deals with i) the kinetics of oxidation of the cyclic secondary alcohols borneol, isoborneol and menthol and the aliphatic alcohols 2-propanol, 2-butanol and 3-methyl-1-butanol by *N*-bromosuccinimide in alkaline medium in the temperature range 303-318 K. ii) the effect of ionic strength on the oxidation rate of the above alcohols using  $K_2SO_4$ .

All the data collected has been collated and suitable reaction mechanisms have been suggested for the oxidation of the cyclic secondary alcohols and aliphatic alcohols under study.

### EXPERIMENTAL

High purity perfumery alcohols were used all the chemicals and reagents used (S.H. Kelkar and Co., Mumbai, Ultra International and Cetex Petrochemical, Mumbai). All other

chemicals and reagents used were of AnalaR Grade; *N*-bromosuccinimide (NBS),  $K_2SO_4$  (SD Fine Chemicals, Mumbai).

The oxidation of the aliphatic and secondary cyclic alcohols was studied under pseudo unimolecular conditions with respect to the oxidizing agent and the progress of the reaction was monitored titrimetrically. The solutions of alcohol and oxidizing agent in requisite amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy  $\pm 0.1$  °C). After the temperature equilibrium was attained, the solutions were mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular intervals and the reaction was controlled by ice. The unreacted *N*-bromosuccinimide was treated with ice cold 10% KI and dilute  $H_2SO_4$  and the liberated iodine was titrated against standard  $Na_2S_2O_3$  using starch as an indicator. The reaction was carried out in the temperature range 303-318 K.

The pseudo first order rate constants were determined from the slopes of the linear plots of  $\log(a-x)$  vs. time. The energy of activation and other thermodynamic parameters were calculated from the Arrhenius plots of  $\log k$  vs.  $T^{-1}$ .  $K_2SO_4$  was used to study the effect of ionic strength ( $\mu$ ) on the oxidation rate in the range  $\mu = 5$  to  $25.0 \times 10^{-2}$  mol  $dm^{-3}$  in accordance

TABLE-1  
RATE CONSTANT DATA FOR THE OXIDATION OF DIFFERENT ALCOHOLS BY *N*-BROMOSUCCINIMIDE (NBS)  
IN ALKALINE MEDIUM; [NaOH] =  $5 \times 10^{-2}$  M, TEMPERATURE = 303 K

[Alc] $\times 10^1$ (mol. dm <sup>-3</sup> )	[NBS] $\times 10^3$ (mol dm <sup>-3</sup> )	Secondary perfumery alcohols			Aliphatic alcohols		
		$k \times 10^3$ s <sup>-1</sup>			$k \times 10^4$ s <sup>-1</sup>		
		Borneol	Isoborneol	Menthol	2-Propanol	2-Butanol	3-Methyl-1-butanol
1.00	2.50	8.70	5.52	2.27	7.76	4.51	2.93
1.00	5.00	9.78	4.61	1.80	6.21	2.97	2.69
1.00	10.00	7.68	3.84	1.51	1.32	2.85	1.93
1.00	15.00	4.61	2.84	1.35	4.99	2.29	1.66
1.00	20.00	3.46	2.27	1.38	2.73	1.87	1.23
1.00	25.00	2.27	1.51	1.10	2.55	1.51	0.96
0.25	5.00	2.10	1.12	0.14	5.13	1.88	1.61
0.50	5.00	4.56	1.51	0.45	7.23	3.62	1.74
0.625	5.00	6.54	1.84	0.65	8.93	7.07	2.42
0.75	5.00	7.84	2.84	0.89	12.30	8.42	2.57
0.875	5.00	9.78	4.61	1.35	15.80	10.20	2.69
1.00	5.00	13.23	5.98	1.80	20.24	13.85	2.78

with the Bronsted-bjerrum equation,  $\log k = \log k_0 + 1.02Z_A Z_B / \mu$ .

## RESULTS AND DISCUSSION

Since *N*-bromosuccinimide (NBS) is a stronger oxidizing agent<sup>7</sup>, the primary aliphatic alcohol, 3-methyl-1-butanol was converted to aldehyde [3-methyl butanal] and then acid [3-methyl butanoic acid]. The secondary alcohols were converted to the corresponding ketones. For all the alcohols under investigation, the rate constant increases with alcohol concentration as expected but decreases with increase in [NBS]. (Table-1, Figs. 1a and 1b). The oxidation rate of 3-methyl-1-butanol was found to be very low.

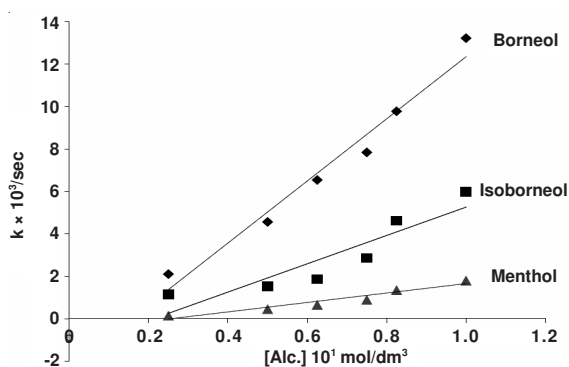


Fig.1a. Variation of rate constant of oxidation of secondary perfumery alcohols with [Alc.]

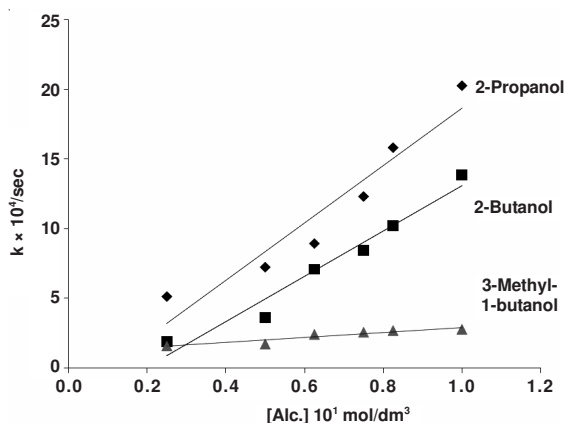
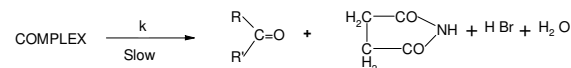
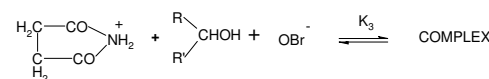
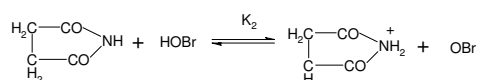
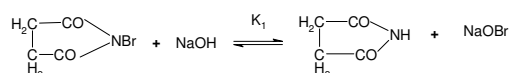


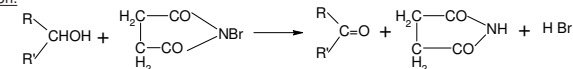
Fig.1b. Variation of rate constant of oxidation of aliphatic alcohols with [Alc.]

**Effect of alcohol concentration and *N*-bromosuccinimide concentration on the oxidation rate:** The oxidation process in alkaline medium 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 product<sup>7</sup>.

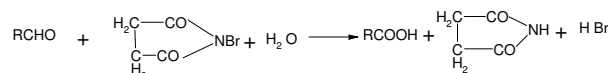
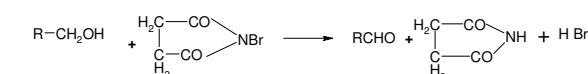
**Reaction mechanism of oxidation:** (i) Reaction mechanism of oxidation of secondary alcohols (**Scheme-I**). (ii) For a primary alcohol the oxidation proceeds by the following reaction (**Scheme-II**).



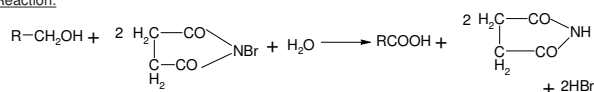
Net Reaction:



(Scheme-I)



Net Reaction:



(Scheme-II)

The products of the oxidation, aldehydes and ketones were identified by 2,4-dinitrophenylhydrazone test and confirmed

TABLE-2  
EFFECT OF IONIC STRENGTH ON THE OXIDATION RATES OF DIFFERENT ALCOHOLS BY *N*-BROMOSUCCINIMIDE  
(IN ALKALINE MEDIUM), [Alc] = 0.1 M, [NaOH] =  $2.5 \times 10^{-2}$  M, [NBS] =  $2.5 \times 10^{-3}$  M, TEMPERATURE = 313 K

$\mu \times 10^2$ (mol dm <sup>-3</sup> )	Secondary perfumery alcohols			Aliphatic alcohols		
	$k \times 10^3$ s <sup>-1</sup>			$k \times 10^4$ s <sup>-1</sup>		
	Borneol	Isoborneol	Menthol	2-Butanol	2-Propanol	3-Methyl-1-butanol
Zero	7.82	3.65	1.56	3.64	3.30	2.48
05.00	9.75	4.61	1.80	3.82	3.51	2.58
10.00	9.78	5.52	2.28	3.92	4.08	2.65
15.00	18.42	6.03	2.84	4.08	5.09	2.69
20.00	26.82	9.67	4.22	4.22	5.28	2.81
25.00	30.16	18.41	5.09	4.41	5.83	2.90

TABLE-3  
THERMODYNAMIC ACTIVATION PARAMETERS OF THE OXIDATION OF ALCOHOLS BY  
*N*-BROMOSUCCINIMIDE IN ALKALINE MEDIUM AT 303 K

Thermodynamic Parameter	2-Propanol	2-Butanol	3-Methyl-1-butanol	Borneol	Isoborneol	Menthol
E <sub>a</sub> (kJ mol <sup>-1</sup> )	13.24	13.63	20.04	12.19	13.36	15.81
K <sup>*</sup> × 10 <sup>16</sup>	5.26	4.54	4.28	3.61	2.93	2.14
ΔH <sup>*</sup> (kJ mol <sup>-1</sup> )	10.72	11.12	17.53	9.68	10.85	13.29
ΔG <sup>*</sup> (kJ mol <sup>-1</sup> )	88.34	88.71	94.64	89.95	89.82	90.60
ΔS <sup>*</sup> (kJ K <sup>-1</sup> mol <sup>-1</sup> )	-0.2572	-0.2570	-0.2473	-0.2664	-0.2555	-0.2553

by TLC. The succinimide and acid were identified by spot tile tests.

The oxidation rates follow the sequences: (1) for aliphatic alcohols, 2-propanol > 2-butanol > 3-methyl-1-butanol. (2) for secondary alcohols, borneol > isoborneol > menthol.

The relative rates of oxidation of the perfumery alcohols under study are consistent with respect to their steric effects on the oxidation. The secondary alcohol menthol has more hindered α-hydrogen hence it is least susceptible to oxidation whereas borneol has the least hindered α-hydrogen hence its oxidation is the fastest. In case of aliphatic alcohols, the oxidation rate is inversely proportional to the length of carbon chain in the alcohol molecules.

**Effect of ionic strength:** Potassium sulfate was used to study the effect of ionic strength ( $\mu$ ) on oxidation rate in dilute solution in the range  $\mu = 5$  to  $25 \times 10^{-2}$  mol. dm<sup>-3</sup> at 313 K (Table-2, Figs. 2a and 2b). The graphs of log  $k$  vs.  $\sqrt{\mu}$  indicate that the oxidation rate depends on ionic strength<sup>7</sup>. This trend is borne out by the reaction mechanism suggested for the oxidation of alcohols under study.

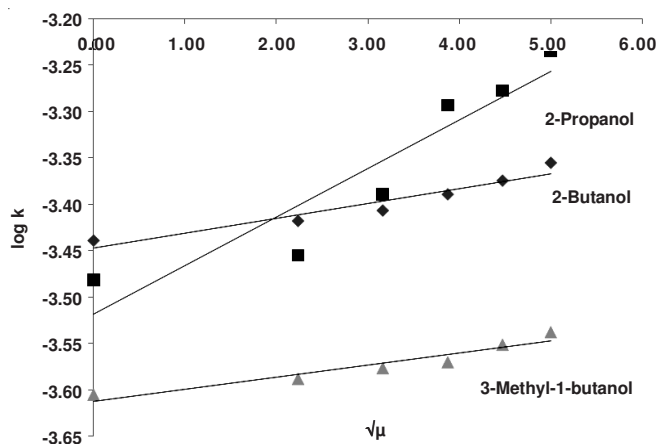


Fig. 2a Variation of rate constant of oxidation of secondary perfumery alcohols with ionic strength.

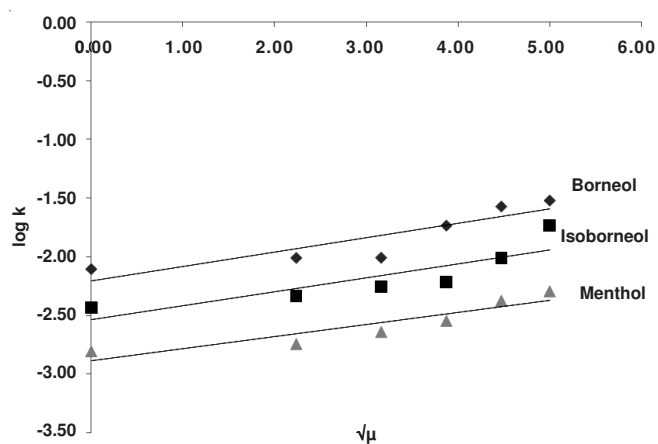


Fig. 2b. Variation of rate constant of oxidation of aliphatic alcohols with ionic strength.

**Effect of temperature:** The oxidation was studied in the temperature range 303-318 K. From the effect of temperature on reaction rate, the energy of activation and other thermodynamic parameters were evaluated (Table-3).

The negative values of  $\Delta S^*$  indicate a decrease in the degrees of freedom due to the formation of a rigid activation complex resulting in an extensive reorientation of solvent molecules. The negative values of  $\Delta S^*$  can be explained by a model in which the water molecules are tightly held to the -OH bond, which is the site of oxidation<sup>8</sup>.

## Conclusion

The oxidation rates follow the sequence: (i) for aliphatic alcohols; 2-propanol > 2-butanol > 3-methyl-1-butanol. (ii) for secondary alcohols; borneol > isoborneol > menthol. The oxidation rate increases with ionic strength in dilute solution.

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