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KINETIC AND THERMODYNAMIC STUDIES OF THE OXIDATION OF ACYCLIC PRIMARY PERFUMERY ALCOHOLS USING $K_2S_2O_8$ AND KIO_4 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 several organic oxidants for the oxidation of alcohols to the corresponding carbonyl compounds but inorganic oxidants have rarely been used. Further, the kinetic and thermodynamic aspects of oxidation of perfumery alcohols have not been investigated. In this paper, we report the kinetic studies of oxidation of acyclic primary perfumery alcohols, Nerol, Citronellol and Geraniol, to aldehydes using $K_2S_2O_8$ and KIO_4 in acidic medium. The oxidation was carried out under first order kinetic conditions with respect to the inorganic oxidants.The progress of reaction was monitored by iodometric estimation of the unreacted oxidants at regular time interval during the course of the reaction. The reaction was found to be independent of ionic strength (μ).The thermodynamic activation parameters have been determined from the variation of oxidation rate with temperature. Suitable reactionmechanism have been suggested for the oxidation of perfumery alcohols.

Keywords: Acyclic primary perfumery alcohols, inorganic oxidants, first order kinetics, ionic strength, thermodynamic activation parameters, entropy of activation.

INTRODUCTION

The quantitative aspects of the oxidation of alcohols using organic oxidants have been widely reported[1-3] but the kinetic and thermodynamic studies of oxidation of alcohols have not been reported. Further, inorganic oxidants have rarely been used for oxidation of alcohols. In our laboratory ,we have studied the kinetics of oxidation of several industrially important alcohols and phenols using a variety of organic and inorganic oxidants.[4-10] This paper reports the kinetic and thermodynamic aspects of the oxidation of acyclic primary alcohols, Nerol, Citronellol and Geraniol using Potassium persulphate ($K_2S_2O_8$)and Potassium periodate(KIO_4) in acidic medium. These alcohols are used in the preparation of perfumery, fragrance and cosmetic formulations. Citronellol is also used as an effective insect repellent.

The effects of substrate and oxidant concentrations, ionic strength and temperature on the oxidation rates of alcohols have been studied. The observed sequence of oxidation rates of the alcohols has been explained on the basis of their steric, structural and isomeric features. Suitable reaction mechanisms have been suggested for the oxidation of the acyclic primary alcohols under investigation.

EXPERIMENTAL

High purityperfumery alcohols were procured from Shaivi Industries, Lucknow, India and distilled prior to use in the oxidation study. All other chemicals and reagents used were of analytical grade. The oxidation of alcohols was studied under first order kinetic conditions with respect to the inorganic oxidants. Aliquots of the reaction mixture were withdrawn at regular intervals and the reaction was arrested by using ice. The progress of the reaction was monitored by iodometric titration of the unreacted oxidant. The first order rate constants were determined from the linear plots of log (a-x) versus time. The effect of ionic strength on oxidation rate was studied using Potassium sulphate (K_2SO_4) in the range μ = 5 to 25 x 10^{-2} mol dm^{-3}. From the Arrhenius plots of log k verses 1/T, the energy of activation and other thermodynamic activation parameters were determined and interpreted.

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RESULTS AND DISCUSSION

The acyclic primary alcohols, Nerol, Citronellol and Geraniol were oxidized to the corresponding aldehydes. It was observed that for all the alcohols under study, the oxidation rates increased with [alc.] but decreased with [ox.](Shown in Tables-1 and 2, Figures-1 and 2).

Reaction mechanism of oxidation of primary alcohols

$K_2S_2O_8$ as oxidant in acidic medium

In acidic medium, $K_2S_2O_8$ forms $H_2S_2O_8$ which is a strong acid and strong oxidizing agent.[11, 12]

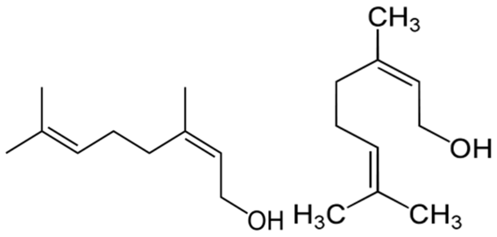
$$RCH_2OH + H_2S_2O_8 \rightarrow RCHO + 2H_2SO_4$$

KIO_4 as oxidant in acidic medium

In acidic medium, KIO_4 forms periodic acid HIO_4 which is a strong acid and a strong oxidizing agent.[13,14] The oxidation of alcohols by KIO_4 results in the formation of the hypohalite ion ,OI^-.

$$RCH_2OH + IO_4^- + 4H^+ \rightarrow RCHO + OI^- + 3H_2O$$

The unreacted oxidants were estimated iodometrically and the products of oxidation viz. aldehyde were identified by 2,4 –dinitrophenylhydrazone test and confirmed by TLC. For $K_2S_2O_8$ oxidant in acidic medium, the rates of oxidation of alcohols followed the sequence, as:



Nerol > Citronellol

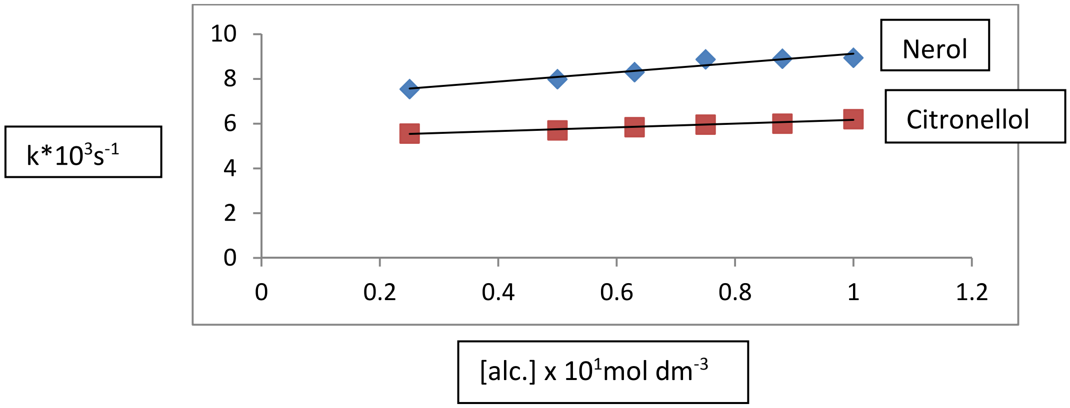
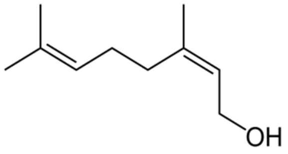
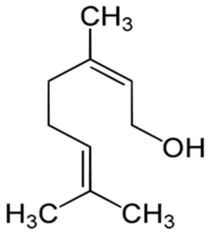
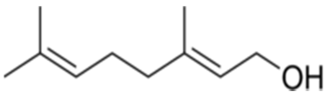


Fig.-1: Variation of rate constant of oxidation of primary alcohols with [alc.] using $K_2S_2O_8$ as oxidant in acidic medium

Citronellol has more hindered alpha –hydrogen than Nerol hence its oxidation is slower than that of Nerol. For KIO_4 oxidant in acidic medium, the rates of oxidation of alcohols followed the sequence:







Nerol > Citronellol > Geraniol

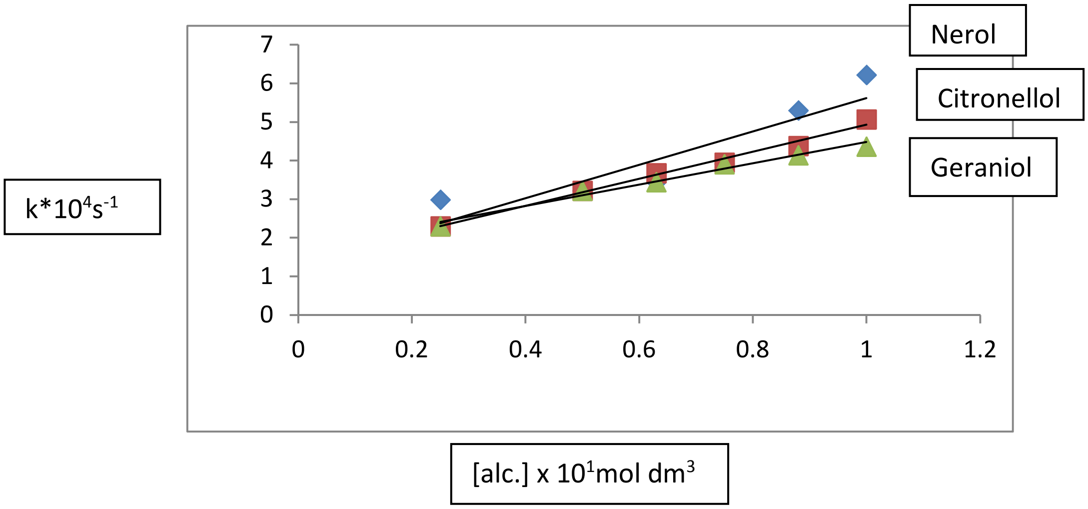


Fig.-2: Variation of rate constant of oxidation of primary alcohols with [alc.]usingKIO_4 as oxidant in acidic medium

The oxidation rates of the primary alcohols are consistent with respect to their steric hindrance effects on the oxidation. The oxidation rates of the three alcohols are relatively close to each other (Figure-2). $K_2S_2O_8$ was found to be a stronger oxidizing agent than KIO_4 for the primary alcohols under study (Tables-1 and 2).

Table-1: Rate constant data for the oxidation of acyclic primary alcohols by $K_2S_2O_8$ in acidic medium. $[H_2SO_4]$ =1M; Temperature=303K

[alc.] $*10^1$ mol dm^{-3}	$[K_2S_2O_8]$ $*10^1$ mol dm^{-3}	Nerol k $*10^3$ s^{-1}	Citronellol k $*10^3$ s^{-1}
1.00	2.50	9.42	6.72
1.00	5.00	9.35	5.78
1.00	10.0	9.17	5.55
1.00	15.0	8.87	5.04
1.00	20.0	7.37	4.84
1.00	25.0	7.28	4.47
0.25	5.00	7.55	5.57
0.50	5.00	7.99	5.71
0.63	5.00	8.31	5.85
0.75	5.00	8.89	5.96
0.88	5.00	8.91	6.01
1.00	5.00	8.96	6.22

Table-2: Rate constant data for the oxidation of acyclic primary alcohols by KIO_4 in acidic medium
$[H_2SO_4]$ =1M; Temperature=303K

[alc.] $*10^1$ mol dm^{-3}	$[KIO_4]$ $*10^1$ mol dm^{-3}	Nerol k $*10^4$ s^{-1}	Citronellol k $*10^4 s^{-1}$	Geraniol k $*10^4$ s^{-1}
1.00	2.50	10.36	4.60	6.22
1.00	5.00	8.75	3.68	5.53
1.00	10.0	8.52	3.22	4.84
1.00	15.0	8.29	3.00	4.60
1.00	20.0	7.83	2.53	3.91
1.00	25.0	7.37	2.30	2.99
0.25	5.00	2.99	2.30	2.30
0.50	5.00	3.22	3.22	3.22
0.63	5.00	3.45	3.68	3.45
0.75	5.00	3.92	3.95	3.91
0.88	5.00	5.30	4.38	4.14
1.00	5.00	6.22	5.07	4.37

Effect of ionic strength on oxidation rates of alcohols

The effect of ionic strength on oxidation rate was in studied in dilute solution using K_2SO_4 in the range of μ = 5 to 25 x 10^{-2} mol dm^{-3} at 303 K (Tables-3 and 4) in accordance with the Bronsted-Bjerrum equation, $\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$

The graphs of log k verses $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis indicating that the oxidation rates of alcohols were independent of ionic strength μ. This observation is supported by the mechanism suggested for the oxidation of alcohols which involves the participation of a nonionic species in the reaction.

Table-3: Effect of ionic strength on oxidation rates of perfumery alcohols using $K_2S_2O_8$ as oxidant
[alcohol] = 0.1M; $K_2S_2O_8]$ = 0.005M; $[H_2SO_4]$ = 0.5 M; Temperature = 303 K

$[K_2SO_4]$ μ x 10^2 mol dm^{-3}	Nerol k x 10^3 s^{-1}	Citronellol k x 10^3 s^{-1}
5	2.58	4.19
10	3.13	4.72
15	2.90	4.37
20	3.38	4.37
25	3.91	4.39

Table-4: Effect of ionic strength on oxidation rates of perfumery alcohol using KIO_4as oxidant
[alcohol] = 0.1 M; $KIO_4]$ = 0.005M; $[H_2SO_4]$ = 0.5 M; Temperature = 303 K

$[K_2SO_4]$ μ x 10^2 mol dm^{-3}	Nerol k x $10^4 s^{-1}$	Citronellol k x $10^4 s^{-1}$	Geraniol k x $10^4 s^{-1}$
5	6.22	4.84	2.76
10	6.22	3.92	2.76
15	4.15	4.15	2.31
20	5.76	4.38	1.60
25	4.38	5.53	1.84

Effect of temperature on oxidation rates of perfumery acyclic primary alcohols

The oxidation was studied in the temperature range 303-318K and the thermodynamic activation parameters were evaluated (Tables-5 and 6). For all the alcohols under study, the rate constants (k) increased with temperature and were inversely proportional to the energy of activation (E). The negative values of entropy of activation can be attributed to the curtailment of the rotational and vibrational modes of motion of the reacting molecules due to the formation of a rigid activated complex and the reorientation of the solvent molecules around the activated complex.[15,16] The constant values of entropy of activation at all temperatures indicate that the site of oxidation i.e. – OH remains the same at all temperatures.

Table-5: Thermodynamic activation parameters of the oxidation of perfumery alcohols by $K_2S_2O_8$ in acidic medium.

a. Nerol

Temp.(K)	k x 10^3 s^{-1}	E kJ mol^{-1}	K* x 10^{15}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
303	7.32	10.92	1.16	8.40	86.98	-0.2590
308	7.83	10.92	1.22	8.36	88.42	-0.2594
313	8.61	10.92	1.32	8.32	89.80	-0.2600
318	8.89	10.92	1.34	8.28	91.25	-0.2603

b. Citronellol

Temp.(K)	k x 10^3 s^{-1}	E kJ mol^{-1}	K* x 10^{15}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
303	6.49	36.34	1.03	33.82	87.01	-0.1750
308	9.07	36.34	1.41	33.78	88.42	-0.1770
313	11.63	36.34	1.78	33.74	89.73	-0.1781
318	12.64	36.34	1.91	33.70	91.17	-0.1805

Table-6: Thermodynamic activation parameters of the oxidation of perfumery alcohols by KIO_4 in acidic medium.

a. Nerol

Temp.(K)	k x 10^4 s^{-1}	E kJ mol^{-1}	K* x 10^{15}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
303	2.30	20.91	1.16	18.39	95.36	-0.2542
308	2.53	20.91	1.22	18.35	96.75	-0.2545
313	2.76	20.91	1.32	18.31	98.11	-0.2546
318	3.45	20.91	1.34	18.27	99.15	-0.2540

b. Citronellol

Temp.(K)	k x 10^4 s^{-1}	E kJ mol^{-1}	K* x 10^{17}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
303	1.15	38.12	1.82	35.60	97.10	-0.2033
308	1.38	38.12	2.15	35.55	98.30	-0.2041
313	1.84	38.12	2.83	35.51	99.16	-0.2036
318	2.30	38.12	3.48	35.47	100.22	-0.2034

c. Geraniol

Temp.(K)	k x 10^4 s^{-1}	E kJ mol^{-1}	K* x 10^{17}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
303	1.61	19.95	2.55	17.43	96.26	-0.2607
308	1.84	19.95	2.87	17.39	97.57	-0.2606
313	2.07	19.95	3.18	17.34	98.86	-0.2600
318	2.33	19.95	3.48	17.30	100.55	-0.2612

CONCLUSION

1. The oxidation rates of primary alcohols follow the sequences:
   For $K_2S_2O_8$ oxidant: Nerol > Citronellol,
   For KIO_4 oxidant: Nerol > Citronellol > Geraniol.
2. Potassium persulphate is a stronger oxidizing agent than Potassium periodate.
3. The oxidation of the primary alcohols under study is independent of ionic strength.
4. The oxidation of the primary alcohols is accompanied by decrease in entropy of activation.

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