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A KINETIC APPROACH TO THE OXIDATION OF 1-HEXANOL AND CYCLOHEXANOL USING INORGANIC OXIDANTS

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ABSTRACT

Several organic oxidants have been used 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 extensively studied but there are few reports of the kinetic investigations of the oxidation of alcohols. The present paper discusses the kinetics of oxidation of 1-hexanol and cyclohexanol using potassium persulphate ($K_2S_2O_8$) and potassium periodate (KIO_4) in acidic medium. 1-hexanol is used in the perfumery industry and cyclohexanol in the manufacture of polymers. Cyclohexanol has an important application as a precursor to nylon.

The oxidation was studied under first order kinetic conditions with respect to the oxidant. The progress of the oxidation was monitored by titrimetric estimation of the unreacted oxidants at regular time intervals during the course of the reaction. For both the alcohols, the oxidation rate increased with alcohol concentration but decreased with oxidant concentration. The oxidation rates followed the sequence: 1-hexanol >cyclohexanol. Potassium persulphate was found to be a stronger oxidising agent than potassium periodate for the alcohols under study. The reaction was found to be independent of ionic strength (μ). From the effect of temperature (303-318K) on the rate of oxidation, the various thermodynamic parameters were determined and interpreted in terms of the molecular dynamics of the oxidation process. Suitable reaction mechanisms have been suggested for the oxidation of the alcohols.

Keywords: alcohol, inorganic oxidant, kinetics, ionic strength, energy of activation, entropy of activation, reaction mechanism.

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INTRODUCTION

The quantitative conversion of alcohols to aldehydes/ketones using organic oxidants has been extensively reported in literature.[1-3] The kinetics of several types of organic reactions using different experimental techniques has also been reported.[4-6] However, there are very few reports available on the kinetic and thermodynamic aspects of the oxidation of alcohols using inorganic oxidants. We have earlier reported the kinetics of oxidation of several industrially important alcohols and phenols using a variety of organic and inorganic oxidants.[7-12]

This paper reports the kinetic study of the oxidation of 1-hexanol and cyclohexanol using potassium persulphate and potassium periodatein acidic medium. The effects of substrate and oxidant concentrations, ionic strength (μ) and temperature on the oxidation rates of alcohols have been studied in detail and the observed sequence of oxidation rates of alcohols has been explained on the basis of their structural features.

EXPERIMENTAL

The alcohols were procured from Shaivi Industries, Lucknow and purified by distillation prior to use in the oxidation study. All other chemicals and reagents used were of analytical grade.

The oxidation of alcohols was carried out under first order kinetic conditions viz. [ox.] << [alc.]. The progress of the reaction was monitored by iodometric estimation of the unreacted oxidant at regular time intervals. The first order rate constants (k) were determined from the linear plots of log (unreacted oxidant) versus time. Potassium sulphate (K_2SO_4) was used in dilute solution to study the effect of ionic strength (μ) on the oxidation rate.

From the Arrhenius plots of log k versus 1/T, the energy of activation and other thermodynamic activation parameters were determined and interpreted.

RESULTS AND DISCUSSION

The primary alcohol, 1-hexanol was oxidised to the corresponding aldehyde, Hexanal and the secondary cyclic alcohol, cyclohexanol was oxidised to the corresponding ketone, cyclohexanone.It was observed that the oxidation rates increased with [alc.] but decreased with [ox.] (Tables-1and 2, Figures-1and 2).

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

[alc.] x 10^1 mol dm^{-3}	$[K_2S_2O_8]$ x 10^3 mol dm^{-3}	1-hexanol k x 10^3 s^{-1}	Cyclohexanol k x 10^3 s^{-1}
1.00	2.50	5.78	-
1.00	5.00	5.53	-
1.00	1.00	5.23	-
1.00	15.00	4.99	0.55
1.00	20.00	4.26	0.46
1.00	25.00	2.99	0.20
0.25	5.00	5.09	0.21
0.50	5.00	6.13	0.30
0.63	5.00	6.45	0.32
0.75	5.00	6.79	0.37
0.88	5.00	7.00	0.46
1.00	5.00	7.18	0.51

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

[alc.] x 10^1 mol dm^{-3}	$[KIO_4]$ x 10^3 mol dm^{-3}	1-hexanol k x 10^3 s^{-1}	Cyclohexanol k x 10^3 s^{-1}
1.00	2.50	-	0.32
1.00	5.00	-	0.28
1.00	1.00	-	0.25
1.00	15.00	0.55	0.23
1.00	20.00	0.46	0.21
1.00	25.00	0.21	0.18
0.25	5.00	0.21	0.16
0.50	5.00	0.30	0.18
0.63	5.00	0.32	0.21
0.75	5.00	0.37	0.23
0.88	5.00	0.46	0.25
1.00	5.00	0.51	0.28

Reaction mechanism of oxidation of 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 oxidising agent.[13,14]

$$\underset{\text{1-hexanol}}{CH_3(CH_2)_5OH} + H_2S_2O_8 \rightarrow \underset{\text{Hexanal}}{CH_3(CH_2)_4CHO} + 2H_2SO_4$$

$$\underset{\text{cyclohexanol}}{(CH_2)_5\,CHOH} + H_2S_2O_8 \rightarrow \underset{\text{cyclohexanone}}{(CH_2)_5\,C{=}O} + 2H_2SO_4$$

KIO_4 as oxidant in acidic medium

In acidic medium , KIO_4 rapidly forms periodic acid HIO_4 which is a strong acid and strong oxidising agent.[15,16] The oxidation of alcohols by potassium periodate results in the formation of the hypohalite ion ,OI^-.

$$CH_3(CH_2)_5OH + IO_4^- + 4H^+ \rightarrow CH_3(CH_2)_4CHO + OI^- + 3H_2O$$

1-hexanol Hexanal

$(CH_2)_5CHOH + IO_4^- + 4H^+ \rightarrow (CH_2)_5\,C{=}O + OI^- + 3H_2O$
Cyclohexanol cyclohexanone

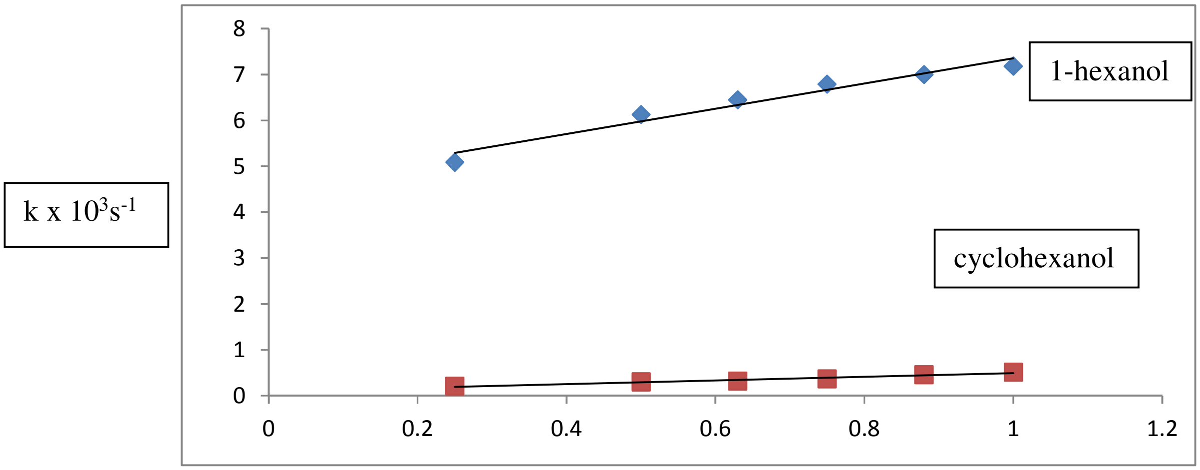

Fig.-1: Variation of rate constant of oxidation of alcohols with [alc.] using $K_2S_2O_8$ in acidic medium

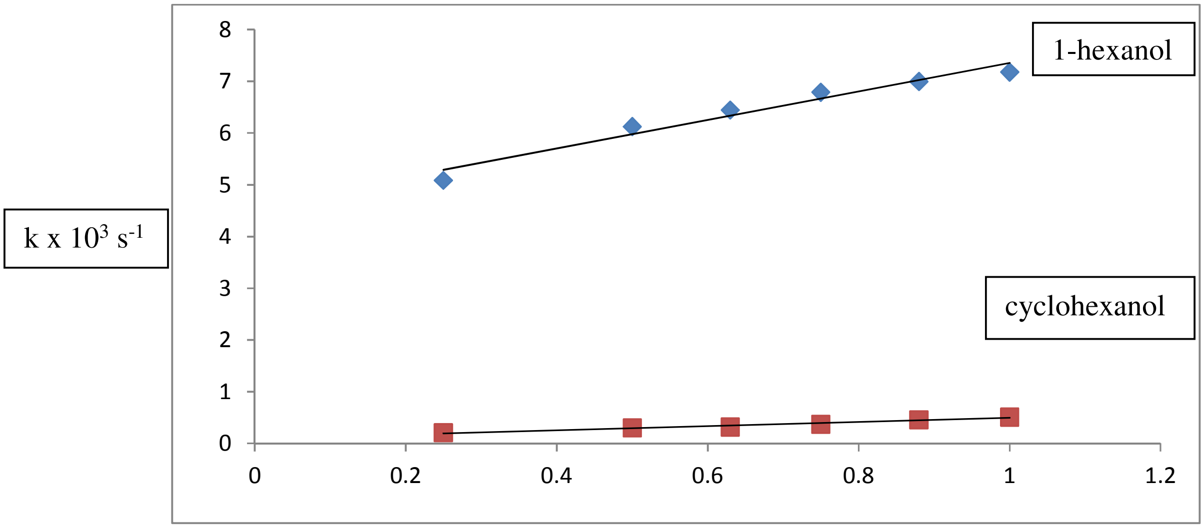

Fig.-2: Variation of rate constant of oxidation of alcohols with [alc.] using KIO_4 in acidic medium.

The unreacted inorganic oxidants were estimated iodometrically, the products of the oxidation viz aldehyde/ketone were identified by 2, 4-dinitrophenyl hydrazone test and confirmed by TLC.

For both the oxidants, the rates of oxidation of alcohols followed the sequence: 1-hexanol > cyclohexanol (Tables-1 and 2, Figures-1 and 2).

The primary aliphatic alcohol, 1-hexanol is more susceptible to oxidation than the secondary cyclic alcohol, cyclohexanol.$K_2S_2O_8$was found to be a stronger oxidant than KIO_4 for the alcohols under study (Tables-1 and 2).

Effect of ionic strength (μ) on oxidation rates of alcohols

K_2SO_4 was used to study the effect of ionic strength (μ) on the rate of oxidation of alcohols in the range, $\mu = 5$ to 25×10^{-2}mol dm^{-3} at 303K (Tables-3 and 4) in accordance with the Bronsted-Bjerrum equation,

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

The graphs of log k versus $\sqrt{\mu}$ 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 borne out by the reaction mechanisms suggested for the oxidation of alcohols.

Variation of oxidation rates of alcohols with temperature (303-318K)

The thermodynamic activation parameters for the oxidation of alcohols are listed in Tables-5 and 6. For both the alcohols, the rate constants (k) increased with temperature and were inversely proportional to the energy of activation (E).

The negative values of entropy of activation (ΔS^*) can be ascribed to the curtailment of the vibrational and rotational modes of the reacting molecules due to the formation of a rigid activated complex and reorientation of the solvent molecules around the complex.[17,18]

The constant values of ΔS^* at all temperatures indicates that the site of oxidation ie –OH remains unchanged at all temperatures.

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

[K_2SO_4] $\mu \times 10^2$ mol dm^{-3}	1-hexanol k x 10^3 s^{-1}	Cyclohexanol k x 10^3 s^{-1}
5	3.27	1.38
10	2.21	2.56
15	2.12	1.82
20	2.03	1.40
25	2.51	1.93

Table-4: Effect of ionic strength on oxidation rates of alcohols using KIO4 as oxidant
[alc.] = 0.1 M; [KIO_4] =0.005 M
[H_2SO_4] = 0.5 M; Temperature = 303 K

[K_2SO_4] $\mu \times 10^2$ mol dm^{-3}	1-hexanol k x 10^3 s^{-1}	Cyclohexanol k x 10^3 s^{-1}
5	0.25	0.53
10	0.25	0.25
15	0.39	0.37
20	0.35	0.48
25	0.32	0.32

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

Temp.(K)	k x 10^3 s^{-1}	E kJ mol^{-1}	K* x 10^{16}	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	ΔS^* kJ K^{-1} mol^{-1}
303	0.74	14.45	1.17	11.93	81.61	-0.2300
308	0.78	14.45	1.22	11.89	83.08	-0.2311
313	0.85	14.45	1.31	11.84	86.84	-0.2400
318	0.97	14.45	1.46	11.81	86.24	-0.2340

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

Temp.(K)	k x 10^3 (s^{-1})	E kJ mol^{-1}	K* x 10^{17}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
1-Hexanol						
303	0.14	21.77	2.18	19.25	86.05	-0.2200
308	0.16	21.77	2.51	19.20	87.52	-0.2220
313	0.18	21.77	2.82	19.17	88.95	-0.2230
318	0.21	21.77	3.13	19.12	90.42	-0.2240
Cyclohexanol						
303	0.09	36.39	1.46	33.87	85.95	-0.1720
308	0.12	36.39	1.79	33.83	87.44	-0.1740
313	0.14	36.39	2.12	33.79	88.88	-0.1760
318	0.18	36.39	2.78	33.75	90.39	-0.1781

CONCLUSION

1. The oxidation rates of alcohols follow the sequence : 1-hexanol >cyclohexanol for both the inorganic oxidants in acidic medium.
2. Potassium persulphate is a stronger oxidant than potassium iodate for the alcohols under study.
3. Ionic strength has no effect on the oxidation rates of alcohols.
4. The oxidation of alcohols is accompanied by decrease in entropy of activation.

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