Kinetic and thermodynamic studies of the oxidation of some industrially important secondary cyclic alcohols using K₂S₂O₈in acidic medium

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Abstract

Inorganic oxidants have rarely been used for the oxidation of alcohols to the corresponding carbonyl compounds. This paper deals with the kinetics of oxidation of industrially important secondary cyclic alcohols,Cyclopentanol, Cyclohexanol and Cyclooctanol by $K_2S_2O_8$ in acidic medium under first order kinetic conditions with respect to the inorganic oxidant.Cyclopentanol is used in the manufacture of perfumes and pharmaceuticals and Cyclohexanol is an important feedstock in the polymer industry as a precursor in the manufacture of nylons and plasticizers. Cyclooctanol also finds use in the preparation of perfumes.

The oxidation was monitored by iodometric titration of the unreacted oxidant during the course of the reaction. From the effect of temperature on the reaction rate, the Energy of activation (E) and other thermodynamic activation parameters (ΔH^*,ΔG^* and ΔS^*) were calculated and interpreted in terms of the molecular dynamics of the oxidation process. Asuitable reaction

mechanism based on the experimental observations has been suggested for the oxidation of the cyclic alcohols under study.

The sequence of oxidation rates of the cyclic alcohols,

Cyclooctanol>Cyclopentanol>Cyclohexanol has been explained on the effect of ring size of the cyclic alcohols on the oxidation rate.

Keywords: secondary cyclic alcohols, inorganic oxidant, kinetics, ring size, thermodynamic activation parameters, energy of activation, entropy of activation.

INTRODUCTION

Oxidation of alcohols is a reaction of prime industrial importance as it yields useful products.The quantitative aspects of the oxidation of alcohols to aldehydes/ketones has been extensively reported but literature survey shows few reports on the kinetic andthermodynamic studies of the oxidation of alcohols[1-5].

We have studied the kinetics of oxidation of some industrially important alcohols and phenols using a variety of organic and inorganic oxidants[6-11].This paper reports the kinetics of oxidation of the industrially important secondary cyclic alcohols, Cyclopentanol, Cyclohexanol and Cyclooctanol using $K_2S_2O_8$ in acidic medium. The effects of alcohol and oxidant concentrations and temperature (303-318K)on the oxidation rates of the cyclic alcohols have been studied in detail. From the variation of oxidation rate with temperature,the thermodynamic activation parameters have been evaluated.

The experimentally observed sequence of oxidation rates of the cyclic alcohols has been explained on the basis of their ring size and other structural features. A suitable reaction mechanism has been suggested for the oxidation of the secondary cyclic alcohols under investigated.

MATERIALS AND METHODS

The cyclic alcohols were procured from E.Merck,Suhuchalt,Germany and used as received. All other chemicals used were of Analytical AR grade.The oxidation was studiedunder firstorder kinetic conditions with respect to the oxidant. The unreacted oxidant was estimated iodometrically at regular time intervals during the course of the reaction. Aliquots of the reaction mixture were withdrawn, quenched using ice and titrated against standard $Na_2S_2O_3$ using starch as indicator.The first order rate constants (k) were determined from the linear plots of log(a-x) versus time.

The oxidation was studied in the temperature range 303-318K and the Energy of activation (E) and other thermodynamic activation parameters were determined from the Arrhenius plots of

log k versus 1/T.

RESULTS AND DISCUSSION

The secondary cyclic alcohols were oxidized to the corresponding ketones by $K_2S_2O_8$ in acidic medium. For all the alcohols studied,the oxidation rate increased with [alc.] but decreased with [oxidant] (Table1, Fig.1).

Reaction mechanism of oxidation of secondary cyclic alcohols

In acidic medium,$K_2S_2O_8$ forms $H_2S_2O_8$ which is a strong acid and strong oxidant [12,13].

For secondary alcohols,the oxidation reaction can be shown as:

RR'CHOH   + $H_2S_2O_8$ ------------$\rightarrow$ RR'C=O   +   2 H_2SO_4
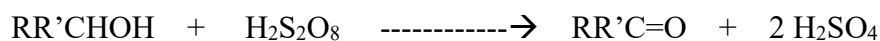
The product of the reaction ie ketone was identified by 2,4-dinitrophenylhydrozone test and further confirmed by TLC.

Sequence of oxidation rates of cyclic alcohols:

Cyclooctanol > Cyclopentano l> Cyclohexanol   (Table1,Fig.1)
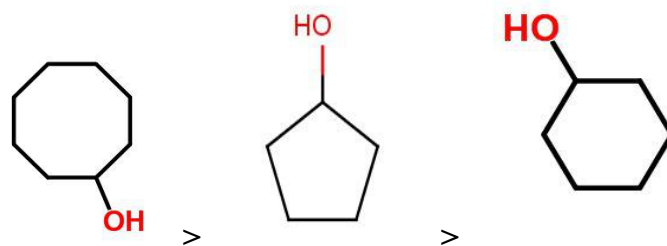
5, 7 and 8 membered rings in cyclic alcohols are more reactive than six membered rings (as in Cyclohexanol)[7,14-16]. This is as per the expectation from a change from a tetrahedral arrangement to a trigonal one abutting the reacting carbon atom.This trend is seen in the sequence of oxidation rates of the cyclic alcohols under study.

Effect of temperature on oxidation rates of secondary cyclic alcohols

The oxidation of alcohols was studied in the temperature range 303-318K. The Energy of activation (E) and other thermodynamic activation parameters were determined from the Arrhenius plots of log k versus 1/T (Tables 2a,2b and 2c).For all the alcohols studied, the entropy of activation $\Delta S^*$is almost constant at all temperatures indicating that the site of oxidation remains the same at all temperatures. The negative values of entropy of activation indicate a decrease in the degrees of freedom of the reacting system due to the formation of a rigid activated complex as a transient intermediate during the course of the reaction.The orientation of solvent molecules around the activated complex also contributes to decrease of entropy [17.18].The decrease of entropy is thus due to the curtailment of the vibrational and rotational motions of the reacting molecules.

Conclusions

1)   The oxidation rates of the secondary cyclic alcohols follow the sequence:
Cyclooctanol > Cyclopentanol > Cyclohexanol

2)   The equilibrium constant K* for the formation of the activated complex from reactants increases with temperature. Hence like rate constant k, K* is also a function of temperature.

3)   The oxidation of the cyclic alcohols results in decrease in entropy of activation.
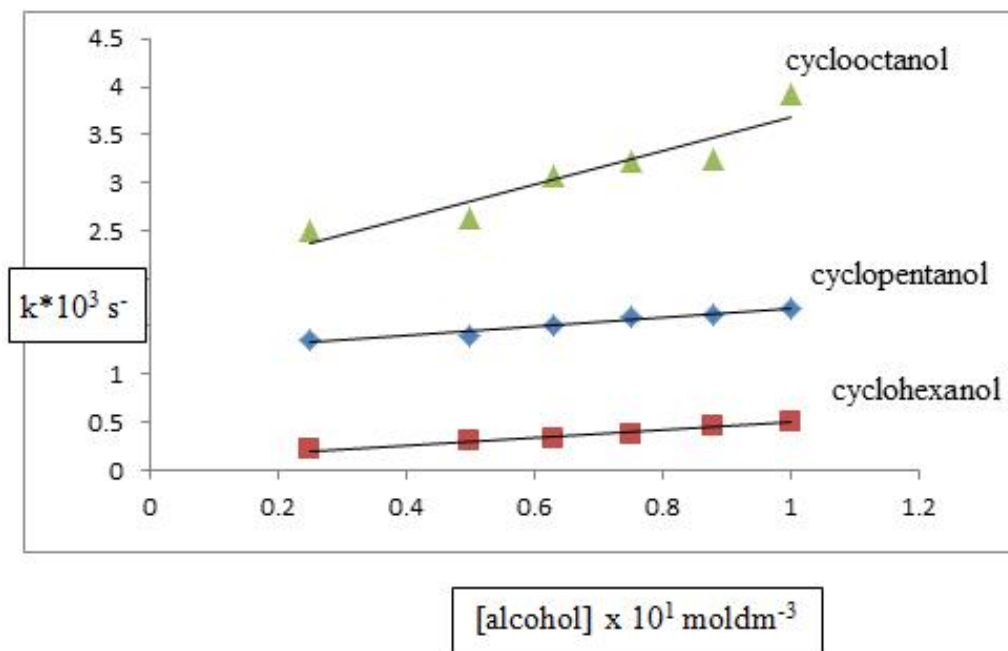
ACKNOWLEDGEMENTS

FIGURES AND TABLES

Fig.1 Variation of rate constant of oxidation with alcohol concentration

TABLE 1

RATE CONSTANT DATA FOR THE OXIDATION OF SECONDARY CYCLIC ALCOHOLS BY K2S2O8 IN ACIDIC MEDIUM

[H2SO4]=1M   Temp. 303K

[alcohol] x 10^1 moldm^{-3}	[$K_2S_2O_8$] x 10^3 moldm^{-3}	Cyclopentanol $k*10^3$ s^{-1}	Cyclohexanol $k*10^3$ s^{-1}	Cyclooctanol $k*10^3$ s^{-1}
1.00	2.50	-	-	-
1.00	5.00	4.10	-	-
1.00	10.00	3.59	-	-
1.00	15.00	3.39	0.55	2.65
1.00	20.00	3.16	0.46	1.93
1.00	25.00	2.97	0.20	1.79
0.25	5.00	1.36	0.21	2.50
0.50	5.00	1.40	0.30	2.63
0.63	5.00	1.52	0.32	3.06
0.75	5.00	1.59	0.37	3.22
0.88	5.00	1.61	0.46	3.25
1.00	5.00	1.68	0.51	3.92

TABLE 2a

THERMODYNAMIC ACTIVATION PARAMETERS Of THE OXIDATION OF CYCLOPENTANOL

BY K2S2O8 IN ACIDIC MEDIUM

[H2SO4] =1M

Temperature (K)	Rate const $k \times 10^3 s^{-1}$	E $kJ\ mol^{-1}$	$K^* \times 10^{16}$	ΔH^* $kJ\ mol^{-1}$	ΔG^* $kJ\ mol^{-1}$	ΔS^* $kJ\ K^{-1}\ mol^{-1}$
303	3.34	12.86	5.29	10.34	88.62	-0.2583
308	3.80	12.86	5.92	10.30	89.81	-0.2581
313	4.05	12.86	6.21	10.26	91.26	-0.2585
318	4.26	12.86	6.43	10.22	92.50	-0.2583

TABLE 2b

THERMODYNAMIC ACTIVATION PARAMETERS OF THE OXIDATION OF CYCLOHEXANOL

BY K2S2O8 IN ACIDIC MEDIUM

[H2SO4] =1M

Temperature (K)	Rate const $k \times 10^3 s^{-1}$	E $kJ\ mol^{-1}$	$K^* \times 10^{16}$	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	1.37	11.84	86.84	-0.2440
318	0.97	14.45	1.46	11.81	86.24	-0.2340

TABLE 2c

THERMODYNAMIC ACTIVATION PARAMETERS OF THE OXIDATION OF CYCLOOCTANOL

BY K2S2O8In ACIDIC MEDIUM

[H2SO4] =1M

Temperature (K)	Rate const $k \times 10^3 s^{-1}$	E $kJ\ mol^{-1}$	$K^* \times 10^{16}$	ΔH^* $kJ\ mol^{-1}$	ΔG^* $kJ\ mol^{-1}$	ΔS^* $kJ\ K^{-1}\ mol^{-1}$
303	3.25	16.96	5.14	14.42	88.69	-0.2452
308	3.38	16.96	5.28	14.38	90.10	-0.2452
313	3.68	16.96	5.65	14.34	91.37	-0.2460
318	4.49	16.96	6.78	14.30	92.36	-0.2450

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