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KINETIC AND THERMODYNAMIC INVESTIGATIONS OF THE OXIDATION OF SOME INDUCTRIALLY IMPORTANT SECONDARY CYCLIC ALCOHOLS BY CHLORAMINET IN ALKALINE MEDIUM

Harichandra. A. Parbat* and D. V.Prabhu.
Department of Chemistry, Wilson College (University of Mumbai, Mumbai 400007
Email: dvprabhu48@gmail.com

Abstract:
The oxidation of secondary cyclic alcohols, Cyclopentanol, Cyclohexanol and Cyclooctanol has been investigated using Sodium-N-chloro-p-toluenesulphonyamide (Chloramine T) in alkaline medium. Cyclopentanol is used in the manufacture of perfumes and pharmaceuticals and Cyclohexanol is an important feedstock in the manufacture of polymers especially nylons and plasticizers. Cyclooctanol is also used in the preparation of perfumes.The kinetics of oxidation of alcohols was studied under first order conditions with respect to the organic oxidant i.e. [CAT] << [alc.].The progress of oxidation was followed by iodometric estimation of the unreacted oxidant at regular time intervals during the course of the reaction.

The effects of alcohol concentration, oxidant concentration, temperature and ionic strength on the reaction rate have been studied and suitable reaction mechanisms and rate laws have been suggested. The thermodynamic activation parameters of the oxidation reaction have been evaluated from the temperature dependence of the oxidation rate on the range 303-318 K. The rate determining step of the oxidation reaction has been identified.

The rate laws suggest a first order dependence on alcohol and oxidant concentrations and inverse first order dependence on OH^- ions. The oxidation is retarded at higher concentrations of the oxidant.

The oxidation rates follow the sequence:Cyclopentanol > Cyclohexanol > Cyclooctanol The sequence have been discussed on the basis of the ring size,structures and isomeric characteristics of the alcohols under study.

Keywords: *secondary cyclic alcohols, oxidation, kinetics, rate determining step, retardation of reaction, ionic strength,energy of activation, entropy of activation.*

*Corresponding Author:
Harichandra. A. Parbat*,
Department of Chemistry,
Wilson College (University of Mumbai,
Mumbai 400007
Email: dvprabhu48@gmail.com

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INTRODUCTON:

The quantitative oxidation of alcohols to the corresponding carbonyl compounds has been exhaustively reported [1-7] but there are relatively few reports of the kinetic and thermodynamic investigations [8-16] of oxidation of alcohols. This paper deals with the kinetic and thermodynamic studies of the controlled oxidation of the secondary cyclic alcohols, Cyclopentanol, Cyclohexanol and Cyclooctanol which are widely used in the perfumery industry. The oxidation was carried out using a mild oxidizing agent; Sodium N-chloro-p-toluenesulphonylamide (Chloramine-T) in NaOH. The oxidation of cyclic alcohols was studied in the temperature range 303 - 318 K to evaluate the thermodynamic activation parameters. K_2SO_4 was used to study the effect of ionic strength on the oxidation rate in dilute solution.

EXPERIMENTAL:

High purity perfumery alcohols were used (S. H. Kelkar and Co.,E. Merck and Co. and Cetex Petrochemicals). AR Grade chemicals and reagents were used throughout: Sodium N-chloro-p-toluenesulphonylamide (Fluka Chemicals), Sodium dodecyl sulphate, and K_2SO_4 (S.D. Fine Chem.)
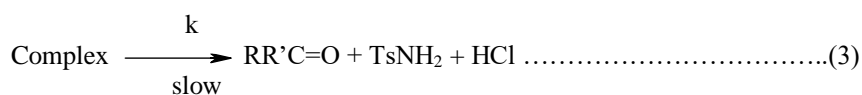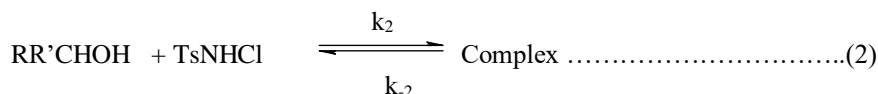
The reaction was studied under first order kinetic conditions with respect to the oxidant. The progress of the reaction was monitored titrimetrically. The solutions of alcohol and oxidant in required amounts were allowed to equilibrate in a thermostat regulated to within +/- 0.1^0C. On attaining temperature equilibrium, the solutions were mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular time intervals and the reaction was quenched using ice. The unreacted oxidant was treated with ice cold 10% KI and dilutes 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 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 (μ) on the oxidation rate in the range μ = 0.5 to 2.5 x 10^{-1} mol dm^{-3} in accordance with the Bronsted-Bjerrum equation, $\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$.

RESULTS AND DISCUSSION:

The secondary cyclic alcohols were oxidized to the corresponding ketones by Chloramine T (CAT) in NaOH. .

Effect of alcohol and oxidant concentration on oxidation rate of alcohols

For all the alcohols under study, the rate constant increased with alcohol concentration as expected but decreased with increase in concentration of Chloramine T . (Tables 1)

Reaction Mechanism of oxidation and rate law equation

In aqueous medium, Chloramine-T (Ts $NCl^- Na^+$) where the tosyl group Ts = H_3C-C_6H_5-SO_2- '
acts as a strong electrolyte and ionizes as follows:

$$\text{Ts } NCl^- Na^+ \longrightarrow \text{Ts } NCl^- + Na^+$$

In alkaline medium, the mechanism suggested is as follows:

$$\text{Ts } NCl^- + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Ts } NHCl + OH^{-1} \dots\dots\dots\dots\dots\dots\dots (1)$$

For a secondary alcohol,

$$RR'CHOH + TsNHCl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex} \dots\dots\dots\dots\dots\dots\dots..(2)$$

$$\text{Complex} \overset{k}{\underset{slow}{\longrightarrow}} RR'C{=}O + TsNH_2 + HCl \dots\dots\dots\dots\dots\dots\dots..(3)$$

.
The product of the reaction, i.e. ketone was identified by 2, 4-dinitrophenylhydrazone test and confirmed by TLC technique.

Applying steady state treatment to steps 1, 2 and 3, we get,

$$[Ts \ NHCl] = \frac{K_1 [TsNCl^-]}{[OH^-]}$$

and

$$[Complex] = \frac{k_2 [Alc][TsNHCl]}{[k_{-2} + k]}$$

$$= \frac{K_1 k_2 [Alc] [TsNCl^-]}{[k_{-2} + k] [OH^-]}$$

Step 3 determines the rate of oxidation hence the rate law equation is as follows:

$$\frac{d \ [Complex]}{dt} = k[Complex]$$

$$= \frac{k \ K_1.k_2. \ [Alc][TsNCl^-]}{[k_{-2} + k] [OH^-]}$$

$$= \frac{k' [Alc] [TsNCl^-]}{[OH^-]}$$

$$\text{where } k' = \frac{k \ K_1 k_2}{[k_{-2} + k]}$$

The rate law equation indicates the first order dependence on alcohol and oxidizing agent and an inverse first order dependence with respect to OH^- ions. A retarding influence of OH^- ions on the oxidation rate has been observed in many reactions involving Chloramine T [17]. This is attributed to the formation of the conjugate acid, $TsNCl^-$. The inverse dependence of oxidation rate on $[OH^-]$ indicates that Ts NHCl is the predominant oxidizing species in alkaline medium [18]. This explains the decrease of oxidation rate with increase in CAT concentration.

The oxidation rates follow the sequences:
Cyclopentanol > Cyclohexanol > Cyclootanol (Table 1, Figure 1).It is generally observed that 5,7 and 8 membered rings in cyclic alcohols are more reactive than six membered rings [19-22]. This trend is seen in the oxidation of the cyclic alcohols studied.

Effect of ionic strength on oxidation rate of alcohols:

The effect of ionic strength on the reaction rate was studied in dilute solution using K_2SO_4 in the range μ = 0.5 to 2.5 x 10^{-1} mol dm^{-3} at 313K (Table 2).. The graphs of log k vs. $\sqrt{\mu}$ were found to be straight lines parallel to the $\sqrt{\mu}$ axis, indicating that the oxidation rate is independent of ionic strength (Figure 2). This observation is borne out by the reaction mechanism and rate law suggested for the oxidation process.

Effect of temperature on oxidation rate of alcohols:
The reaction was studied in the temperature range 303 to 318K and the thermodynamic activation parameters were calculated.(Table3). The negative values of ΔS^* indicate an extensive reorientation of the solvent molecules as a result of the formation of a rigid activated complex [23] and can perhaps be explained by a model in which the water molecules are tightly held to the -OH bond which is the site of oxidation of the alcohols . The decrease in entropy is thus due to decrease in the vibrational and rotational motions of the reaction system.

Table 1.Rate constant data for the oxidation of secondary cyclic alcohols by Chloramine T (in NaOH)
[NaOH] = 5 x10^{-2}M,   Temperature = 303 K

[alc]x 10^1 mol dm^{-3}	[CAT] x 10^3 mol dm^{-3}	k x 10^4 s^{-1}		
		Cyclopentanol	Cyclohexanol	Cyclooctanol
1.00	2.50	9.88	7.88	5.58
1.00	5.00	9.34	5.84	4.47
1.00	10.00	4.51	3.52	3.13
1.00	15.00	2.36	1.69	2.33
1.00	20.00	2.13	1.60	2.12
1.00	25.00	1.73	1.46	3.25
0.25	5.00	2.45	2.27	1.18
0.50	5.00	6.37	5.38	2.05
0.625	5.00	7.00	6.04	3.10
0.75	5.00	8.70	7.30	4.22
0.875	5.00	9.90	8.24	5.38
1.00	5.00	10.10	8.90	5.88

Table 2.Effect of Ionic Strength on the oxidation rates of secondary cyclic alcohols by Chloramine T (in NaOH) [Alc] = 0.1 M, [NaOH] = 2.5 x10^{-2}M, [CAT] = 2.5 x10^{-3} M , Temperature = 313 K

μ x10^2 mol dm^{-3}	k x 10^4 s^{-1}		
	Cyclopentanol	Cyclohexanol	Cyclooctanol
Zero	9.88	7.88	5.58
05.00	9.74	7.84	5.47
10.00	9.51	7.72	5.53
15.00	9.56	7.69	5.53
20.00	9.63	7.60	5.42
25.00	9.73	7.76	5.65

Table 3.Thermodynamic activation parameters for the oxidation of secondary cyclic alcohols by CAT (in NaOH)

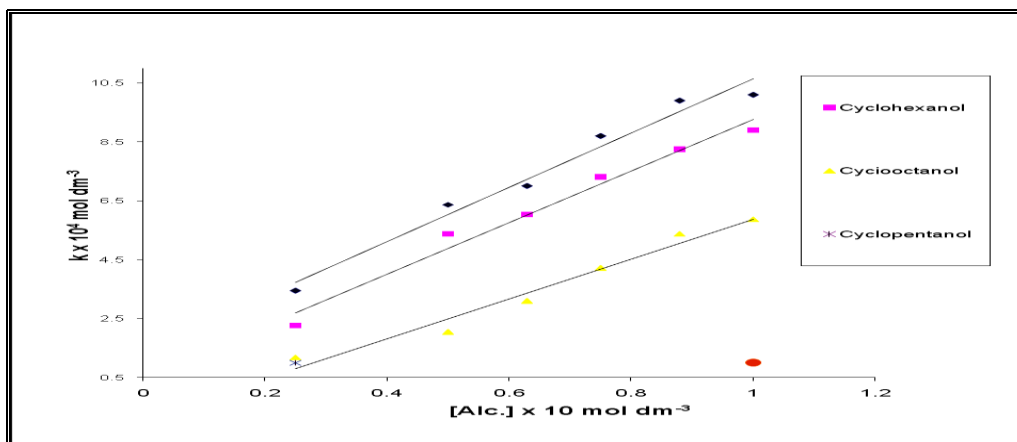| Temperature (K)	k x 10^4 s^{-1}	E kJ mol^{-1}	K* x 10^{17}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ K^{-1} mol^{-1}
Cyclopentanol						
303	6.25	51.63	9.9	49.06	95.87	-0.1521
308	6.58	51.63	10.3	48.72	95.79	-0.1520
313	6.98	51.63	10.7	48.69	95.71	-0.1519
318	7.14	51.63	10.6	48.65	97.66	-0.1518
Cyclohexanol						
303	2.77	52.92	4.68	50.35	93.05	-0.1486
308	3.68	52.92	6.56	50.24	94.44	-0.1485
313	5.68	52.92	7.89	50.13	95.83	-0.1485
318	7.02	52.92	9.90	50.10	97.26	-0.1484
Cyclooctanol						
303	1.18	83.98	1.87	81.46	97.05	-0.0514
308	2.77	83.98	4.32	81.41	96.50	-0.0489
313	3.68	83.98	5.64	81.37	97.37	-0.0511
318	5.70	83.98	8.61	81.31	97.81	-0.0518

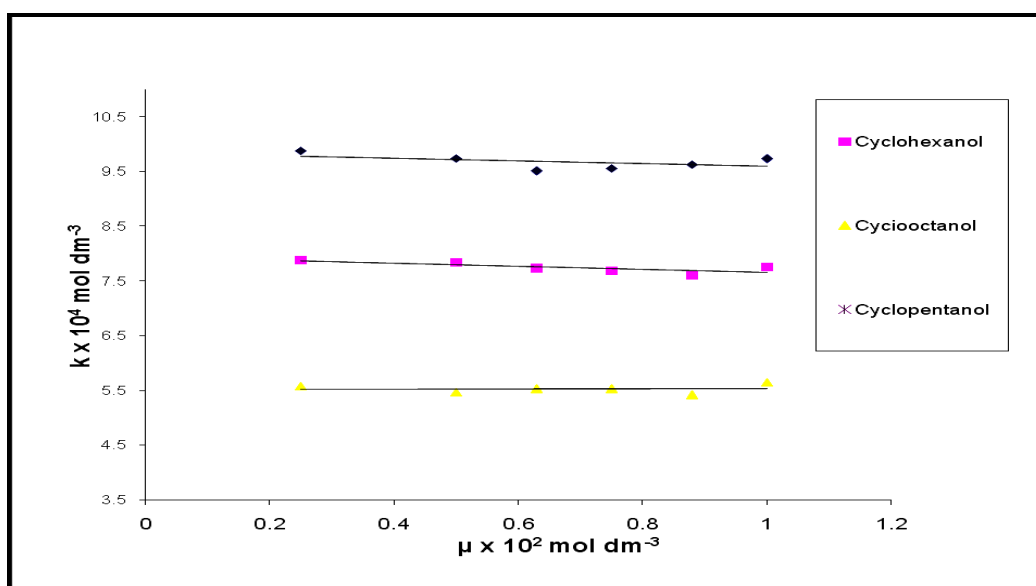**Fig.. 1: Variation of rate constants of oxidation of secondary cyclic alcohols with [alc.]**

Fig. 2:Effect of Ionic strength on the rate constant of oxidation of secondary cyclic alcohols by CAT.

REFERENCES:

1.E.J.Corey and J.W.Suggs, Tetrahedron Lett., 2675(1975).

2.E.J.Corey and D.L.Bayer, Tetrahedron Lett., 240(1978).

3.J.C.Collins and W.W.Hess, Organic Synth., 5,42(1972).

4.E.J. Corey and G.Schmidt,Tetrahedron Lett., 399(1979).

5.F.S.Guizec and F.A.Luzziv,Synthesis, 691(1980)

6.G.Piancatelli,A.Scettri and M.D'Auria , Synthesis 245(1982)

7.V.M.Deshpande, N.B.Laxmeshwar and D.V.Prabhu
 Proceedings of International Conference of Chemistry (Indian Chemical Society),

December1999, Kolkatta, India, B-14

8.P.K.Choudhary , P.K.Sharma and K.K.Banerji Intl. J. Chem.Kinetics, 1979;31:469.

9.K.K.Banerji , J.Chem Soc., Perkin Trans.,1985;2: 547.

10.K.K.Banerji   .et   al.,J.Indian   Chem Soc.,1998;75,,42.

11.K.Das Asim, J.Indian Chem Soc.,2000;77:225.
P.K.Sharma and Manju Baghmar , Proc. Indian Acad. Sci,(Chem. Sci.),2001;113:139.

12.D.V.Prabhu , J Ind. Chem. Soc.,2007;84:1135.

13.D.V.Prabhu , Asian J.Chem,2008;20(2):1186.

14.D.V.Prabhu, Asian J.Chem. 2008;20(3):1886.

15.D.V.Prabhu, Proceedings of Third International Congress of Chemistry and Environment. (Research

Journal of Chemistry and Environment and Kuwait Society of Engineers), November, 2007, Kuwait City. pp 126-132.

16.Puttaswamy, J.Ind. Chem.Soc.,1999; 76:438.

17.T.Demappa and S.Ananda , Asian J.Chem.1999;11(2):377.

18.H.C.Brown and H.Herstein, J Am.Chem. Soc.,1952;74:2929.

19.H. G. Kuivila and B.T.Becker, J.Am,Chem.Soc., 1952;74:5329.

20.H. C. Brown,R.S.Fletcherand and B.Johannesen, J.Am.Chem.Soc.,1957; 79:212.

21.D.V.Prabhu, Oriental Journal of Chemistry,2008;24(1):163.

22.G.L.Eichhorn and I.M.Trachtenberg, J.Am.Chem.Soc.,1952;76:5185.