Kinetic and reaction mechanism of the oxidation of some cyclic alcohols in the micellar phase using chloramine T in alkaline medium

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ABSTRACT

The kinetics of oxidation cyclopentanol, cyclohexanol and cyclooctanol using Chloramine T in NaOH has been studied in the micellar phase using sodium dodecyl sulphate in the temperature range 30°C to 50°C to correlate the oxidation rate with the ring size of the cyclic alcohols.

The effect of alcohol concentration, concentration of oxidising agent, ionic strength and temperature on the oxidation rate have been studied in detail.
The oxidation rates follow the sequence:
Cyclooctanol > Cyclopentanol > Cyclohexanol,

A suitable reaction mechanism has been suggested for the oxidation of the cyclic alcohols under study. From the effect of temperature on reaction rate the thermodynamic activation parameters have been evaluated

Key words: Cyclic alcohols, oxidation, chloramine T, micellar phase.

INTRODUCTION

The oxidation of alcohols is an industrially important reaction. The quantitative aspects of the oxidation of alcohols to carbonyl compounds have been extensively studied[1-7] but there are relatively few reports in literature on the kinetics study of oxidation of alcohols. The study of reaction kinetics in invaluable for.

1. Determining the reaction mechanism and rate law equation and
2. Suggesting modifications in experimental conditions of ensure better yield of the products.

We report herein the kinetics of oxidation of Cyclopentanol, Cyclohexanol and Cyclooctanol using Chloramine T (in NaOH) in order to study the effect of ring size on oxidation rate. All the data has been collated and a suitable reaction mechanism has been suggested.

EXPERIMENTAL

All the chemicals and reagents used were of A.R. Grade-Cyclopentanol, Cyclohexanol and Cyclooctanol (E Merck Schuchadt) Chloramine T (Fluka Chemicals) and Sodium dodecyl sulphate (Loab Chemie). AR Grade KCl was used study the effect of ionic strength on the reaction rate.

The oxidation of the cyclic alcohols was studied under pseudounimolecular conditions and its progress was monitored titrimetrically. The solutions of alcohol and oxidising 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 initiate the reaction. Aliquots of the reaction mixture were withdrawn at regular intervals and the reaction was arrested using ice. The unreacted Chloramine T 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 towards the end.

The reaction was studied in the temperature range 30°C to 50°C under pseudounimolecular conditions with respect to the oxidising agent. The plots of log (a-x) vs. time were found to be straight lines and the pseudo first order rate constants were calculated from the slopes of the graphs. From the Arrhenius plots of log k vs1/T, the energy of activation and other thermodynamic activation parameters K*,ΔH*, ΔG* and ΔS* were calculated. The effect of ionic strength (μ) on the oxidation rate was studied in dilute solution in the range μ=0.1M to 0.5M using KCl.

RESULTS AND DISCUSSION

The secondary alcohols, Cyclopentanol (A), Cyclohexanol (B) and Cyclooctanol (C) were oxidised using Chloramine T (in NaOH) in micellar phase using Sodium dodecyl sulphate (SDS).

Effect of alcohol concentration and oxidising agent concentration rate

The rate constant increases with alcohol concentration as expected but decreases as the concentration of Chloramine T increases (Table 1).

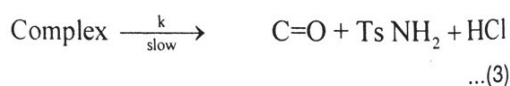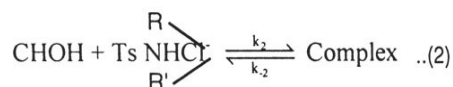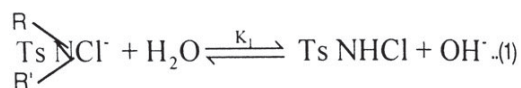### Reaction mechanism of oxidation and rate law equation

In aqueous medium, Chloramine T (Ts. NCl^- Na^+) acts as strong electrolyte and ionises as follows.

$$Ts\ NCl^-\ Na^+ \rightarrow Ts\ NCl^-\ Na^+$$

Where

$$Ts = [H_3C\text{-}C_6H_5\text{-}SO_2]$$
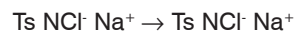
In alkaline medium, the mechanism suggested is as follows.

$$\underset{R'}{\overset{R}{\diagdown}}Ts\ NCl^- + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} Ts\ NHCl + OH^- \quad ..(1)$$

$$CHOH + Ts\ NHCl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Complex \quad ..(2)$$

$$Complex \xrightarrow[slow]{k} C{=}O + Ts\ NH_2 + HCl \quad ...(3)$$

Table 1: Rate constant data for the oxidation of Cyclopentanol (A), Cyclohexanol (B) and Cyclooctanol (C) by Chloramine T (in NaOH) [Na OH]=0.05M, [SDS] = 0.05 M, Temp = 303 K

[Alc] × 10² mol dm⁻³	[Ox] × 10² mol dm⁻³	k × 10⁴ s⁻¹ A	B	C
10.00	0.25	4.36	1.51	5.82
10.00	0.50	4.20	1.18	3.87
10.00	1.00	5.53	3.45	5.70
10.00	1.50	4.50	1.54	5.25
10.00	2.00	3.58	0.99	4.93
10.00	2.50	2.96	0.63	4.39
2.50	0.50	1.73	0.88	1.88
5.00	0.50	2.55	1.32	3.07
6.25	0.50	3.89	1.50	3.75
7.50	0.50	3.92	1.60	4.38
8.75	0.50	4.52	1.70	5.02
10.00	0.50	5.05	1.83	5.70

The product of the reaction i.e. ketone was identified by 2,4 dinitrophenyl hydrazone test and confirmed by tlc.

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

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

$$and\,[complex] = \frac{k_2\,[Alc]\,[Ts\,NHCl]}{[k_{-2} + k]}$$

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

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

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

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

$$= \frac{k'\,[Alc]\,[Ts\,NCl^-]}{[OH^-]}$$

where

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

The rate law equation indicates as first order dependence on alcohol and oxidising agent and an inverse first order dependence with respect to OH⁻ ions on the oxidation rate has been observed in several reactions involving Chloramine T (in NaOH)[8]. This is attributed to the formation of the conjugate acid. Ts NCl⁻. Thus the inverse dependence of oxidation (OH⁻) indicates that Ts. NHCl is the predominant oxidising species in alkaline medium[9]. 5,7 and 8 membered rings in cyclic alcohols are more reactive than six membered rings (as in cyclohexanol)[10-12]. This is in accordance with the normal expectation from a change from the tetrahedral to trigonal arrangement abutting the reaching carbon atom. This trend is seen in the sequence of oxidation rates of the cyclic alcohols under study viz.
Cydooctanol > Cyclopentanol > Cyclohexanol (Table 1)

Effect ionic strength

The effect of ionic strength (μ) on the oxidation rate of the cyclic alcohols was studied in dilute solutions using KCl in the range $\mu = 0.1$ to 0.5M at 40°C (Table 2). The graphs of log k vs μ were straight lines parallel to the μ axis indicating that the oxidation rate was independent of ionic strength.

Table 2: Effect of ionic strength on the oxidation rate of Cyclopentanol (A), Cyclohexanol (B) and Cyclooctanol (C) [Alc] = 0.1M, [Ox] = 0.01M [NaOH] = 0.025 M, [SDS] = 0.05M, Temp = 313 K

μ mol. dm⁻³	$k \times 10^4 s^{-1}$		
	A	**B**	**C**
Zero	5.73	4.37	6.65
0.1	4.86	3.95	6.90
0.2	4.65	3.51	7.93
0.3	4.88	3.95	7.52
0.4	5.18	3.59	6.13
0.5	4.90	3.42	7.55

Effect of temperature

The reaction was studied in the temperature range 30° to 50°C and the thermodynamic activation parameters were calculated. The negative values of ΔS^* (-0.2425 kJ K⁻¹ mol⁻¹ for A, - 0.2559 kJ K⁻¹ mol⁻¹ for B and (-0.2483 kJ K⁻¹ mol⁻¹ for C). Indicates an extensive reorientation of solvent molecules as a result of the formation of the activated complex[13] 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.

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