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Comparative Study of the Oxidation of 1-Hexanol and Cyclohexanol by Chloramine B in Acidic Medium

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The kinetics of oxidation of 1-hexanol and cyclohexanol to the corresponding carbonyl compounds by Chloramine B in HCl has been studied in the micellar phase using sodium lauryl sulphate in the temperature range 30-50 ºC. The oxidation rate increases with alcohol concentration but decreases with the concentration of Chloramine B. From the effect of temperature on oxidation rate, the themodynamic activation parameters have been calculated. The negative values of ΔS^* indicate the reorientation of solvent molecules around the rigid activated complex formed during the course of the reaction. Ni(II), Cu(II) and Zn(II) have been used as effective catalysts for the oxidation of the alcohols under study. Suitable reaction mechanism have been suggested for the oxidation of the alcohols in the presence and absence of metal ions. The oxidation rates follows the sequence 1-hexanol > cyclohexanol.

Key Words: Oxidation, 1-Hexanol, Cyclohexanol, Chloramine B.

INTRODUCTION

The quantitative aspect of oxidation of a variety of alcohols has been studied in detail in this laboratory[1,2]. In the present study, the kinetics and reaction mechanism of oxidation of 1-hexanol and cyclohexanol by Chlormine B (in HCI) in the presence and absence of Ni(II), Cu (II) and Zn(II) has been reported. The effect of alcohol concentration, concentration of oxidising agent and temperature on the oxidation rate has been studied. The oxidation rates follow the sequence 1-hexanol > cyclohexanol. The rate law equation suggests a first order dependence on alcohol, oxidant and acid. The thermodynamic activation parameters have been evaluated from the effect of temperature on the oxidation rate.

EXPERIMENTAL

AR grade chemicals and reagents were used, 1-hexanol and cyclohexanol (E-Merck), chloramine B (CAB) (Fluka Chemicals) sodium lauryl sulphate (SLS) (Lobo Chemie). All metal salts required for the catalytic study of oxidation of alcohols were of AnalR Grade (B.D.H.).

The oxidation of the alcohols was studied under pseudo unimolecular conditions with respect to the oxidizing agent. The solutions of alcohol and oxidizing agent were allowed to equilibrate in a previously adjusted thermostat (accuracy ± 0.1 ºC). After the attainment of temperature equilibrium, the solutions were mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular intervals and the reaction was arrested using ice. The unreacted chloramine B 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 30-50 ºC. The pseudo first order rate constants were evaluated from the linear plots of log (a-x) *vs.* time. The energy of activation was calculated from the Arrhenius plots of log k *vs.* 1/T. From the effect of temperature on reaction rate, the themodynamic activation parameters. PZ, K*, ΔH*, ΔG* and ΔS* were calculated.

A similar procedure was used to study the catalytic effect of metal ions on the oxidation rate in the concentration range [M(II)] = 0.5 to 2.5 × 10^{-3} mol dm^{-3} at 30 ºC. The plots of log (a-x) *vs.* time were found to be straight lines and the rate constants were determined from the slopes of these linear plots.

RESULTS AND DISCUSSION

Chloramine B (in HCl) oxidizes 1-hexanol to 1-hexanal and cyclohexanol to cyclohexanone.

Effect of alcohol concentration and oxidant concentratiom on reaction rate: The rate constant increases with alcohol concentration as expected but decreases as the concentration of chloramine B increases (Table 1).

Reaction mechanism of oxidation and rate law equation: In aqueous medium, chloramine B ($RNCl^- Na^+$) acts as a strong electrolyte and ionizes as follows:

$$RNCl^- Na^+ \longrightarrow RNCl^- + Na^+ \quad \text{where } R = [C_6H_5\text{-}SO_2]$$

In acidic medium, the mechanism suggested is as follows:

$$RNCl^- + H^+ \xrightleftharpoons{K_1} RNHCl \qquad (1)$$

RNHCI is the predominant oxidizing species in the acidic medium

$$RCH_2OH + RNHCl \xrightleftharpoons[k_{-2}]{k_2} \text{Complex} \qquad (2)$$

$$\text{Complex} \xrightleftharpoons[\text{Slow}]{k} RCHO + RNH_2 + HCl \qquad (3)$$

In the case of a secondary alcohol, the corresponding ketone is produced. The product of oxidation *i.e.* aldehyde or ketone was identified by 2,4-dinitrophenyl hydrozone test and confirmed by TLC.

TABLE-1
RATE CONSTANT DATA FOR THE OXIDATION OF 1-HEXANOL AND CYCLOHEXANOL BY CHLORAMINE B (IN HCl)
[HCl] = 0.1 M, [SLS] = 0.05 M, Temp. = 303 K

[Alc] × 10^1 (mol dm^{-3})	[CAB] × 10^3 (mol dm^{-3})	k × 10^5 (s^{-1})	
		1-Hexanol	Cyclohexanol
1.000	1.00	30.70	22.10
1.000	2.00	37.60	13.10
1.000	3.00	20.60	7.80
1.000	4.00	11.70	5.00
1.000	5.00	6.20	4.60
0.250	1.00	14.80	12.30
0.500	1.00	23.00	15.10
0.625	1.00	24.60	21.10
0.750	1.00	29.80	24.60
0.875	1.00	30.70	22.10
1.000	1.00	34.00	16.00

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

$$[RNHCl] = K_1[RNCl^-]\,[H^+]$$

$$\text{and [complex]} = \frac{k_2[Alc][RNHCl]}{[k_{-2}+k]}$$

$$= \frac{K_1k_2[Alc][RNCl^-][H^+]}{[k_{-2}+k]}$$

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

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

$$= \frac{kK_1k_2[Alc][RNCl^-][H^+]}{[k_{-2}+k]}$$

$$= K^1\,[Alc]\,[RNCl^-]\,[H^+]$$

$$\text{where } K^1 = \frac{K_1kk_2}{[k_{-2}+k]}$$

Thus the rate law equation indicates a first order dependance on alcohol, Chloramine B and acid. The decrease of oxidation rate with increase in chloramine B concentration (Table-1) is due to the retardation of the protonation of $RNCl^-$ at high [CAB]. The SO_2 group in CAB is an electron withdrawing group and makes nitrogen less basic. This hinders the protonation of $RNCl^-$ resulting in the decreasing of oxidising rate with increasing [CAB]. The oxidation rates of the alcohols under study follow the sequence 1-hexanol > cyclohexanol.

Effect of temperature on oxidation rate: The reaction was studied in the temperature range 30-50 ºC. The negative value of ΔS^* (-0.1801 kJ K^{-1} mol^{-1} for 1-hexanol and -0.1348 kJ K^{-1} mol^{-1} for cyclohexanol) indicate a decrease in the degrees of freedom due to the formation of a rigid activation complex resulting in an extensive reorientation of solvent molecules. The negative values of ΔS^* can be explained by a model in which the solvent molecules are hightly held to the -OH bond which is the site of oxidation[3].

Effect of metal ions on the oxidation rate: Metal ions *viz.*, Ni(II), Cu(II) and Zn(II) were used as catalysts in the concentration range [M(II)] = 0.5 to 2.5 × 10^{-3} mol dm^{-3} at 30 ºC. The rate constants of the catalyzed reaction are listed in Table-2 (1-hexanol) and Table-3 (cyclohexanol). It is observed that for each of the metal ion catalysts, the oxidation rate varies linearly with [M(II)] (Tables 2 and 3).

TABLE-2
RATE CONSTANT DATA FOR METAL ION CATALYZED OXIDATION OF I-HEXANOL BY CHLORAMINE B (IN HCl)
[Alc] = 0.1 M, [CAB] = 0.005 M, [SLS] = 0.05 M, [HCl] = 0.1 M, Temp. = 303 K

M(II) × 10^3 (mol dm^{-3})	k × 10^5 (s^{-1})		
	Ni(II)	Cu(II)	Zn(II)
In absence	12.40	12.40	12.40
0.50	13.40	18.40	23.00
1.00	15.30	20.10	25.10
1.50	23.00	20.90	25.50
2.00	24.00	26.30	29.40
2.50	27.00	27.70	30.30

The reaction mechanism proposed for the metal ion catalyzed oxidation of alcohols is as follows:

Chloramine B ($RNCl^-$ Na^+) acts as a strong elctroloyte in aqueous medium and ionizes as follows:

$$RNCl^- Na \longrightarrow RNCl^- + Na^+ \text{ where } R = [C_6H_5\text{-}SO_2]$$

In acidic medium,

$$RNCl^- + H^+ \xrightleftharpoons{K_1} RNCl \qquad (1)$$

RNHCI is the predominant oxidizing species in the acidic medium

$$RCH_2OH + M(II) \xrightleftharpoons{K_2} \underset{\text{Complex}}{(RCH_2OH)\ M(II)} \qquad (2)$$

$$\text{Complex} + \text{RNHCl} \underset{\text{Slow}}{\overset{k}{\rightleftharpoons}} \text{RCHO} + \text{RNH}_2 + \text{HCl} + \text{M(II)} \qquad (3)$$

In the case of a secondary alcohol, the corresponding ketone is produced.

The catalytic effect of transition metal ions is inversely proportional to the stablity of their complexes which may be formed as short lived intermediates during the course of reaction. The stability of the complexes generally depends on the charge density of the metal ion involved in addition to several other factors. Thus the stability order for the metal ions under study is expected to be Cu(II) > Zn(II) > Ni(II)[4-6] and their catalytic efficiency is expected to follow the sequence Ni(II) > Zn(II) > Cu(II). However such generalizations are only approximate guides to metal ion behaviour[7] and discrepancies have been observed and reported in the relative values of stability constants of complexes and catalytic efficiency of metal ions.

In the present investigation the catalytic efficiency follows the sequence. 1-hexanol: Zn(II) > Cu(II) > Ni(II); Cyclohexonal: Cu(II) > Zn(II) > Ni(II) (Tables 2 and 3).

TABLE-3
RATE CONSTANT DATA FOR METAL ION CATALYZED OXIDATION OF CYCLOHEXANOL BY CHLORAMINE B (IN HCl)
[Alc] = 0.1 M, [CAB] = 0.005 M, [SLS] = 0.05 M, [HCl] = 0.1 M, Temp. = 303 K

$M(II) \times 10^3$ (mol dm^{-3})	$k \times 10^5$ (s^{-1})		
	Ni(II)	Cu(II)	Zn(II)
In absence	14.49	14.49	14.49
0.50	14.70	18.00	15.90
1.00	15.00	20.72	16.69
1.50	15.35	21.10	19.80
2.00	16.80	21.75	20.15
2.50	17.91	22.40	21.87

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