KINETICS OF OXIDATION OF ALCOHOLS BY CHLOROPENTAMINE COBALT(III) CHLORIDE IN NaOH MEDIUM.
A MECHANISTIC STUDY

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Abstract:

Kinetics of alcohol oxidation by chloropentamine cobalt(III) chloride in NaOH medium was investigated. The rate was first order with respect to [oxidant] and [alcohol] and zero order in [OH^-]. Variation of ionic strength did not have any significant influence on the rate of oxidation, indicating that a non-ionic specie is involved in the rate limiting step. Addition of reaction mixture to aqueous acrylonitrile solution did not initiate polymerization, showing absence of free radicals. Michaelis-menten plot showed the presence of an intermediate complex. Oxidation products were identified from spectral studies and R_f values. Activation parameters were evaluated from the values obtained from temperature studies. Therefore, based on the kinetic results, reaction stoichiometry and oxidation products, a suitable mechanism was proposed.

Introduction:

Alcohols are generally weaker acid than water. Alcohols, most especially the primary and secondary alcohols have been oxidized by various researchers using different organic and inorganic oxidants like tripropylammonium fluorochromate [1], quinolinium bromochromate [2], hydrogen peroxide [3], Enneamolybdomanganate(IV) [4], hypervalent iodine [5], Benzimidazolium Fluorochromate [6], butyltriphenyl phosphonium dichromate[7], N-Bromoacetamide [8], quinolinium fluorochromate[9]. However, the kinetics of the oxidation of alcohols by chloropentamine cobalt(III) chloride has not been reported, hence the need for this study.

Experimental

Materials and Methods:

The reagents utilized were ethanol, propanol, butanol and isopropyl alcohol (all AR grade), sodium hydroxide and potassium nitrate (Both BDH (AR) grade). Chloropentamine cobalt(III) chloride was obtained from Aldrich chemical company.

Spectral measurement

The maximum absorption of the oxidant, $[Co(NH_3)_5Cl]Cl_2$ was reported to be 510nm. All kinetic studies were undertaken at this fixed wavelength.

Kinetic measurement

The rate of oxidation as a function of oxidant, substrate, ionic strength and temperature were studied using a uv-1800 Shimadzu spectrophotometer with a thermostated cell compartment and interfaced with a computer. Appropriate quantities of the solution of alcohol, potassium nitrate, sodium hydroxide were measured into the cuvette. Consequently, the reaction was kick started by adding requisite volume of the oxidant solution (All stock solutions were kept in the water bath for 30 minutes before the kinetic runs). The kinetic data were obtained via pseudo- first order condition with the concentration of the substrate in large excess compared with the oxidant concentration. The pseudo- first order rate constant (k_{obs}) were calculated from the plot of In(A_∞-A_t) versus time.

Product Analysis

The IR showed absorption at 1725 cm^{-1} and 2 weak bands at 2750 cm^{-1} and 2850 cm^{-1} which are attributed C=O and C-H stretching of aldehydes. The R_f obtained were within the range 2.5-3.0.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration under the conditions used for the kinetic study i.e large excess of alcohol over the oxidant. The stoichiometry was evaluated from plots of absorbance vs [alcohol] curve. Stoichiometry of the reaction was found to be 1:1, i.e one mole of substrate consumed one mole of the oxidant.

$$RCH_2OH + [Co(NH_3)_5Cl]Cl_2 \rightarrow RCHO + [Co(NH_3\ )_5Cl] + 2HCl$$

Result and Discussion:

Oxidation of alcohols like ethanol, propanol, butanol and isopropyl alcohol were carried out in alkaline chloropentaminecobalt(III) chloride solution via pseudo-first condition throughout the experiment.

Effect of varying [oxidant]

The effect of the oxidant concentration on the reaction was determined by monitoring the reaction at various initial oxidant concentrations. The linear plot of In(A_∞ - A_t) vs. time indicated a first order dependence on the oxidant. There was no appreciable change in k_{obs} with oxidant concentration (Table I).

Table I: Dependence of k_{obs} with [oxidant]

10^3[oxidant]/M	$10^3k_{obs}/s^{-1}$			
	Ethanol	Propanol	Butanol	Isopropylalcohol
0.80	1.95	1.91	1.37	0.168
1.00	2.14	1.93	1.35	0.168
1.50	2.00	1.88	1.35	0.162
2.00	2.11	1.91	1.36	0.169
2.50	2.12	1.92	1.38	0.166

[Alcohol] 3.00 x 10^{-2}M [OH^-] 1.00 x 10^{-2} M[KNO_3] 0.30M T= 298K

Effect of [substrate]

The effect of substrate concentration on the rate of oxidation was determined by varying the initial substrate concentration and keeping all other parameters constant. It was observed that the pseudo- first order rate constants, k_{obs} increases with increase in substrate concentration (Table II). However, values for the second order rate constants obtained from the slope of the plot of k_{obs} versus [S] were as follows: Ethanol 0.341$M^{-1}S^{-1}$;Propanol 0.315$M^{-1}S^{-1}$;Butanol 0.304$M^{-1}S^{-1}$; Isopropylalcohol 0.340 $M^{-1}S^{-1}$. The plot of Ink_{obs} vs. In[S] were found to be linear for all the substrates with slope 1, indicating a first order dependence with respect to the substrates. The linearity of a plot of Ink_{obs} vs. In[S] shows that the rate of reaction increases with substrate concentration, indicating that the complex formation took place between substrate and the oxidant. Micaelis-menton plot of 1/k_{obs} vs. 1/[S] gave an intercept, showing the presence of an intermediate complex(Fig.I).

Table II: Dependence of k_{obs} with [Alcohol]

10^2[Alcohol]/M	$10^3k_{obs}/s^{-1}$			
	Ethanol	Propanol	Butanol	Isopropylalcohol
2.00	0.54	0.67	0.67	0.067
4.00	1.37	1.18	1.24	0.15
5.00	1.72	1.63	1.64	0.173
6.00	1.98	1.88	1.72	0.205
7.00	2.36	2.23	2.20	0.236

[Co^{3+}] 1.50 x 10^{-3}M [NaOH] 1.00 X 10^{-2}M [KNO_3] 0.30M T= 298K

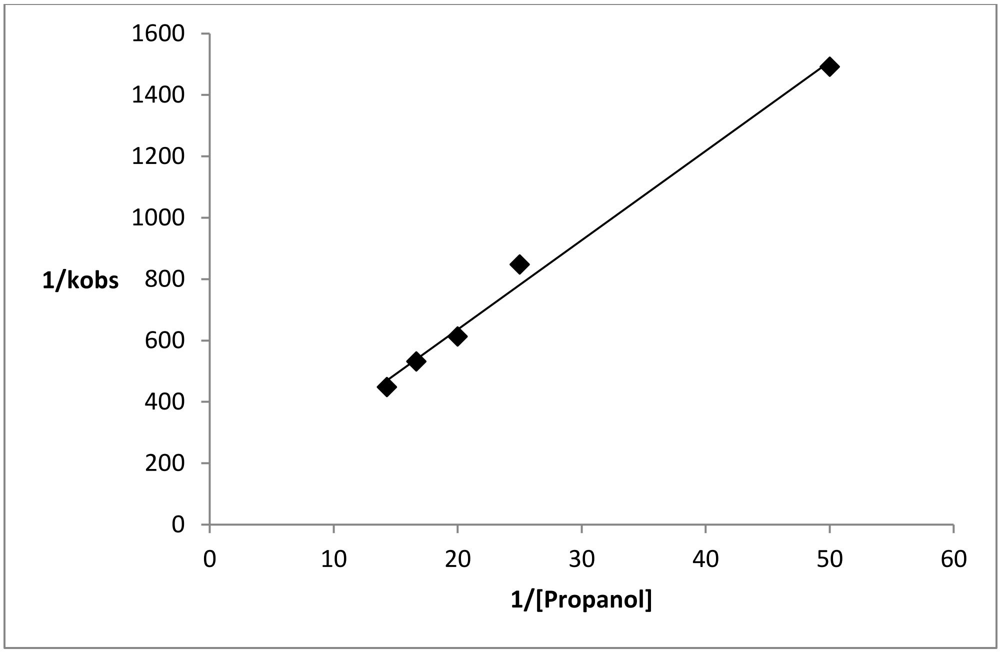

Fig.I: Plot of 1/kobs vs 1/[Propanol]

Effect of [OH$^-$]

Dependent study of [OH$^-$] on the rate of oxidation showed that the reaction was unaffected by [OH$^-$] as there was no significant change in the observed rate constant with [OH$^-$] for all the substrates (Table III). Plots of In k_{obs} vs. In[OH$^-$] showed a zero order dependence on [OH$^-$]. The zero order dependence has also been reported for the kinetic study of the oxidation of proranolol by sodium-N-chloro-p-Toluene sulphonamide in NaOH medium[10].

Table III: Dependence of k_{obs} with [OH$^-$]

10^2[OH$^-$]/M	10^3k_{obs}/s^{-1}			
	Ethanol	Propanol	Butanol	Isopropylalcohol
0.20	1.64	1.02	1.31	0.15
0.40	1.62	1.03	1.34	0.16
0.60	1.67	1.01	1.33	0.15
0.80	1.65	1.02	1.32	0.16
1.00	1.67	1.01	1.33	0.15

[Co^{3+}] 1.50 x 10^{-3}M [Alcohol] 4.00 x 10^{-2}M [KNO_3] 0.30M T= 298K

Effect of Ionic strength

The rate constants in the presence of KNO_3 was studied. There was no significant change in the observed rate constants with respect to [KNO_3]. This suggests that a non-ionic specie is involved in the rate limiting step as evident in the plot of In k_{obs} vs. $I^{1/2}$ (Fig.II).

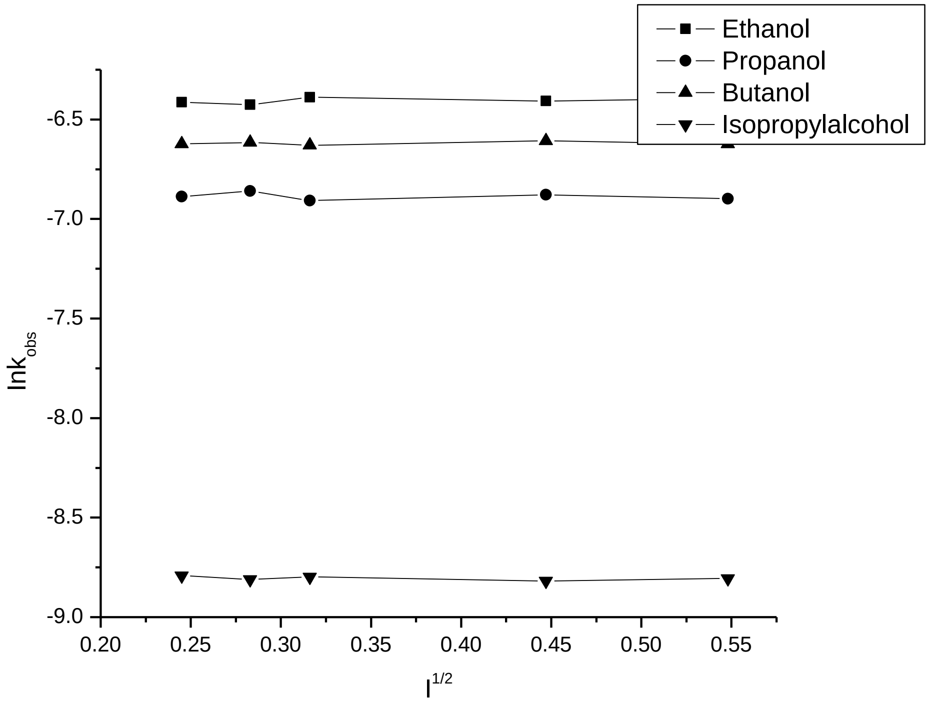

Fig.II: Plot of Ink$_{obs}$ vs. I$^{1/2}$

Effect of Temperature

Evaluation of various activation parameters were determined from the temperature dependent study by varying the temperature of the reaction medium within the range 298K-318K while the initial concentrations of all the reactants remained constant. The observed rate constant increased with increase in temperature. Plots of In k_{obs} vs. 1/T were linear and the activation parameters obtained are shown in Table IV. The thermodynamic parameters were obtained from the relationship[11]:

Table IV: Activation parameters

Alcohol	Ea(kJmol^{-1})	ΔH$^{\#}$(kJmol^{-1})	ΔS$^{\#}$(KJK^{-1}mol^{-1})	ΔG$^{\#}$(kJmol^{-1})
Ethanol	29.64	28.43	-0.19	207.08
Propanol	66.61	76.40	-0.05	207.08
Butanol	68.86	61.82	-0.18	207.16
Isopropylalcohol	64.75	60.29	-0.11	206.88

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$E_a = \Delta H^{\#} + RT$$

$$\Delta G^{\#} = 2.303RT(\log \frac{RT}{Nh} - \log k)$$

$$\Delta S^{\#} = 2.303R \log A - \log \frac{e^{RT}}{Nh}$$

Conclusion:

Mechanism and Rate Law:

The below mentioned kinetic and spectral results helped in the formulation of the mechanism:

(i) An alcohol is a weaker acid than water, an alkoxide is not prepared by the reaction of alcohol with sodium hydroxide, but rather by the reaction of alcohol with active metal [12].

(ii) The non-dependence of the oxidation reaction on ionic strength indicates the presence of a neutral molecule in the rate determining step.

(iii) Same values of $\Delta G^{\#}$ indicates same mechanism for the reaction and negative values of $\Delta S^{\#}$ revealed entropy decrease upon achieving the transition state, which often indicate an associative mechanism and it shows that the reaction occurred between ions of similar charges.

(iv) The IR spectrum of the product showed C=O stretching at 1725 cm^{-1} and two weak bands of C-H stretching at 2750 cm^{-1} and 2850 cm^{-1}, these can be attributed to the presence of aldehyde.

(v) Michaelis-menton plot showed the presence of an intermediate complex.

Therefore, the below mechanism was proposed based on the kinetic results and spectral analyses carried out.

$$RCH_2OH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCH_2O^- + H_2O$$

$$RCH_2OH + [Co(NH_3)_5Cl]Cl_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Complex \xrightarrow{k_3} RCHO + [Co(NH_3)_5Cl] + 2HCl$$

The rate law is given by:

$$[Alcohol]_T = [Alcohol] + [Alkoxide]$$

$$[Alcohol]_T = [Alcohol] + k_1[Alcohol][OH^-]$$

Since, alcohols are weaker acids than water, alkoxides are not likely to be formed in solution[12].

$$[Alcohol]_T = [Alcohol]$$

$$k_2[Alcohol][Co^{3+}] = (k_{-2} + k_3)[Complex]$$

$$[Complex] = \frac{k_2[Alcohol][Co^{3+}]}{(k_{-2} + k_3)}$$

$$Where\ K_2 = \frac{k_2}{k_{-2}}$$

k_3 *is negligible as* k_3 *is less than* k_{-2} *, dividing by* k_{-2} *we get*

$$[Co^{3+}]_T = [Co^{3+}] + [Complex]$$

$$= [Co^{3+}] + K_2[Alcohol][Co^{3+}]$$

$$= [Co^{3+}](1 + K_2[Alcohol]$$

$$[Co^{3+}] = \frac{[Co^{3+}]_T}{1 + K_2[Alcohol]}$$

$$[Complex] = \frac{K_2[Alcohol]_T[Co^{3+}]_T}{1 + K_2[Alcohol]_T}$$

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

$$Rate = \frac{-d[Co^{3+}]_T}{dt} = k_3[Complex]$$

$$Rate = \frac{k_3 k_2[Alcohol]_T[Co^{3+}]_T}{1 + K_2[Alcohol]_T}$$

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