



The Kinetics and Mechanism of Alcohol Oxidation in Alkaline 12-Tungstocobaltate (III)

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ABSTRACT

The kinetics of the oxidation of alcohol by 12-tungstocobaltate(III) in alkaline medium as a function of oxidant, alcohol, OH^- , ionic strength and temperature were studied spectrophotometrically at λ_{max} 624nm under pseudo first order conditions. The kinetic study showed first order dependence on $[\text{CoIIIW12}]$, $[\text{Alcohol}]$ and $[\text{OH}^-]$. Ionic strength effect on the reaction showed that the charges on the ions at the rate determining step are opposite and the reaction between alcohols and 12-tungstocobaltate(III) in alkaline medium exhibits 1:1 stoichiometry. The oxidative products were identified by FTIR spectroscopy. Salt effect was investigated by using NaNO_3 and KCl . Michaelis-Menten plot showed the presence of an intermediate complex. Thermodynamic parameters were evaluated and a mechanism related to this reaction is proposed.

Keywords: 12-tungstocobaltate(III); Ethanol; Butanol; Pentanol; Isopropylalcohol; NaOH ; KNO_3

INTRODUCTION

12-tungstocobaltate(III) have been widely used to investigate several oxidation reactions involving reductants like hydroxylammonium ion [1], L-cysteine [2,3], doils [4], iodide and thiocyanate ions [5], sugars [6] and Atenolol drugs [7].

However the dynamics of the alkaline oxidation of alcohols in any heteropolyacids have not been reported most especially with respect to 12-tungstocobaltate(III) where the CoIII is in a tetrahedral environment. And unlike FeIIIW12 where both the tungsten and the central Iron are involved in oxidative reactions, only CoIII is found to be responsible for oxidative reaction in CoIIIW12 .

Moreover, unlike in polyacids CoIII is octahedrally surrounded by water molecules in aquocobaltic ion. Therefore, this study shall examine the oxidation of alcohols in CoIIIW12 , where CoIII has a tetrahedral symmetry with the view to comparing it with the oxidation of alcohols in aquocobaltic ion where CoIII has octahedral symmetry.

EXPERIMENTAL

Materials

12-tungstocobaltate(III) complex was prepared by the method of Baker and Mc Cutcheon and characterized spectrophotometrically by using uv-visible spectra. Stock solution of $[\text{CoIIIW12}]$ was standardized via spectrophotometric titration method with a standard solution of FeII .

Alcohols (BDH), KNO_3 and NaOH (Analar grade) were utilized without further purification.

Kinetics

The reactions were performed under pseudo-first order conditions by maintaining a large excess ($\times 10$ or greater) of alcohol over CoIIIW12 . The kinetic data were obtained by monitoring increase in absorbance of CoIIIW12 at absorption maximum at 624nm as a function of time with a uv- 1800 Shimadzu spectrophotometer connected to a thermostated cell compartment and interfaced with a computer. Appropriate quantities of the solution of alcohol, potassium nitrate, sodium hydroxide and CoIIIW12 were measured into the cuvette. Consequently, the reaction was kick started by adding requisite volume of the CoIIIW12 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 sugar in large excess compared with the oxidant concentration. The pseudo- first order rate constant (k_{obs}) were calculated.

Stoichiometry

Reaction mixtures of constant $[CoIIIW12]$ at $1.02 \times 10^{-4} \text{ mol dm}^{-3}$ and varied $[Alcohol]$ from 0.50×10^{-2} to $4.50 \times 10^{-2} \text{ mol dm}^{-3}$, $[NaOH]$ $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 0.25 \text{ mol dm}^{-3}$ at 298K were prepared. The absorbances of the solution were taken at 624nm after the reaction had gone to completion after 24hours. The stoichiometry was evaluated from the plots of absorbance versus $[Alcohol]$ curve. The stoichiometry was found to be 1:1 that is one mole of $CoIIIW12$ per one mole of Alcohol.

Product analysis

A reaction mixture containing $[CoIIIW12]$ $1.02 \times 10^{-4} \text{ mol dm}^{-3}$, $[Alcohol]$ $3.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[NaOH]$ $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 0.25 \text{ mol dm}^{-3}$ was prepared and allowed to stand for two days. The product sample was frozen in the freezer and then loaded into the freeze dryer under the following conditions:

1. Condenser temperature -55oC
2. Period of drying - 15hrs

Then the product was analysed using Agilent Cary 630 FTIR Spectrometer.

Effect of $[CoIIIW12]$

The observed first order rate constant (k_{obs}) increases with increase in the $[CoIIIW12]$ as shown in table 1. The order with respect to oxidant is unity by the linearity of pseudo-first order plot of $\ln [CoIIIW12]$ against time and the slope of the plot of $\ln k_{obs}$ vs $\ln [CoIIIW12]$ gave 1.

Table 1: Dependence of k_{obs} with [oxidant]

$10^5 [Co^{3+}]/M$	$10^3 k_{obs}/s^{-1}$			
	Ethanol	Butanol	Pentanol	Isopropylalcohol
5.08	1.12	0.85	0.89	1.04
7.62	1.41	1.32	1.22	1.45
10.2	1.95	1.65	1.57	1.8
12.7	2.3	1.91	1.96	2.21
15.2	2.62	2.48	2.52	2.56

Effect of $[Alcohol]$

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 2). However, values for the second order rate constants obtained from the slope of the plot of k_{obs} versus $[S]$ were as follows: Ethanol $6.46 \times 10^{-2} M^{-1} s^{-1}$; Butanol $5.56 \times 10^{-2} M^{-1} s^{-1}$; Pentanol $5.52 \times 10^{-2} M^{-1} s^{-1}$; Isopropylalcohol $6.31 \times 10^{-2} M^{-1} s^{-1}$. The plot of $\ln k_{obs}$ vs. $\ln [S]$ 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 $\ln k_{obs}$ vs. $\ln [S]$ shows that the rate of reaction increases with substrate concentration, indicating that the complex formation took place between substrate and the oxidant. Micaelis-Menten plot of $1/k_{obs}$ vs. $1/[S]$ gave an intercept, showing the presence of an intermediate complex (Figure 1).

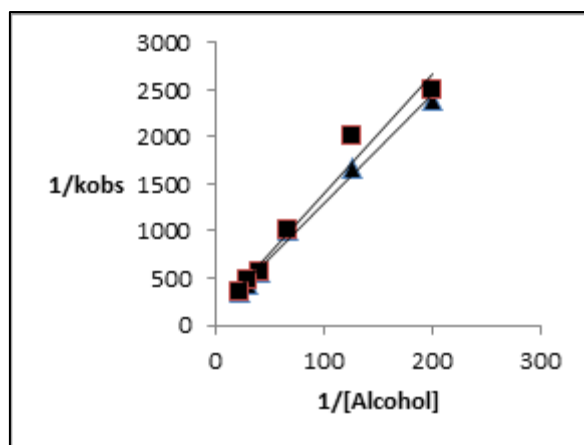


Figure 1: Plot of $1/k_{obs}$ versus $1/[Alcohol]$

Table 2: Dependence of kobs with [Alcohol]

10 ² [Alcohol]/M	Ethanol	Butanol	Pentanol	Isopropylalcohol
0.5	0.42	0.25	0.22	0.4
0.8	0.6	0.5	0.46	0.5
1.5	1	0.91	0.85	1
2.5	1.75	1.42	1.4	1.75
3.5	2.26	1.89	1.83	2.1
4.5	2.8	2.5	2.25	2.8
[Co ³⁺] 1.02 × 10 ⁻⁴ M [OH ⁻] 1.00 × 10 ⁻² M I= 0.25M				

Effect of [OH⁻]

The effect of [OH⁻] on the rate of oxidation showed that the reaction was affected by [OH⁻] as kobs increases with increase in [OH⁻] (Table 3). Plots of ln kobs vs. ln [OH⁻] showed a first order dependence on [OH⁻].

Table 3: Dependence of kobs with [OH⁻]

10 ² [OH ⁻]/M	10 ³ k _{obs} /s ⁻¹			
	Ethanol	Butanol	Pentanol	Isopropylalcohol
0.2	0.62	0.51	0.42	0.82
0.4	1	0.72	0.65	1.22
0.6	1.3	1	1.08	1.44
0.8	1.62	1.31	1.28	1.63
1	1.96	1.65	1.59	1.83
[Co ³⁺] 1.02 × 10 ⁻⁴ M [Alcohol] 3.00 × 10 ⁻² M I= 0.25M				

Salt effect

The effect of salts like NaNO₃ and KCl was carried out in order to ascertain the outer/inner sphere mechanistic point of view. The concentration [KCl] and [NaNO₃] were varied between 0.05 to 0.60 mol dm⁻³ keeping constant [CoIIIW12] at 1.02 × 10⁻⁴, [Alcohol] at 3.00 × 10⁻² mol dm⁻³, [NaOH] at 1.00 × 10⁻² mol dm⁻³ and I=0.25 mol dm⁻³. The result showed that the rate of reaction is dependent on [Salt] as shown in figure 2, indicating that the reaction went via outer sphere mechanism.

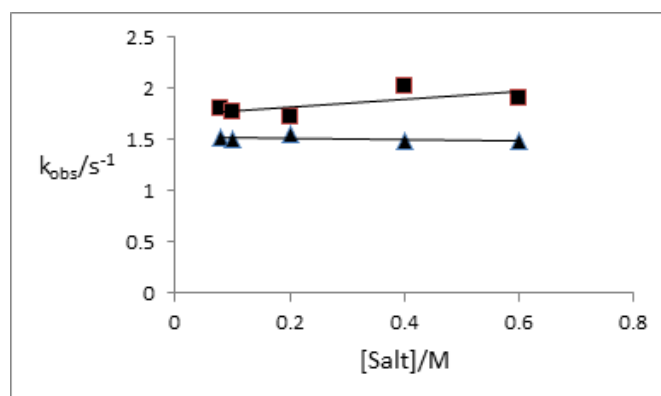


Figure 2: Plot of kobs versus [Salt]

Effect of ionic strength

The effect of ionic strength was investigated by varying the ionic strength of the reaction mixture between 0.10-0.80 mol dm⁻³ and keeping constant [CoIIIW12] 1.02 × 10⁻⁴ mol dm⁻³, [Alcohol] 3.00 × 10⁻² mol dm⁻³ and [OH⁻] 1.00 × 10⁻² mol dm⁻³. A decrease in kobs with increase in ionic strength was observed as shown in table 4, therefore a plot of ln kobs vs I^{1/2} would give a negative slope (figure 3), suggesting opposite charges on the ions participating at the rate determining step.

Table 4: Dependence of kobs with Ionic strength

10I/M	10 ³ k _{obs} /s ⁻¹			
	Ethanol	Butanol	Pentanol	Isopropylalcohol
1	2.01	1.81	1.59	2.06
3	1.88	1.7	1.32	1.82
5	1.69	1.65	1.16	1.71
7	1.52	1.5	1	1.55
8	1.29	0.8	0.86	1.31
[Co ³⁺] 1.02 × 10 ⁻⁴ M [Alcohol] 3.00 × 10 ⁻² M [NaOH] 1.00 × 10 ⁻² M				

Effect of temperature

The effect of temperature was monitored at constant [CoIIIW12] of 1.02×10^{-4} mol dm⁻³, [Alcohol] 3.00×10^{-2} mol dm⁻³, [NaOH] 1.00×10^{-2} mol dm⁻³, I= 0.25 mol dm⁻³ and varying temperature range (298K-313K). The activation energies and the activation parameters (ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) for the reaction were obtained from the below relationship and are given in table 5.

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

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{k'}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right)$$

$$\ln\left(\frac{k'}{h}\right) = 23.76$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

K = Rate constant

T= Temperature

ΔH^\ddagger = Enthalpy of activation

ΔS^\ddagger = Entropy of activation

ΔG^\ddagger = Free Gibb's energy of activation

R= Molar gas constant

k/= Boltzmann's constant

h= Plank's constant

Table 5 : Activation parameters

Alcohol	Ea(kJmol ⁻¹)	ΔH^\ddagger (kJmol ⁻¹)	ΔS^\ddagger (kJK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJmol ⁻¹)
Ethanol	20.9	18.5	-0.24	90.02
Butanol	17.84	15.26	-0.25	89.76
Pentanol	13.39	10.6	-0.26	88.08
Isopropylalcohol	26.25	23.53	-0.22	89.09

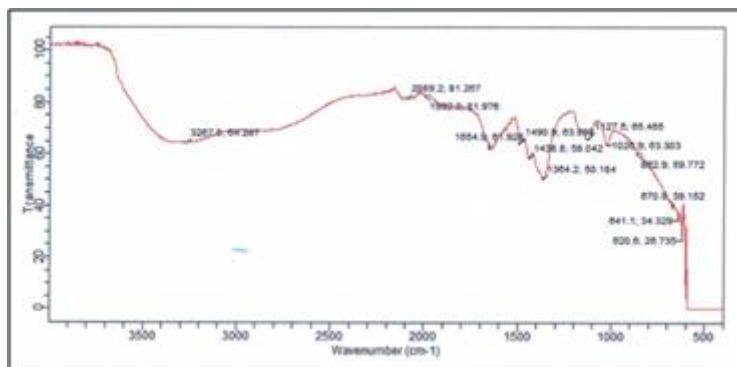
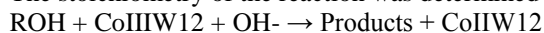


Figure 3: FTIR Spectrum of product

RESULTS AND DISCUSSION

The stoichiometry of the reaction was determined to be 1:1 mole ([CoIIIW12]: [Alcohol])

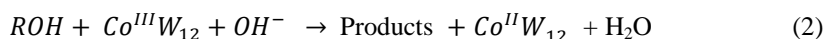


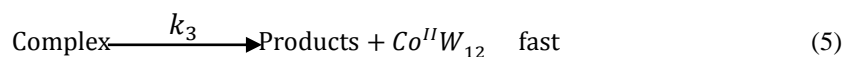
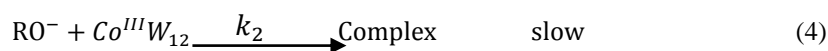
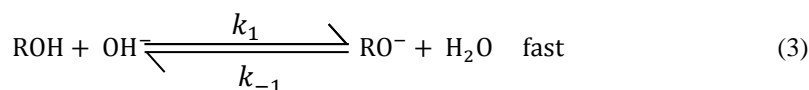
A plot of $1/k_{obs}$ vs. $1/[Alcohol]$ gave a straight line graph with an intercept (figure 1), indicating the presence of an intermediate complex in the course of the reaction. The dependence of the reaction rate on the ionic strength of the solution showed that ions of opposite charges are present at the rate determining step. Salt effect indicated an inner sphere mechanism as the reaction rate is dependent on the [NaNO₃] and [KCl].

Moreover, similar values of ΔG^\ddagger suggests same mechanism for all the substrates. The IR spectrum of the product showed very broad -OH stretching at 3400-2400 cm⁻¹, C=O stretching at 1730-1700 cm⁻¹ and C-O stretching between 1320-1210 cm⁻¹ which can be attributed to the presence of carboxylic acid. Relatively low values of ΔH^\ddagger shows the absence of high energy free radicals.

Therefore, for the reaction of alcohols with CoIIIW₁₂ in alkaline medium, the stoichiometry and kinetic data are consistent with the rate equation (1)

$$\frac{-d[CoIIIW_{12}]}{dt} = k'[CoIIIW_{12}][ROH][OH^-] \quad (1)$$





The reaction scheme proposed above gives the rate law (6) when steady state approximation is applied to it assuming equation (4) is the slow step.

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}]}{dt} = \frac{k_1 k_2 [\text{ROH}][\text{Co}^{\text{III}}\text{W}_{12}][\text{OH}^-]}{k_{-1} + k_2 [\text{Co}^{\text{III}}\text{W}_{12}]}$$

Limiting Conditions

If $k_{-1} \gg k_2 [\text{Co}^{\text{III}}\text{W}_{12}]$

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}]}{dt} = \frac{k_1 k_2 [\text{ROH}][\text{Co}^{\text{III}}\text{W}_{12}][\text{OH}^-]}{k_{-1}}$$

$$\frac{-d[\text{Co}^{\text{III}}\text{W}_{12}]}{dt} = K_1 k_2 [\text{Co}^{\text{III}}\text{W}_{12}][\text{ROH}][\text{OH}^-] \quad (6)$$

CONCLUSION

The oxidation reaction is first order each with respect to $[\text{Co}^{\text{III}}\text{W}_{12}]$, $[\text{ROH}]$ and $[\text{OH}^-]$. The oxidative product is carboxylic acid as revealed by FTIR spectrum. Salt effect showed an inner sphere mechanism. The rate determining step involves ions of opposite charges and the presence of an intermediate complex during the course of the reaction is revealed. The absence of high energy free radicals is confirmed.

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REFERENCES

- [1] GA Ayoko; MA Olatunji. *Transition Met Chem* **1985**, 10, 218-220
- [2] PK Satpathy; GC Dash; Dp Mohanty. *Ind J Chemistry* **2008**, 47, 1199-1203.
- [3] GA Ayoko; MA Olatunji. *Polyhedron* **1983** 7, 577-582.
- [4] MA Olatunji; GA Ayoko. *Bulletin De La Societe Chimique de France* **1985**, 5, 705-708.
- [5] MA Olatunji; GA Ayoko. *Polyhedron* **1984**, 3(2), 191-197.
- [6] BD Bhosale; GS Gokavi. *Adv Applied Sci Res*, **2012** 3(2), 785-792.
- [7] BB Nagolkar; LD Chavan; TK Chondhekar TK; Shankarwar SG. *J Chem Chemical Sci* **2016**. 6(1), 1-8.