The Kinetics and Mechanisms 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 [Co^{III}W_{12}], [Alcohol] and [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. Moreover, unlike in polyacids, Co^{III} is octahedrally surrounded by water molecules in aquocobaltic ion. Therefore, this study shall examine the oxidation of alcohols in Co^{III}W_{12}, where Co^{III} has a tetrahedral symmetry, with the view to comparing it with the oxidation of alcohols in aquocobaltic ion where Co^{III} has octahedral symmetry.

MATERIALS AND METHODS

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 [Co^{III}W_{12}] was standardized via spectrophotometric titration method with a standard solution of Fe^{II}. Alcohols (BDH), KNO₃ and NaOH (Analar grade) were utilized without further purification.

INTRODUCTION

12-tungstocobaltate(III) has 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 Co^{III} is in a tetrahydral environment. And unlike Fe^{III}W_{12} where both the tungsten and the central Iron are involved in oxidative reactions, only Co^{III} is found to be responsible for oxidative reaction in Co^{III}W_{12}.
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 ($k_{\text{obs}}$) were calculated.

**Stoichiometry**

Reaction mixtures of constant [Co$^{III}$W$_{12}$] at $1.02 \times 10^{-4}$ mol dm$^{-3}$ and varied [Alcohol] from $0.50 \times 10^{-2}$ to $4.50 \times 10^{-2}$ mol dm$^{-3}$, [NaOH] $1.00 \times 10^{-2}$ mol dm$^{-3}$ and I= 0.25 mol dm$^{-3}$ at 298K were prepared. The absorbance of the solution was 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 Co$^{III}$W$_{12}$ per one mole of Alcohol.

**Product Analysis**

A reaction mixture containing [Co$^{III}$W$_{12}$] $1.02 \times 10^{-4}$ mol dm$^{-3}$, [Alcohol] $3.00 \times 10^{-2}$ mol dm$^{-3}$, [NaOH] $1.00 \times 10^{-2}$ mol dm$^{-3}$ and I= 0.25 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 -55°C
2. Period of drying, 15hrs

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

**Table 1:** Dependence of $k_{\text{obs}}$ with [Oxidant].

<table>
<thead>
<tr>
<th>$10^4$[Co$^{III}$]/M</th>
<th>$10^4$k$_{\text{obs}}$/s$^{-1}$</th>
<th>Ethanol</th>
<th>Butanol</th>
<th>Pentanol</th>
<th>Isopropylalcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.08</td>
<td>1.12</td>
<td>0.85</td>
<td>0.89</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>7.62</td>
<td>1.41</td>
<td>1.32</td>
<td>1.22</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>10.2</td>
<td>1.95</td>
<td>1.65</td>
<td>1.57</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>12.7</td>
<td>2.30</td>
<td>1.91</td>
<td>1.96</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>2.62</td>
<td>2.48</td>
<td>2.52</td>
<td>2.56</td>
<td></td>
</tr>
</tbody>
</table>

[Alcohol] $3.0 \times 10^{-2}$M, [OH$^{-}$] $1.00 \times 10^{-2}$M I= 0.25M

**Effect of [Co$^{III}$W$_{12}$]**

The observed first order rate constant ($k_{\text{obs}}$) increases with increase in the [Co$^{III}$W$_{12}$] as shown in Table 1. The order with respect to oxidant is unity by the linearity of pseudo-first order plot of ln [Co$^{III}$W$_{12}$] against time and the slope of the plot of ln$k_{\text{obs}}$ vs ln[Co$^{III}$W$_{12}$] gave 1.

**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, $k_{\text{obs}}$ increases with increase in substrate concentration (Table 2). However, values for the second order rate constants obtained from the slope of the plot of $k_{\text{obs}}$ 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 $5.52 \times 10^{-2}$ Isopropylalcohol $6.31 \times 10^{-2}$ M$^{-1}$S$^{-1}$. The plot of ln$k_{\text{obs}}$ 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$k_{\text{obs}}$ 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$_{\text{obs}}$ vs. 1/[S] gave an intercept, showing the presence of an intermediate complex (Figure 1).
**Table 2:** Dependence of $k_{obs}$ with [Alcohol].

<table>
<thead>
<tr>
<th>10[^4] [Alcohol]/M</th>
<th>10[^3] $k_{obs}$/s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethanol</td>
</tr>
<tr>
<td>0.50</td>
<td>0.42</td>
</tr>
<tr>
<td>0.80</td>
<td>0.60</td>
</tr>
<tr>
<td>1.50</td>
<td>1.00</td>
</tr>
<tr>
<td>2.50</td>
<td>1.75</td>
</tr>
<tr>
<td>3.50</td>
<td>2.26</td>
</tr>
<tr>
<td>4.50</td>
<td>2.80</td>
</tr>
</tbody>
</table>

[Co^{3+}] = 1.02 x 10^-4 M [OH^-] = 1.00 x 10^-2 M I = 0.25 M

**Figure 1:** Plot of 1/$k_{obs}$ versus 1/[Alcohol]
- ■ Isopropyl alcohol
- ▲ Ethanol
**Effect of [OH⁻]**

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

**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 [Co³⁺W₁₂] at 1.02x10⁻⁴, [Alcohol] at 3.00x10⁻² mol dm⁻³, [NaOH] at 1.00x10⁻² 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.

**Table 3: Dependence of $k_{obs}$ with [OH⁻]**

<table>
<thead>
<tr>
<th>$10^2$[OH⁻]/M</th>
<th>$10^2k_{obs}$/s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethanol</td>
</tr>
<tr>
<td>0.20</td>
<td>0.62</td>
</tr>
<tr>
<td>0.40</td>
<td>1.00</td>
</tr>
<tr>
<td>0.60</td>
<td>1.30</td>
</tr>
<tr>
<td>0.80</td>
<td>1.62</td>
</tr>
<tr>
<td>1.00</td>
<td>1.96</td>
</tr>
</tbody>
</table>

[Co³⁺] 1.02 x 10⁻⁴M [Alcohol] 3.00 x 10⁻²M I= 0.25M

**Figure 2: Plot of $k_{obs}$ versus [Salt]**

( ■ KCl ▲ NaNO₃)
**Table 4: Dependence of $k_{\text{obs}}$ with Ionic Strength.**

<table>
<thead>
<tr>
<th>$10^{-3}$I/M</th>
<th>$10^3k_{\text{obs}}$/s$^{-1}$</th>
<th>Ethanol</th>
<th>Butanol</th>
<th>Pentanol</th>
<th>Isopropylalcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>2.01</td>
<td>1.81</td>
<td>1.59</td>
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<tr>
<td>3.00</td>
<td>1.88</td>
<td>1.70</td>
<td>1.32</td>
<td>1.82</td>
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<tr>
<td>5.00</td>
<td>1.69</td>
<td>1.65</td>
<td>1.16</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>7.00</td>
<td>1.52</td>
<td>1.50</td>
<td>1.00</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td>1.29</td>
<td>0.80</td>
<td>0.86</td>
<td>1.31</td>
<td></td>
</tr>
</tbody>
</table>

[Co$^{3+}$] $1.02 \times 10^{-4}$M [Alcohol] $3.00 \times 10^{-2}$M [NaOH] $1.00 \times 10^{-2}$M

**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 [Co$^{III}W_{12}$] $1.02 \times 10^{-4}$ mol dm$^{-3}$, [Alcohol] $3.00 \times 10^{-2}$ mol dm$^{-3}$ and [OH$^{-}$] $1.00 \times 10^{-2}$ mol dm$^{-3}$. A decrease in $k_{\text{obs}}$ with increase in ionic strength was observed as shown in Table 4, suggesting opposite charges on the ions participating at the rate determining step.

**Effect of Temperature**

The effect of temperature was monitored at constant [Co$^{III}W_{12}$] of $1.02 \times 10^{-4}$ mol dm$^{-3}$, [Alcohol] $3.00 \times 10^{-2}$ mol dm$^{-3}$, [NaOH] $1.00 \times 10^{-2}$ mol dm$^{-3}$, I= $0.25$ mol dm$^{-3}$ and varying temperature range (298K-313K). The activation energies and the activation parameters ($\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$) for the reaction were obtained from the below relationship and are given in Table 5.

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

\[
\ln \left( \frac{k}{T} \right) = \frac{-\Delta H^\#}{RT} + \ln \left( \frac{k}{h} \right) + \left( \frac{\Delta S^\#}{R} \right)
\]

\[
\ln \left( \frac{k}{h} \right) = 23.76
\]

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

$K$ = Rate constant
$T$ = Temperature
$\Delta H^\#$ = Enthalpy of activation

$\Delta S^\#$ = Entropy of activation
$\Delta G^\#$ = Free Gibb’s energy of activation
$R$ = Molar gas constant
$k$ = Boltzmann’s constant
$h$ = Plank’s constant

**RESULTS AND DISCUSSION**

The stoichiometry of the reaction was determined to be 1:1 mole ([Co$^{III}W_{12}$]: [Alcohol])

ROH + Co$^{III}W_{12}$ + OH$^{-}$ → Products + Co$^{II}W_{12}$

A plot of $1/k_{\text{obs}}$ vs. $1/[$Alcohol$]$ gave a straight line graph with an intercept(fig. 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 [NaNO$_3$] and [KCl].

Moreover, similar values of $\Delta G^\#$ 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 $\Delta H^\#$ shows the absence of high energy free radicals.

Therefore, for the reaction of alcohols with Co$^{III}W_{12}$ in alkaline medium, the stoichiometry and kinetic data are consistent with the rate Equation(1).
Table 5: Activation Parameters.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$E_a$(kJmol$^{-1}$)</th>
<th>$\Delta H^\circ$(kJmol$^{-1}$)</th>
<th>$\Delta S^\circ$(kJK$^{-1}$mol$^{-1}$)</th>
<th>$\Delta G^\circ$(kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>20.90</td>
<td>18.50</td>
<td>-0.24</td>
<td>90.02</td>
</tr>
<tr>
<td>Butanol</td>
<td>17.84</td>
<td>15.26</td>
<td>-0.25</td>
<td>89.76</td>
</tr>
<tr>
<td>Pentanol</td>
<td>13.39</td>
<td>10.60</td>
<td>-0.26</td>
<td>88.08</td>
</tr>
<tr>
<td>Isopropylalcohol</td>
<td>26.25</td>
<td>23.53</td>
<td>-0.22</td>
<td>89.09</td>
</tr>
</tbody>
</table>

Figure 3: FTIR Spectrum of Product.

$$\frac{-d[Co^{III}W_{12}]}{dt} = k'[Co^{III}W_{12}][ROH][OH^-] \tag{1}$$

$ROH + Co^{III}W_{12} + OH^- \rightarrow$ Products $+ Co^{III}W_{12} + H_2O \tag{2}$

ROH + OH$^- \xrightleftharpoons[k_1]{k_{-1}}$ RO$^- + H_2O \quad \text{fast} \tag{3}$

$RO^- + Co^{III}W_{12} \xrightarrow{k_2}$ Complex $\quad \text{slow} \tag{4}$

Complex $\xrightarrow{k_3}$ Products $+ Co^{III}W_{12} \quad \text{fast} \tag{5}$

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.

$$\frac{-d[Co^{III}W_{12}]}{dt} = \frac{k_1k_2[ROH][Co^{III}W_{12}][OH^-]}{k_{-1} + k_2[Co^{III}W_{12}]} \tag{6}$$
Limiting Conditions:

\[
\begin{align*}
\frac{d[Co^{III}W_{12}]}{dt} &= k_{-1}
-\frac{d[Co^{III}W_{12}]}{dt} = k_{1}k_{2}[ROH][Co^{III}W_{12}][OH^{-}] \\
-\frac{d[Co^{III}W_{12}]}{dt} &= K_{1}k_{2}[Co^{III}W_{12}][ROH][OH^{-}] 
\end{align*}
\]

CONCLUSION

The oxidation reaction is first order each with respect to [Co\textsuperscript{III}W\textsubscript{12}], [ROH] and [OH\textsuperscript{-}]. 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


SUGGESTED CITATION


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