Alcohol Oxidation by Metallic Benzoquinone Complexes

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Introduction

Linck and Taube discovered that p-benzoquinones and chromium oxidized ethanol.

Further Study

A later, in depth study on the reaction of chloranilic acid, chromium, and ethanol provides some very important information:

- Two chromium atoms per benzoquinone atom are, in fact, necessary for alcohol oxidation
- The reduced chromium and chloranilic acid complex is a semiquinone bridged polynuclear complex

Objectives

What kind of alcohols are more easily oxidized?

Which benzoquinones are more effective oxidizing agents?

How will changing the metal effect the reaction?
Solutions Analyzed

Seventeen alcohols of differing characteristics were used.

Two p-benzoquinones were used, Chloranilic acid and Bromanilic acid.

Two metals were used, chromium (III) and aluminum.
Solution Preparation

Enough benzoquinone to identify carbonyl compounds with GCMS. At least 2.5-1 metal moles per benzoquinone moles.

Four solutions per alcohol:

1. Chromium and chloranilic acid
2. Chromium and bromanilic acid
3. 1-1 Chromium and chloranilic acid in excess of aluminum
4. Aluminum and chloranilic acid
Chloranilic Acid and Chromium

Chloranilic Acid and Aluminum

Bromanilic Acid and Chromium

Chloranilic Acid, Chromium, and Aluminum
Methods of Analysis

Two principle methods of analysis were used:

• UV-vis spectroscopy to identify reduced benzoquinone

• Gas chromatography and mass spectroscopy to identify oxidized alcohol
The Reduced 2-1 Complex Spectrum
The 1-1 Complex Spectrum
Using Gas Chromatography
Using Mass Spectroscopy
### Results: Cr\(^{3+}\) and C.A.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>GCMS</th>
<th>UV-Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl Alcohol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2-Butene-1,4-diol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>3-Butene-1-ol</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>2-Butyn-1-ol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2-Bromoethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanolamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>2-Chloroethanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2-Propanol</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1,2-Propanediol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-(Trifluoromethyl)-benzyl alcohol</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Results: Which Metal?

• Chromium was much more effective than the other two metal combinations

• Chromium and aluminum were more effective than aluminum alone
Results: Which Metal?

Aluminum was least effective, but some solutions’ UV-visible spectra still contained sharp peaks.
Results: Which Benzoquinone?

Chloranilic acid was the better oxidizing agent; more solutions contained oxidized alcohol and more UV-visible spectra contained sharp peaks.
Alcohol Dehydration

Most solutions contained a dehydrated product of the alcohol.

Ex:

- Required metal
- Independent of benzoquinone
- Independent of time
Future Work

Stoichiometry

- Is the reaction cyclic?
- Does aluminum react in the same way as chromium?

GCMS analysis using a derivatization method

Investigation of the dehydration of alcohol catalyzed by Cr$^{3+}$