**LAB 16: ALCOHOLS, PHENOLS, ALDEHYDES & KETONES:**

**STRUCTURE & PROPERTIES**

**PURPOSE:** To discover the physical and chemical properties of alcohols, phenols, aldehydes, and ketones.

To identify an unknown oxygen compound by comparing it to known samples.

**SAFETY CONCERNS:**
Always wear safety goggles. Observe waste disposal procedures.

**ALCOHOLS & PHENOLS:**

**Alcohols** are hydrocarbons that contain an –OH bonded to a regular carbon. Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) according to the type of carbon to which they are bonded.

<table>
<thead>
<tr>
<th>1° Alcohol</th>
<th>2° Alcohol</th>
<th>3° Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>OH</td>
<td>OH</td>
</tr>
<tr>
<td>CH₃—C—H</td>
<td>CH₃—C—CH₂—CH₃</td>
<td>CH₃—C—CH₃</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CH₃</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2-butanol</td>
<td>2-methyl-2-propanol</td>
</tr>
<tr>
<td>(Ethyl alcohol)</td>
<td>(sec-butyl alcohol)</td>
<td>(t-butyl alcohol)</td>
</tr>
</tbody>
</table>

**Phenols** are aromatics that contain the alcohol group. Although concentrated solutions of phenol are toxic, dilute solutions and derivatives of phenol are used as antiseptics and can be found in cough drops and sore throat sprays.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H—C—O—H</td>
<td>H—C=C—C—O—H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Methanol</td>
<td>Phenol</td>
</tr>
<tr>
<td>(Methyl alcohol)</td>
<td></td>
</tr>
</tbody>
</table>
**ALDEHYDES AND KETONES:**
A carbon that is double bonded to an oxygen (C=O) is called a **carbonyl**. Carbonyl groups where the carbon is also bonded to at least 1 hydrogen is called an **Aldehyde**. A carbonyl that is in between 2 carbons is called a **ketone**.

<table>
<thead>
<tr>
<th>A Carbonyl group</th>
<th>Aldehyde</th>
<th>Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Aldehyde Structure" /></td>
<td>Methanal (Formaldehyde)</td>
<td>Propanone (Acetone)</td>
</tr>
<tr>
<td><img src="image2.png" alt="Ketone Structure" /></td>
<td>Ethanal (Acetaldehyde)</td>
<td>2-butane (Ethyl Methyl Ketone)</td>
</tr>
</tbody>
</table>

**PHYSICAL PROPERTIES:**

**Solubility:**
Alcohols with four or fewer carbons are usually water soluble due to the polarity of the –OH group. However, with more than four carbons the nonpolar character of the C-H bond dominates and the long chain alcohols become insoluble in water.

The carbonyl group, C=O, although slightly polar is less polar than the OH making aldehydes and ketones less soluble than alcohols but more soluble than non-oxygen containing hydrocarbons.

<table>
<thead>
<tr>
<th>Attraction of Compounds to water</th>
<th>Methanol</th>
<th>Propanone (Acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image3.png" alt="Atoms" /></td>
<td><img src="image4.png" alt="Atoms" /></td>
<td><img src="image5.png" alt="Atoms" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Attraction of Compounds to themselves</th>
<th>Methanol</th>
<th>Propanone (Acetone)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image6.png" alt="Atoms" /></td>
<td><img src="image7.png" alt="Atoms" /></td>
<td><img src="image8.png" alt="Atoms" /></td>
</tr>
</tbody>
</table>
**Boiling Point:**
The polarity of the –O-H bond causes alcohols to attract and so hydrogen bond with each other. As a result of this attraction to one another, alcohols require more energy to vaporize than other hydrocarbons of comparable size.

The slight polarity of the carbonyl group, C=O, enables some polar attraction between aldehydes and ketones that is weaker than the hydrogen bonds between alcohols. Thus, aldehydes and ketones have lower boiling points than alcohols of comparable size.

<table>
<thead>
<tr>
<th>Groups with similar Molar Mass</th>
<th>Alkane</th>
<th>Ketone</th>
<th>Aldehyde</th>
<th>Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Propane (FW=44.10)</td>
<td>Ethanal (FW=44.05)</td>
<td>Ethanol (FW=46.07)</td>
<td></td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-42.1°C</td>
<td>21 °C</td>
<td>78 °C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Groups with similar Molar Mass</th>
<th>Butane (FW=58.12)</th>
<th>Propanone (FW=58.08)</th>
<th>Propanal (FW=58.08)</th>
<th>1-Propanol (FW=60.10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point</td>
<td>-0.5 °C</td>
<td>56 °C</td>
<td>46-50 °C</td>
<td>97 °C</td>
</tr>
</tbody>
</table>

**CHEMICAL PROPERTIES:**

**Acidity**
In the same way that water ionizes to form hydronium ions (H₃O⁺) and hydroxide ions (OH⁻), water soluble alcohols can also ionize in water. The amount of ionization can be expressed in an equilibrium expression for acids and characterized by the acid dissociation constant, Ka. The Ka can be further simplified as a pKa. The acidity of alcohols is very similar to the acidity of water so we do not consider alcohols to belong to the family of acids.

\[ K_a = \frac{[H_3O^+][A^-]}{[HA]} \]
\[ pK_a = -\log K_a \]

**Ionization of Water:**

\[ \text{Hydronium ion} \quad \text{Hydroxide ion} \]
\[ pK_a = 15.7 \quad \text{H-O-H} + \text{H-O-H} \rightleftharpoons \text{H-O-H}^+ \quad \text{H-O-}^- \quad \text{H-O-}^- \]

**Ionization of Methanol:**

\[ \text{Methoxide ion} \]
\[ pK_a = 15.5 \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

**Ionization of Phenol:**

\[ \text{Phenoxide ion} \]
\[ pK_a = 10 \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
Oxidation/Reduction

Primary alcohols (1°) easily oxidize to form aldehydes with can then oxidize to form carboxylic acids. Secondary alcohols (2°) oxidize to ketones. Tertiary alcohols (3°) do not oxidize. Oxidation of alcohols or aldehydes requires an oxidizing agent that itself will get reduced. A common oxidizing agent is sodium dichromate (Na2Cr2O7), a bright orange compound that in the course of the reaction forms a green chromium compound. Oxidations can be verified by this color change.

\[
\begin{align*}
1° \text{ Alcohol} & \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Aldehyde} \rightarrow \text{Ketone} \rightarrow \text{Carboxylic Acid} + \text{Cr}_2(\text{SO}_4)_3 \\
2° \text{ Alcohol} & \rightarrow \text{Aldehyde} \rightarrow \text{Ketone} \rightarrow \text{Carboxylic Acid} \rightarrow \text{Cr}_2(\text{SO}_4)_3
\end{align*}
\]

Reduction is the reverse of oxidation so carboxylic acids reduce to aldehydes which then can reduce to primary alcohols. Ketones reduce to form secondary alcohols.

Tollén’s Test: Aldehydes react with silver ions (from AgNO₃) to form carboxylic acids and silver metal. The silver metal coats the inside of the test tube to form a silver mirror.

Other Characterization Reactions

Phenols: Compounds containing a Phenol group can be identified because a phenol group will grab onto yellow Ferric chloride (FeCl₃) to give a purple complex.

\[
\text{Phenol (yellow)} + \text{FeCl}_3 \rightarrow \text{FeCl}_4^- (\text{violet color}) + \text{HCl}
\]

Aldehydes & Ketones: Compounds containing an Aldehyde or Ketone carbonyl group will react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones that are usually yellow to red colored solids. Each of these solids formed has a distinct melting point that can be used for identification.

\[
\text{Aldehydes or Ketones} + \text{2,4-dinitrophenylhydrazine} \rightarrow \text{a yellow to red solid 2,4-dinitrophenylhydrazone}
\]
PROCEDURES:

ACTIONS:

I. PHYSICAL PROPERTIES:

A. Solubility in Water:
1. Obtain 9 stoppered test tubes (labeled #1-8), each containing 1 mL of water.

2. Leave tube #1 as a control for comparison.
   Into tube #2 put 5 drops ethanol, (ethyl alcohol).
   Into tube #3 put 5 drops of 1-propanol, (n-propyl alcohol).
   Into tube #4 put 5 drops 1-butanol, (n-butyl alcohol).
   Into tube #5 put 5 drops 1-pentanol, (n-amyl alcohol).
   Into tube #6 put 5 drops 1-hexanol, (n-hexyl alcohol).
   Into tube #7 put 5 drops 1-octanol, (n-octyl alcohol).
   Into tube #8 put rice sized kernel of phenol (carbolic acid).
   Into tube #9 put 5 drops of an unknown containing oxygen.

Stopper the tubes and shake each to mix.

3. Check each tube for layers or insoluble droplets.
   Record your observations about the solubility of each organic oxygen compound in water. Use ‘S’ for soluble, and ‘I’ for insoluble.

4. Save these tubes for use in Parts IB & IIA.

B. Density:
5. For each insoluble (‘I’) organic oxygen compound in Part IA observe the positioning of the hydrocarbon layer relative to water. The more dense substance will be on the bottom.

6. Record the density of each insoluble hydrocarbon relative to water on the report sheet. Report M for more dense than water, and L for less dense than water.

II. CHEMICAL PROPERTIES:

A. Reactivity with Iron (III) Chloride:
7. Select the following tubes of samples in water from part IA
   Tube #1 Water (as a control)
   Tube #8 Phenol
   Tube #9 Your unknown oxygen compound

8. Into each of these samples drop 3 drops of 0.1 M Ferric chloride (FeCl₃) solution. Note and record any resulting color changes.

9. Indicate on the report sheet (next to the colors recorded) whether this is a positive (+) or negative (-) test for the presence of phenols (aromatic alcohols).

NOTES:

¹This measurement does not need to be exact, so measure the 1 mL for the first tube with a graduated cylinder and then eyeball the levels of the rest to match.

²Phenol is caustic and can cause burns. Avoid contact with bare skin.

³You will be given a sample of an unknown oxygen compound that you will endeavor to characterize by class. If your unknown is a solid then put a rice kernel sized crystal into 1 mL of water. Your unknown will be a ¹ alcohol, a ² alcohol, a ³ alcohol, a phenol, an aldehyde, or a ketone. Your unknown may also be small or large which may influence its water solubility.

⁴Sometimes the light optics due to curvature of the test tube looks like a layer when it is not. Compare to plain water in a tube. If you are still not certain that an insoluble layer is forming then add a couple more drops of reagent and see if your layer gets bigger.

⁵Phenols are weakly acidic because the phenoxide ion formed is stabilized by resonance with the electrons in the aromatic ring.

⁶A purple color formed upon addition of FeCl₃ indicates the presence of a phenol (+ test). If the color remains yellow, no reaction has occurred (-).

CH105 Lab 16: Alcohols, Phenols, Aldehydes, & Ketones (F14) 65
II. CHEMICAL PROPERTIES CONTINUED:

1. Obtain enough clean and dry white spot plates to test 8 samples with 2 reagents (you’ll need 16 wells).

2. As shown in the notes, enter the following compounds to be tested in each row of the plates:
   - Into 2 wells of row #1 put 4 drops water, (as a control).
   - Into 2 wells of row #2 put 4 drops ethanol, (ethyl alcohol).
   - Into 2 wells of row #3 put 4 drops of 2-propanol, (isopropyl alcohol).
   - Into 2 wells of row #4 put 4 drops 2-methyl-2-propanol, (t-butyl alcohol).
   - Into 2 wells of row #5 put 4 drops of phenol solution, (carbolic acid).
   - Into 2 wells of row #6 put 4 drops, propanal (propionaldehyde).
   - Into 2 wells of row #7 put 4 drops propanone, (acetone).
   - Into 2 wells of row #8 put 4 drops of an unknown compound.

B. Oxidation:

1. Into each well of column B add
   - 1 drop of Sodium Dichromate (Na₂Cr₂O₇) solution followed by
   - 1 drop of 6M Sulfuric Acid (H₂SO₄) solution.
   Observe any color changes.

2. Watch for a couple of minutes and then record final results. Indicate on the report sheet (next to the colors recorded) whether this is a positive (+) or negative (-) test for the presence of oxidizable alcohols or aldehydes.

3. Into each well of column C drop 3 drops of 2,4-Dinitrophenylhydrazine solution. Indicate if any immediate yellow to red precipitates are formed. (For example; if an orange precipitate forms record orange-ppt. If no immediate solid forms indicate no reaction, NR)

C. Reactivity with 2,4-Dinitrophenylhydrazine:

4. Indicate on the report sheet (next to the colors recorded) whether this is a positive (+) or negative (-) test for the presence of aldehydes or ketones.

D. Unknown Oxygen Compound:

5. You have observed the behavior of an unknown compound in solubility, density, reaction with ferric chloride, oxidation with sodium dichromate, and reaction with 2,4-dinitrophenylhydrazine. On the report sheet characterize your unknown as a 1° or 2° alcohol, a 3° alcohol, a phenol, an aldehyde, or a ketone. Justify your answer.

6. Dispose in the designated waste containers.

---

The glassware must be very clean and dry. Impurities may cause a false positive test.

Pattern of spot plate wells:

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

Use the phenol dissolved in water from Part IA tube 8.

The loss of the red-orange color of Cr⁺⁺ and the formation of a blue-green color of the Cr⁺⁺⁺ is a sign that the chromium has been reduced indicating a positive test for the presence of oxidizable alcohols or aldehydes.

1° Alcohol + Na₂Cr₂O₇ + Aldehyde + H₂SO₄ (orange) → Aldehyde or Ketone + Cr₂(SO₄)₃ (green)

If the orange color turns to green within 1-2 minutes, oxidation has taken place (+). If the color remains orange, no reaction has occurred (-).

Aldehydes and Ketones react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones that are usually yellow to red colored solids.
LAB 16: ALCOHOLS & ALDEHYDES

PRE LAB EXERCISES

1. Draw the structural formula for each of these hydrocarbons:

<table>
<thead>
<tr>
<th>2-propanol</th>
<th>t-butyl alcohol</th>
</tr>
</thead>
</table>

Match the following statements with the structure that it best fits:

A. ![Structure A]

B. ![Structure B]

C. ![Structure C]

D. ![Structure D]

1. Would form a solid with 2,4-dinitrophenylhydrazine.
2. Would turn violet with FeCl₃.
3. Would cause orange Na₂Cr₂O₇ to turn blue-green.
4. Would show no reaction (NR) with either FeCl₃, Na₂Cr₂O₇, nor 2,4-DNP.

Complete the following reactions showing the organic products only: (use structural formulas)

**Oxidation of cyclohexanol with Sodium Dichromate in the presence of Sulfuric Acid:**

![Reaction](cyclohexanol_oxidation)

**Reaction of Propionaldehyde (Propanal) with 2,4-Dinitrophenylhydrazine:**

**Reaction of Phenol with Iron (III) Chloride:**
# Lab 16: Alcohols & Aldehydes

**NAME________________**  
**PARTNER________DATE___**

## I. Physical Properties:

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>A. Solubility in Water (S or I)</th>
<th>B. Density (If Insoluble)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water (control)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Ethanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. 1-propanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. 1-butanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. 1-pentanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. 1-hexanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. 1-Octanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Phenol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Results Summary:**

1. What do your experimental results indicate concerning the relationship between the length of the carbon chain and the water solubility of alcohols?
   - A. The greater the number of carbons the **more** soluble it will be in water.
   - B. The greater the number of carbons the **less** soluble it will be in water.
   - C. There is no general rule

2. As the chain length of an alcohol increases at what point (at what number of carbons) does solubility noticeably decrease? Give the number.

3. My results show that the density of insoluble organic oxygen compounds is generally ________ water.
   - A. more than  
   - B. less than  
   - C. unrelated to.

**Explanation/Analysis:** Why were the results as they were? Explain any anomalies.
## II. CHEMICAL REACTIVITY:

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Classification (1°, 2°, or 3° alcohol, phenol, aldehyde, or ketone)</th>
<th>A. Reactivity w/ FeCl₃ Color and (+ or -)</th>
<th>B. Oxidation w/ Na₂Cr₂O₇ Color and (+ or -)</th>
<th>C. Reactivity w/ 2,4-DNP Color/ppt? (+ or -)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. 2-propanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. t-butyl alcohol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Phenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Propanal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Propanone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Unknown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Results Summary:

1. My results show that the following compounds react with FeCl₃ to form a violet color:
   - A. 1° alcohol
   - B. 2° alcohol
   - C. 3° alcohol
   - D. phenol
   - E. aldehyde
   - F. ketone
   - G. None

2. My results show that the following compounds easily oxidize with Na₂Cr₂O₇: (List all)
   - A. 1° alcohol
   - B. 2° alcohol
   - C. 3° alcohol
   - D. phenol
   - E. aldehyde
   - F. ketone
   - G. None

3. My results show that the following compounds form solid precipitates with 2,4-DNP: (List all)
   - A. 1° alcohol
   - B. 2° alcohol
   - C. 3° alcohol
   - D. phenol
   - E. aldehyde
   - F. ketone
   - G. None

### Explanation/Analysis: Why were the results as they were? Explain any anomalies

### D. Unknown

<table>
<thead>
<tr>
<th>#</th>
<th>Belongs to what family of compounds? (circle one)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1° or 2° alcohol  3° alcohol  phenol  aldehyde  ketone</td>
</tr>
</tbody>
</table>

### Explanation/Analysis: Justify your conclusion. Explain any anomalies
### Related Exercises:

Write balanced chemical equations to represent the following reactions: (Use structures rather than simple formulas for the major organic reactants and products. If no reaction occurs write NR)

1. Reaction of Phenol (a weak acid) with Sodium Hydroxide (a strong base):
   
   \[
   \text{Phenol} + \text{NaOH} \rightarrow \text{Phenoxide}^-
   \]

2. Oxidation of isopropyl alcohol with Sodium Dichromate in the presence of Sulfuric Acid:

3. Oxidation of Acetone with Sodium Dichromate in the presence of Sulfuric Acid:

4. Formation of the 2,4-dinitrophenylhydrazone of acetophenone:
   
   \[
   \text{Acetophenone} + \text{Hydrazine} \rightarrow \text{2,4-dinitrophenylhydrazone}
   \]
Reference Search:
5. In your textbook or a chemistry handbook, look up and draw the condensed structural formulas of each of the following: Indicate where each can be found in nature and potential uses.

<table>
<thead>
<tr>
<th></th>
<th>Thymol</th>
<th>Menthol</th>
<th>Cuminaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sources in nature/ Uses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Camphor</td>
<td>Vanillin</td>
<td>Cinnamaldehyde</td>
</tr>
<tr>
<td>Sources in nature/ Uses</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Go on a chemical scavenger hunt. Find alcohols (-ol), aldehydes (-al), and ketones (-one). Go to the kitchen, bathroom, medicine cabinet, garage, etc. and find different items that contain the needed functional groups on the label. List your findings below.

<table>
<thead>
<tr>
<th>Group</th>
<th>Product Brand Name / Use</th>
<th>Chemical Name on the Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldehyde</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketone</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>