Experiment 24
Alcohols

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Name:

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Key Objectives

1. Structure of alcohols
2. Reactions of alcohols
3. Differences between Primary (1°), Secondary (2°) and Tertiary (3°) Alcohols
4. Diagnostic tests for alcohols
5. Solubility and combustibility of alcohols

Discussion

A. Structure of Alcohols

Alcohols are organic compounds containing a hydroxy (hydroxyl) (R−OH) functional group bonded to a carbon atom that is not bonded to a carbonyl carbon (C=O). Those molecules will be explored in a future experiment. If the hydroxy group is bonded to an aromatic ring (benzene ring), a class of compounds called phenols are form, which have properties different than regular alcohols, and will not be used in this experiment.

Alcohols can be separated into three subclasses, primary (1°), secondary (2°) and tertiary (3°) based on the number of alkyl (R-) groups attached to the carbon atom with the hydroxy (−OH) group attached.

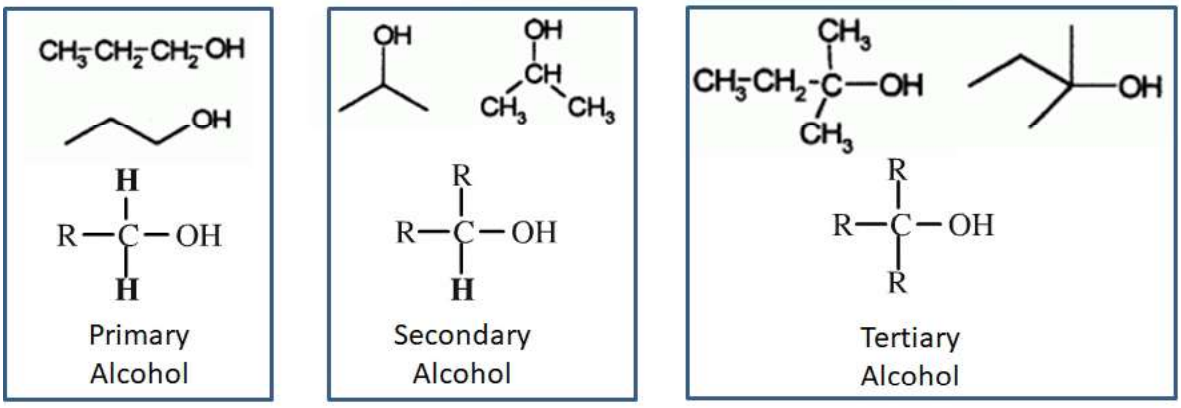

Figure 24.1: The location of an alcohol functional group determines many of its chemical properties. credit: author

Physical Properties of Alcohols

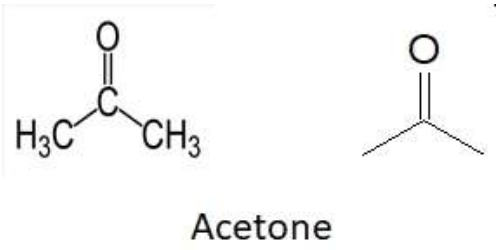

Figure 24.2: Propanone (common name acetone) is a common solvent in organic chemistry. credit: author

The most common alcohols are colorless liquids at room temperature. Their melting and boiling points are considerably higher than those of alkanes, alkenes, and alkynes of similar size due to the ability to hydrogen bond (See Hein 13.8). The ability to form hydrogen bonds also makes low molar mass alcohols soluble in water, however, as the alkane portion of the molecule increases in size the solubility decreases, because the hydrogen bonds formed by the alcohol group can not counteract the non-polar alkane part. Solubility in acetone will also be tested, as it is a widely used organic solvent because of its ability to dissolve a wide variety of compounds. We will also examine the combustion of several common alcohols.

Chemical Properties

Chemically alcohols undergo two main categories of reactions: oxidation and dehydration. There are several common oxidizing agents (compounds that will oxidize organic molecules). These include:

1. Potassium Permanganate: $\xrightarrow[\Delta]{KMnO_4/H_2O}$
2. Chromic Acid: $\xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4}$
3. Tollens reagent: $2Ag^+ \xrightarrow[H_2O]{NH_3}$
4. Fehling/Benedicts reagent: $2Cu^{2+} \xrightarrow[H_2O]{NaOH}$
5. Generic: $\xrightarrow{[O]}$

Generally we will be unconcerned with the identity of the oxidizing agent, and will use the generic representation. Due to the complex reaction mechanisms and balancing required, we will focus on the organic compounds formed in the reactions only. Depending on the classification of alcohol (primary, secondary, tertiary) they will be oxidized to different classes of molecules. The reaction results in the replacement of the $-OH$ group by either an Aldehyde, Carboxylic Acid or Ketone functional group.

- Primary Alcohol $\xrightarrow{[O]}$ Aldehyde + H_2O $\xrightarrow{[O]}$ Carboxylic Acid
- Secondary Alcohol $\xrightarrow{[O]}$ Ketone + H_2O $\xrightarrow{[O]}$ NR

- Tertiary Alcohol $\xrightarrow{[O]}$ NR

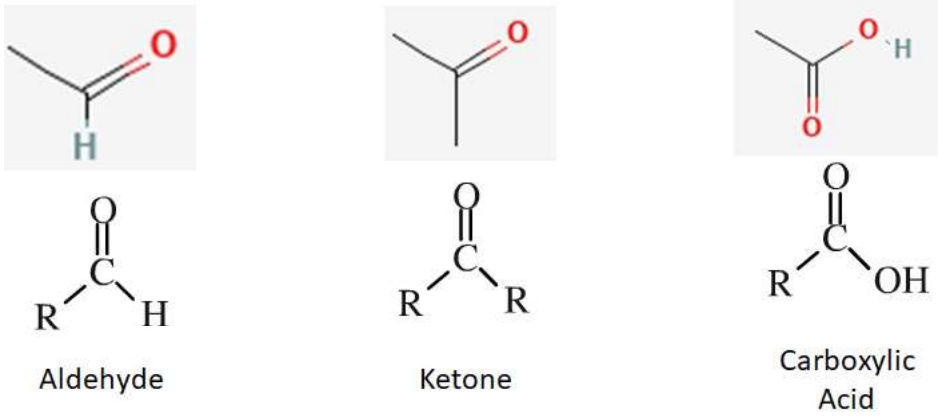

Figure 24.3: Structure of Aldehydes, Ketones and Carboxylic Acid functional groups that result from oxidation reactions of alcohols. credit: author.

A general test for oxidation of compounds is by reaction with Potassium Permanganate. This test is non-specific and will give a positive result for a variety of compounds (including alkenes and alkynes as seen in a previous experiment). The reaction is catalysed by the addition of base or acid to the reaction. The reaction is characterized by the disappearance of the purple color and in some cases the formation of a precipitate.

$$\underset{\text{Purple}}{\mathrm{R{-}OH + KMnO_4(aq)}} \xrightarrow{[\text{acid/base}]} \underset{\substack{\text{Aldehyde}\\ \text{or Ketone}}}{\mathrm{R{=}O(s)}} + \mathrm{KOH(aq) + H_2O(l)} + \underset{\text{Brownish ppt}}{\mathrm{MnO_2(s)}}$$

Figure 24.4: Bayer Test/Potassium Permanganate oxidation test for alcohols. credit: author

A specific test for oxidizing alcohols is the Chromic Acid test. A color change from orange to green or to blue-green within 5 seconds is a positive test, indicating the alcohol has been oxidized.

$$1^\circ \text{ or } 2^\circ\text{Alcohol} \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} \text{Aldehyde/Ketone (Color Change : Orange/Red to Blue/Green)}$$

$$3^\circ\text{Alcohol} \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} \text{NR}$$

Another useful chemical property of alcohols is their reaction with a solution of hydrochloric acid in the presence of zinc chloride to form alkyl chlorides. This reaction is commonly referred to as the Lucas Test. This test is important because of the different rates of reactions between primary, secondary and tertiary alcohols. Generally Tertiary alcohols react immediately, secondary alcohols require 5-15 minutes to react, and primary alcohols will show little or no reactivity after 30 minutes. The evidence of a positive reaction is the conversion of a soluble alcohol to an insoluble alkyl chloride which forms a milky suspension in the solution.

$$\mathrm{R{-}OH + HCl(aq) \xrightarrow{[ZnCl_2]} R{-}Cl(s) + H_2O}$$

Tertiary (3°) = immediate
Secondary (2°) = slow (5-15 min)
Primary (1°) = very slow (> 30 min)

Figure 24.5: Lucas Reagent/Zinc Chloride test for alcohols. credit: author

Procedure

A. Combustion

1. Perform the following test in the hood.
2. Remember hot things are hot.
3. Place about 1 mL of the substance to be tested in an evaporating dish.
4. Ignite the liquid using the lighter provided.
5. Record your observations noting the characteristics of each flame along with any evidence of residue left behind in the evaporating dish.
6. Repeat for each of the substance to be tested.

B. Solubility Tests - Water

1. Test the solubility of each of the listed substances with water by adding 1 mL (20 drops) of the substance to be tested to 5 mL of water in a test tube.
2. Mix each of the test tubes vigorously for 15 seconds. Wait 30 seconds. Sketch a picture of your results. In the sketch, label each liquid in the test tube. Note which pairs are miscible and which are not.
3. Wait an additional 5 minutes and record your results.
4. For any solutions that are insoluble note the relative density of the hydrocarbons with respect to water.
5. Dispose of the solutions in the waste bottle labeled "E22 Waste".

C. Solubility Tests - Acetone

1. Test the solubility of each of the listed substance with acetone by adding 1 mL (20 drops) of the substance to be tested to 5 mL of acetone in a clean dry test tube.
2. Mix each of the test tubes vigorously for 15 seconds. Wait 30 seconds. Sketch a picture of your results. In the sketch, label each liquid in the test tube. Note which pairs are miscible and which are not.
3. Wait an additional 5 minutes and record your results.

4. For any solutions that are insoluble note the relative density of the hydrocarbons with respect to acetone.

5. Dispose of the solutions in the waste bottle labeled "E22 Waste".

D. Oxidation - Potassium Permanganate

1. Be especially careful with the Potassium Permanganate solution as it is it will stain skin and clothes. If spilled on the skin rinse immediately with cold water and inform your instructor.

2. Perform the test on the Control (water) first and then on your sample.

3. In a test tube add 3 mL of water + 1 mL of alcohol.

4. Add 2 drops of 3M Sulfuric Acid. Record your observations.

5. Add 1 drop of the Potassium Permanganate solution to test tubes.

6. Swirl the tubes gently to mix them.

7. Note any observations (color change, formation of a ppt etc).

8. Note how long it takes each reaction to occur.

9. Dispose of the contents of the test tubes in the waste bottle labeled "E22 Waste".

E. Oxidation - Chromic Acid

1. Be especially careful with the chromic acid solution as it is very corrosive. If spilled on the skin rinse immediately with cold water and inform your instructor.

2. In a clean dry test tube place 1 mL of acetone.

3. Add 5 drops of the alcohol to be tested.

4. Swirl the tubes gently to mix them.

5. Add 2 drops of the chromic acid reagent to the test tube.

6. Note any results after 5 seconds. Record any color changes.

7. Dispose of the contents of the test tubes in the waste bottle labeled "E22 Waste".

F. Oxidation - Lucas Test

1. Be especially careful with the Lucas reagent as it is very corrosive. If spilled on the skin rinse immediately with cold water and inform your instructor.

2. In a clean test tube place 1 mL of the Lucas Reagent.

3. To the solution add 4 drops of the alcohol to be tested.

4. Swirl the tubes gently to mix them.
5. Note any results after 1 minute, 5 minutes, 15 minutes, and 30 minutes. Record any color changes or the formation of a cloudy mixture.
6. Dispose of the contents of the test tubes in the waste bottle labeled "E22 Waste".

G. Identity of an Unknown Alcohol

1. You must complete the tests all of the previous tests before doing testing your unknown.
2. Determine which class of alcohol (primary, secondary, or tertiary) that your unknown belongs to by reacting it with chromic acid and the Lucas reagent as directed in parts E and F.
3. Be sure to record the identity of your unknown solution.
4. Record any required observations about your unknown.

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Results

A. Combustion

Compound	Observations	Lewis Structure
ethanol		
1-butanol		
2-butanol		
1-hexanol		
1-decanol		
2-methyl-2-propanol		
cyclohexanol		

Table 24.1: Results - Combustion

B. Solubility Tests - Water

Mixture	Observation/Sketch	Miscible/Immiscible	
		30 seconds	5 minutes
ethanol			
1-butanol			
2-butanol			
1-hexanol			
1-decanol			
2-methyl-2-propanol			
cyclohexanol			

Table 24.2: Results - Solubility in Water

C. Solubility Tests - Acetone

Mixture	Observation/Sketch	Miscible/Immiscible	
		30 seconds	5 minutes
ethanol			
1-butanol			
2-butanol			
1-hexanol			
1-decanol			
2-methyl-2-propanol			
cyclohexanol			

Table 24.3: Results - Solubility in Acetone

D. Oxidation - Potassium Permanganate

Compound	**Observations (+/-)** **Color Changes**	**Write the Complete Reaction**
Control (H_2O)		
ethanol		
1-butanol		
2-butanol		
1-hexanol		
1-decanol		
2-methyl-2-propanol		
cyclohexanol		

Table 24.4: Results - Chromic Acid Test

E. Chromic Acid Test - Oxidation of Alcohols

Compound	**Observations (+/-)** **Color Changes**	**Write the Complete Reaction**
Control (H_2O)		
ethanol		
1-butanol		
2-butanol		
1-hexanol		
1-decanol		
2-methyl-2-propanol		
cyclohexanol		

Table 24.5: Results - Chromic Acid Test

F. Lucas Reagent - Conversion of Alcohols to Alkyl Chlorides

Compound	Observations: A milky suspension occurring				$1°, 2°, 3°$
	1 Minute	**5 Minute**	**15 Minute**	**30 Minute**	
Control (H_2O)					
ethanol					
1-butanol					
2-butanol					
1-hexanol					
1-decanol					
2-methyl-2-propanol					
cyclohexanol					

Table 24.6: Results - Lucas Reagent

G. Analysis of an Unknown Alcohol

Unknown ID: _____

Observations	**Conclusions** (1°, 2°, 3°) **+ Explanation**
Chromic Acid Test:	
Lucas Reagent:	

Table 24.7: Results - Unknown Alcohol

Questions

A. Combustion

1. Which compounds completely combusted:

2. Which compounds showed incomplete combustion:

3. Comment on any trends noticed in your observations of luminosity.

4. Comment on any trends noticed in your observations on complete/incomplete combustions.

B. Solubility - Water

1. Which compounds were completely soluble in water:

2. Which compounds were insoluble in water:

3. Comment on any trends noticed in your observations of solubility and insolubility in water.

C. Solubility - Acetone

1. Which compounds were completely soluble in acetone:

2. Which compounds were insoluble in acetone:

3. Comment on any trends noticed in your observations of solubility and insolubility in acetone.

4. Comment on the differences in the solubility results between water and acetone. What properties of acetone make it a much better solvent for alcohols than water. (Hint: Draw/consider the structure of acetone compared to water.)

D. Potassium Permanganate

1. What was the purpose of the control?

2. What is the evidence of a positive test?

3. Did any of the compounds tested behave unexpectedly. Explain. Why might this have occurred?

4. What trends were observed for the time required for oxidation in the basic, acid and neutral solution?

5. What trends were observed for the time required for oxidation based on the molecular size?

6. What trends were observed for the time required for oxidation based on the type of alcohol (primary, secondary, tertiary)?

7. Write the complete (balanced) reaction for the oxidation of methanol with potassium permanganate.

E. Chromic Acid Test

1. What was the purpose of the control?

2. What is the evidence of a positive test?

3. Did any of the compounds tested behave unexpectedly. Explain. Why might this have occurred?

F. Lucas Reagent

1. What was the purpose of the control?

2. What is the evidence of a positive test?

3. Did any of the compounds tested behave unexpectedly. Explain. Why might this have occurred?

4. What type of reaction occurred? Write a complete (balanced) reaction for ethanol.

G. Unknown

1. Is it necessary to perform both the Chromic Acid test and the Lucas test to classify your unknown?

2. What advantages does the Chromic Acid test have over the Lucas test?

3. What advantages does the Lucas test have over the Chromic Acid test?

4. Why might we perform both tests to help identify an unknown?

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Prelab Questions

1. Draw the Lewis structure of all molecules in Part A of the Results section, and show it to your instructor before beginning the laboratory.

2. Answer the following questions about hydrogen bonding:

   (a) What is hydrogen bonding?

   (b) What are the requirements for hydrogen bonding to occur?

   (c) Sketch an example of hydrogen bonding between two water molecules.

   (d) Sketch an example of hydrogen bonding between two ethanol molecules.

3. How can you use the Lucas test to tell if an alcohol is a primary, secondary or tertiary alcohol?

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