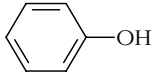


EXPERIMENT #8 – PROPERTIES OF ALCOHOLS AND PHENOLS

Introduction

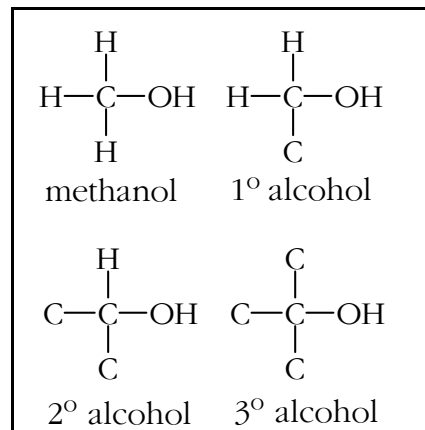
As has been mentioned before, over 20 million organic compounds have been identified. If each substance had to be studied as an entity completely separate from all the other substances, the study of organic chemistry as a whole would be impossible; that is to say, even more impossible than you currently believe it to be. Fortunately, the subject can be organized and it is often organized around the concept of the *functional group*. A functional group is an atom or group of atoms, bonded together in a certain way, that, as part of a molecule, will impart certain physical and chemical characteristics to the molecule as a whole. It is the case that the rest of the molecule can modify the characteristics of the functional group. It is also the case that if the rest of the molecule is an alkyl group the modifications may be modest. On the other hand, other functional groups in the molecule, especially if they are close by, are more likely to profoundly modify the characteristics of the functional group in question.

The functional group we are considering in this experiment is the hydroxy (or hydroxyl) functional group, -OH. This group shows up in a number of guises in organic compounds. Some of the common ones are shown in the table below.

Functional Group Structure	Compound Generic Name	Comments
$\begin{array}{c} \\ -\text{C}-\text{OH} \\ \end{array}$	alcohol	In an alcohol, the -OH is attached to a tetrahedral carbon atom. Very weakly acidic.
$\begin{array}{c} -\text{C}=\text{C}-\text{OH} \\ \quad \end{array}$	enol	Two functional groups attached to the same carbon. It's an <i>alkene</i> and an <i>alcohol</i> . Usually unstable.
	phenol	-OH <i>directly</i> bonded to an aromatic ring. Weekly acidic.
$\text{C}-\text{O}-\begin{array}{c} \\ \text{C}-\text{OH} \\ \end{array}$	hemiacetal	Two functional groups attached to the same carbon. Formed from reaction between an alcohol and an aldehyde or ketone.
$\begin{array}{c} -\text{C}-\text{OH} \\ \\ \text{O} \end{array}$	carboxylic acid	Two functional groups attached to the same carbon. Moderately acidic.

$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{S}-\text{OH} \\ \\ \text{O} \end{array}$	sulfonic acid	Very acidic.
--	---------------	--------------

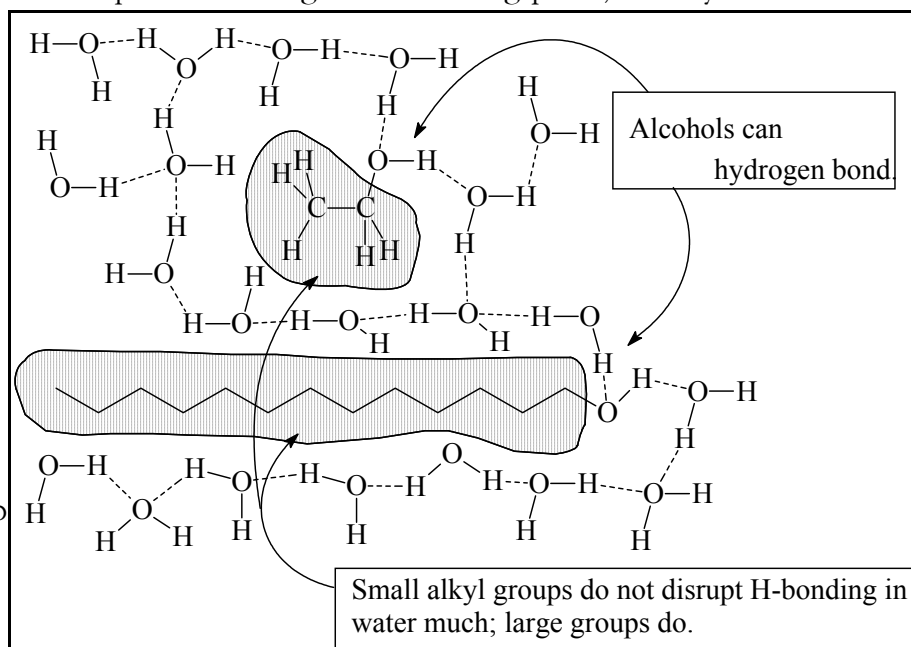
The functional groups we will consider in this experiment are alcohols and phenols. In alcohols the -OH group is attached to a tetrahedral carbon atom. If the carbon atom is bonded to three hydrogens in addition to the -OH, the alcohol is methanol. If the carbon that is bonded to the -OH is bonded to one carbon and two hydrogens, the alcohol is a primary (1°) alcohol. If the carbon that is bonded to the -OH is bonded to two carbons and one hydrogen, the alcohol is a secondary (2°) alcohol. If the carbon that is bonded to the -OH is bonded to three carbons, the alcohol is a tertiary (3°) alcohol. All of these alcohols share some characteristics but other characteristics are different owing to their different structures.



In phenols the -OH group is directly attached to a carbon that is part of an aromatic ring. Alcohols and phenols are similar in some ways, but there are enough differences so that they are considered different functional groups. One major difference is that phenols are typically about a million times more acidic than alcohols. Addition of sufficient aqueous sodium hydroxide to a phenol will cause the -OH group of most of the molecules present to be deprotonated; this will not happen to an alcohol.

Physical Properties

The larger an alcohol or phenol the higher the boiling point, usually. As the alcohol size increases the probability that the alcohol will be a solid increases. Many phenols are solids. Small alcohols are water soluble because the hydroxyl group can hydrogen bond with water molecules. But as the size of the alkyl group increases the solubility in water decreases. This is the result of the alkyl group disrupting hydrogen bonding among the water molecules. If the



disruption becomes large enough the water molecules, in effect, expel the alcohol molecules to reestablish hydrogen bonding. A cartoon showing this is seen above.

The situation is similar for phenols. If nonpolar groups (like alkyl groups) are attached to the aromatic ring the water solubility of the phenol decreases. [This is why nonpolar groups are sometimes called *hydrophobic*.]

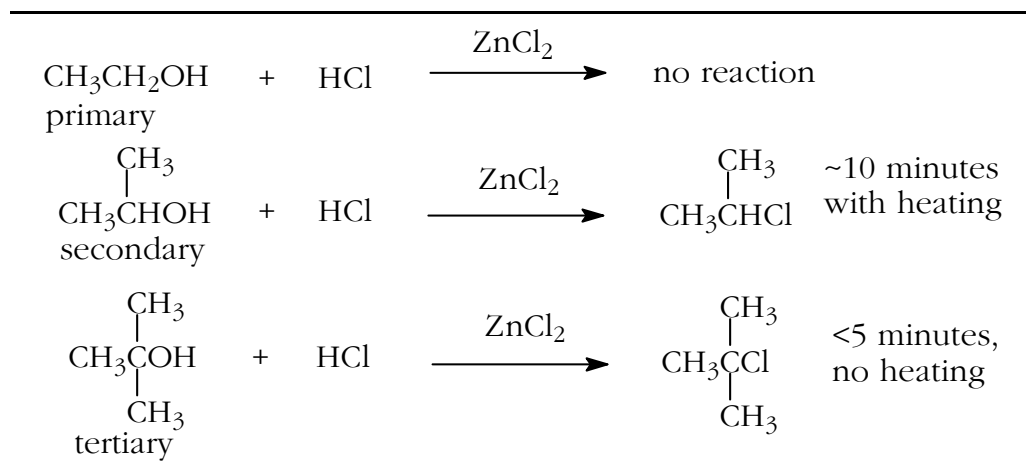
Chemical Properties

We shall focus on chemical reactions that can help to distinguish alcohols from phenols and to distinguish among the classes of alcohols.

1. Lucas Test.

This test is used to distinguish among primary, secondary, and tertiary water-soluble alcohols. Lucas reagent is a mixture of concentrated hydrochloric acid and zinc chloride. Zinc chloride is a Lewis acid, which when added to hydrochloric acid makes it even more acidic.

Water soluble tertiary alcohols react with Lucas reagent almost immediately to form an alkyl chloride which is insoluble in the aqueous solution. The formation of a second liquid phase in the test tube almost as soon as the alcohol initially dissolves is indicative of a tertiary alcohol. A secondary alcohol reacts slowly to form a chloride and, after heating a little, gives a second phase, usually within 10 minutes. Primary alcohols and methanol do not react under these conditions. In the case of tertiary alcohols the chloride is usually attached to the carbon that held the hydroxyl group. In the case of secondary alcohols, it is often the case that the chlorine is attached to the carbon that held the hydroxyl, but rearrangements are possible.

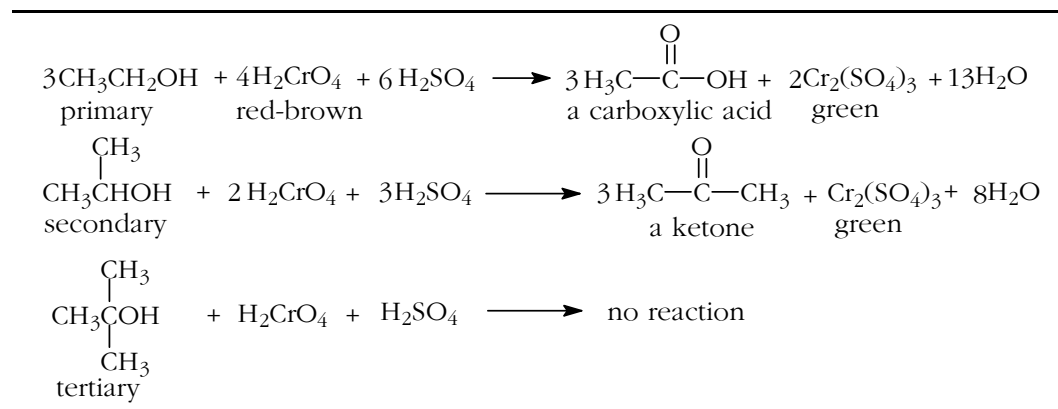


2. Chromic Acid Test.

Primary alcohols are oxidized to carboxylic acids by chromic acid. The Cr^{+6} in the chromic acid, which is red-brown, is reduced to Cr^{+3} , which is green. Secondary alcohols are oxidized to ketones by chromic acid. The chromium reduction is the same here as

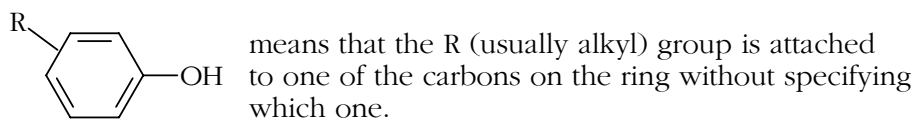
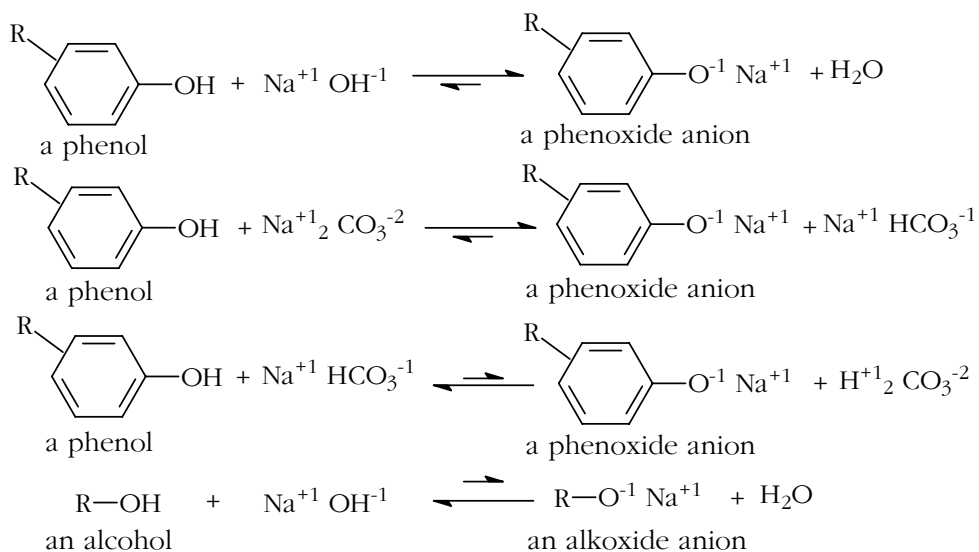
for the primary alcohols. Tertiary alcohols are not oxidized by chromic acid. Thus this reaction can distinguish between primary and secondary alcohols, on the one hand, and tertiary alcohols, on the other.

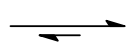
Phenols are usually oxidized to a brown tar by chromic acid.

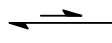


3. Acidity of Phenols.

Most phenols are weaker acids than carboxylic acids and stronger acids than alcohols. When phenols react with a base the phenol is converted into a phenoxide anion (see reactions below). The phenoxide anion is more soluble in water than the corresponding phenol. Consequently, if a water-insoluble phenol is treated with an aqueous solution of a base that is strong enough to convert most of the phenol to the phenoxide anion, that phenol will dissolve in the aqueous base (as the phenoxide salt). Aqueous sodium hydroxide and sodium carbonate are strong enough bases to dissolve most water-insoluble phenols, while aqueous sodium bicarbonate is not. None of the above-mentioned bases is strong enough to convert a substantial amount of a typical alcohol into an alkoxide anion (which would cause a water-insoluble alcohol to dissolve as its alkoxide anion).



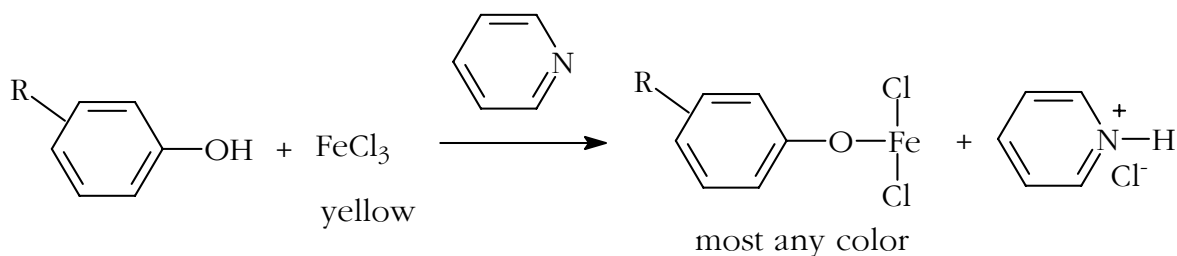

 means that equilibrium favors the reaction; products will form and reactants will mostly be used up. The stronger acid and stronger base are on the left side.


 means that equilibrium does not favor the reaction; reactants will hardly react and little product will form. The weaker acid and weaker base are on the left side.

The order of basicity of the bases appearing on the left in the above equations is, from most basic to least basic: sodium hydroxide, $\text{NaOH} >$ sodium carbonate, $\text{Na}_2\text{CO}_3 >$ sodium bicarbonate, NaHCO_3 .

4. Iron(III) Chloride Test.

Addition of iron(III) chloride dissolved in chloroform (trichloromethane) to a phenol dissolved in chloroform, gives a colored solution upon addition of pyridine. Depending on the structure of the phenol the color of the product can be most anything from red to violet. Alcohols do not give this test.



Objectives of the Experiment –

1. To learn something about the physical and chemical properties of alcohols.
2. To use the information obtained about chemical properties to identify an unknown as a primary, secondary, or tertiary alcohol or phenol.

Procedure –

Caution!

Chromic acid is very corrosive. If you get any on yourself wash the affected area with lots of water immediately! Phenol is extremely corrosive. If any of the solid or a solution of phenol comes in contact with you, wash the affected area with lots of water immediately! Wear gloves when handling these chemicals, and as usual, goggles.

Solubility of Alcohols and Phenols

In each of the following cases you will attempt to make an approximately 10% (by weight) solution of the alcohol or phenol in water (very polar) and in hexane (nonpolar) to see if the compound is soluble to at least that extent.

1. Label clean dry test tubes as follows: 1-propanol, 1-butanol, 1-pentanol, phenol, 5-isopropyl-2-methylphenol. Place 10 drops (= ~0.5 ml = ~0.5 g) of the appropriate compound into each test tube. In the case of phenol add 0.5 g. Using a 10 ml graduated cylinder, add 4.5 ml (= 4.5 g) of deionized water to each tube. Agitate the tubes to mix the contents. (Note that, in general, liquids that are miscible will dissolve in each other quickly. Solids that are soluble may take some time and require encouragement like stirring with a stirring rod.) Record on the report sheet whether the compound is completely soluble, partially soluble, or insoluble in the water. Discard the contents of the tubes into the sink and wash down the drain with water. Rinse the test tubes with water, then with a small portion of acetone, then with a small portion of hexane. Invert the tubes in a beaker and allow them to dry for a couple of minutes. Rinse the graduated cylinder with acetone and then hexane.
2. Again place 10 drops (in the case of phenol 0.5 g) of each compound into the corresponding test tube. Using the 10 ml graduated cylinder, add 6.8 ml of hexane (~4.5 g) to each tube. Agitate the tubes to mix the contents. Note on the report sheet whether the compound is completely soluble, partially soluble, or insoluble in the hexane.

Discard the contents of the tubes into the sink and wash down the drain with water. Rinse the test tubes with water, then with a small portion of acetone. Allow to drain.

Chemical Tests

Label the clean dry test tubes as follows: 1-butanol, 2-butanol, 2-methyl-2-propanol, phenol, and unknown.

1. Lucas Test –

Place 5 drops of each sample into the appropriate tube. Add 1 ml of Lucas reagent. Stopper the test tube with a cork and agitate the contents of the tube vigorously by holding the top of the tube with the thumb and index finger of one hand and striking the bottom of the tube horizontally with the index finger of the other hand. After the contents are thoroughly mixed, remove the cork and allow the tube to stand for five minutes. Look for any cloudiness or separation of a second layer that has developed in this 5 minute time span. Record results on the report sheet. Allow the tubes to sit for another 5 minutes and again observe the ones that had been clear to see if there is any cloudiness or second layer of liquid. Place any tubes that still have one clear layer into a 60°C water bath for 15 minutes. Again look for cloudiness or a second layer of liquid and record your results on the report sheet.

2. Chromic Acid Test –

Place 5 drops of each sample into the appropriate clean dry test tube. To each test tube add 10 drops of acetone and 2 drops of chromic acid. Stopper the tube with a cork and agitate. Remove the cork and place the tube in a 60°C water bath for 5 minutes. Note the color of each solution and any other characteristics. Record your observations.

3. Iron(III) Chloride Test –

Place 10 drops of each sample into the appropriate clean dry test tube. Add 10 drops of trichloromethane (chloroform) to each tube. Add 5 drops of iron(III) chloride in chloroform to each tube. Add 2 drops of pyridine to each tube. Agitate the tube. Record your observations.

Structures of Alcohols

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 1-propanol

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 1-butanol

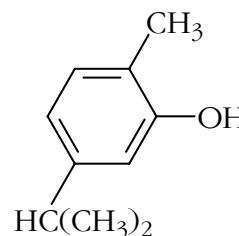
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 1-pentanol

$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$ 2-butanol

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CCH}_3 \\ | \\ \text{OH} \end{array}$ 2-methyl-2-propanol

Structures of Phenols

 phenol

 5-isopropyl-2-methylphenol

4. Acidity –

Place 5 drops of each sample into the appropriate clean, but not necessarily dry, test tube. To each test tube add 5 drops of deionized water. Use a clean glass stirring rod to stir each sample and then touch the wet tip of the rod to a piece of pHDrion paper. After 15 seconds compare the color of the paper with the colored scale that accompanies the test paper. Record the pH of the mixture on your report sheet.

Based on these tests you should be able to identify your unknown as a primary alcohol, secondary alcohol, tertiary alcohol, or a phenol.