Chemistry 136

Organic Qualitative Analysis

Objective:

During this experiment, you will determine the structure of an unknown compound by using a series of classification tests and by preparing derivatives. This is the way things were done prior to the advent of modern instrumentation. Although these chemical techniques have been largely replaced by sophisticated equipment, they do illustrate many aspect of chemical reactivity that will enable you to handle and identify unknown organic compounds using instrumental methods.

Background:

You will be given 1000 mg of an unknown material that is either a ketone or an amine. You will then use the physical properties and reactivity of your unknown to deduce its structure. By following the simple scheme described below, you will be able to determine which functional groups your unknown contains, learn about the reactivity of the compound, and prepare a sufficient number of derivatives to identify the compound beyond reasonable doubt. Along the way, you will be asked to make observations about the state of your unknown and its behavior under a variety of conditions that will prove useful in determining the structure of your compound.

PART I. *Physical Properties and Functional Group Classification*.

Step 1. Physical Properties

Examine your unknown and answer the following questions:

A. Appearance/Color?_____

B. Solid or Liquid?_____

Determination of the melting point of a solid.

Place *ca*. 5 mg of the solid in a capillary tube that has been sealed at one end (these are available in the laboratory). It may be necessary to shake the sample to the closed end of the tube by dropping the capillary (closed end first) several times down a length of glass tubing held vertically on the bench top. Take the melting point in the normal manner.

Determination of the boiling point of a liquid: Microscale Technique.

The boiling point of a liquid can be determined with surprising accuracy on samples as small as 2 microliters using the following method. Place *ca*. 10 microliters (enough to fill the capillary to a depth of *ca*. 5 mm) of the unknown liquid in a capillary tube that has had one end sealed. Put this tube aside. Take a fresh melting point capillary and heat it gently in a Bunsen flame. When the glass has softened, remove the glass from the flame and draw out the glass to form a micro capillary tube. Ideally this tube will be *ca*. 0.2 mm in diameter. It will take a few tries before you get the "perfect" micro capillary. Allow the glass to cool and then break off one of the ends of the micro capillary, being sure to leave *ca*.1 cm of the micro capillary on the other end. Seal the end of the micro capillary by passing it quickly through the flame. Break off about 5 mm of the sealed micro capillary and place it, open end down, into the capillary tube containing your unknown. Make sure that the micro capillary is all the way to the bottom of the unknown. Now place the capillary containing your unknown and the micro capillary into the melting point apparatus and warm it until there is a steady stream of bubbles flowing from the open end of the micro capillary. Turn off the heat and observe the sample. As it cools, the rate of flow of bubbles will decrease. Eventually the bubbles

will stop flowing all together and the unknown liquid will be drawn up into the micro capillary. The temperature at which this occurs is the boiling point of the unknown liquid. This procedure may be repeated to ensure that the boiling point that you obtain is accurate.

C. M.P. or B.P._____

Step 2. Solubility

The solubility of an unknown material in various solvents can often provide very useful information regarding the structure of the unknown. The compounds in this experiment are all ketones or amines. Solubility in dilute acid provides a convenient and easy method to distinguish these two functional groups from one another.

The Hydrochloric Acid Test.

Place *ca*. 3 mL of water in a clean test tube. Add one drop or a spatula tip of your unknown. Swirl the mixture. If your unknown is soluble, test the pH of the solution. An alkaline pH is indicative of an amine. If your unknown is not soluble in water, add 3 mL of 5% HCl solution. If your unknown dissolves in the acid solution, an amine is indicated. If the unknown is not soluble in the acid solution, your unknown is likely a ketone.

D. Soluble in Water?_____

E. Mark the appropriate blank indicating the functional group in your unknown.

Ketone_____ Amine_____

PART II. Additional Functional Group Tests and Formation of Derivatives.

Now that you know the main functional group in your unknown, you will now be able to develop, using additional tests, a more refined picture of your unknown. Tests for ketones and amines are described separately. Be sure to conduct the experiments for the type of unknown that you have.

The Following Tests are for Ketone containing Unknowns

If you have an amine containing unknown, skip to **Step 6**.

Step 3. Presence of Unsaturation.

To determine if your unknown contains an alkene, you may conduct the Bayer test for unsaturation. This test uses the decolorization of bromine to show the presence of unsaturation.

The Bayer Test for Unsaturation.

Dissolve 2 drops or a spatula tip full of your unknown in *ca*. 2 mL of dichloromethane. Add one drop of a 1% solution of bromine in dichloromethane to your solution of unknown. The immediate disappearance of the brown color of the bromine is indicative of the presence of a double bond. All aliphatic ketones will brominate over time, so be sure that the disappearance of color is immediate.

F. Unsaturation? (y/n)_____

Step 4. Presence of a Methyl Ketone

The presence of a methyl ketone may be determined by examining the reaction of the unknown ketone with iodine in the presence of the base. If there is a methyl ketone in the unknown, the methyl group will be oxidized and displaced as iodoform, which precipitates as a light yellow solid from the reaction mixture.

The Iodoform Test for Methyl Ketones.

Dissolve 10 drops or a spatula tip full of your unknown in 2 mL of diglyme. Add 2 mL of 10% sodium hydroxide solution. In a separate test tube, dissolve 0.5 g of iodine in a solution composed of 4 mL of water and 1 g potassium iodide (this is the iodoform reagent). Place 2 mL of the sample solution (the solution of the unknown) in a 20 mL test tube. Add iodoform reagent dropwise until a dark color just persists. Then heat the solution in a warm water bath at *ca*. 60°C. While heating, add additional iodoform reagent at a rate such that the color is just maintained. Continue to heat the solution for *ca*. 2 min. after the last addition. Then add 10% sodium hydroxide solution to remove

any residual iodine color. Now dilute the solution with a volume of water equal to the total volume of solution. If the test is positive (i.e. you have a methyl ketone), a yellow precipitate of iodoform should be observed within 10 min.

G. Methyl Ketone (y/n)_____

Step 5. Derivative for Ketones.

Among the most common and also highly crystalline derivatives for ketones are the 2,4-dinitrophenylhydrazones. These materials may be formed by reaction of the hydrazine with the unknown ketone under the following conditions.

The 2,4-Dinitrophenylhydrazone Derivative for Ketones.

Place 5 mL of a saturated solution of 2,4-dinitrophenylhydrazine in ethanol in a test tube. To this solution add 5-10 drops of the unknown ketone. Warm the solution to reflux in a warm water bath for *ca*. 2 min. Add 1-2 drop of concentrated hydrochloric acid to the solution. At this point, the color usually changes to bright yellow or orange. Heat the solution at reflux in a hot water bath for 2 min. while adding water dropwise until the solution becomes turbid or crystallization begins. Cool the solution in an ice bath and obtain the crystals by filtration (be sure to rinse the crystals to remove any residue). It is generally the case that these hydrazones do not require recrystallization. Dry the crystals under vacuum and obtain a melting point. Lists of melting points of 2,4-dinitrophenylhydrazones of many ketones are available in many organic qualitative analysis text in the laboratory.

H. Melting point of 2,4-DNP_____

The Following Tests are for Amine containing Unknowns

If you have a ketone containing unknown, go back to **Step 3**.

Step 6. Primary or Secondary Amines.

Primary and secondary amines may be distinguished from tertiary and aromatic amines by formation of the sulfonamides. This experiment, known as the Hinsberg test, is based on the fact that primary and secondary amines react with benzenesulfonyl

chloride to give N-substituted sulfonamides. The tertiary amines do not give derivatives. The sulfonamides of primary amines react with base to give salts that are usually water soluble. Sulfonamides of secondary amines do not have any acidic protons and therefore do not show pH dependent solubility.

The Hinsberg Test for Amines.

Place 10 drops or two spatula tips full of the amine unknown in 10% KOH solution. Add 0.4 mL benzenesulfonyl chloride to this solution. Stopper the mixture and shake with cooling if necessary. The mixture should still be strongly basic. If it is not, add a few drops 4 M KOH. If the mixture has formed two layers, separate the layers and test the organic phase for solubility in 10% HCl. Tertiary amines will be soluble. Sulfonamides of secondary amines will not be soluble. Some higher molecular weight amines form benzenesulfonamides that have low solubility in aqueous base. They may give the same solubility characteristics as the sulfonamides of secondary amines. In order to differentiate between these possibilities, you should bring the separated aqueous phase to a pH of 4 by addition of 6 M HCl. A precipitate indicates the formation of the sulfonamide of a primary amine.

If the original mixture did not separate into two layers, a soluble salt of a benzenesulfonamide of a primary amine was formed. This can be confirmed by bringing the pH of the solution to 4 by drop wise addition of 6 M HCl, at which time a precipitate should form. If you did obtain a sulfonamide of a primary or secondary amine, collect the crystals by filtration, rinse them with water, dry them under vacuum, and obtain a melting point. You may compare the melting point of your sulfonamide to those in the qualitative analysis texts in the laboratory to confirm the structure of your unknown.

I. Primary, Secondary or Tertiary Amine?_____

J. If primary or secondary, M. P. of benzenesulfonamide_____

Step 7. Tertiary Amines.

If, by the Hinsberg test, you have determined that you have a tertiary amine, you will need to make a derivative of this compound to confirm its structure. The most convenient derivative for tertiary amines is the methyl iodide alkylation product. These quaternary ammonium salts are almost always crystalline, but are very hygroscopic.

Place 10 drops or two spatula tips of your unknown tertiary amine in a test tube. Add 0.5 mL of methyl iodide to the test tube and warm the mixture for a few in a hot water bath. Upon cooling, the mixture should solidify to give the methiodide adduct as a crystalline solid. The solid obtained from these reactions is often amorphous, but can be recrystallized from ethanol or ethyl acetate. You may compare the melting point of your methiodide to those in the qualitative analysis texts in the laboratory to confirm the structure of your unknown.

K. M. P. of Methiodide_____

PART III. Determination of the Structure

Based on the tests you have performed and derivatives you have prepared, you should be able to deduce the structure of the unknown compound. Give that structure in the space provided below. Make sure that the properties of your proposed structure are consistent with all data available on your unknown. Write the number of your unknown in the space provided.

Structure

Unknown Number

Questions

Attach additional pages as necessary to answer to following questions regarding these experiments.

1. Why are amines soluble in acidic water and generally not soluble in basic water?

2. Describe how you might be able to distinguish between an alkane and a carboxylic acid based on solubility properties.

3. A) Using acetophenone (phenyl methyl ketone) as the methyl ketone, write a complete mechanism for the formation of iodoform during the iodoform test.
   B) What is the other organic product that is formed during the iodoform test?

4. Using butyl amine as the primary amine, write a complete mechanism for the formation of (N-butyl)benzenesulfonamide from benzenesulfonyl chloride under basic conditions.

5. Why are the benzenesulfonamides of primary amines soluble in strong base and the benzenesulfonamides of secondary amines not?