Lab 13: Qualitative Analysis

Prelab Assignmet
Date, Title, Introduction. You will complete the procedures during the lab period as you plan for each test.

Introduction
In this experiment you will be determining the identity of an unknown compound. The object of this experiment is to identify an unknown organic compound through the use of physical observations, solubility tests, classification tests, preparation of chemical derivatives, and a limited amount of spectroscopic analysis. Your unknown will be one of the chemicals listed in the handout that you will get in lab (~300 chemicals). The unknown may be a solid or a liquid and may be an alcohol, a ketone, or an aldehyde with or without double/ triple bonds and or a halogen. Furthermore, your unknown may contain halogens or double bonds.

Procedure
You will perform the following tests on your unknown. For each of the chemical tests it is imperative that you run controls first so that you can determine what a positive result should look like AND what a negative test should look like. ***You may be able to determine what your unknown is before running all of the tests, but you should still perform all of the tests.*** You will receive about 1.0 mL of your sample, so be sure to use it wisely and to store it properly.

1. Observe the physical appearance.
    a. Color
    b. Odor
    c. Physical State
2. Check the solubility in water
3. Run the Belstein's test for halogens.
4. Run the bromine and $KMnO_4$ (Baeyer Test) test for unsaturation.
5. Ceric nitrate test
6. 2,4-dinitrophenylhydrazine test (Brady's Reagent)
7. Chromic acid test (Jones reagent)
8. Tollen's test
9. Preparation of derivatives and MP of derivatives
    a. Alcohols → 3,5-dinitrobenzoyl chlorides
    b. Aldehydes and ketones → 2, ,4-dinitrophenylhydrazine
10. After the completion of the above tests, take your lab book to your instructor with saved samples of your prepared derivatives for approval.
    a. After approval you may be able to take an IR (at your instructors discretion) of you sample for analysis.
    b. Measure the refractive index if your unknown is a liquid. Be sure to correct your refractive index with the formula below.

$$n_D^{20^oC(corrected)} = n^{Ambient\ temp} + (T^{ambient} - 20.0000^oC)x(0.00045)$$

11. As an option, you may take the boiling point of your liquid unknown.

Remember your controls: It is imperative that each test have at minimum two types of controls- one that will yield positive results and one that will yield negative results. You will be graded on which controls you use, so be sure to pick them carefully and make good observations in your lab book!

Tests

Belstein's Test

Organic compounds that contain chlorine, bromine or iodine and hydrogen decompose on ignition in the presence of copper oxide to yield the corresponding hydrogen halides. These hydrogen halides react to form the volatile cupric halides that impart green or blue-green colors to a flame. It is a very sensitive test, but some nitrogen containing compounds and some carboxylic acids also give positive tests.

Procedure

Place a piece of copper wire into a cork to act as an insulator (these may be provided to you at the back of the lab). Heat the wire in a flame until the color becomes negligible. Place an large drop of your unknown or a few crystals if solid onto the tip of your **COOLED** copper wire. Gently heat the wire in the flame. Sometimes it is easier to see the color if you place the copper wire above the flame slightly. The characteristic blue/green color will become evident if chloride, iodide, or bromide is present. It is often a quick flash, so be certain to run controls first so that you know what to look for!

Test for Unsaturation:

Bromination of Alkenes

Unsaturated hydrocarbons (non-aromatic) react readily with bromine (Br_2). We will be using aqueous bromine for this test. (Do you recall the mechanism for this reaction?) The test is based on the decolorization of the bromine (brown). Be sure to note the time that it takes for the controls to respond. You may see two layers forming here because most of your samples are not water soluble.

CAUTION: Be sure that your Br_2(aq) stock solution is dark orange. If left out for too long the Br_2 dissipates out of the water. ALSO NOTE: Bromine is highly toxic and can cause burns. Treat this reagent with respect!

Procedure

In a 10 x 75-mm test tube, place 2 drops of a liquid unknown (~15 mg if a solid) followed by approximately 2 drops of the Br_2 aqueous solution. Add dropwise while shaking the mixture. Additional points: aldehydes and ketones can interfere with this test.

Oxidation with Potassium Permanganate (Baeyer Test)

This test is positive for non-aromatic double bonds and for triple bonds. The reaction dihydroxylates unsaturated bonds and forms the brown precipitate MnO_2. Other compounds that can be easily oxidized can also give positive tests (aldehydes, certain alcohols, and aromatic amines).

Procedure

In a 10 x 75-mm test tube, place 2 drops of a liquid unknown (~15 mg if a solid) followed by approximately 6 drops of the $KMnO_4$ aqueous solution. Add dropwise while shaking the mixture. Permanganate solutions slowly decompose from the purple $KMnO_4$ into the brown manganese dioxide precipitate over time, so be careful to not confuse this with a positive test.

Ceric nitrate test

Primary, secondary, and tertiary alcohols having fewer than10 carbons give a positive test as indicated by a change in color from yellow to red.

$$(NH_4)_2Ce(NO_3)_6 + RCH_2OH \rightarrow \text{Alcohol} + \text{reagent}$$
YELLOW RED

Procedure

Place 5 drops of test reagent in a test tube. Add 1-2 drops of the unknown sample (~5 mg if solid). Stir with a glass rod to mix the components and observe any color change.

2,4-dinitrophenylhydrazine test (Brady's Reagent)

Aldehydes and ketones react readily with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones. These derivatives range in color from yellow to red, depending on the degree of conjugation in the carbonyl compound.

Procedure

In a test tube, place 7-8 drops of 2,4-dinitrophenylhydrazine reagent solution (be sure to get some gloves from your instructor). Add 1 drop of a liquid unknown. If your unknown is a solid, dissolve 10mg of your sample in 10 drops of 95% ethanol. The mixture is stirred with a thin glass rod. The formation of red-to-yellow precipitate is a positive test. **NOTE: The reagent 2,4-dinitrophenylhydrazine is orange-red. Be careful to not mistake this as your derivative.**

Additional notes

Reactive esters or anhydrides react with the reagents to give a positive test. Allylic or benzylic alcohols may be oxidized to aldehydes or ketones, which can in turn give a positive test.

Chromic acid test (Jones reagent)

The Jones oxidation is a rapid method for distinguishing primary and secondary alcohols from tertiary alcohols. A positive test is indicated by a color change from orange (Cr(VI), the oxidizing agent) to a greenish-blue (Cr(III), reduced form).

The test is based on the oxidation of a primary alcohol to a carboxylic acid and a secondary alcohol oxidized to a ketone.

Procedure

Place one or two drops of your unknown (10 mg if a solid) into your test tube. Add two drops of the Jones reagent and observe any color changes (the reaction should be fairly fast but you should make your observations over a period of 5 minutes)

NOTES:

- Be sure to work with gloves here.
- Do not forget to run proper controls (which ones do you need here?).
- Run a blank with acetone as an additional control
- Aldehydes give a positive test since they can be oxidized to carboxylic acids (what other controls do you need?)

$ZnCl_2$/ HCl test (Lucas reagent) (ask your instructor- we may skip this test)

The Lucas test is used to distinguish between primary, secondary, and tertiary alcohols with fewer than 6 carbons.

$$R\text{-}OH\ (aq) + H_3O^+\ (aq) \rightarrow RCl\ (ppt) + H_2O$$

The test requires that the alcohol initially be soluble in the Lucas reagent. A positive test is indicated by the formation of a precipitate of the corresponding alkyl chloride. See you notes from last semester for the reaction mechanism. Primary (very slow) alcohols react much slower than secondary (~3-10 min) or tertiary (immediate reaction) alcohols.

Procedure

In a 3-ml conical vial equipped with an air condenser, add 2 drops of your unknown (or 10 mg if solid) followed by 10 drops of the Lucas reagent. Shake or stir the reaction with a glass rod to mix the solutions while noting the presence of a ppt *and* the time that it takes for the ppt to form. You may gently heat this solution if needed.

Tollen's test

This reaction involves the oxidation of aldehydes to the corresponding carboxylic acid using an alcoholic solution of silver ammonium hydroxide. A positive test is indicated by the formation of a silver-mirror, or a black precipitate of finely divided silver.

$$RCHO + 2\ Ag(NH_3)_2OH \rightarrow 2\ Ag(s) + RCOO^- + NH_4^+ + H_2O + 3\ NH_3$$

Procedure

Use one of the disposable sample test tubes provided by your instructor. Place 1.0 mL of 0.1M $AgNO_3$ (aq) and 1 drop of 10% NaOH (aq) into the prepared test tube. Now add concentrated aqueous ammonia dropwise into the test tube (usually about 1.5 drops) with shaking until the precipitate of silver oxide just dissolves. Add 1 drop of the unknown (10 mg if solid) with shaking and allow the mixture to stand for 10 minutes at room temperature. If no reaction has occurred, place the test tube in a sand bath at 40^0C for 5 minutes.

Additional Important Points to Consider:

- Avoid a large excess of ammonia.
- Use piperonaldehyde for your positive control.
- Reagents must be mixed well. Stirring is recommended.
- This reagent must be freshly prepared for each test. It should not be stores since decomposition occurs with the formation of AgN_3 (look up the HAZ-MAT for this) which is explosive!
- This oxidizing agent is very mild and does not oxidize alcohols. Ketones do not react.

CAUTION:

The reagent should be prepared immediately before use and all residues disposed of immediately after use. Dispose of any residues by acidifying them with 5% hydrochloric acid and then placing them in a waste container designated for this waste. On standing, the reagent tends to form silver fulminate, a very explosive substance. (Pavia, et al)

Preparation of Derivatives

You will now prepare a derivative of your compound. By doing this you will gain another important piece of information that you can use to help you narrow down your choices.

Alcohols

In a 3-mL conical vial containing a boiling stone, and equipped with an air condenser with calcium chloride filled drying tube, add 75-mg of pure 3,5-dinitrobenzoyl chloride and six drops of your unknown. Heat the mixture to about 10^{o}C below the boiling point of the alcohol (but not over 100^{o}C) in a water bath for about 5 minutes. Most of the solid should dissolve during this heating. Cool the reaction, add 0.90mL of DI water and then place the vial in an ice bath to further cool. Collect the ester product by vacuum filtration (get a precut piece of filter paper to aid in the collection in your Hirsch funnel) and wash the solid with three 0.5mL portions of 2% Na_2CO_3 (aq) followed by 0.5 mL of DI water. Recrystallize the product using an ethanol-water mixture with a test-tube. Dissolve the solid in boiling 95% ethanol and then add water dropwise until the solution is just cloudy. Cool in an ice bath and collect the crystals by vacuum filtration (get a precut piece of filter paper to aid in the collection in your Hirsch funnel). Allow the product to dry and take the melting point.

Aldehydes and Ketones

Aldehydes and ketones react readily with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones. These derivatives range in color from yellow to red, depending on the degree of conjugation in the carbonyl compound.

Procedure

In a 3-mL conical vial, place 28-32 drops of 2,4-dinitrophenylhydrazine reagent solution. Add 6 drops of a liquid unknown. If your unknown is a solid, dissolve 10mg of your sample in 10 drops of 95% ethanol. The mixture is stirred with a thin glass rod. The formation of red-to-yellow precipitate is a positive test. Collect the solid via vacuum filtration (get a precut piece of filter paper to aid in the collection in your Hirsch funnel) and recrystallize the derivative using 95% ethanol.