ORGANIC FUNCTIONAL GROUP ANALYSIS

I. OBJECTIVES AND BACKGROUND

This experiment will introduce you to some of the more common functional groups of organic chemistry. The functional group is that portion of the molecule that undergoes a structural change during a chemical reaction. The functional groups that will be studied in this experiment are carboxylic acid, amines, aldehyde, ketone, alcohols and alkenes.

You will learn chemical tests that will allow you to distinguish one functional group from another. You will use the chemical tests to identify the functionality of an unknown organic compound. In addition, you will use a water solubility test to determine whether your organic compound is of high or low formula weight.

The chemical tests you will perform make up a sequence of experiments designed to determine the absence of or suggest the presence of particular functional groups. The complete sequence is shown in the flow diagram on page 8. This diagram can serve you in several ways:

- It is a summary of the procedure that you are to follow in classifying your unknown as one of the functional group types.
- It can order your thoughts as you read the discussion of each test, and help you to understand the significance of that test.
- It can enhance your appreciation for and enjoyment of this experiment. Your role is that of chemist and detective: you will employ this cleverly devised scheme to sleuth out the identity of your unknown's functionality.
Discussion of Chemical Tests

1. Water Solubility: Diagnosis of a Low Formula Weight Compound
Most organic compounds are slightly soluble or insoluble in water. Water solubility is uncommon and if observed is an indication of a molecule of low molecular weight. A litmus paper test of the solution’s pH will provide additional information about the water-soluble molecule.

A. Acidic Response to Litmus: Diagnosis of a Low Molecular Weight Organic Acid
Carboxylic acids with fewer than five carbon atoms are generally water soluble and form solutions that give an acidic response to litmus (acidic response: blue litmus paper turns red).

\[ \text{RCO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RCO}_2^- + \text{H}_3\text{O}^+ \]

B. Basic Response to Litmus: Diagnosis of a Low Molecular Weight Organic Base
Amines are the organic derivatives of ammonia, and like ammonia, they are weak bases. Amines that have fewer than five carbon atoms are generally water soluble and form solutions that give a basic response to litmus (basic response: red litmus paper turns blue).

primary amine: \[ \text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ + \text{OH}^- \]

secondary amine: \[ \text{R}_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{NH}_2^+ + \text{OH}^- \]

tertiary amine: \[ \text{R}_3\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{R}_3\text{NH}^+ + \text{OH}^- \]

C. Neutral Response to Litmus: Diagnosis of Low Molecular Weight Neutral Compound
Neutral compounds (ketones, aldehydes, alcohols, alkenes) with fewer than five carbons are generally water soluble, and the resulting solutions are neither acidic nor basic. The solutions give a neutral response to litmus (neutral response: litmus paper does not change colors).
2. **Solubility in 5% NaOH: Diagnosis of a High Molecular Weight Organic Acid**

A carboxylic acid with five or more carbons, though insoluble in water, will be soluble in 5% NaOH solution because of the formation of the sodium salt of the acid.

\[
\text{R} \overline{\text{C}} \text{OH} + \text{NaOH} \rightleftharpoons \text{R} \overline{\text{C}} \text{O}^- \text{Na}^+ + \text{H}_2\text{O}
\]

3. **Solubility in 5% HCl: Diagnosis of a High Molecular Weight Organic Base**

An amine with five or more carbon atoms, though insoluble in water, will be soluble in 5% HCl solution because of the formation of an ammonium chloride salt.

- **Primary amine:** \( \text{RNH}_2 + \text{HCl} \rightleftharpoons \text{RNH}_3^+\text{Cl}^- \)
- **Secondary amine:** \( \text{R}_2\text{NH} + \text{HCl} \rightleftharpoons \text{R}_2\text{NH}_2^+\text{Cl}^- \)
- **Tertiary amine:** \( \text{R}_3\text{N} + \text{HCl} \rightleftharpoons \text{R}_3\text{NH}^+\text{Cl}^- \)

*If the compound is not soluble in either dilute acid or dilute base, then it is a neutral compound (ketone, aldehyde, alcohol, alkene) of high molecular weight.*

4. **Reaction with 2,4-Dinitrophenylhydrazine (2,4-DNP): Diagnosis of Aldehyde or Ketone**

Aldehydes and ketones are detected by the formation of an orange or red-orange 2,4-dinitrophenylhydrazone precipitate.

\[
\text{R}' \overline{\text{C}} \text{O} \rightleftharpoons \text{H}_2\text{N} \overline{\text{N}} \text{H} \overline{\text{N}} \text{H} \text{O}_2\text{N} \text{NO}_2 + \text{H}_2\text{O}
\]

\[
\text{R}' \overline{\text{C}} \text{N} \overline{\text{N}} \text{H} \text{O}_2\text{N} \text{NO}_2 + \text{H}_2\text{O}
\]

\( \text{R}' = \text{alkyl or H} \quad 2,4\text{-DNP} \quad \text{orange 2,4-DNP precipitate} \)
5. Tollens’s Test: Diagnosis of Aldehyde

Aldehydes can be distinguished from ketones by the Tollens’s Test because aldehydes can be easily oxidized to acids, but ketones cannot. The Tollens’s reagent contains a silver-ammonia complex ion in a basic solution. Silver(I) ion is reduced to silver metal as the aldehyde is oxidized to acid.

\[
\text{R-CHO} + 2 \text{Ag(NH}_3\text{)}_2^+ + 2 \text{OH}^- \rightarrow \text{R-CO}^- + \text{NH}_4^+ + 2 \text{Ag(s)} + \text{H}_2\text{O} + 3\text{NH}_3
\]

An aldehyde is indicated by the appearance of a silver mirror on the wall of the test tube or a precipitate of silver metal.

6. Reaction with Chromic Acid: Diagnosis of Alcohol

Primary and secondary alcohols are oxidized by chromic acid to carboxylic acid and ketone, respectively.

- **Primary alcohol:**
  \[
  \text{R-CH}_2\text{-OH} \xrightarrow{\text{H}_2\text{CrO}_4} \text{R-C} \xrightarrow{\text{H}_2\text{CrO}_4} \text{R-COOH}
  \]

- **Secondary alcohol:**
  \[
  \text{R'-CH-OH} \xrightarrow{\text{H}_2\text{CrO}_4} \text{R'-C} \xrightarrow{\text{H}_2\text{CrO}_4} \text{no visible reaction}
  \]

- **Tertiary alcohol:**
  \[
  \text{R''-C} \xrightarrow{\text{H}_2\text{CrO}_4} \text{no visible reaction}
  \]

An alcohol is indicated by disappearance of the orange color of the chromic acid reagent and the formation of a green or blue-green solution.
7. Decolorization of Bromine: Diagnosis of Alkene
The halogen bromine will rapidly react with alkenes at room temperature to produce the dibromoalkane.

\[
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \quad \text{+} \quad \text{Br}_2 \quad \rightarrow \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\]

Colorless \quad red solution \quad colorless or light yellow solution

Bromine solutions are reddish-brown; alkenes and bromoalkanes are colorless. Rapid decolorization of bromine is a positive indication of an alkene.

III. PROCEDURE
The following procedures are to be carried out first on samples of known compounds so that positive responses for each test can be observed. When you feel confident that you can recognize a positive test for each procedure, obtain an unknown from your instructor. Substitute your unknown for the known compound in each test. Use the flow diagram on page 8 to follow your progress in identifying the functionality and molecular weight (high or low) of your unknown.

Known compounds to be tested for solubility properties: ethanoic acid, propanone, cyclohexene, diethylamine, benzaldehyde, 1-pentanol.

1. Water Solubility: Diagnosis of a Low Molecular Weight Compound
Add \(\approx 1\) mL of water to \(\approx 0.5\) mL of the known compound. Agitate the mixture thoroughly by holding the test at the top and flicking the base with your finger. A liquid that is insoluble in water will form a second phase.

Visualization of two liquid phases in a few drops of mixture can be difficult; holding the test tube nearly horizontal should make the liquid-liquid interface readily observable.

If the compound is soluble in water, it is a low molecular weight compound, and the solution should be tested with litmus paper to determine whether the compound is a carboxylic acid, an amine, or a neutral compound (ketone, aldehyde, alcohol or alkene).

If the compound is insoluble in water, it is a high molecular weight compound. The compound's solubility properties in 5% NaOH and 5% HCl will yield information about its functionality. Record your observations and draw conclusions about each compound tested.
2. **Solubility in 5% NaOH: Diagnosis of a High Molecular Weight Organic Acid**

Add ~1 mL of 5% NaOH dropwise, with agitation, to ~0.5 mL of the known compound. A high molecular weight carboxylic acid will be soluble in 5% NaOH because of the formation of the sodium salt of the acid. High molecular weight amines and neutral compounds will not be soluble in 5% NaOH; these functionalities will be distinguished by their differing solubilities in 5% HCl. Record your observations and draw conclusions about each compound tested.

3. **Solubility in 5% HCl: Diagnosis of a High Molecular Weight Organic Base**

Add ~1 mL of 5% HCl dropwise, with agitation, to ~0.5 mL drops of the known compound. High molecular weight amines will be soluble in 5% HCl because of the formation of the ammonium chloride salt. High molecular weight neutral compounds (ketones, aldehydes, alcohols, alkenes) will not be soluble in 5% HCl. Record your observations and draw conclusions about each compound tested.

4. **Reaction with 2,4-Dinitrophenylhydrazine (2,4-DNP): Diagnosis of Aldehyde or Ketone**

*Known compounds to be tested: propanone, benzaldehyde*

Place ~1 mL of the 2,4-DNP solution in a small test tube. Add two drops of the known compound and swirl the mixture. Aldehydes and ketones will react with the reagent and produce an orange or red-orange precipitate. Record your observations for each compound tested.

5. **Tollen's Test: Diagnosis of Aldehyde**

*Known compounds to be tested: propanone, benzaldehyde*

Place ~2 mL of 5% aqueous AgNO₃ in a medium-size, very clean test tube. (Obtain a new test tube from the stockroom for this test.) Add one drop of 10% NaOH solution; a powdery brown precipitate of silver oxide should form. Add 5% NH₃ dropwise, with agitation, until the muddiness of the mixture clears (it is OK if a few pieces of the brown solid remain near the bottom of the test tube). *Do not use excess ammonia.* Add to this mixture one drop of the known compound and shake thoroughly by holding the test tube at the top and swirling for a minute or two. An aldehyde is indicated by the formation of a silver mirror on the wall of the test tube. Record your observations for each compound tested.

Be sure to follow these directions carefully. Excess ammonia, too much unknown, or a dirty test tube will all give poor results. Upon completion of the test, discard the reaction mixture in the waste container.
provided and rinse the test tube thoroughly. It may deposit explosive products upon standing or drying out.

6. Reaction with Chromic Acid: Diagnosis of Alcohol

**Known compound to be tested: 1-pentanol**

Place ~1 mL of the known compound in a test tube. Add 1 drop of the chromic acid reagent and swirl the mixture.

An alcohol is indicated by the disappearance of the orange color of the chromic acid reagent and the formation of a green or blue-green solution.

Record your results for each compound tested.

7. Decolorization of Bromine: Diagnosis of Alkene.

**Known compound to be tested: cyclohexene.**

Place two drops of the known compound in a dry test tube. Add dropwise a 1% solution of Br₂ in dichloromethane (CH₂Cl₂).

An alkene will rapidly decolorize at least ten drops of the bromine solution. Record your results for each compound tested.
Laboratory Experiments for GOB Chemistry

Flow Diagram for Determination of Functionality
Report Sheet: Experiment 1

Name ___________________________________ Date ____________
Partner's Name ___________________________ Instructor's Initials _____

KNOWN Compound Functional Group Tests

Tests 1,2,3. Solubility

<table>
<thead>
<tr>
<th>Known Compounds</th>
<th>Observations</th>
<th>Conclusions</th>
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<tr>
<td></td>
<td>Water/Litmus</td>
<td>5% NaOH</td>
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<tr>
<td>enthanoic acid</td>
<td></td>
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<tr>
<td>diethylamine</td>
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<tr>
<td>propanone</td>
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<tr>
<td>benzaldehyde</td>
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<tr>
<td>l-pentanol</td>
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<tr>
<td>cyclohexene</td>
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Test 4. Reaction with 2-4-Dinitrophenylhydrazine

Known compound tested: propanone

Observations:

Chemical equation:
Test 4, continued. Reaction with 2-4-Dinitrophenylhydrazine

Known compound tested: benzaldehyde
Observations:

Chemical equation:

Test 5. Tollen's Test

Known compound tested: propanone
Observations:

Chemical equation:

Test 6. Reaction with Chromic Acid

Known compound tested: 1-pentanol
Observations:

Chemical equation:

Test 7. Decolorization of Bromine

Known compound tested: cyclohexene
Observations:

Chemical equation:
**UNKNOWN Compound Functional Group Tests**

Unknown Number_________________

<table>
<thead>
<tr>
<th>Chemical Test</th>
<th>Observations</th>
<th>Conclusions</th>
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<tr>
<td>Water Solubility/Litmus</td>
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<tr>
<td>5% NaOH Solubility</td>
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<tr>
<td>5% HCl Solubility</td>
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<tr>
<td>Reaction with 2,4-Dinitrophenylhydrazine</td>
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<td>Tollen's Test</td>
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<tr>
<td>Reaction with Chromic Acid</td>
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<tr>
<td>Decolorization of Bromine</td>
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Functional Group Present in Unknown________________________

Molecular Weight of Unknown (high or low)________________________