EXPERIMENT 4

Expt #4 - Properties of Aldehydes, Ketones, Carboxylic Acids, and Amines – Acid/Base and Redox Reactions

**Materials Needed**

cyclohexanone, acetone, benzaldehyde, benzoic acid, acetic acid, cyclohexylamine
18 small test tubes
4 mL 5% AgNO₃(aq), 12 mL 5% NaOH(aq), 5% NH₃(aq) (to prepare Tollens’ reagent)
6 mL copper(II) citrate solution (Benedict's reagent)
distilled water, hexane, 3 M HCl(aq), 3 M NaOH(aq)

**Additional Reading Assignment**

Denniston, chap 13.7, 14.1, 14.4, 15.1, 16.1

**Introduction**

In this lab we will again examine how the structure of a molecule determines the properties of the compound. In particular, you will explore the chemical properties of four families of organic compounds, aldehydes (RCHO), ketones (R₂CO), carboxylic acids (RCOOH) and amines (RNH₂). The solubility of each compound in water and hexane will be tested. The reactivity of each compound with a strong acid (3 M HCl(aq)) and a strong base (3 M NaOH(aq)) will be determined. The aldehyde and two ketones will also be tested using Benedict’s and Tollens’ tests for oxidizability. In addition, you will look up literature values for the melting point and boiling point of all of the compounds tested.

As in previous experiments, you should make a note of as many characteristics of the substances to be tested as possible. Use the in-lab observations/data sheet to record your observations on each compound individually as well as on the results of each test. Make sure you record all observations as carefully as you can and is much detail as possible.

**Background**

**Water Solubility.** The general rule for solubility is "like dissolves like". Hence water, a very polar solvent, dissolves only the most polar organic compounds, for example, salts of organic acids, salts of organic bases, polyhydroxy compounds (e.g., triols, tetraols, etc), and low-molecular-weight alcohols, amines, and carboxylic acids.

**Hexane Solubility.** Only relatively non-polar compounds will dissolve in this very non-polar alkane solvent.

**Reactivity with 3 M HCl(aq).** Hydrochloric acid is a strong acid that reacts with basic organic compounds such as amines. The lone pair of electrons on nitrogen are used to form a bond to the H⁺ from the acid. Signs of reaction include heat evolution and dissolution. If a compound does not dissolve in water but does dissolve in HCl(aq) then it must be reacting with the HCl. (See equation 1 on the next page.)

**Reactivity with 3 M NaOH(aq).** Sodium hydroxide is a strong base that reacts with acidic organic compounds such as carboxylic acids. The hydroxide ion accepts an H⁺ from the carboxylic acid and forms water plus a carboxylate anion. Signs of reaction include heat evolution and dissolution. If a compound does not dissolve in water but does dissolve in NaOH(aq) then it must be reacting with the NaOH. (See equation 2 on the next page.)

**Acid/Base Summary.** The solubility of a water-insoluble compound in acidic (e.g., HCl) or basic solution (e.g., NaOH) results from acid/base reactions that convert the insoluble compound to an ion which, because of its charge, is much more polar and, hence, more soluble in the aqueous solvent, than the parent compound. (See equations on next page.)
1. Amines are basic and dissolve in HCl(aq):

\[
\text{CH}_3\text{(CH}_2)_6\text{CH}_2\text{-NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{(CH}_2)_6\text{CH}_2\text{-NH}_3 + \text{Cl}^- \quad (1)
\]

\begin{array}{c}
\text{an amine = organic base} \\
\text{an ammonium ion}
\end{array}

(1)

\begin{array}{c}
\text{acid} \\
\text{soluble}
\end{array}

(2)

2. Carboxylic acids dissolve in NaOH(aq)

\[
\text{CH}_3\text{(CH}_2)_6\text{C-OH} + \text{OH}^- \rightarrow \text{CH}_3\text{(CH}_2)_6\text{C-O}^- + \text{HOH} \quad (2)
\]

\begin{array}{c}
a \text{carboxylic acid} \\
\text{a carboxylate ion}
\end{array}

(2)

\begin{array}{c}
\text{base} \\
\text{soluble}
\end{array}

(3)

Tollens' and Benedict's Tests

Aldehydes are easily oxidized due to the presence of the hydrogen attached to the carbonyl carbon. Such a hydrogen is not present in ketones or carboxylic acids and both of these functional groups are, therefore, much harder to oxidize. The oxidation of an aldehyde yields a carboxylic acid as the product (eq 3.5). Even air will oxidize an aldehyde slowly over time (eq 3).

\[
\text{H} \quad \text{OH}
\]

\begin{array}{c}
\text{R-C=O} \\
\text{OH}
\end{array}

(3)

\begin{array}{c}
\text{(aldehyde) } \\
\text{(carboxylic acid)}
\end{array}

(3)

Other oxidizing agents can bring about this reaction. One of these is **Tollens' reagent**, a basic solution of the silver complex ion, Ag(NH\(_3\))\(_2^+\). The silver(I) cation is reduced (gains one electron) at the same time the aldehyde is oxidized. This produces metallic silver (Ag\(_0\)), which often forms a shiny "mirror" on the sides of the container (eq 4). Thus, Tollens' reagent can be used to detect the presence of an aldehyde functional group – if a mirror forms then the compound tested is an aldehyde.

\[
\text{H} \quad \text{OH}
\]

\begin{array}{c}
\text{R-C=O} \\
\text{OH}
\end{array}

(4)

\begin{array}{c}
\text{(Tollens' reagent) } \\
\text{(silver mirror)}
\end{array}

(4)

**Benedict's reagent** can also oxidize aldehydes. This reagent is a basic solution of copper(II) citrate. The copper(II) ion is the oxidizing agent for the reaction (eq 5). The conversion of the clear, blue copper(II) citrate to insoluble, reddish copper(I) oxide indicates a positive test for the presence of the aldehyde functional group.

\[
\text{H} \quad \text{OH}
\]

\begin{array}{c}
\text{R-C=O} \\
\text{OH}
\end{array}

(5)

\begin{array}{c}
\text{(Benedict's reagent) } \\
\text{(copper(I) oxide)}
\end{array}

(5)
LABORATORY PROCEDURE

SAFETY PRECAUTIONS

- Wear your safety goggles at all times.
- If you spill a solution on your skin, be sure to flush the area promptly with lots of water.
- Carry out all tests while working in a fume hood.
- Wear gloves when carrying out the solubility and reactivity tests.
- Do not let the Tollens' reagent stand around, since it may form explosive substances.
- Dispose of all solutions in the appropriately labeled waste beakers provided.

General procedure for solubility tests

Place approx. 0.5 mL (10 drops) of the liquid or approx. 0.1-0.2 g (1 small spatula tip - don't overdo it!) of the solid to be tested, in a test tube and add a total of approx. 2 mL of the solvent (either distilled water or hexane) in several portions. Cover the tube with a cork or rubber sleeve stopper and shake it vigorously so as to mix the contents thoroughly after each addition of solvent. If the substance dissolves completely, record it as soluble. Continue shaking for at least five minutes if the substance does not dissolve at first in order to make sure you have allowed adequate time for dissolution to take place.

As in previous labs, when testing liquid samples, be sure to look carefully for a layer of undissolved liquid, which may be either lying on top or at the very bottom of the test tube.

Solubility in H₂O. Test all six compounds using distilled water as the solvent. (Use the general procedure given above.) For insoluble liquids observe whether the substance is more or less dense than water.

Solubility in hexane. Test the solubility of all six compounds using hexane as the solvent, again using the general procedure given above. Discard the resulting solutions in the bottle labeled "waste hexane" in the hood.

Reactivity with 3 M NaOH(aq). Use the general procedure for solubility tests to test only the compounds that did not dissolve in water. Use 3 M NaOH(aq) as the solvent. Watch carefully for any sign of reaction as discussed in the background.

Reactivity with 3 M HCl(aq). Use the general procedure for solubility tests to test only the compounds that did not dissolve in water. Use 3 M HCl(aq) as the solvent. Watch carefully for any sign of reaction as discussed in the background.

Tollens' Test. The reagent must be prepared fresh. Wash a medium-size test tube thoroughly with soap and water and rinse with distilled H₂O. Place 4 mL of 5% AgNO₃ in the test tube, and add 2 drops of 5% NaOH, mixing thoroughly. A dark brown precipitate of silver oxide (Ag₂O) will form. Now dissolve the precipitate by adding 5% aqueous NH₃ (conc. NH₄OH) until the solid disappears and a clear colorless solution is obtained.

Test only the aldehyde and the two ketones. Divide the fresh Ag(NH₃)₂⁺ reagent approximately equally between three clean test tubes. Add 3 drops of the compound being tested to each tube. Make sure you label the tubes to keep them straight. Observe the solutions carefully. If no precipitate forms or mirror appears, heat the tubes gently in a warm water bath for 5-10 minutes.

Benedict's Test. Test only the aldehyde and the two ketones. Measure 2 mL of Benedict's solution into each of three clean test tubes. Add 20 drops of the compound being tested to each tube. Make sure you label the tubes to keep them straight. Heat the test tubes in a boiling water bath for 10 minutes. Watch for the appearance of reddish Cu₂O.
1. Give the structures of the compounds being tested in this lab: cyclohexanone, acetone, benzaldehyde, benzoic acid, acetic acid, cyclohexylamine. All of these you will be able to find in the Denniston textbook or be able to figure out from nomenclature rules.
IN-LAB OBSERVATIONS/DATA

Expt #4 - Properties of Aldehydes, Ketones, Carboxylic Acids, and Amines – Acid/Base and Redox Reactions

Names ____________________________________________________________________ Date __________

Cyclohexanone:
  general observations _____________________________________________________________________
  solubility in water _____________________________________________________________________
  solubility in hexane _____________________________________________________________________
  reactivity with 3 M NaOH __________________________________________________________________
  reactivity with 3 M HCl __________________________________________________________________
  Tollens’ test ____________________________________________________________
  Benedict’s test ___________________________________________________________

Acetone:
  general observations ___________________________________________________________________
  solubility in water _____________________________________________________________________
  solubility in hexane _____________________________________________________________________
  reactivity with 3 M NaOH __________________________________________________________________
  reactivity with 3 M HCl __________________________________________________________________
  Tollens’ test ___________________________________________________________
  Benedict’s test __________________________________________________________

Benzaldehyde:
  general observations ___________________________________________________________________
  solubility in water _____________________________________________________________________
  solubility in hexane _____________________________________________________________________
  reactivity with 3 M NaOH __________________________________________________________________
  reactivity with 3 M HCl __________________________________________________________________
  Tollens’ test ___________________________________________________________
  Benedict’s test __________________________________________________________
EXPT #4 IN-LAB OBSERVATIONS/DATA (continued)

Benzoic acid:

- **general observations**

- solubility in water ____________________________

- density (if insoluble) _________________________

- solubility in hexane ___________________________

- reactivity with 3 M NaOH _______________________

- reactivity with 3 M HCl _________________________

Acetic acid:

- **general observations**

- solubility in water ____________________________

- solubility in hexane ___________________________

- reactivity with 3 M NaOH _______________________

- reactivity with 3 M HCl _________________________

Cyclohexylamine:

- **general observations**

- solubility in water ____________________________

- solubility in hexane ___________________________

- reactivity with 3 M NaOH _______________________

- reactivity with 3 M HCl _________________________
**REPORT - EXPERIMENT 4**

**EXPT 4 - Properties of Aldehydes, Ketones, Carboxylic Acids, and Amines – Acid/Base and Redox Reactions**

Name __________________________________________________________ Date __________

| Compound Name and Structure | Appearance | Results of Solubility/Reactivity Tests | lit bp (°C)
|----------------------------|------------|---------------------------------------|--------------|
|                            |            | H₂O/density | hexane | 3 M NaOH | 3 M HCl | Tollens’ | Benedict’s | lit mp (°C)
| __________________________ |------------|------------|--------|---------|--------|----------|------------|------------|
| cyclohexanone              |            |            |        |         |        |          |            |            |
| acetone                    |            |            |        |         |        |          |            |            |
| benzaldehyde               |            |            |        |         |        |          |            |            |
| benzoic acid               |            |            |        |         |        | N.A.     | N.A.       |            |
| acetic acid                |            |            |        |         |        | N.A.     | N.A.       |            |
| cyclohexylamine            |            |            |        |         |        | N.A.     | N.A.       |            |

*Reference used for literature values ________________________________*

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QUESTIONS

1. Which compounds reacted with NaOH? Which were expected to react? Write equations for the reactions that were observed and try to explain any erroneous results.

2. Which compounds reacted with HCl? Which were expected to react? Write equations for the reactions that were observed and try to explain any erroneous results.

3. Which compounds of the ones tested have the highest boiling points? Explain in detail why these three compounds have high bps compared to the other three.

4. Which compounds were found to be water-soluble? Was this as expected? Explain why these compounds are water-soluble while the other compounds tested are not.
5. Which compound(s) reacted with Tollens’ reagent? Which reacted with Benedict's reagent? Are these results as expected? Write equations for these reactions and explain why the compounds that gave negative tests did not react.

6. Potassium benzoate is an ingredient in Diet Coke. Give the structure of potassium benzoate.

7. 4-Hydroxy-3-methoxybenzaldehyde is the major constituent of vanilla extract. (a) Draw its structure and predict its behavior in each of the tests carried out in this lab. (b) Why is it best to use fresh vanilla extract for your baking rather than several-year old stuff?