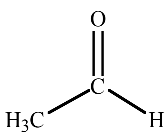
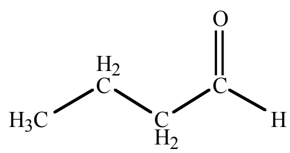
Experiment 7 – Aldehydes, Ketones, and Carboxylic Acids

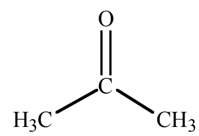
Aldehydes and ketones are molecules that contain a carbonyl group, which is an oxygen atom with a double bond to a carbon atom. In an aldehyde, the carbonyl group is on the end of the molecule. In a ketone, the carbonyl group is somewhere in the middle of the molecule. Example structures of aldehydes and ketones are given below.



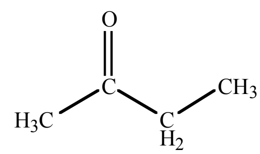
An aldehyde



An aldehyde

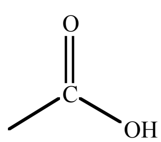


A ketone

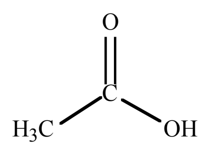


A ketone

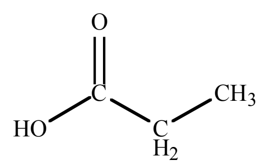
Carboxylic acids contain the carboxyl functional group, shown below.



A carboxyl group



A carboxylic acid



A carboxylic acid

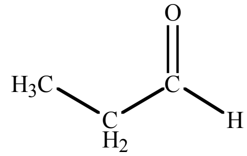
Physical Properties

Aldehydes and ketones are polar because they contain a carbonyl group (oxygen is very electronegative compared to carbon). Aldehydes and ketones can form hydrogen bonds with water, so small aldehydes and ketones are water-soluble. However, they cannot form hydrogen bonds to each other, so their boiling points are not very high. (Their boiling points are higher than the corresponding alkanes, but lower than the corresponding alcohols.) Carboxylic acids are polar and can form hydrogen bonds with water. Small carboxylic acids are therefore water-soluble. They can also form hydrogen bonds with each other, so they have relatively high boiling points.

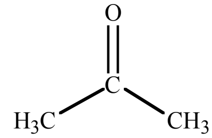
As a comparison, the following molecules have very similar molar masses, but different boiling points. The differences in the boiling points are thus due to differences in polarity and hydrogen-bonding ability.

$CH_3CH_2CH_2CH_3$

Butane (MM = 58)
bp = 0°C



Propanal (MM = 60)
bp = 50°C

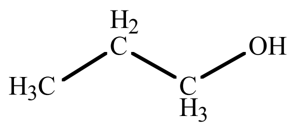


Acetone (MM = 60)
bp = 56°C

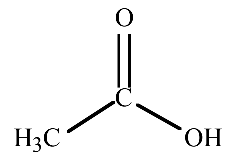
Many aldehydes and ketones have pleasant odors. Examples of good-smelling aldehydes are vanillin, cinnamaldehyde, and benzaldehyde. Because aldehydes and ketones are somewhat polar but not extremely polar, they are good solvents for organic reactions.

Oxidation

Aldehydes can be oxidized to carboxylic acids by almost any oxidizing agent.



Propanol (MM = 60)
bp = 97°C



Acetic acid (MM = 60)
bp = 118°C

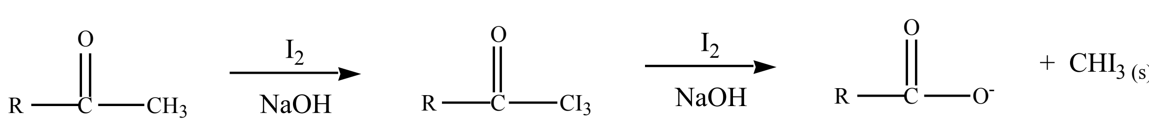
Some common oxidizing agents are chromic acid, Benedict's reagent, and Fehling's reagent. Chromic acid is an orange solution and it contains chromium in the +6 oxidation state. It can be reduced to a green solution of chromium (III) ion (in the +3 oxidation state). This reaction is useful, because the reduction of chromium is accompanied by a color change from orange to green. If the test solution turns green when chromic acid is added, it means that the test solution is being oxidized.

Fehling's reagent and Benedict's reagent are blue solutions that contain copper ions under basic conditions. The copper ions are in the +2 oxidation state, and can be reduced to the +1 oxidation state, where they form a red precipitate of Cu_2O in a basic solution. Therefore, the formation of a red precipitate in the blue solution is a visual indication that the compound being tested has been oxidized.

Ketones and carboxylic acids cannot be oxidized and therefore will not react with chromic acid or Benedict's reagent.

Iodoform Test

Compounds that contain a methyl group attached to a carbonyl carbon will react with I_2 in a basic solution to produce a yellow precipitate of iodoform (CHI_3). Many (but not all) ketones will undergo this reaction.



Acidity

Carboxylic acids are weak acids, and will ionize to a slight extent in water. A solution of a carboxylic acid in water will be acidic. The most common carboxylic acid is acetic acid, which contains only two carbons. (This is the acid present in vinegar.)

Because they are weak acids, carboxylic acids will react with strong bases. The product of the reaction is a carboxylate ion, and because it is charged it is much more soluble in water than the corresponding uncharged acid. Therefore, one method of making an acid more soluble in water is by reacting it with a strong base to deprotonate it.

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COO^- Na^+_{(aq)} + H_2O_{(l)}$$

Acids will also react with bicarbonate ion to produce carbon dioxide gas. This is another useful reaction, since it shows a visible change – if the reaction occurs, you will see bubbles appear in the solution. This reaction is shown below.

$$CH_3COOH_{(aq)} + NaHCO_{3\,(aq)} \rightarrow CH_3COO^- Na^+_{(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

Aldehydes and ketones are not acidic and will not react with sodium bicarbonate.

In this experiment, you will make some models of aldehydes, ketones, and carboxylic acids. You will test the water solubility of several compounds. You will carry out several reactions on various aldehydes, ketones, and carboxylic acids. You will then identify an unknown compound based on its reactivity.

Safety Precautions:

- Organic compounds are extremely flammable. Use small amounts of the compounds, and do not use Bunsen burners in the organic chemistry laboratory.
- Keep the organic solvents under the fume hood.
- Avoid touching the chemicals.
- Wear your safety goggles.

Waste Disposal:

- All waste must be placed in the **organic** waste containers (which have a pink label) in one of the fume hoods.

Procedure

Part 1: Structures of Aldehydes, Ketones, and Carboxylic Acids

1. Using the molecular model kits, make models of acetaldehyde, acetone, and acetic acid. Write the condensed structural formula for each of these and also for 2-methylpropanal, cyclohexanone, benzaldehyde and benzoic acid.

Part 2: Solubility

2. You will be testing the following compounds: propionaldehyde (propanal), benzaldehyde, acetone, cyclohexanone, propanoic acid, butanoic acid (butyric acid), hexanoic acid, and your unknown. Label eight test tubes and place 5 drops of each compound in its own separate test tube. Add about 2 mL (40 drops) of

deionized water to each test tube, and shake each test tube side to side to mix. If the substance is soluble in water, you will see a clear solution with no separate layers. If it is insoluble, you will see separate layers or a cloudy solution. Record your observations.

Part 3: Oxidation: Chromic Acid

3. In this part, you will test the following compounds: propanal, 2-butanone, acetic acid, and your unknown. On a white spot plate, place 1 drop of each substance to be tested in separate wells. Add 5-8 drops of alcohol-free acetone to each well and stir each mixture with a thin glass rod. Make sure to rinse and wipe off the stirring rod between solutions so that you don't accidentally contaminate the solutions (this would give you ambiguous results). Add 1 drop of the chromic acid reagent to each well and stir with the glass rod (again rinsing between solutions). Observe any color change that happens within the first 10 seconds. If the orange color changes to green, reaction has taken place. Record your observations.
4. Predict the products in each case where a reaction occurred. If no reaction took place, write "NR".

Part 4: Oxidation: Benedict's Reagent

5. In this part, you will test propanal, 2-butanone, acetic acid and your unknown. Label 4 test tubes and place 10 drops of the liquid to be tested in its own tube. Add 5 mL of Benedict's reagent to each tube and shake the tubes to mix them. Place the tubes in a boiling water bath on a hot plate for 5 minutes. A reddish-orange precipitate of Cu_2O indicates a positive test. If a small amount of Cu_2O is formed, it will blend with the blue color of the solution to form a greenish or rust-colored precipitate. Record your observations.

Part 5: Iodoform Test

6. In this part, you will test 2-methylpropanal, butanal, 2-butanone, acetone, and your unknown. Place about 1 mL of water (20 drops) in each of 5 test tubes. Add 5 drops of the liquid to be tested. Add 10 drops of 10% $NaOH_{(aq)}$ and mix by shaking each tube side to side. Add 10 drops of KI/iodine solution and shake to mix. A yellow precipitate indicates a positive reaction.

Part 6: Acidity (pH Test)

7. You will test acetic acid, propanoic acid, solid salicylic acid, acetone, and your unknown. Place about 2 mL of deionized water in each of 5 test tubes. Add 6 drops of each liquid to be tested to separate test tubes. (For the solid salicylic acid, use a few crystals.) Shake each tube thoroughly. To test the pH of the solution, dip a (clean) glass stirring rod in the solution and touch it to a piece of pH paper. Read the pH of the sample, using the scale on the label of the pH paper. Rinse off the stirring rod between solutions.

Part 7: Solubility in Base

8. Place 1 mL of deionized water in one test tube and 1 mL of 10% $NaOH_{(aq)}$ in another tube. Add 2 drops of hexanoic acid to each tube. Shake each tube

thoroughly. Record the relative solubility of hexanoic acid in each of the solutions.

Part 8: Sodium Bicarbonate Test

9. In this part, you will test propanoic acid, acetic acid, acetone, and your unknown. Label four test tubes and add 3 mL of 10% $NaHCO_{3\ (aq)}$ to each tube. Add 10 drops of each substance to be tested to the appropriate tube. While you are adding the substances to the sodium bicarbonate solution, watch for the formation of bubbles, which indicate a positive reaction. Record your observations.

Part 9: Identification of the Unknown Substance

10. Based on the results from each of the experiments, discuss what you know about the structure of your unknown. Identify it as an aldehyde, ketone, or carboxylic acid, and include any additional conclusions based on your results.

<u>Questions</u>

1. Draw the condensed structural formulas for each of the following compounds.

   a. benzaldehyde

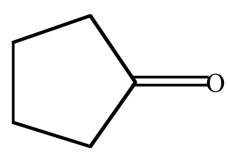
   b. 3-chlorobutanoic acid

   c. 1,4-cyclohexanedione

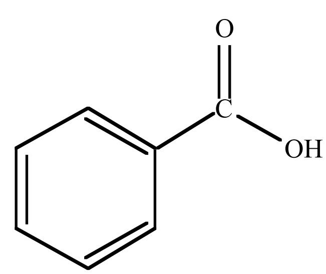
   d. 3-ethyl-2,2-dimethylpentanal

2. Name each of the following compounds.

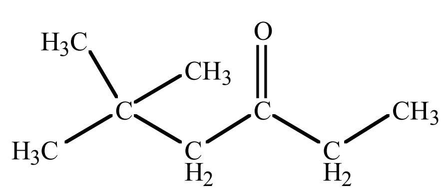
   a.



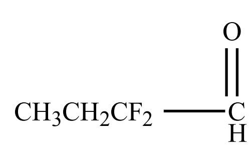
   b.



   c.

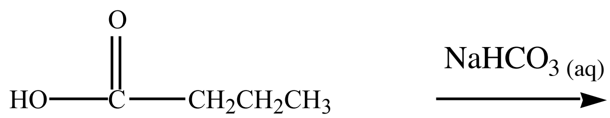


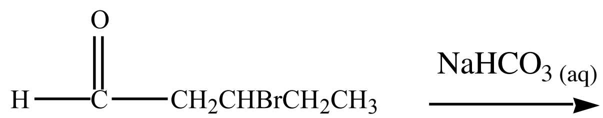
   d.

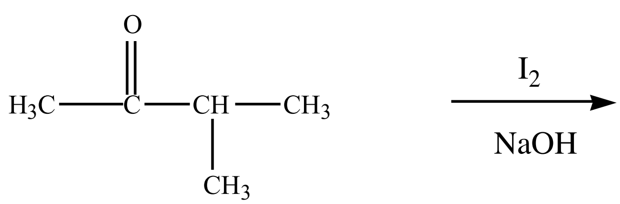


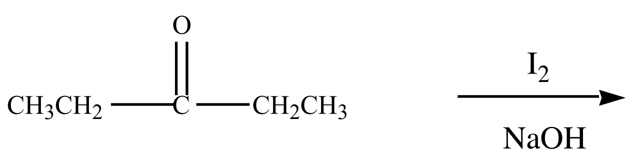
3. An unknown has a chemical formula of C_3H_6O. When chromic acid was added to the unknown, the solution remained orange. The unknown was soluble in water. When NaOH and KI/iodine were added to the unknown, a yellow precipitate formed. What is the structure of the unknown compound?

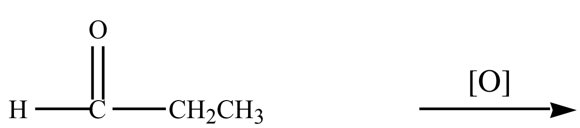
4. Write the structure of the product(s) of each of the following reactions. Also include a description of the changes you would expect to <u>see</u> (if any) in each solution.

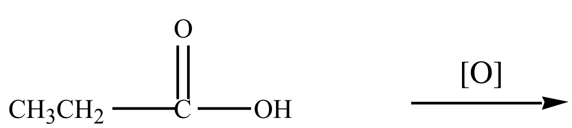
a. 

b. 

c. 

d. 

e. 

f. 

5. Would you expect 2-octanone to be soluble in water? Would you expect butanal to be soluble in water? Would either of them be more soluble in hexane than in water? Explain.

6. Would you expect pentanal to give a positive iodoform test? Would you expect acetaldeyde to give a positive iodoform test? Explain.