Objectives

- Use qualitative tests to study and distinguish aldehydes and ketones
- Identify an unknown aldehyde or ketone

Background

Differences between Aldehydes and Ketones

There are multiple functional groups that feature a carbonyl group, in which a carbon has a double bond to an oxygen. The presence of the electronegative oxygen gives carbonyl compounds some similar characteristics to alcohols. However, the oxygen does not have an attached hydrogen, so hydrogen bonding is only possible in the presence of other molecules with the necessary N-H or O-H bond. The lack of hydrogen bonding a pure sample of most carbonyl compounds generally decreases their melting and boiling points compared to alcohols.

Beyond the C=O bond, the atoms attached to the carbon in the carbonyl group dictate the specific functional group present and determine the properties and reactivity. A carbonyl that appears at the end of an organic molecule is known as an aldehyde. An aldehyde has at least one hydrogen bonded to the carbonyl carbon and has a name ending in *-al*. A carbonyl that appears in the middle of an organic molecule is known as a ketone. A ketone has a carbon attached to both sides of the carbonyl carbon and has a name ending in *-one*.

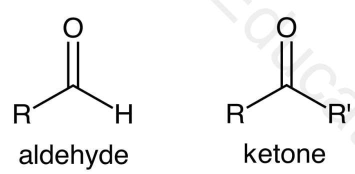

Figure 1 Generic structures of aldehydes and ketones

One main reactivity difference between the two functional groups derives from the presence of the hydrogen on the carbonyl carbon for the aldehyde. An aldehyde can be further oxidized without breaking a C-C bond. A ketone, on the other hand, cannot be easily oxidized as a C-C bond would need to be broken.

Qualitative Tests for Aldehydes and Ketones

Functional groups with different reactivity, like aldehydes and ketones, can be distinguished by qualitative tests. In general, qualitative tests have some apparent visual change indicating when a reaction has occurred. To best understand qualitative tests, it is important to identify a positive and negative result by testing with known compounds. Control tests ensure that the reagents are working properly and that you know what the different results look like.

2,4-DNP Test for Aldehydes and Ketones

The 2,4-dinitrophenylhydrazine test, also known as the 2,4-DNP test, indicates the presence of an aldehyde or ketone through the formation of a precipitate. 2,4-DNP is a hydrazine that reacts with an aldehyde or ketone through a condensation reaction to form the insoluble hydrazone adduct, as shown in Figure 2. The reaction occurs in an alcohol solvent with acid present. If a sample contains a ketone or an aldehyde, it will react with a 2,4-DNP solution to form a yellow-orange precipitate. Note that the precipitate can have multiple colors or even sometimes appear oily depending on the ketone or aldehyde.

Although the test does not have distinct reactivity for aldehydes and ketones, the 2,4-DNP test does create a solid precipitate derivative that can have its melting point analyzed to help identify the specific starting carbonyl molecule.

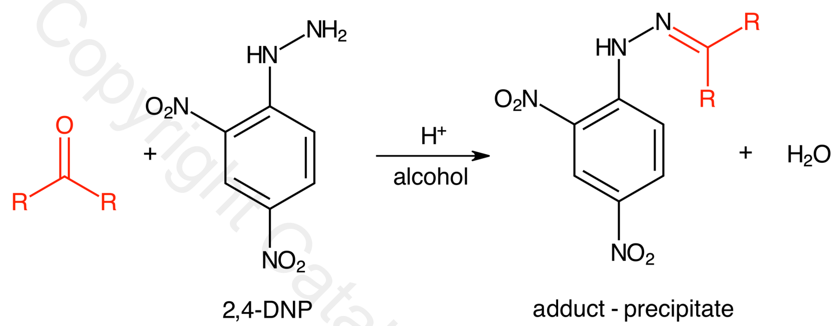

Figure 2 Reaction that occurs in a positive 2,4-dinitrophenylhydrazine test

Chromic Acid Test for Aldehydes

The chromic acid test is an oxidation that works with aldehydes as well as primary and secondary alcohols. Ketones, like tertiary alcohols, do not react with the chromic acid test because an oxidation would require breaking a C-C bond.

The general form of the chromic acid test, shown in Figure 3, starts with an alcohol and uses chromium(VI) to oxidize an alcohol to a carboxylic acid, for primary alcohols, or a ketone, for secondary alcohols. Formation of an aldehyde in the first oxidation step of a primary alcohol supports the positive test for aldehydes. The counterpart in each successful oxidation is the reduction of chromium(VI) to chromium(IV). Two chromium(IV) cations undergo a disproportionation reaction to form a chromium(V) ion and the stable chromium(III) ion. The chromium(III) ion turns the solution a shade of green dependent on the other compounds present.

The chromium(VI) ion used in the test can be prepared in a couple ways. One way is to use chromium trioxide and sulfuric acid. The other way, used in this lab, is to slowly add concentrated acid to a sodium dichromate solution. Once the chromic acid reagent is prepared, its addition to an aldehyde, results in the formation of the greenish chromium(III) ion. Note that the reagent is aqueous so the test may result in two layers. A green color in either layer represents a positive test.

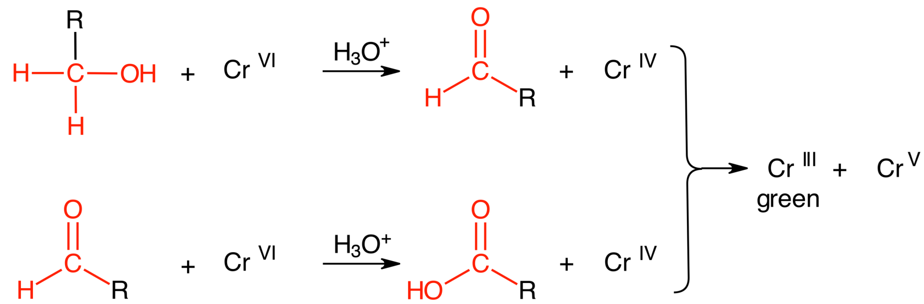

Figure 3 Reaction that occurs in a positive chromic acid test

Tollens's Test for Aldehydes

The Tollens's test can also be used to distinguish between aldehydes and ketones. The test uses silver ions to oxidize the aldehyde to a carboxylate, as shown in Figure 4. Ketones cannot be oxidized in this way. In the process of oxidation, silver ions are reduced to neutral silver, which has a silver mirror appearance.

The Tollens's reagent is a complex ion with silver metal and ammonia ligands. The Tollens's reagent is prepared from silver nitrate mixed with sodium hydroxide and ammonium hydroxide until a clear solution is formed. Once the Tollens's reagent is formed, it can be mixed with the organic sample. A positive test for aldehydes will result in the appearance of a silver mirror or possibly a dark gray precipitate in the test tube.

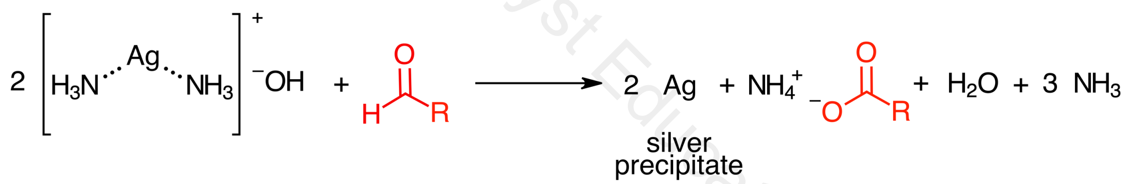

Figure 4 Reaction that occurs in a positive Tollens's test

Iodoform Test for Methyl Substituent on Carbonyl

In the iodoform test, a methyl group next to an oxidizable carbonyl or alcohol group is used to form insoluble iodoform. Thus, the iodoform test indicates methyl ketones or an alcohol with an alpha methyl group next to the functional group. Because of the methyl group next to the carbonyl, the aldehyde acetaldehyde can also give a positive result.

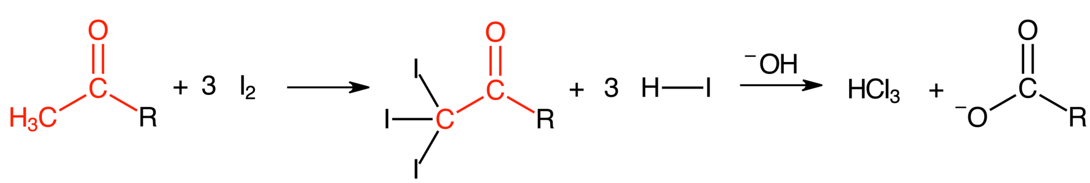

Figure 5 Reaction that occurs in a positive iodoform test

To start the test with an alcohol, iodine and sodium hydroxide are mixed to form sodium hypoiodite, as shown in Figure 5. The hypoiodite ion oxidizes the alcohol to the methyl ketone, which is why methyl ketones also give a positive test result. The iodine can then react with the methyl group, replacing the hydrogens with iodines. The triiodomethyl group is now a better leaving group in the presence of the hydroxide. When the triiodomethyl group leaves, insoluble iodoform, CHI_3, forms as a yellow precipitate.

Materials

- Acetone
- Benzaldehyde
- Butanal
- Cyclohexanone
- Unknown aldehyde or ketone
- 2,4-DNP reagent
- 6M HCl
- 10% sodium dichromate
- 3M NaOH
- Tollens's reagent
- Iodine solution
- Test tubes

Safety goggles are required!

All work should be performed in the fume hood.

2,4-dinitrophenylhydrazine and its derivatives are carcinogenic and should be handled with care; the solution will stain hands and clothing.

Chromic acid is corrosive and toxic, and chromium is a possible carcinogen.

Tollens's reagent can form potentially explosive silver fulminates when stored; wash thoroughly if skin contact is made.

Procedure

Qualitative Tests for Aldehydes and Ketones

You will be assigned at least one test to perform for the known positive and the known negative test as well as performing all tests on your unknown.

You will compare your results with the group or groups that performed the known positive and known negative tests.

Solubility Tests

1. Write the identification code for your unknown on the space provided on the data sheet.
2. Place 0.5 mL of each of the following: acetone, benzaldehyde, butanal, cyclohexanone, and your unknown in a small test tubes.
3. Add 1 mL of deionized water to each.
4. Shake the contents of the tube well to see if they mix. Describe each as soluble, insoluble, or slightly soluble on the data sheet.
5. Dump the contents of the tubes in the non-halogenated waste container, and wash the test tubes with soap and water.

2,4-DNP Test for Aldehydes and Ketones

1. Place 8 drops of the following in separate test tubes: acetone, benzaldehyde, butanal, cyclohexanone, and your unknown.
2. Add 1 mL of the 2,4-DNP reagent to each test tube.

3. Wait about five minutes to see if a precipitate forms.
4. Decant the liquid into the non-halogenated waste, careful not to lose any precipitate.
5. Add 1 mL of water to each of the test tubes and shake well.
6. Decant the added water into the non-halogenated waste.
7. Record your observations. Pay attention to the color of the precipitate, as this may be important to determine your unknown.
8. Discard the solutions in the non-halogenated waste container, and wash the test tubes with soap and water.

Chromic Acid Test for Aldehydes

1. Prepare the chromic acid solution by thoroughly mixing 2 mL of 6 M HCl in a test tube with 20 drops of 10 % sodium dichromate ($Na_2Cr_2O_7$).
2. Place 4 to 5 drops of the following in separate test tubes: acetone, benzaldehyde, butanal, cyclohexanone, and your unknown.
3. Add 10 drops of acetone to each tube and mix well.
4. Add the prepared chromic acid solution dropwise to each tube for up to 10 drops. Mix well between drops and observe any changes.
5. Dump the contents of the tubes in the **halogenated** waste container, and wash the test tubes with soap and water.

Tollens's Test for Aldehydes

1. Take three small test tubes and fill them half full of 3 M NaOH to clean them. Let them soak for a few minutes.
2. Dump the contents of each tube in the non-halogenated waste container, and rinse the test tubes with water. The tubes do not need to be dry.
3. Add 3 to 5 drops of an aldehyde, a ketone, and your unknown to each of the three tubes.
4. Add 10 to 12 drops of the Tollens's reagent to each test tube and shake well.
5. Set the tubes aside; it may take up to 5 minutes to form the silver mirror. A positive test is either a silver mirror or a black (dark gray) precipitate.
6. Dump the contents of the tubes in the non-halogenated waste container, and wash the test tubes with soap and water.

Iodoform Test for Methyl Substituent on Carbonyl

1. Place 3 to 5 drops of the following in separate test tubes: acetone, butanal, cyclohexanone, and your unknown.
2. Dilute the acetone and butanal with 2 mL of water and mix well.
3. Add 1 mL of methanol to the cyclohexanone to dissolve it.
4. Determine whether to add water or methanol to your unknown based on your solubility tests and add that solvent to your unknown test tube.

5. Add 2 mL of 3 M NaOH to each test tube and mix well again.
6. Add 3 mL of the iodine solution to each mixture and mix well once more. Record your observations for each.
7. Dispose of the content of the tube in the **Halogenated Waste** container. Wash the test tube with soap and water.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What is the functional group that determines if a compound is an aldehyde or a ketone?

2. What observation is expected for a positive iodoform test?

3. What observation is expected for a positive Tollens's test?

4. Write the equation for the Tollens's test reaction with an aldehyde.

5. Explain why aldehydes and ketones have a higher boiling point than the corresponding hydrocarbons.

Lab 8: Aldehydes and Ketones Report Sheet

Name ______________________ Section ______________________

Date ______________________ Instructor ______________________

Qualitative Tests for Aldehydes and Ketones

UNKNOWN CODE: ___________________________

Solubility Tests

Aldehyde or ketone	Water solubility
acetone	______________________
benzaldehyde	______________________
butanal	______________________
cyclohexanone	______________________
Unknown	______________________

2,4-DNP Test for Aldehydes and Ketones

Aldehyde or ketone	Observations
acetone	______________________
benzaldehyde	______________________
butanal	______________________
cyclohexanone	______________________
Unknown	______________________

Chromic Acid Test for Aldehydes

Aldehyde or ketone	Observations
acetone	______________________
benzaldehyde	______________________
butanal	______________________

cyclohexanone	______________________
Unknown	______________________

Tollens's Test for Aldehydes

Aldehyde or ketone	Observations
aldehyde (butanal)	______________________
ketone (cyclohexanone)	______________________
Unknown	______________________

Iodoform Test for Methyl Substituent on Carbonyl

Aldehyde or ketone	Observations	Is CH_3-C=O present?
acetone	______________________	________
butanal	______________________	________
cyclohexanone	______________________	________
Unknown	______________________	________

Describe the information you have gathered from the tests about your unknown.

Post-lab Questions

1. What test(s) distinguished your unknown compound as an aldehyde or ketone?

2. How certain are you that your compound is an aldehyde or ketone?

3. If you compare your unknown compound results to the tested known compounds, which compound do you think your unknown is? Explain your answer.