Identification of an Unknown Aldehyde or Ketone

Background

Structures of unknown compounds can be determined by comparing physical properties, performing functional group tests, and checking melting points of derivatives against those of known compounds reported in the literature.

In this experiment, you will analyze an unknown aldehyde or ketone by performing classification tests, by measuring the refractive index and boiling point, and by preparing a derivative and measuring its melting point. You will identify your unknown by comparing its data with literature values.

Classification tests

Classification tests are qualitative tests that determine the presence or absence of certain structural features of a molecule. For example, certain classification tests indicate the presence of a particular functional group, such as an aldehyde or an alcohol. Other tests indicate a functional group that easily undergoes oxidation or the presence of an acidic hydrogen. Classification tests are designed to be easily evaluated visually. For example, a positive test may be indicated by a color change, formation of precipitate, formation of gas, or solution layers forming or becoming miscible.

When performing classification on an unknown, it is often helpful to also run known compounds. Perform the test on a known compound that will result in a positive test (known positive) and on one that will result in a negative test (known negative) in addition to the unknown compound. This direct visual comparison of the results confirms that the reagents are good and you are performing the test properly.

The following classification tests are performed in this experiment:

The Tollens Test

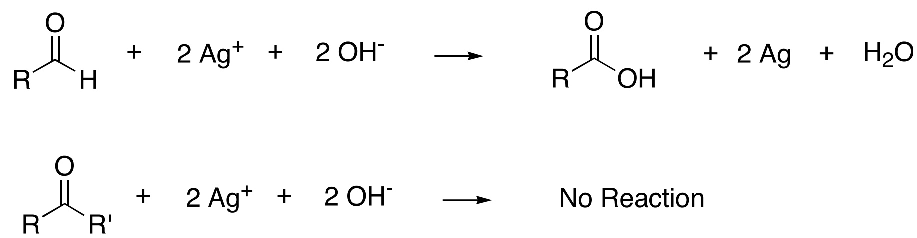
Aldehydes are easily oxidized to carboxylic acids by silver ions, a mild and selective oxidizing agent. A positive test results in a mirror finish deposited on the sides of the test tube, or sometimes a heavy black precipitate.

The test must be performed in basic conditions. Ammonia is added to prevent precipitation of silver oxide.

$$2\ Ag^+(aq) + 2\ OH^-(aq) \rightarrow Ag_2O\ (s) + H_2O\ (l)$$

$$Ag_2O\ (s) + 4\ NH_3\ (aq) + H_2O(l) \rightarrow 2\ Ag(NH_3)_2^+(aq) + 2\ OH^-(aq)$$

As the aldehyde is oxidized, the silver ion (Ag^+) is reduced to silver metal (Ag^0). Some aldehydes require several minutes to form a silver mirror. Ketones do not react under these conditions. The conditions are not strong enough to oxidize alcohols.



The Schiff Test

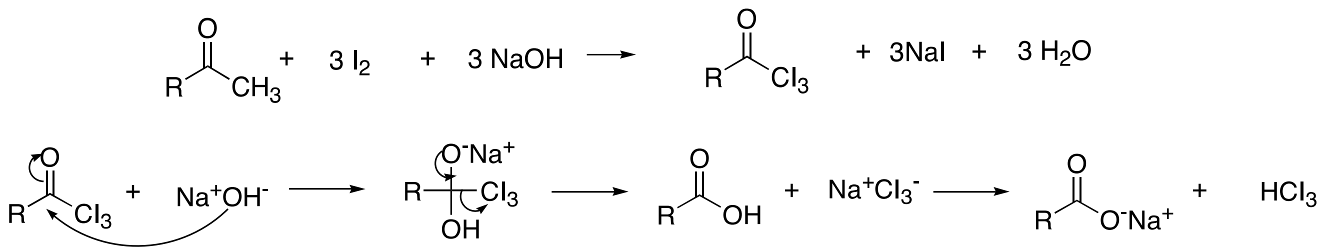
In a complex series of reactions that is not completely understood, Schiff reagent reacts only with aldehydes to produce a fuchsia solution. A faint pink color results from the initial reagent and does not constitute a positive test. The Schiff test is the most sensitive for aldehydes. However, the Schiff test is subject to giving false positives and false negatives.

Iodoform Test

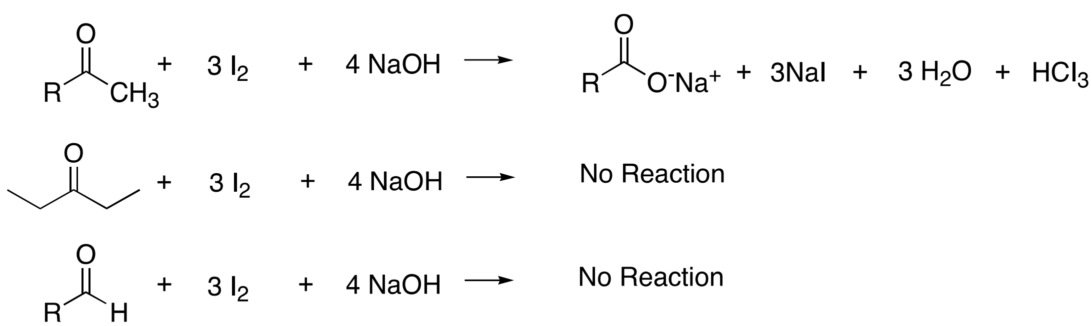
The iodoform test is for methyl ketones. Elemental iodine is first formed in situ by oxidizing iodide (I^-) with hypochlorite (OCl^-).

$$2I^- \text{ (aq)} \quad + \quad OCl^- \text{ (aq)} \quad + \quad H_2O \text{ (l)} \quad \rightarrow \quad I_2 \quad + \quad Cl^- \text{ (aq)} \quad + \quad 2\ OH^- \text{ (aq)}$$

The methyl ketone undergoes three alpha substitutions with the iodine resulting in an inductively stabilized carbon (CI_3) that can act as a leaving group.



The protonated leaving group, known as iodoform (HCI_3), is a yellow insoluble precipitate. Its formation indicates a presence of a methyl ketone (or acetaldehyde). No precipitate is formed with other types of ketones or aldehydes.



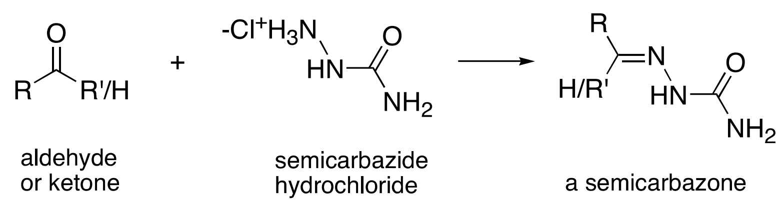
Secondary alcohols having an adjacent methyl group are oxidized to methyl ketones by the iodoform test reagent thus resulting in a positive iodoform test. Note that acetone is a methyl ketone, so acetone should not be used to rinse test tubes before the iodoform test. Methyl ketones that have low solubility in the iodoform reagent may give false negatives.

Derivatives

Unknown compounds can be reacted with various reagents to give new compounds called derivatives. Derivatives are crystalline solids. The melting point of derivatives can be compared to literature values to help identify unknowns. For any derivative, purity is more important than yield. Several derivatives can be made to confirm an unknown aldehyde or ketone.

Semicarbazone Derivatives

Semicarbazone derivatives can be made from aldehydes and ketones. They are rapidly formed and easily crystallized. Semicarbazide is reacted with an aldehyde or ketone to form the semicarbazone as shown below in the reaction below.



Ketones and aldehydes both form semicarbazones. The melting point of the derivative can be compared to the literature melting points to help identify the compounds.

Physical Properties of Aldehydes			
Name	bpt (◦C)	Refractive index (at 20◦C)	Semicarbazone mpt (◦C)
2-furaldehyde	161	1.5260	202
Cyclohexane-carbaldehyde	162	1.4500	173
3-cyclohexene-carbaldehyde	164	1.4745	154
Octanal	171	1.4183	101
Benzaldehyde	178	1.5450	217
Phenylacetaldehyde	194	1.5290	156
Salicylaldehyde	196	1.5720	231
p-tolualdehyde	204	1.5460	221
2-phenylpropanal	205	1.5170	154
o-chlorobenzaldehyde	208	1.5660	233
3-phenylpropanal	224	1.5230	127
p-anisaldehyde	248	1.5730	210
cinnamaldehyde	252	1.6220	215

Physical Properties of Ketones			
Name	bpt (◦C)	Refractive index (at 20◦C)	Semicarbazone mpt (◦C)
2-heptanone	150	1.4080	127
Cyclohexanone	155	1.4500	166
2-methylcyclohexanone	163	1.4480	195
3-methylcyclohexanone	169	1.4450	180
Cycloheptanone	181	1.4610	163
5-nonane	187	1.4190	90
Acetophenone	200	1.5325	198
Propiophenone	218	1.5258	174
Butyrophenone	230	1.5195	187
valerophenone	242	1.5143	166

Procedure

Preparing a Semicarbazone Derivative

1. Prepare a hot-water bath heated to 80°C and an ice water bath. Mix 3 mL of 95% ethanol and 3 mL of distilled water in the test tube. Cool the ethanol-water mixture in the ice-water bath for later use.

2. Add 1 mL of 95% ethanol to a second test tube. Add 5 drops of the unknown. Mix the solution until it is homogeneous.

3. Place 0.15 g of semicarbazide hydrochloride, 0.15 g of sodium acetate and 2 mL of D.I. water to a third test tube. Shake to dissolve the solids. Pour the semicarbazide solution into the test tube containing the unknown. Shake the test tube to mix, then shake again once a minute for the next 5 minutes until a precipitate forms. Cool the test tube in the ice-water bath for 10 mins.

4. Vacuum filter the semicarbazone and rinse with 25 mL of D.I. water.

5. To recrystallize the semicarbazone, transfer the semicarbazone precipitate to a clean test tube. Add 2 mL of distilled water, 2 mL of 95% ethanol, and a boiling chip. Heat the tube in the hot-water bath until the semicarbazone dissolves. If some of the semicarbazone remains undissolved, add 1 mL of 95% ethanol and heat again. Continue adding ethanol until the solid completely dissolves. Do not add more than 8 mL of ethanol. When the semicarbazone dissolves, remove the tube from the hot-water bath. Allow the solution to cool to room temperature, then chill for up to 10 minutes in the ice bath.

6. Vacuum filter the semicarbazone. Rinse the semicarbazone with the 6 mL of chilled 1:1 95% ethanol-water mixture.

7. Allow the product to dry at least 30 minutes before taking a melting point. Compare your results with the literature melting points.

Waste: Acetone waste jug: Filtrates, extra 95% ethanol
"Carbonyl Unknown" jar: solid waste

Performing the Tollens test for aldehydes.

1. Obtain 3 clean test tubes. Add 1 mL of 5% silver nitrate to each tube. Add 0.5 mL of 10% sodium hydroxide to each test tube. Next add concentrated ammonium hydroxide dropwise, with mixing, until the initial precipitate just dissolves.

2. Add 2 drops of p-anisaldehyde to test tube 1. Mix well.
Add 2 drops of acetophenone to tube 2 Mix well.
Add 2 drops of the unknown to test tube 3. Mix well.

3. For each tube, note whether or not a silver mirror or a heavy black precipitate forms. Record your observations. If there is not visible change within 5 min, place the tube in a 80 °C hot-water bath for 15 sec. Do not overheat the tube.

Waste: "Hydrophobic waste": contents of all test tubes, rinse each tube with ≈ 1 mL of 3 M nitric acid to destroy any residual Tollens reagent. Add this rinse to the to the same waste container. Wash the test tubes with soap and water.

Performing the Schiff Test for Aldehydes

1. Obtain three test tubes and add 2 mL of Schiff solution to each test tube.

2. Add 1 drop of p-anisaldehyde to test tube 1. Mix well.
   Add 1 drop of acetophenone to test tube 2. Mix well.
   Add 1 drop of unknown to test tube 3. Mix well.

3. Shake each tube well for about 5 minutes. Note the color in each tube and record your observations. A faint pink color results from the initial reagent and does not constitute a positive test. A fuchsia color constitutes a positive test. Several minutes may be required for color development.

Waste: "Carbonyl Unknown" waste jar: Pour contents of all tubes.

Performing the Iodoform Test for Methyl Ketones

1. Prepare a hot-water bath (80 °C).

2. Obtain 3 test tubes and add 2 mL of iodoform test solution to each test tube. Warm the tubes in the hot-water bath for 30 sec.

3. Add 1 drop of p-anisaldehyde to test tube 1. Mix well.
   Add 1 drop of acetophenone to test tube 2. Mix well.
   Add 1 drop of unknown to test tube 3. Mix well.

4. Immediately add 2 mL of 1.0M NaOH to each tube and mix. Note whether or not a yellow precipitate forms immediately and record your observations.

Waste: "Carbonyl Unknown" waste jar: Pour contents of all tubes.

Refractive index.
Measure the refractive index of your unknown. Record the lab temperature at the time of the measurement.

Boiling point.
Measure the boiling point of your unknown using a simple distillation apparatus.

Chemicals:
95% ethanol, semicarbazide hydrochloride, sodium acetate, silver nitrate, 10% sodium hydroxide, conc. ammonium hydroxide (ammonia), p-anisaldehyde, acetophenone, Schiff reagent, Iodoform reagent, 5% sodium hypochlorite.

Adapted from:

William Simek, California Polytechnic State University.