

Aldehydes and Ketones

READ: Landgrebe pp 542-546

I. Introduction

Aldehydes and ketones are two of several types of compounds that contain the carbonyl group. Reactions that occur because of the presence of the carbonyl group include nucleophilic addition reactions and base catalyzed condensations. Aldehydes are also easily oxidized, which provides a convenient means to distinguish them from ketones.

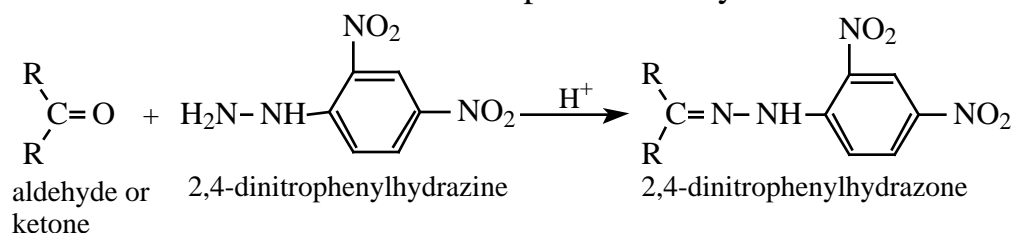
The carbonyl group in aldehydes and ketones is highly polarized; the carbonyl carbon bears a substantial partial positive charge and is susceptible to nucleophilic attack. Further, since it is sp² hybridized it is relatively open to attack. Because the carbonyl contains no good leaving group, addition occurs rather than substitution.

Aldehydes and ketones are polar compounds; however, the pure compounds do not undergo hydrogen bonding as the alcohols do. Thus the boiling points of aldehydes and ketones are lower than alcohols, but higher than alkanes or ethers. Low molecular weight carbonyl compounds are water soluble.

Each of the tests in this experiment will be performed on known compounds first to familiarize you with the test procedure and the interpretation of results. You will also perform these tests on an unknown, to determine if the compound is an aldehyde or a ketone, and if it is a ketone whether it is a methyl ketone. You will then identify the specific compound by making one or more solid derivatives and comparing the melting points of these derivatives with the listed melting points in the table below.

1. 2,4-Dinitrophenylhydrazone Test

Aldehydes and ketones react with a number of nitrogen containing compounds through nucleophilic addition and subsequent loss of water to give products that have a carbon nitrogen double bond. These reactions are useful in distinguishing an aldehyde or ketone from other functional groups. Two reagents that are often used for this purpose are 2,4-dinitrophenylhydrazine and semicarbazide. The solid products resulting from these reagents are also used as solid derivatives for the identification of specific aldehydes and ketones.

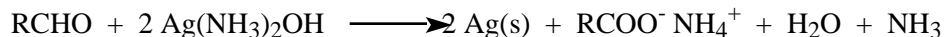


The color of the hydrazone precipitate formed is often a guide to the amount of conjugation in the original aldehyde or ketone. Unconjugated ketones such as

cyclohexanone often give a yellow solid, while conjugated ketones such as acetophenone give orange to red solids. Compounds which are highly conjugated give red solids. However, the 2,4-dinitrophenylhydrazine is itself orange-red; thus the color must be judged with caution. In rare cases, compounds which are either strongly acidic or strongly basic will precipitate the unreacted reagent from solution.

2. Tollens Test

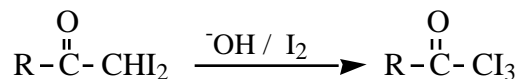
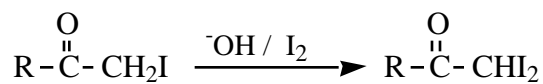
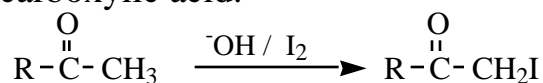
Aldehydes are very easily oxidized to yield carboxylic acids or their salts if the reaction is done in basic media. Since ketones are not readily oxidized, this test is a useful method of differentiating between aldehydes and ketones. The ammoniacal silver hydroxide solution used in the Tollens Test is a very mild oxidizing agent (actually the Ag^{+1} ion). The silver ion is reduced to metallic silver in a positive reaction. Sometimes a silver mirror forms on the test tube.



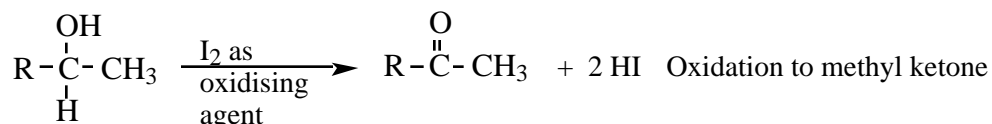
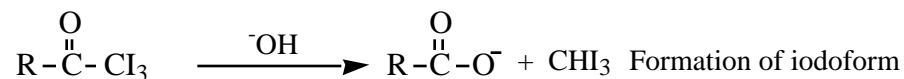
Ordinary ketones do not give a positive result in this test. The test should be used only if it has already been shown that the unknown compound has a carbonyl group. It should be noted that certain aromatic amines, phenols and amino ketones are also able to reduce ammoniacal silver nitrate.

3. Iodoform Test

Methyl ketones can be distinguished from other ketones by their reaction with iodine in a basic solution to yield iodoform (CHI_3) as a yellow colored precipitate. However, acetaldehyde (CH_3CHO) and alcohols with their hydroxyl groups at the 2 position of the chain will also form iodoform under these same conditions. Alcohols of the type described are easily oxidized to methyl ketones under the conditions of the iodoform reaction (I_2 is an oxidizing agent). The other product of the iodoform reaction is the sodium or potassium salt of a carboxylic acid.



Successive iodination leading to triiodomethyl substituent



II. Overview

- A. Obtain from your lab instructor, an unknown aldehyde or ketone. It will be one of those in the table below.

COMPOUND	BOILING PT	DNP mp	SEMICARBAZIDE mp
acetone.....	56.....	126.....	187
methyl ethyl ketone.....	80.....	116.....	135
3-methyl-2-butanone.....	94.....	117.....	113
2-pentanone	102.....	144.....	113
3-pentanone	102.....	154.....	156
2-butenal (Crotonaldehyde)	104.....	190.....	199
methyl isobutyl ketone	117.....	95.....	132
cyclopentanone.....	131.....	144.....	210
5-methyl-2-hexanone	144.....	95.....	142
heptanal.....	153.....	108.....	109
cyclohexanone.....	156.....	162.....	166
furfural.....	162.....	230.....	202
3-methylcyclohexanone.....	169.....	155.....	179
4-methylcyclohexanone.....	169.....	134.....	203
benzaldehyde.....	179.....	237.....	222
acetophenone.....	202.....	239.....	199
Tolualdehyde	202.....	234.....	215

- B. Your unknown will be due at the end of the next lab period.

III. Procedure

You will identify your unknown through the following procedures

1. The melting point of the DNP derivative (I have substituted a better procedure, below, for the one shown in the lab text on page 543).

Run this reaction with acetone first to see what you should expect. Don't isolate the product or take the melting point of the derivative from acetone.

PROCEDURE:

- a. The 2,4-DNPH reagent has already been prepared by the lab assistant by warming a mixture of 1 g of 2,4-dinitrophenylhydrazine and 30 mL of diglyme (2-methoxy ethyl ether). The final warm solution was then filtered.
- b. A solution of 0.3 g of your carbonyl compound in 3 mL of 95% ethanol is prepared in a 25-mL or 50-mL Erlenmeyer flask or beaker, and 15 mL of the 2,4-DNPH reagent is added.
- c. Up to nine drops of concentrated hydrochloric acid is added to the mixture. If the derivative does not precipitate immediately after introduction of the acid, water is added dropwise until separation of a solid does occur. Warning! If your compound does not form a DNP, large amounts of water will cause the starting

dinitrophenylhydrazine to precipitate out and you will think you have isolated a DNP product.

2,4-Dinitrophenylhydrazine has a melting point of 199-200 degrees. If your "DNP" derivative melts near that temperature and has the same color as starting material, be suspicious.

- d. The crude dinitrophenylhydrazone is filtered with suction and washed with cold ethanol or 50% aqueous ethanol. Recrystallize the product, if necessary, from ethanol, aqueous ethanol, or ethyl acetate. (Derivatives obtained by this procedure are reported to be sufficiently pure to eliminate the need for recrystallization.)
2. The Tollens Test (in place of the procedure on page 544, use the procedure, below.). **WARNING.** Tollens reagent will denature your protein. Do not get it on you.
 - a. In a thoroughly clean test tube place 2 mL of a 5% solution of silver nitrate, and add a drop of dilute sodium hydroxide solution (10%). A black precipitate of silver oxide will form. Add a very dilute solution of ammonia (about 10% NH_4OH) drop by drop, with constant shaking, until the precipitate of silver oxide just dissolves. In order to obtain a sensitive reagent it is necessary to avoid a large excess of ammonia.
 - b. To this solution add about 10 drops of a 10% solution of your compound in 50% aqueous absolute alcohol.. Stir the solution well and let stand. (As a test try heptanal from the hood.)
 3. The iodoform test (L. p545). Run this test on acetone first.
 - a. Add 4 drops of acetone to 5 mL of dioxane in a test tube and shake until all the sample has gone into solution. You may need to stopper the test tube to get adequate shaking. Add 1 mL of 10% sodium hydroxide solution, and then iodine-potassium iodide solution, with shaking, until a slight excess yields a definite dark color of iodine. If less than 2 mL of the iodine solution is decolorized, place the test tube in a water bath maintained at a temperature of 60° . If the slight excess of iodine already present is decolorized, continue the addition of iodine solution with shaking until a slight excess of iodine solution again yields a definite dark color. The addition of iodine is continued until the dark color is not discharged by 2 minutes' heating at 60° . This excess of iodine is removed by the addition of a few drops of 10% sodium hydroxide solution with shaking. Now fill the test tube with water and allow to stand for 15 minutes. Observe the results. Iodoform is a light yellow solid.
 4. The infrared spectrum. This spectrum should help verify whether the compound is aromatic, has a double bond, or is an aldehyde or ketone.

-
5. If you are not able to draw a clear conclusion as to what your unknown is, then prepare a semicarbazone (see instructor for procedure). Semicarbazone derivatives are difficult to make from hindered ketones. If you do not get a solid derivative, you may have such a compound.
 6. Be able to show balanced equations for any given aldehyde or ketone with any of the reagents used in this experiment.

Aldehydes and Ketones

Name _____

Unknown Report Sheet

Aldehydes and Ketones

Record the results of each test performed as well as the chemical reactions (using acetone and propanal as examples) on the Report Sheet, below. Attach to this report the interpreted IR.

Unknown Number _____ Color _____

DNP Melting Point _____ Semicarbazone Melting Point (if done) _____

- a. Reaction of your unknown (actual structure) with DNP

- b. Reaction of your unknown (actual structure) with Semicarbazone (use acetone as the unknown if you didn't do this)

Tollins Test

- a. Results

- b. Equations for reactions of your unknown (actual structure)

Iodoform Test

- a. Results

- b. Equations for reactions of your unknown (actual structure)

Functional groups (with wavenumbers) indicated on infrared spectrum (attached).

Functional Group Indicated	Wavenumber	Peak size

FINAL CONCLUSIONS:

First choice for name of unknown_____

Second choice for name of unknown_____