#### Aldehydes and Ketones

**Objective**: To study some chemical reactions that are used to distinguish aldehydes and ketones, especially oxidation of aldehydes.

#### Introduction

Aldehydes and ketones both contain the carbonyl functional group, which imparts similar chemical reactivities to these two classes of compounds with some reagents. Aldehydes are much more susceptible to oxidation because a hydrogen atom is attached to the carbonyl, which is the basis for some of the chemical reactions that distinguish between these two classes of compounds.



The oxidation of aldehydes can be performed with a mild oxidizing agent, such as  $Ag^+$  in ammonia solution used in the Tollens test or  $Cu^{2+}$  in alkaline solution used in Fehling's test. If the Tollens test is performed in a scrupulously clean glass vessel, the silver metal is plated on the walls of the glass to form a silver mirror; contaminants may result in the reduced silver forming a gray sludge in the bottom of the tube. Fehling's reagent is a deep blue  $Cu^{2+}$  solution that forms a brick-red precipitate of  $Cu_2O$  in the presence of aldehydes.

Tollens' Silver Mirror Test

| $R-C-H + AgNO_3 \xrightarrow{NH_4OH}$    | O<br>R-C-O <sup>-</sup> + Ag + NH₄ <sup>+</sup> |
|--|---|
| Fehling's Test                           | Silver<br>Mirror                                |
| $R-C-H + Cu^{+2} + OH^{-1}$<br>Blue soln | $\rightarrow R - C - O^{-} + Cu_2O$<br>Red ppt  |

A stronger oxidant such as chromic acid, which was used to oxidize alcohols in the previous experiment, will also oxidize aldehydes readily, but generally does not oxidize ketones. The chromic acid in Bordwell-Wellman reagent is an orange-yellow solution that forms the green  $Cr^{3+}$  ion when it is reduced by alcohols or aldehydes. Ketones should give no reaction.

#### Materials and Reagents

Test tubes, 6 M sodium hydroxide, 6 M ammonium hydroxide, dilute nitric acid, Fehling's solutions A and B, Bordwell-Wellman reagent, iodine in potassium iodide solution, acetone, benzaldehyde, acetaldehyde, cyclohexanone and unknowns.

#### Procedure

Begin Here: Add 100 mL of tap water to a 250 mL beaker and heat it on a hot plate for Part B.

#### Part A. Tollens' Silver Mirror Test (Start this after setting up hot water bath)

**Note**: Test tubes must be scrupulously clean for the silver mirror test to work. Be sure to rinse tubes well with deionized water. The chloride ions in tap water interfere with mirror formation.

- 1. Wash 5(or 6 if working in pairs) test tubes thoroughly with soap/detergent and water and rinse well. Give at least 2 final rinses with **<u>deionized</u>** water.
- 2. Add 10 drops of 6 M sodium hydroxide (NaOH) to each test tube and swirl the tube. Allow the NaOH solution to remain in the tube for about 1 min, then discard the NaOH solution in the sink. DO **NOT** RINSE THE TEST TUBES!!!
- 3. Add about 1 mL of 0.1 M silver nitrate solution to each test tube. A brown precipitate of silver hydroxide (AgOH) may form.
- 4. Add a few (2 to 4) drops of 6 M ammonium hydroxide ( $NH_4OH$ ) solution to get the brown precipitate to dissolve. Shake to completely dissolve the brown precipitate. Add a few more drops of  $NH_4OH$  solution, if needed, until the precipitate completely dissolves. The solution should be clear, with no precipitate or solid material in it.
- 5. Add 3 drops of acetone to tube 1; 3 drops of benzaldehyde to tube 2; 3 drops acetaldehyde solution to tube 3; 3 drops cyclohexanone to tube 4 and 3 drops of unknown to tube 5.
- 6. Mix each well and allow to stand without further shaking for 5 to 10 min and look for the formation of mirrored glass on the walls of the test tube (or gray sludge in the bottom).
- 7. Record your observations on the Report Sheet, Table 1.

#### 8. **Dispose of these reagents in the "Liquid Waste" container in the hood.**

9. Add dilute nitric acid (HNO<sub>3</sub>) to the mirrored glass tubes to remove the silver deposits. Dispose of the nitric acid in the hazardous waste bottle and flush with plenty of water in the sink.

#### Part B. Fehling's Test

The water bath you set up earlier should be boiling. Set the hot plate temperature control to a medium setting. Use 5 clean test tubes if working alone, or 6 test tubes if working in pairs.

- Add 5 (or 6) mL of Fehling's Solution A to a small beaker and mix 5 (or 6) mL of Fehling's Solution B with it. Notice the change in color of the Cu<sup>2+</sup> ion when these solutions are mixed.
- 2. Add about 2 mL of the mixture prepared in step 1 to each of 5 (or 6) clean test tubes.
- 3. Add 5 drops of the following test compounds (aldehydes/ketones) to the Fehling's reagent in each test tube. Acetone in tube 1; benzaldehyde in tube 2; acetaldehyde in tube 3; cyclohexanone in tube 4; and unknown in tube 5 (and 6).
- 4. Make sure the tubes are properly labeled before placing them in the boiling water bath.
- 5. After heating the mixtures for 5 minutes, take note of any changes in color or formation of a red precipitate at the bottom of the tube.
- 6. Record your observations on the Report Sheet, Table 1.
- 7. Turn off the hot plate, the water bath is no longer needed.

#### Dispose of these reagents in the "Liquid Waste" container in the hood.

#### Part C. Oxidation with Chromic Acid

## CAUTION!! Concentrated sulfuric acid in the Bordwell-Wellman reagent is very corrosive. Handle it with care.

- 1. Add 6 to 8 drops of each of the following test compounds (aldehydes/ketones) to 5 (or 6 if working in pairs) clean test tubes: acetone in tube 1; benzaldehyde in tube 2; acetaldehyde in tube 3; cyclohexanone in tube 4; and unknown(s) in tube(s) 5 (and 6).
- 2. Add 1 or 2 drops of Bordwell-Wellman reagent solution to each of the test tubes containing the test aldehydes or ketones from step 1.
- 3. Mix well and note any color changes after a few minutes. If there is a reaction, the color should change from yellow/orange to green or brown.
- 4. Record your observations on the Report Sheet, Table 1.

#### Dispose of these reagents in the "Liquid Waste" container in the hood.

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### Aldehydes and Ketones Experiment #4

**Pre-Lab Exercise** 

1. Describe the difference between an aldehyde and a ketone, and indicate how each differs from an alcohol.

2. Name one aldehyde or ketone that is used widely by consumers. Be sure to give the correct name and indicate its use.

3. Describe what is meant by oxidation and reduction in relation to organic compounds, giving one example of oxidation of an organic compound and one example of reduction of an organic compound. The compound you use for the example may be the same or different for the oxidation and the reduction reactions. Be sure to indicate what oxidizing agent is used and what reducing agent is used for each example.

4. The simplest aldehyde, formaldehyde (methanal), is a common aldehyde found in our food and environment. Give at least one source of human exposure to formaldehyde and indicate at least one health condition that can result from this aldehyde. (See supplement to chapter 15 or internet sources and cite your source).

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# Aldehydes and KetonesExperiment #4Data & Report Sheet

<u>Table 1. Tests for Aldehydes and Ketones.</u> [indicate whether you observed a positive reaction (+) or no reaction (-) in each test <u>and</u> note any color changes or other changes].

Unknown #

|               | Tollens<br>Test | Fehling's<br>Test | Chromic Acid Test |
|---------------|-----------------|-------------------|-------------------|
| Acetone       |                 |                   |                   |
| Benzaldehyde  |                 |                   |                   |
| Acetaldehyde  |                 |                   |                   |
| Cyclohexanone |                 |                   |                   |
| Unknown #     |                 |                   |                   |

#### Questions

1. After looking at the results in Table 1, to what class of compound would you conclude your unknown belongs? (Aldehyde, ketone, or aromatic aldehyde)

2. Which one of the tests performed in this experiment would be most useful in differentiating butanal (a straight chain aldehyde) and benzaldehyde (an aromatic aldehyde). Which of the test compounds (acetone, acetaldehyde, benzaldehyde or cyclohexanone) should react in the same way as butanal in these tests? Explain your answer.

3. Did any of these three reagents (Tollens, Fehling's or chromic acid) react differently with benzaldehyde than it did with other aldehydes? Which one?

4. Why would benzaldehyde react differently than other aldehydes?