# Experiment 25
# Aldehydes and Ketones

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Name:



Date:

## Key Objectives

1. Carbonyl carbon structure and properties
2. Structure of aldehydes and ketones
3. Reactions of aldehydes and ketones
4. Diagnostic tests for aldehydes and ketones
5. Solubility and combustibility of aldehydes and ketones

## Discussion

### Structure of Aldehydes and Ketones

Aldehydes and Ketones are organic compounds containing a carbonyl carbon (C=O) (Figure 25.1) functional group. Carboxylic Acids and Esters also contain a carbonyl carbon, and will be explored in a future experiment. The carbonyl carbon is a polar group with the carbon having a slight excess of positive charge and the oxygen atom having a slight excess of negative charge. A carbonyl carbon located at the end of a molecule is considered an aldehyde functional group. If the carbonyl carbon is located in the middle of the molecule it is considered a ketone functional group. A carbonyl carbon paired with a hydroxy group at the end of the molecule is a carboxylic acid, which often form salts by replacing the hydroxy hydrogen with a metal cation.

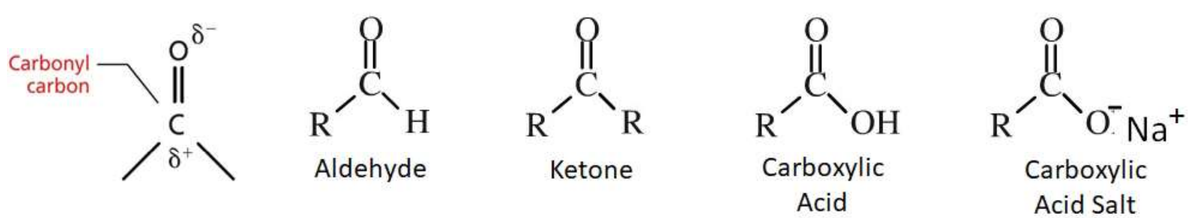
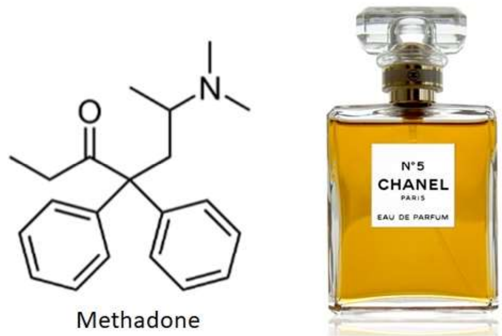



Figure 25.1: Structure of (a) aldehydes (b) ketones and (c) carboxylic acids. credit: author

### Important Uses of Aldehydes and Ketones

The variety of uses of Aldehydes and Ketones is immense and can be read about in your text book for more detail. A few interesting uses are as a drug treatment (Methadone), ingredient in perfumes, and as a product in metabolism as shown in Figure 25.2.




| | |
|---|---|
| Heptanal ($C_7H_{14}O$) | Occurs naturally in sage leaf and has an herbal odor |
| Octanal ($C_8H_{16}O$) | Has a citrusy scent, specifically smells like oranges |
| Nonanal ($C_9H_{18}O$) | Smells like roses |
| Decanal ($C_{10}H_{20}O$) | Has a smell strongly reminiscent of orange-rind |
| Undecanal ($C_{11}H_{22}O$) | Occurs naturally in coriander leaf and has a "clean" smell |
| Duodecanal ($C_{12}H_{24}O$) | Smells like lilacs and violets |
| Tridecanal($C_{13}H_{26}O$) | Has a citrusy scent, specifically smells like grapefruit |
| Tetradecanal ($C_{14}H_{28}O$) | Famous for its peach-skin smell in *Mitsouko* |

Figure 25.2: Important uses of aldehydes and ketones (a) structure of methadone used in drug treatments and (b) use in perfumes. credit: `https://www.ck12.org/c/chemistry/aldehydes-and-ketones/lesson/Aldehydes-and-Ketones-CHEM/`

## Reactions of Aldehydes and Ketones

Aldehydes and ketones are created by the mild oxidation of primary and secondary alcohols. The following general scheme is observed.

- Primary Alcohol $\xrightarrow{[O]}$ Aldehyde + $H_2O$
- Secondary Alcohol $\xrightarrow{[O]}$ Ketone + $H_2O$

Chemically aldehydes and ketones both contain a carbonyl carbon and thus have similar chemical reactivities. However, aldehydes are more susceptible to oxidation because of the hydrogen atom attached to the carbonyl group. This is the basis for distinguishing between these two classes of compounds. Several tests are useful for differentiating between aldehydes and ketones.

The typical diagnostic tests for aldehydes and ketones rely on oxidation-reduction (redox) reactions where a metal ion is reduced while the corresponding organic molecule is oxidized. The signs on paper that a redox reaction has occurred are shown in Figure **??**.

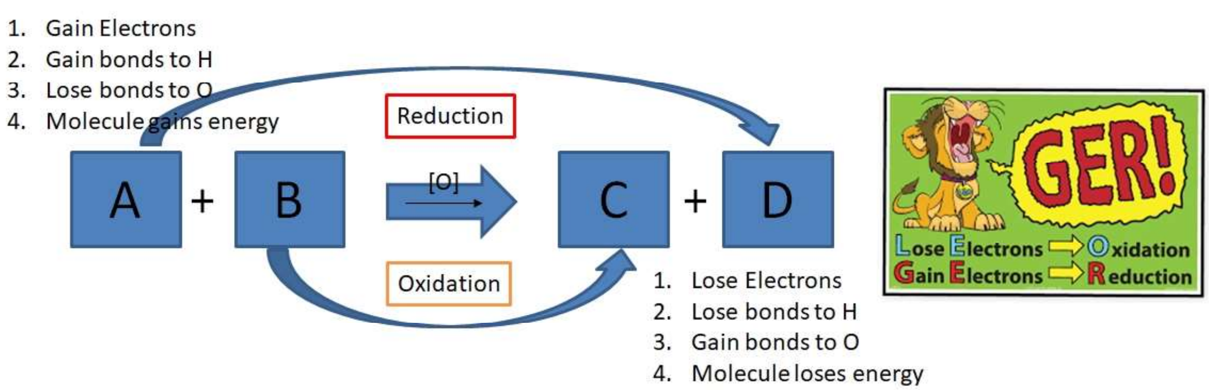



Figure 25.3: Signs an oxidation/reduction or redox reaction has occurred. credit: author

## Copper Wire Oxidation Test

One such method to oxidize alcohols is with copper (II) oxide. Upon heading, copper wire ($Cu^0$) in an open flame leads to the formation of copper (II) oxide. The copper (II) oxide formed on the wire is then reacted with an alcohol to form an aldehyde or ketone, copper (I) oxide and water. In this reaction the aldehyde or ketone is oxidized (loses electrons) while the copper is is reduced (gains electrons).

Heating a copper wire to test multiple solutions is difficult and time consuming and risks igniting the sample. Instead scientists have used a variety of other metals in compounds such as silver (Ag), copper (Cu) or Chromium (Cr) ions in solution as discussed below in the Tollens, Fehlings and Jones tests.

## Chromic Acid or Jones Test

A stronger oxidant such as chromic acid which was used previously to oxidize alcohols can also be used to oxidize aldehydes to carboxylic acids. The chromic acid in the Bordwell-Wellman reagent is an orange-yellow solution that is reduced to $Cr_3^+$ which is a green color. The reaction is quite complicated and in general we will simplify it by only including the organic products that are oxidized (the aldehyde and carboxylic acid) and indicate a color change occurred and ignore the other reactants and products which are reduced and produce the color change.

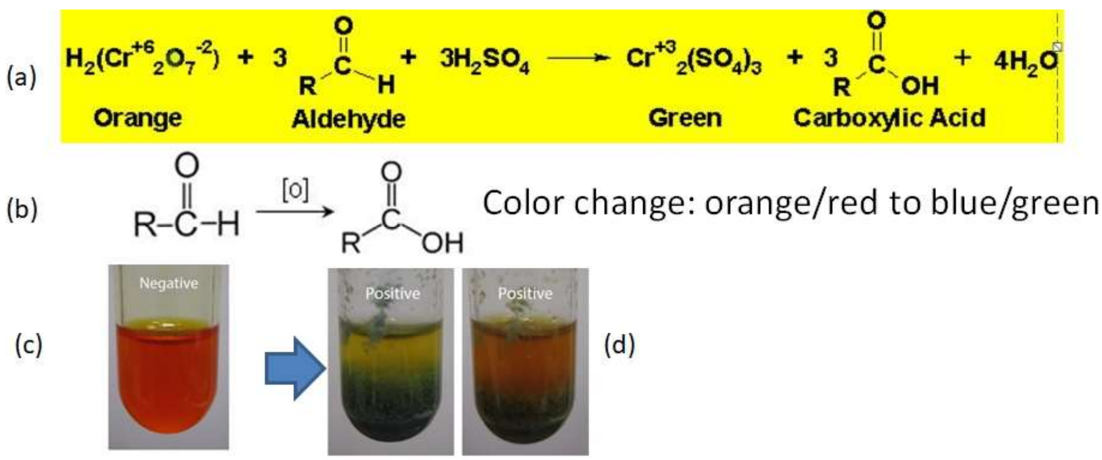



Figure 25.4: (a) Full reaction for the Chromic Acid test showing the oxidation of the aldehyde and the corresponging reduction of the chromium ion from +6 to +3) (b) Simplified version of the chromic acid reaction used in class (c) Negative result (d) Positive results credit: author and Individual Tests. (2021, August 4). Butte College. `https://chem.libretexts.org/@go/page/95742`

## Tollens or Silver Mirror Test

The first test is referred to as the Tollens' or Silver Mirror test shown in Figure 25.5. The Tollens test uses $Ag^+$ ions to oxidize the aldehyde to a carboxylic acid, as a result the silver ions are reduced to silver metal and either plated out on the surface of the reaction container, or forms a dark silver metal precipitate.

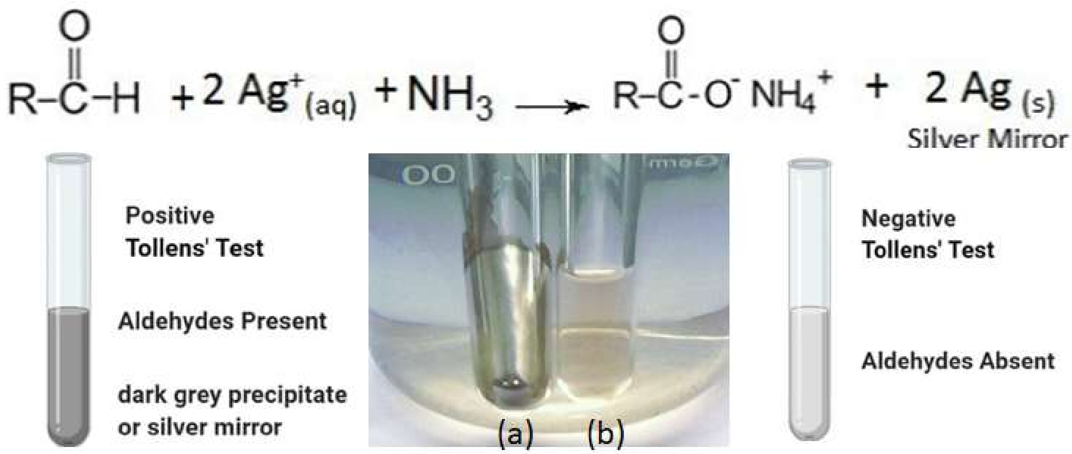



Figure 25.5: (a) Positive Tollens Test (b) Negative Tollens Test. credit: author modified, https://en.wikipedia.org/wiki/Tollens

## Fehling's Test

A second test for differentiating aldehydes and ketones is the Fehling's test showin in Figure 25.6. The Fehling's reagent uses $Cu_2^+$ ions to oxidize the aldehyde into a carboxylic acid salt and in turn the copper ions are reduced to form copper (I) oxide which is a reddish precipitate.

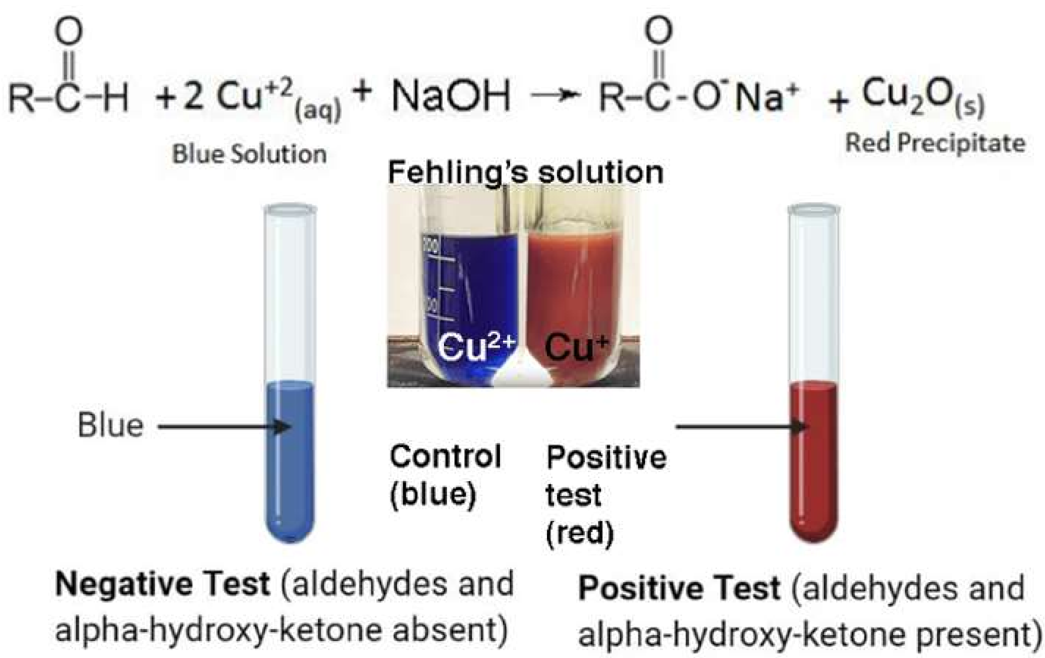



Figure 25.6: Postitive and Negative test results for Fehlings test. credit: author modified unknown

# Procedure

## A. Odors of Aldehydes and Ketones

1. Carefully detect the odor of all the compounds by carefully wafting.

## B. Solubility - Water

1. Test the solubility of each of the listed substance with water by adding 1 mL (20 drops) of the substance to be tested to 5 mL of water in a test tube.
2. Mix each of the test tubes vigorously for 15 seconds. Wait 30 seconds. Sketch a picture of your results. In the sketch, label each liquid in the test tube. Note which pairs are miscible and which are not.
3. For any solutions that are insoluble note the relative density of the compounds with respect to water.
4. Dispose of the solutions in the appropriately labeled waste bottle labeled .

## C. Oxidation of Alcohols - Copper (II) Oxide

1. Place 2 mL of methanol in a test tube.
2. Obtain a 20 cm piece of copper wire wire with several spiral turns on one end.
3. Using a Bunsen burner, warm the alcohol slightly to promote alcohol vapors in the tube. Do not overheat the tube as methanol is highly flammable.
4. Heat the copper coil to a glowing orange color. Do not overheat the wire as it will melt.
5. While the copper wire is hot, lower part way into the tube (but not into the liquid) and note the results.
6. Heat the wire again and lower it into the tube slowly, finally dropping it into the liquid alcohol.
7. Remove the wire and gently waft the vapors from the tube to your nose to detect the odor.
8. Dispose of the solutions in the appropriately labeled waste bottle labeled .

## D. Tollens' Silver Mirror Test

1. This test is very sensitive to impurities, and the glassware used must be scrupulously clean in order for a silver mirror to form.
2. Obtain 6 NEW test tubes from your instructor.
3. Add 10 drops of 6 M NaOH to each test tube, and swirl to rinse the bottom half of the tube. Leave the NaOH solution in the test tube for 1 minute, then discard the solution in the sink.

4. Add about 1 mL of the 0.1 M $AgNO_3$ solution to each test tube. A brown precipitate of AgOH may form.

5. Add 15-20 drops of 6 M $NH_4OH$ solution and swirl until the brown precipitate completely dissolves. If the brown precipitate does not dissolve, add several more drops of 6 M $NH_4OH$ to the test tube until it does dissolve.

6. Add 3 drops of the aldehyde or ketone to be tested to the test tube and swirl slightly to mix.

7. Allow the test tube to stand for 5-10 minutes without further disturbing it, then record your observations.

8. Repeat for all of the aldehydes and ketones to be tested.

9. Dispose of the solutions in the appropriately labeled waste bottle labeled .

## E. Fehling's Test

1. Fill a 1000 mL beaker 70% full of tap water and begin heating it over a bunsen burner.

2. Add 2 mL of the Fehling's Solution A and 2 mL of Fehling's Solution B to a test tube.

3. Add 1 mL of the compound to be tested to the Fehlings's reagent.

4. Swirl the tubes gently to mix them.

5. Place the tube in the boiling water bath.

6. After 5 minutes, record your observations (color changes or precipitates).

7. Dispose of the solutions in the appropriately labeled waste bottle labeled .

## F. Oxidation with Chromic Acid

1. Add 2 drops of the chromic acid solution to a test tube.

2. Add 6-8 drops of the compound to be tested to the test tube.

3. Swirl well and note any color changes after 1 minute.

4. Dispose of the solutions in the appropriately labeled waste bottle labeled .

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# Results

## A./B. Structures, Odors and Solubility Tests - Water

| Compound | Structure | Odor | Solubility Obs. | Miscible/Immiscible |
|---|---|---|---|---|
| Methanal | | | | |
| Butanal | | | | |
| benzaldehyde | | | | |
| propanone | | | | |
| 2-butanone | | | | |
| cyclohexanone | | | | |

Table 25.1: Results - Misc. Tests

1. What trends were observed in the solubility of aldehydes and ketones in water?

## C. Oxidation of Alcohols - Copper (II) Oxide

| **Observations** |
| --- |
| **Heating the copper coil:** |
| **After heated coil is immersed in methanol:** |

Table 25.2: Results - Oxidation of Alcohols

1. What evidence of a chemical reaction did you observe when you heated Cu spiral?

2. Write the **complete** (balanced and states) reaction for the oxidation which occurred when the copper spiral was heated and reacted with oxygen gas.

3. What evidence of a chemical reaction did you observe after the heated Cu spiral was lowered into the methanol vapors?

4. Write the **complete** (balanced and states) reaction for the oxidation-reduction reaction between methanol and copper (II) oxide.

## D/E/F/ Oxidation Tests

Clearly indicate whether you observed a positive (+) or negative (-) results. Also include any additional observations you made.

| **Compound** | **Tollens** | **(+/-)** | **Fehlings** | **(+/-)** | **Chromic Acid** | **(+/-)** |
|---|---|---|---|---|---|---|
| methanal | | | | | | |
| butanal | | | | | | |
| benzaldehyde | | | | | | |
| propanone | | | | | | |
| 2-butanone | | | | | | |
| cyclohexanone | | | | | | |

Table 25.3: Results - Oxidation Tests

## Questions

1. For the Tollens test did any compounds tested not react as expected? Explain.

2. Write a **complete** (balanced and states) chemical reaction for the oxidation product formed when butanal reacts with the Tollens Reagent.

3. For the Fehlings test did any compounds tested not react as expected? Explain.

4. Write a **complete** (balanced and states) chemical reaction for the oxidation product formed when butanal reacts with the Fehlings Reagent.

5. For the Chromic Acid test did any compounds tested not react as expected? Explain.

6. Write a **complete** (balanced and states) chemical reaction for the oxidation product formed when butanal reacts with the Chromic Acid Reagent. (Remember you can exclude the jones reagent from the reaction).

7. What advantages does the Tollens test have over the Fehlings test?

8. What advantages does the Fehlings test have over the Tollens test?

9. Which one of the tests performed in this experiment would be most useful in differentiating butanal and benzaldehyde. Explain how you would interpit the results.

10. Draw the structure **AND** write the name for all the aldehyde (4) and ketone (3) isomers of $C_5H_{10}O$

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## Prelab Questions

1. Draw the Lewis structure of all molecules in Part B of the Results section (on that page), and show it to your instructor before beginning the laboratory.

2. The Tollens test is + for what functional group and negative for what functional group? What is the evidence of a positive result in the Tollens test?

3. The Fehlings test is + for what functional group and negative for what functional group? What is the evidence of a positive result in the Fehlings test?

4. The Chromic Acid test is + for what functional group and negative for what functional group?What is the evidence of a positive result in the Chromic Acid test?

5. Based on your knowledge of chemistry, act like Nostradamus and indicate which of the following reactions will occur or not occur. Write Yes or No in each box below.

| **Compound** | **Soluability in $H_2O$** | **Tollens** | **Fehlings** | **Chromic Acid** |
|---|---|---|---|---|
| methanal | | | | |
| butanal | | | | |
| benzaldehyde | | | | |
| propanone | | | | |
| 2-butanone | | | | |
| cyclohexanone | | | | |

Hello. We may as well get to know each other. What is your favourite color?