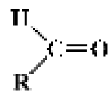
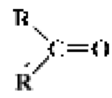
Identification of Aldehydes and Ketones

Aldehydes are compounds of the general formula RCHO; ketones are compounds of the general formula RŔCO. The groups R and Ŕ may be aliphatic or aromatic, and in one aldehyde, formaldehyde, R is hydrogen.

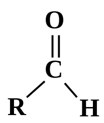


the general formula for aldehydes

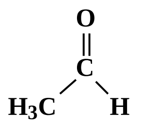


the general formula for ketones

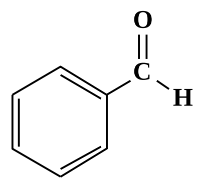
Both aldehydes and ketones contain the carbonyl group, C=O, and are often referred to collectively as carbonyl compounds. It is this carbonyl group that largely determines the chief chemical and physical properties of aldehydes and ketones.



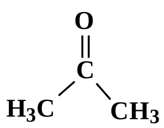
formaldehyde



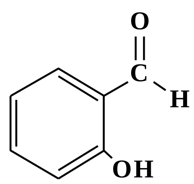
acetaldehyde



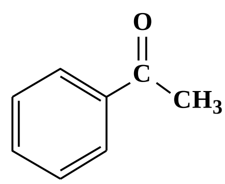
benzaldehyde



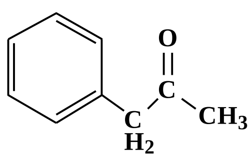
acetone



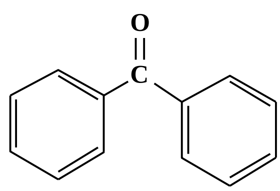
salicylaldehyde



acetophenon



benzyl methyl ketone



benzophenone

Aldehydes and ketones differ from alcohols in having two less hydrogen atoms. Removal of these two hydrogens from a primary alcohol as a result of oxidation yields an aldehyde; where as their removal from a secondary alcohol gives a ketone. The relation between these carbonyl compounds and alcohols is, therefore, oxidation-reduction relation. Tertiary alcohols can't undergo this reaction.

Physical properties

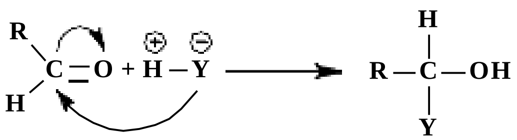
- All aldehydes and ketones are liquids except formaldehyde, which is gas (boiling point -21˚C), and benzophenone, which is solid (melting point 48˚C). Formaldehyde is handled either as an aqueous solution (*formalin*, an aqueous solution of 40% formaldehyde and 15% methanol.) or as one of its solid polymers: paraformaldehyde, $(CH_2O)_n$, or trioxane, $(CH_2O)_3$.
- Low molecular weight aldehydes and ketones (less than 5 carbons) are appreciably soluble in water, although they do not have the ability to form hydrogen bonds (unlike alcohols), aromatic ones are insoluble in water, and all of them are soluble in organic solvents.
- They are colorless except benzaldehyde, which has a pale yellow colour (due to oxidation) with a characteristic odour.
- The boiling points of aldehydes and ketones are lower than those of the alcohols from which they are derived; isopropyl alcohol boils at 82.5˚C while its oxidation product, acetone, boils at 56˚C, ethanol boils at 78˚C while its oxidation product, acetaldehyde, boils at 21˚C.
- Aliphatic aldehydes and ketones burn with a blue flame (without smoke) while aromatic ones burn with a yellow smoky flame.

Solubility classification

Aldehydes and ketones that are soluble in water are soluble in ether too and are classified under class $\boldsymbol{S_1}$(*e.g.*, formaldehyde and acetone).Aldehydes and ketones that are insoluble in water are classified under class ***N*** such as benzaldehyde and benzophenone.

Chemical properties

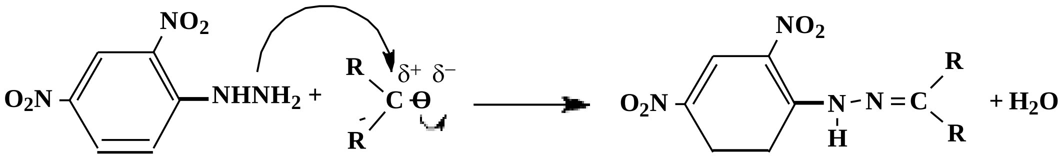
- All reactions of aldehydes and ketones are related to the carbonyl group (the active group).
- Aldehydes contain a hydrogen atom attached to its carbonyl while ketones don't. This difference in the chemical structure affects their chemical properties in two ways:
  a) aldehydes are easily oxidized to the corresponding acids and have reducing properties while ketones are not oxidized under similar conditions and do not show reducing properties.
  b) aldehydes are usually more reactive than ketones towards nucleophilic addition, the characteristic reaction of carbonyl group.



- Both aldehydes and ketones are neutral compounds that don't change the color of litmus paper.

1. General test (2,4-Dinitrophenylhydrazine reagent)

Both aldehydes and ketones give yellow or orange precipitate with 2,4-dinitrophenylhydrazine reagent.



Procedure

To 2 drops of the compound add 3 drops of the reagent, a yellow or orange precipitate will be formed. If the compound is insoluble in water, dissolve it in 1 mL of methanol and then add the reagent.

2. Differentiation between aldehydes and ketones

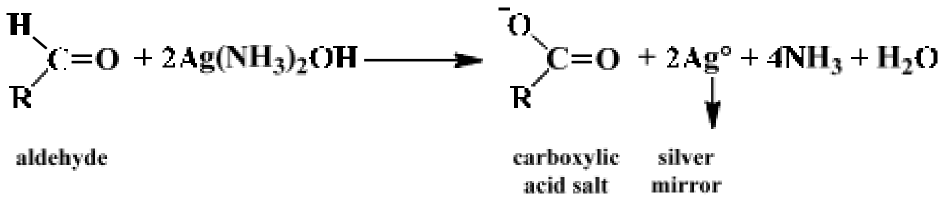
Differentiation between aldehydes and ketones is achieved by taking the advantage of the fact that aldehydes can be easily oxidized while ketones cannot (they need stronger oxidizing agents).Two reagents can be used for this purpose, Tollen's reagent or Fehling's reagent. Only aldehydes give positive results with these two reagents.

a) Tollen's test (Reduction of ammoniacal silver nitrate)

Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. Aldehydes show positive result with this reagent because the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid with an accompanying reduction of the silver ions from this reagent to silver element in the form of silver mirror on the inner side of the test tube.

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{brown ppt.}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow 2Ag(NH_3)_2OH + 3H_2O$$



The oxidation process requires an alkaline medium; therefore sodium hydroxide solution is used, and in order to overcome the formation of the brown silver oxide precipitate (Ag_2O), ammonium hydroxide is used to serve as a complexing agent for this precipitate making it a water soluble complex. Note that since the medium is alkaline, salts of the produced carboxylic acid are formed rather than the acid itself.

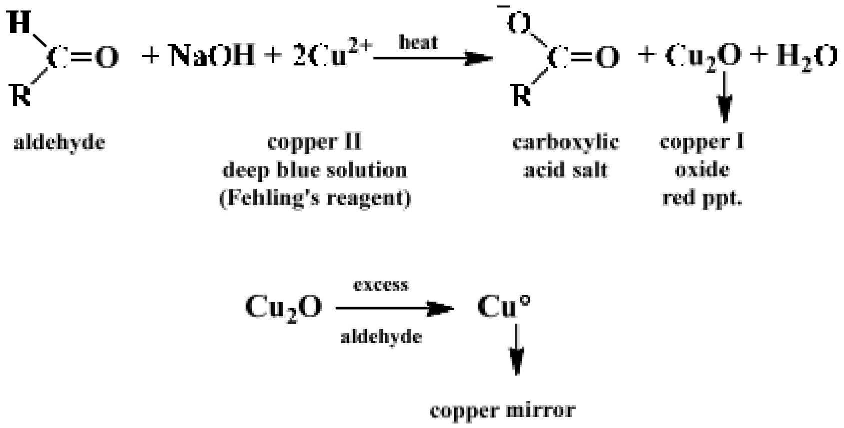
Procedure

- Preparation of Tollen's reagent
  To 3mL of silver nitrate solution add 2-3 drops of 10% sodium hydroxide solution, and then add drop wise very dilute ammonia solution with continuous shaking until all the brown precipitate of silver oxide is dissolved. This reagent should be freshly prepared prior before use.
- Add 2-3 drops of the compound to 2-3 mL of Tollen's reagent, a silver mirror will be formed. If no reaction occurs, warm the test tube in water bath for few minutes (note that excessive heating will cause the appearance of a false positive test by decomposition of the reagent).

The formed silver mirror can be washed using dilute nitric acid. If the test tube is not very clean, silver metal forms merely as a granular gray or black precipitate. False-negative tests are common with water insoluble aldehydes. A negative result indicates that the compound is a ketone.

b) **Reduction of Fehling's reagent**

This test, like Tollen's test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling's reagent (a deep blue solution) to give a red cuprous oxide precipitate.



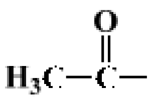
Procedure

- Preparation of Fehling's reagent
  Fehling's reagent is prepared by mixing exactly equal volumes of Fehling's A and Fehling's B solution in a 1:1 ratio immediately before use (usually 1 mL of each).Fehling's A solution is an aqueous solution of copper sulfate pentahydrate ($CuSO_4.5H_2O$) with few drops of concentrated sulfuric acid whereas Fehling's B solution is an aqueous solution of potassium sodium tartrate ($C_4H_4KNaO_6,4H_2O$) and sodium hydroxide.
- Add 5 drops of the compound to 1 mL of Fehling's solution, and then heat in water bath for 5 minutes (with shaking for water insoluble compounds).

Aldehydes change the color of Fehling's solution from blue to green, orange precipitate, and then red precipitate or copper mirror. Ketones don't change the color of this reagent. On the other hand, this test does not give a sharp result with aromatic aldehydes.

3. Special tests for aldehydes and ketones containing a terminal methyl group

These compounds include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone. All of them have a methyl group attached to the carbonyl group:



a) Iodoform (Haloform) test

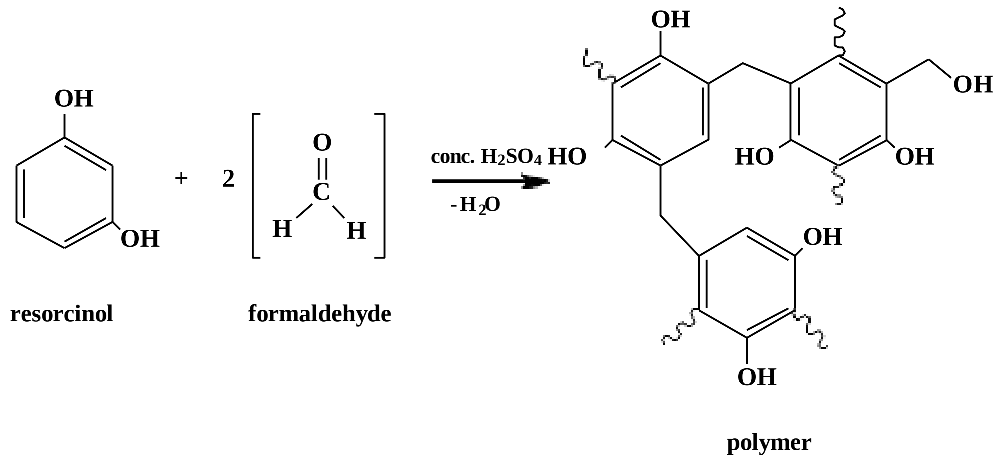
Follow the same procedure of iodoform test mentioned earlier (identification of alcohols).

b) Sodium nitroprusside test

To few drops of the compound add 1 mL of sodium nitroprusside ($Na_2[Fe(CN)_5NO].2H_2O$) solution and excess of 30% sodium hydroxide solution, a red color complex is a positive test.

4. Polymerization reaction

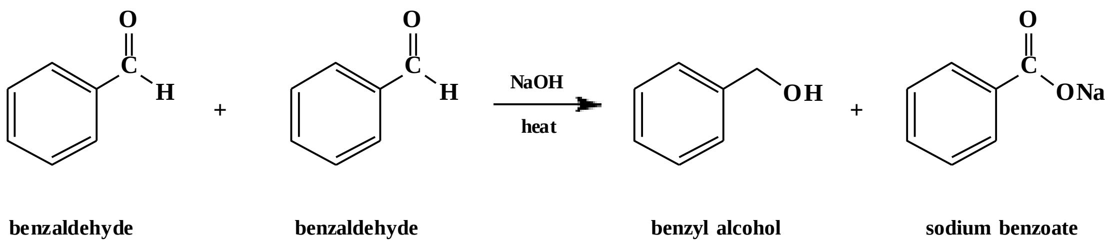
To 0.5 mL of formaldehyde or salicylaldehyde add 0.2 gm of resorcinol and drop-by-drop concentrated sulfuric acid to get a red or reddish violet color, or a white ring that changes to a reddish violet ring.



5. Cannizzaro reaction

Benzaldehyde, salicylaldehyde, and formaldehyde can undergo Cannizzaro reaction because they do not have an alpha hydrogen atom.

In this type of reactions the aldehyde undergoes a self oxidation-reduction in the presence of a strong basic medium to yield a mixture of the corresponding alcohol and the salt of the corresponding carboxylic acid (or the acid itself). Therefore, one molecule of the aldehyde serves as the oxidizing agent while the other serves as the reducing agent.



Procedure

To few drops of benzaldehyde (or the other aldehydes) add 0.5 mL of 30% sodium hydroxide solution and heat gently on a water bath with shaking for five minutes. A precipitate of sodium benzoate is produced. Dissolve this precipitate by adding few drops of distilled water, and then add drops of concentrated hydrochloric acid to liberate benzoic acid as a white precipitate.

As mentioned earlier formaldehyde can undergo this reaction ; however, this reaction can't be relied on for testing formaldehyde since the acid produced, formic acid, is liquid that can't be observed separately as compared to the solid benzoic acid resulted from benzaldehyde.

What is paraformaldehyde and from what aldehyde is it from? Write down its molecular formula.