2. ALDEHYDES&KETONES

Introduction

Aldehydes are compounds of the general formula **RCHO**. **Ketones** are compounds of the general formula **RŔCO**. See figure 1.

*The groups **R** and **Ŕ** may be **aliphatic or aromatic**, and in one aldehyde, **formaldehyde**, **R** is hydrogen.*

***Both aldehydes and ketones contain a 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.*

*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 relationship between these carbonyl compounds and alcohols is oxidation-reduction relationship**. **Tertiary alcohols can't undergo this reaction.***

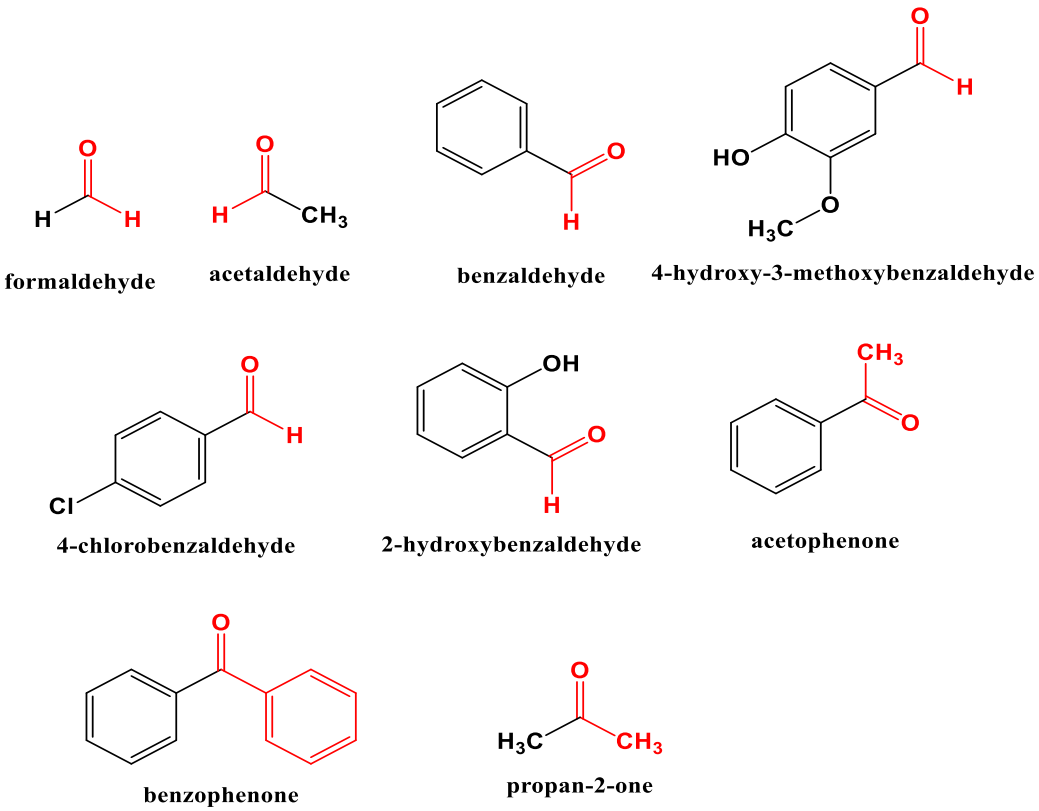


Figure 1: some examples of aldehydes and ketones

Physical Properties

All aldehydes and ketones are liquids except formaldehyde, which is gas and benzophenone, which is solid.
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 odor.
The boiling points of aldehydes and ketones are lower than those of the alcohols from which they are derived **[WHY?]**; 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.

Chemical Properties

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

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:***

1. ***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.***
2. ***Aldehydes are usually more reactive than ketones towards nucleophilic addition, the characteristic reaction of carbonyl group.***

Identification Of Aldehydes and Ketones

GENERAL TEST

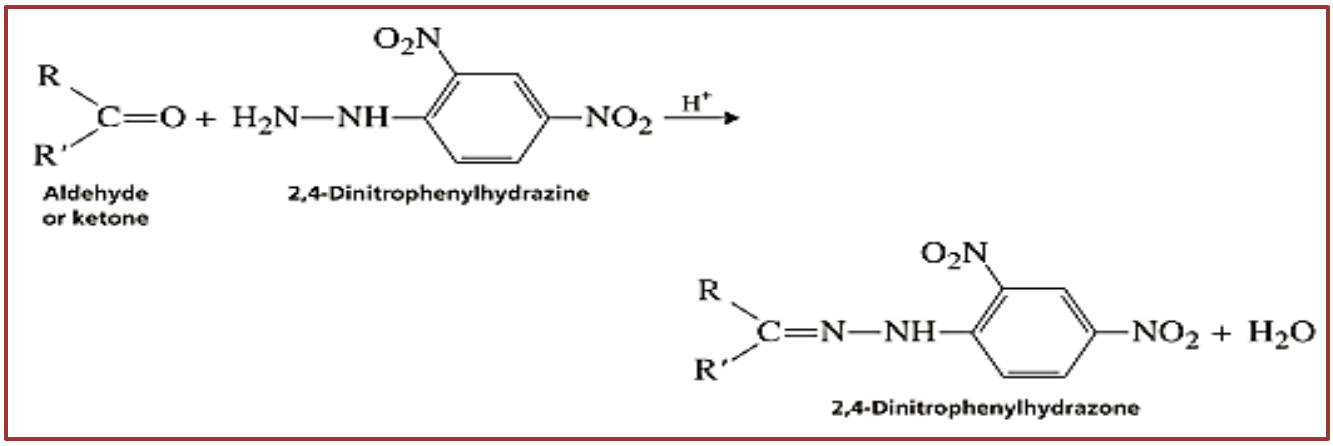
2,4-DINITROPHENYL HYDRAZINE

Both aldehydes and ketones give ***yellow to red*** *precipitate with* ***2,4-dinitrophenyl hydrazine*** *reagent.*

PROCEDURE

Place **1 drop** of the liquid unknown in a small test tube and add **10 drops** of the ***2,4-dinitrophenyl hydrazine*** reagent. If the unknown is solid, dissolve about **10mg** in

minimum amount of ***95% ethanol*** before adding the reagent. Shake the mixture vigorously. Most aldehydes and ketones will give ***yellow to red*** precipitate immediately. However, some compounds will require up to ***15 minutes***, or even ***gentle heating***, to give a precipitate. A precipitate indicates a ***positive test***.



Identification Of Aldehydes and Ketones

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, Tollens reagent or Fehling's reagent. ***Only aldehydes give positive results with these two reagents.***

→ Tollens Test (Reduction of Ammoniacal Silver Nitrate)

The reagent must be prepared immediately before use*. To prepare the reagent, mix 1mL of Tollen's solution A [****Dissolve 3.0g of silver nitrate in 30mL of water****] with 1mL of Tollen's solution B [****10% sodium hydroxide solution****]. A precipitate of silver oxide will form. Add enough dilute* **(10%)** *ammonia solution (dropwise) to the mixture to dissolve the silver oxide just barely.* ***The reagent so prepared can be used immediately for the following test****.*

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.

PROCEDURE

Dissolve **1drop** of a liquid aldehyde or **10mg** of a solid aldehyde in the minimum amount of diethyl ether. Add this solution, a little at a time, to the **2–3mL** of reagent contained in a small test tube. Shake the solution well. ***If a mirror of silver is deposited on the inner walls of the test tube, the test is positive***. ***In some cases, it may be necessary to warm the test tube in warm-water bath***.

$$2AgNO_3 + 2NaOH \rightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O$$

Brown ppt.

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

$$RCHO + 2\,Ag(NH_3)_2OH \longrightarrow 2\,Ag + RCOO^-NH_4^+ + H_2O + NH_3$$

Identification Of Aldehydes and Ketones

Special Tests For Aldehydes And Ketones Containing Terminal Methyl Group

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

→ Iodoform (Haloform) Test

Follow the same procedure of iodoform test mentioned in identification of lactic acid.