IDENTIFICATION OF ALDEHDES AND KETONES

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

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Both contain the carbonyl group (C=O), which lends to their chief chemical and physical properties. Examples of them include formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde ,salicylaldehyde, acetophenone, benzyl methyl ketone, and benzophenone.

**Physical Properties:**

1. All aldehydes and ketones are liquids except formaldehyde which is a gas (boiling point = -21°C) and benzophene, which is a solid (milting point=48°C). Formaldehyde is handled either as an aqueous solution (*formalin*)or as one of its solid polymers: Para formaldehydes,(CH2O)n, or trioxune, (CH2O)3 .
2. The lower aldehydes and ketones are appreciably soluble in water (containing five or less carbon atoms), aromatic one are insoluble in water, and all of them are soluble in organic solvents.
3. They are colorless except benzaldehyde, which has a pale yellow color(due to oxidation) with characteristic odors.
4. The boiling points of aldehydes and ketones are lower than those of the alcohols from which they are derived. For example, isopropyl alcohol boils at 82.5°C while its oxidation product, acetones, boils at 56°C;ethanol boils at 78 °C while its oxidation product, acetaldehyde, and boils at 21°C .
5. Ignition: Aliphatic aldehydes and ketones burn with a blue flame (without smoke) while aromatic ones burn with a smoky yellow flame.

**Solubility Classification:**

Aldehydes and ketones, unlike alcohols, have no ability to form hydrogen bonding.

1. Aldehydes and ketones that are water –soluble are soluble in ether too and are classified under class *S*1(e.g. formaldehyde and acetone).
2. Aldehydes and ketones that are not soluble in water are classified under class N such as benzaldehyde and benzophenone.

**Chemical Properties:**

1. All reactions of aldehydes and ketones are related to the carbonyl group (the active group).
2. Aldehydes contain a hydrogen atom attached to its carbonyl while ketones don, t.This difference in the chemical structure effects their chemical properties in tow ways:
3. 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.
4. Aldehydes are usually more reactive than ketones towards nucleophilic addition, the characteristic reaction of carbonyl groups.



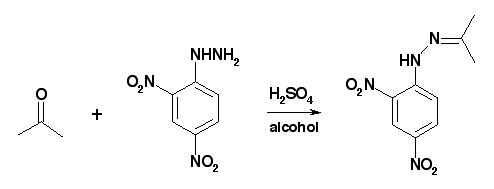
3. Aldehydes and ketones differ from alcohols by tow hydrogen atoms. Removel of these tow hydrogens from a primary alcohol as a result of oxidation yields an aldehyde; whereas their removal from a secondary alcohol as a result of oxidation gives a ketone. The relation between them and alcohol is oxidation-reduction reaction.Tertiary alcohols can, t undergo this reaction.

4. Both aldehydes and ketones are neutral compounds that don, t change the color of litmus paper.

**Chemical reactions:**

1-General test (2,4-dinitrophenylhydrazine reagent) (Brady test):

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



2,4dinitrophenylhydrazine Yellow-orange ppt.

2,4dinitrophenylhydrazine(Imine)

**Procedure:**

1-Add to 2 drops of the compound 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-Tests for differentiation between aldehydes and ketones.

Differentiation between aldehydes and ketones is achieved by taking the advantage of the fact that aldehydes can easily oxidizing while ketones cannot (they need stronger oxidizing agents).

Two reagents can be used for this purpose, Tollen,s reagent or Fehlings reagent. Only aldehydes give positive results with these tow reagents.

2-A. Tollen,s test (Reduction of ammonical silver nitrate).

Tollen,s reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. This reagent gives a silver

mirror in the presence of aldehydes becuese the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid with an accompanying reduction of silver ion from this reagent to silver element in the form of a silver mirror.

2AgNO3  + 2NaOH Ag2O + 2NaNO3 + H2O

Ag2O + 4NH4OH 2Ag(NH3 )OH + 3 H2O

RCHO + 2Ag(NH3 )OH RCOO- + 2Ag° + 4NH3 + H2O

Aldehyde carboxylic acid silver

Salt Mirror

The oxidation process needs alkaline medium, Therefore sodium hydroxide solution is used, and in order to overcome the formation of the brown silver oxide precipitate (Ag2O), 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 produced carboxylic acid are formed rather than the acid itself.

**Procedure :**

**Preparation of Tollen,s reagent**

To 5 ml of silver nitrate solution add 2-3 drops of 10% of sodium hydroxide solution, and then add very dilute ammonia solution drop by drop with continues shaking until

all brown precipitate of silver oxide is dissolved. This reagent should be freshly prepared prior to 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

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**2.B.Reduction of Fehlings 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 Cu2O.

NaO

RCHO + 2Cu+2  + NaOH Cu2O + C=O + H2O

R

Aldehyde Cupper II deep Cupper I oxide

Blue solution

excess

Cu2O Cu°

Aldehyde copper mirror

**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).

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 hands, this test does not give sharp results with aromatic aldehydes.

3-Test for aldehydes and ketones containing a terminal methyl group. (CH3C=O)

These include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone.

**3.a. Iodoform(Haloform) test.**

For details about the procedure of this test see in page 33/34(identification of alcohols).

**3.b.Sodium nitroprusside test. (Na2[Fe(CN)5NO].2H2O)**

To few drops of the compound add 1ml of sodium nitroprusside solution and ecsses of 30% Na OH solution, a red color complex is a positive test

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**4-Polymerization Reaction (test) .**

To 0.5 ml of formaldehyde or salicylaldehyde add 0.2 gm a red or reddish violet color, or a white ring that change to reddish violet ring.



**5-Cannizzaro reaction:**

Benzaldehyde, Salicaldehyde, and formaldehyde can undergo this reaction because they do not contain an alpha hydrogen.

CH3C=O

In this type of reaction 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 aldehyde) add 0.5 ml of 30% of sodium hydroxide solution and heat slowly with shaking for 5 minutes. A precipitate of sodium benzoate is produced. Dissolve this precipitate by adding of distilled water, and then add drops of conc. HCl to liberate benzoic acid as a white precipitate. As mentioned earlier formaldehyde can undergo this reaction; however, this reaction cannot be considered for testing formaldehyde since the acid produced, formic acid is liquid and cannot be seen as compared to the solid benzoic acid resulted from benzaldehyde.

**Questions:**

1-what are para formaldehyde, and what compound is it forms?

2- write the equations for the following reaction:

a) Acetaldehyde plus ammonical silver nitrate.

b) Acetaldehyde plus 2,4-dinitrophenylhydrazine.

c) Acetaldehyde plus Fihling,s reagent.