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Identification of Aldehydes & Ketones

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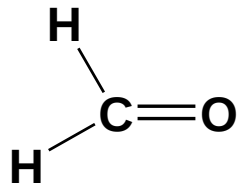
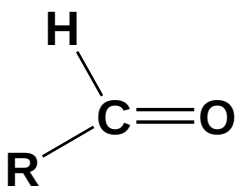
Structure

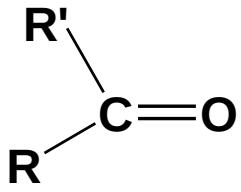
Aldehydes are cpd.s of the general formula RCHO ; Ketones are cpd.s of the general formula RŔCO. The groups R and Ŕ may be aliphatic or aromatic, and in one aldehyde, formaldehyde, R is hydrogen.



Formaldehyde

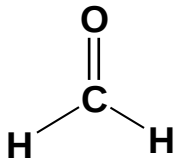


Aldehyde

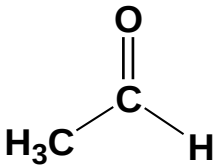


Ketone

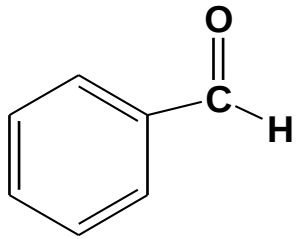
Both aldehydes and ketones contain the carbonyl group, (C=O) , and are often referred to collectively as carbonyl compounds. It is this carbonyl group that largely determines the chief chemical and physical properties of aldehydes and ketones.



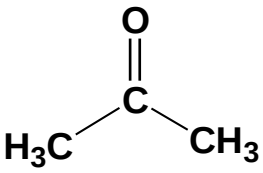
Formaldehyde



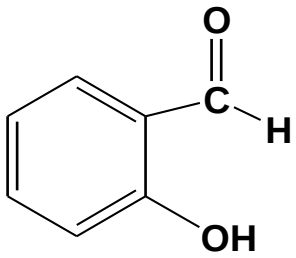
Acetaldehyde



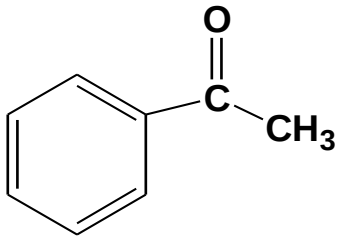
Benzaldehyde



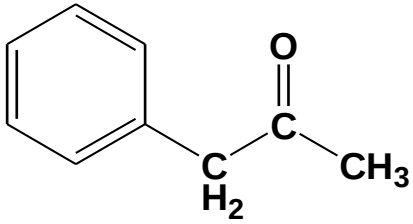
Acetone



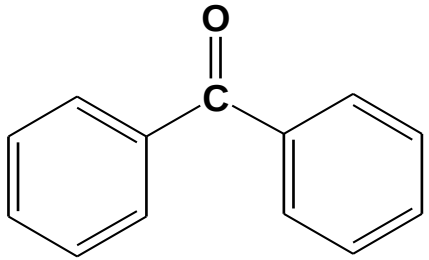
Salicylaldehyde



Acetophenone



Benzyl methyl ketone



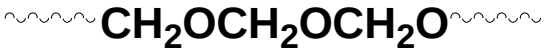
Benzophenone

- **Aldehydes & 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;** *whereas* **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 .**

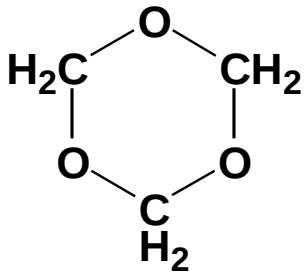
Physical properties

- **All aldehydes and ketones are liquids except formaldehyde , which is gas and benzophenone , which is solid .**

Formaldehyde, b.p. -21 °C , is handled either as an aqueous solution (formalin , an aqueous solution of 40% formaldehyde and 15% methanol) or as one of it's solid polymers: paraformaldehyde (CH_2O)$_n$, or trioxane (CH_2O)$_3$.



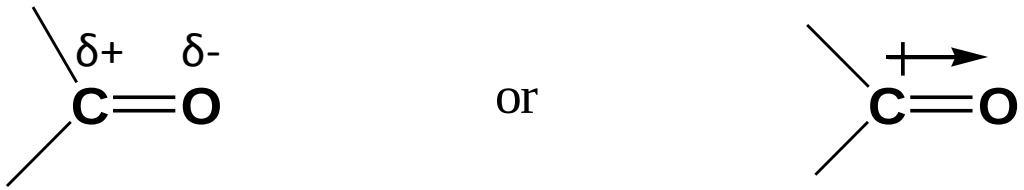
Paraformaldehyde



Trioxane

- **They are colorless except benzaldehyde, which has a pale yellow color (due to oxidation) with a characteristic odor .**
- **Aliphatic aldehydes and ketones burn with a blue flame (without smoke) , while aromatic ones burn with a yellow smoky flame .**
- **The polar carbonyl group makes aldehydes & ketones polar cpd.s, & hence they have higher boiling points than non-polar cpd.s of comparable molecular weight.**

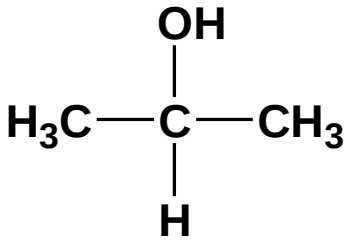
The polarization of carbonyl group can be represented by various ways,



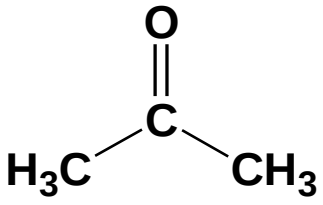
- **By themselves, they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids.**

For example, isopropyl alcohol boils at 82.5˚C while its oxidation product, acetone, boils at 56˚C.

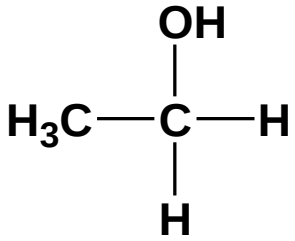
Another example is ethanol which boils at 78˚C while its oxidation product, acetaldehyde, boils at 21˚C.



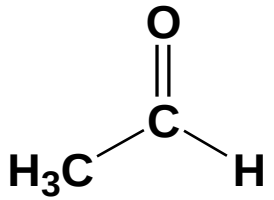
Isopropyl alcohol
B.p. 82.5 °C



Acetone
B.p. 56 °C

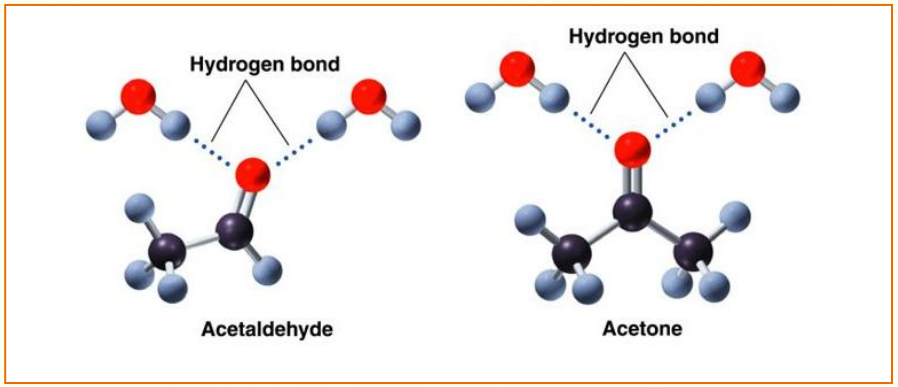


Ethyl alcohol
B.p. 78 °C



Acetaldehyde
B.p. 21 °C

- **The lower aldehydes and ketones are appreciably soluble in water, presumably because of H-bonding between solute and solvent molecules; borderline solubility is reached at about 5 carbons.**



Aromatic aldehydes & ketones are insoluble in water & all of them are soluble in the usual organic solvents

Solubility classification

Aldehydes and ketones that are soluble in water are soluble in ether too and are classified under class 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.

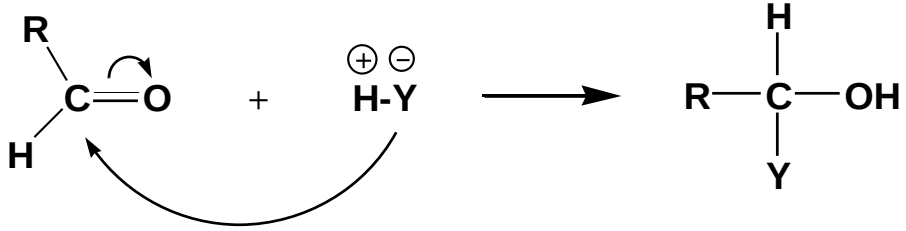
Chemical properties

1- All reactions of aldehydes & ketones are related to the carbonyl group (the active group) .

2- Aldehydes contain a hydrogen atom attached to it's 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 & do not show reducing properties.

b) Aldehydes are usually more reactive than ketones towards nucleophilic addition , the characteristic reaction of carbonyl group .



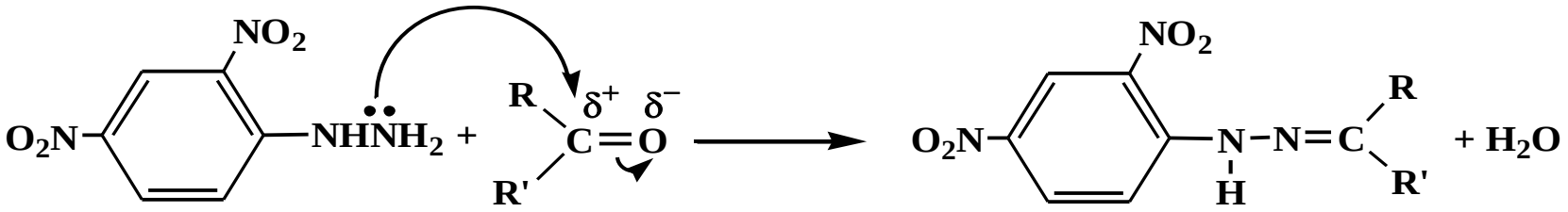
3- Both aldehydes & ketones are neutral cpd.s that don't change the color of litmus paper.

Identification of aldehydes & ketones

1- General test:

2,4-Dinitrophenylhydrazine reagent:

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



2,4-dinitrophenylhydrazine

2,4-dinitrophenylhydrazone
(imine)
yellow-orange ppt.

* *An imine* **is a functional group or chemical cpd. containing a carbon–nitrogen double bond .**

Procedure:

- **To 2 drops of the cpd. add 3 drops of the reagent, a yellow or orange precipitate will be formed.**
- **If the cpd. is insoluble in water, dissolve it in 1 mL of methanol & 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 can not (they need stronger oxidizing agents).

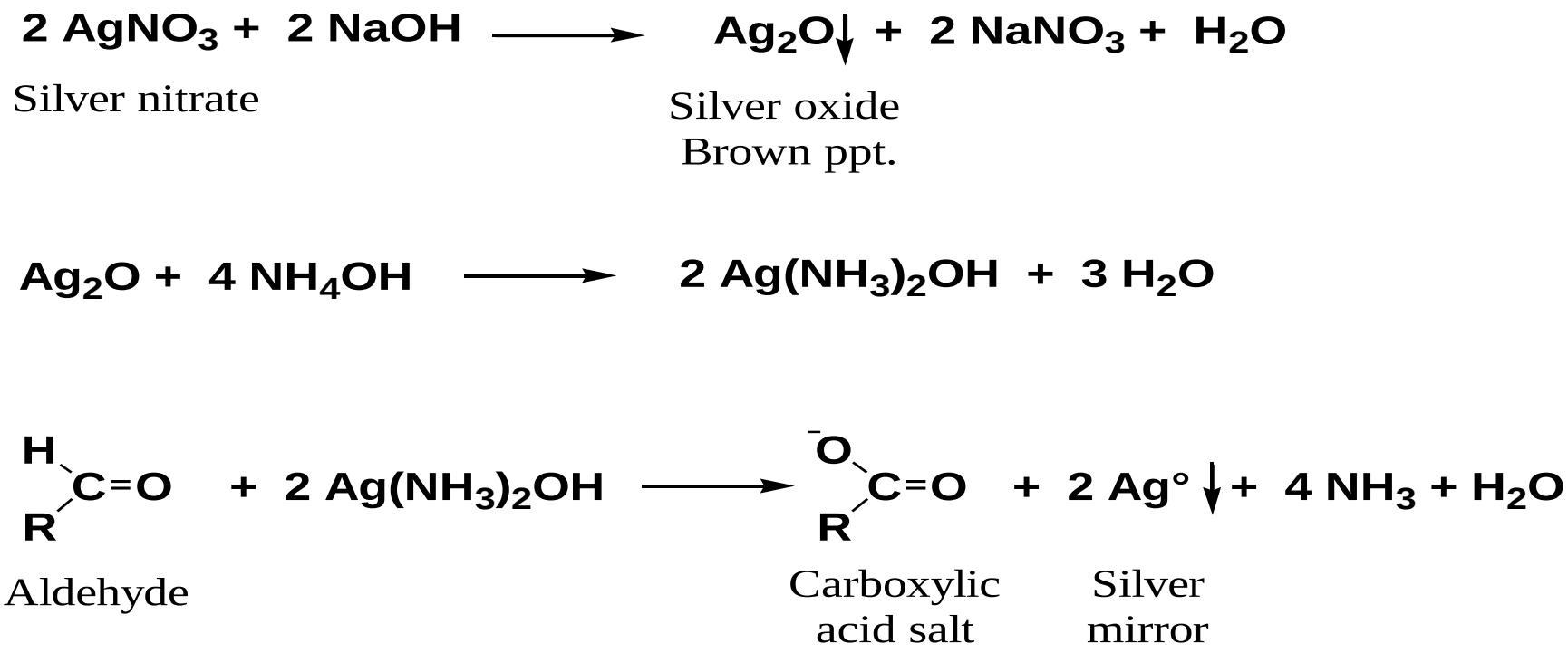
Two reagents can be used for this purpose, Tollen's reagent or Fehling's reagent.

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.**



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 3 mL of silver nitrate solution add 2-3 drops of 10% NaOH solution, & 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 cpd. 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.**

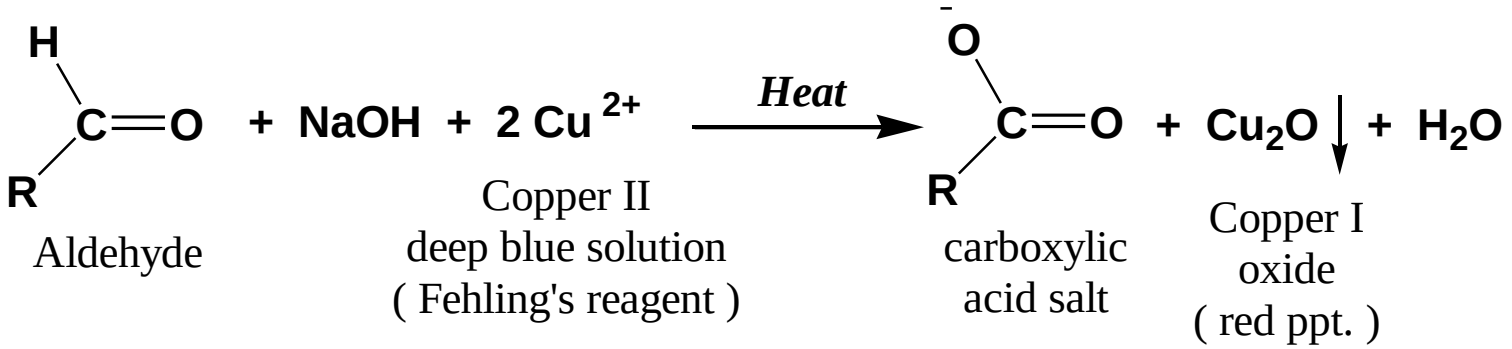
Notes:

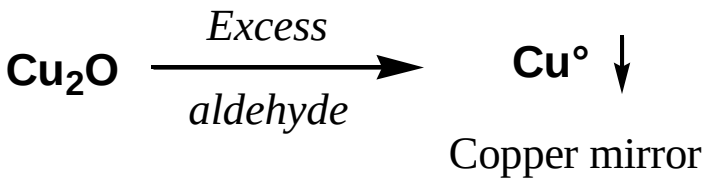
* If the test tube is not very clean , silver metal forms merely as a granular gray or black ppt. .
* False - negative tests are common with water insoluble aldehydes .
* A negative result indicates that the compound is a ketone .

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 & 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.

Fehling's B solution is an aqueous solution of potassium sodium tartrate ($C_4H_4K\ NaO_6.4H_2O$) and sodium hydroxide.

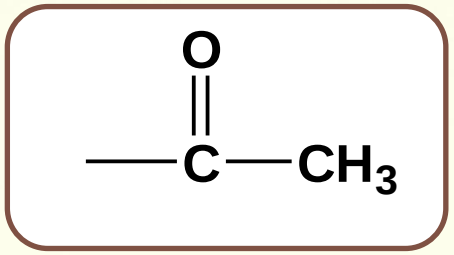
- **Add 5 drops of the compound to 1 mL of Fehling's solution, and then heat in water bath for 5 minutes (with shaking for water insoluble compounds).**

- **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:

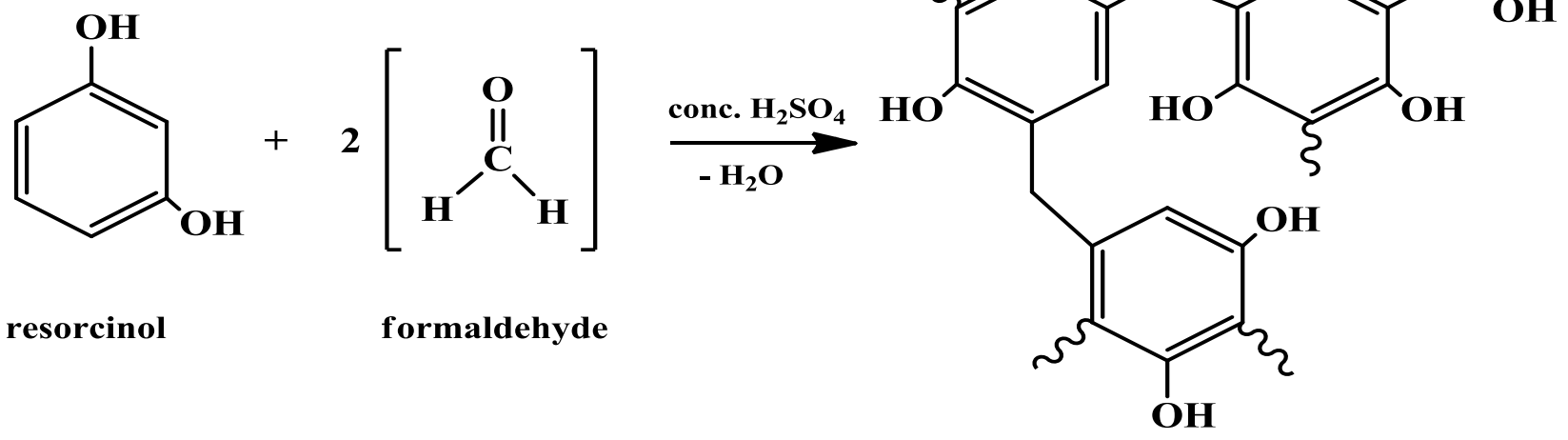
Follow the same procedure of iodoform test mentioned earlier (identification of alcohols).

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.



resorcinol formaldehyde polymer

Acid catalysis reaction by protonating formaldehyde and increasing the electron deficiency of the carbonyl carbon.

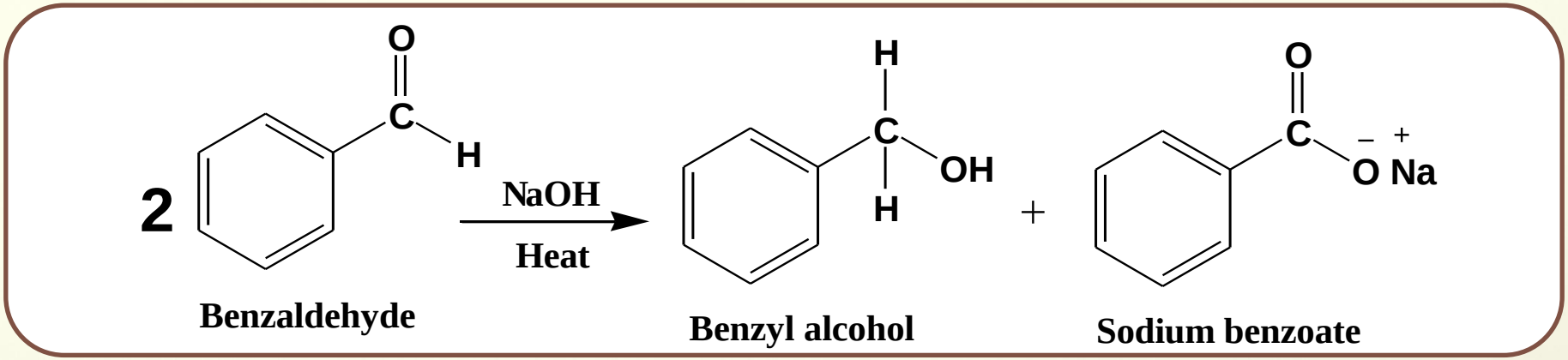
So, the first stage can be viewed as both electrophilic substitution on the ring by the electron – deficient carbon of formaldehyde , and nucleophilic addition of the aromatic ring to the carbonyl group.

5- Cannizzaro reaction:

In the presence of concentrated alkali, aldehydes containing no α- hydrogens undergo self oxidation – reduction to yield a mixture of the corresponding alcohol & a salt of the corresponding carboxylic acid. This reaction is known as Cannizzaro reaction.

Therefore, one molecule of the aldehyde serves as the oxidizing agent while the other serves as the reducing agent.

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



Benzaldehyde — Benzyl alcohol — Sodium benzoate

Procedure:

- **To few drops of benzaldehyde (or other aldehydes) add 0.5 mL of 30% NaOH solution & heat gently on a water bath with shaking for 5 minutes.**

A precipitate of sodium benzoate is produced.

- **Dissolve this precipitate by adding few drops of distilled water, & then add drops of concentrated HCl to liberate benzoic acid as a white precipitate.**

Note :

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.

Questions & Exercises :

1- Sketch the hydrogen bonding between benzaldehyde and water.

2- Aldehydes and ketones have higher boiling points than hydrocarbons , but have lower boiling points than alcohols, explain why?

3- What is paraformaldehyde, and from which aldehyde is formed? Write down it's molecular formula.

4- Aldehydes are usually more reactive than ketones towards nucleophilic addition, explain why?

5- Write the imine product formed in the reaction of each of the following :

a- Acetaldehyde and benzylamine, $C_6H_5CH_2NH_2$.

b- Benzaldehyde and butylamine, $CH_3CH_2CH_2CH_2NH_2$.

6- Using chemical tests how would you distinguish among 1-pentanol , 2-pentanone , 3-pentanone , and pentanal ?

7- Which of the following compounds give positive Cannizzaro test ? Why ?
Benzaldehyde , Acetaldehyde , Salicylaldehyde .

8- Cannizzaro reaction can't be relied on for testing formaldehyde, explain why and write the equation of the reaction .

References

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* Shriner R.L. , Hermann C.K.F. , Morrill T.C., Curtin D.Y. and Fuson R.C. : *" Chemical tests for functional groups "* . **The Systemic Identification of Organic Compounds** , (8^{th}) edition, John Wiley and Sons Inc., New York. 2004; 247-350.

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