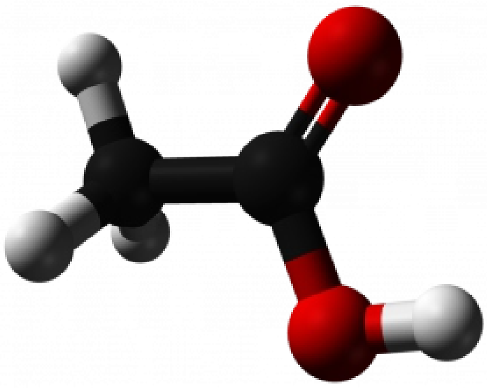
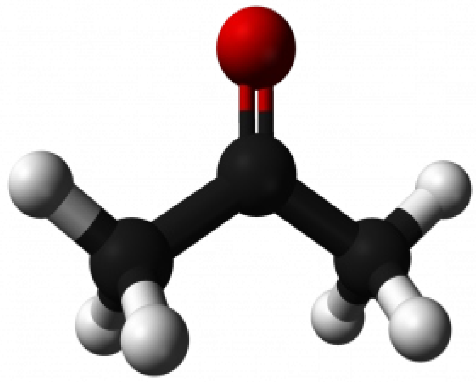
CHAPTER 8

CARBOYNL COMPOUNDS 1: ALDEHYDES AND KETONES

Teaching Periods	**04**	**Assessment**	**01**	**Weightage %**	**03**





Students will be able to:

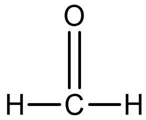
- ✓ Explain the physical properties and structure of aldehydes and ketones. (Understanding)
- ✓ Explain the preparation of aldehydes and ketones by ozonolysis of alkenes, hydration of alkynes, oxidation of alcohols and Friedel Craft's acylation of aromatics. (Applying)
- ✓ Describe reactivity of aldehydes and ketones. (Understanding)
- ✓ Explain acid and base catalysed nucleophilic addition reactions of aldehydes and ketones. (Applying)
- ✓ Explain reactions of aldehydes and ketones. (Applying)
- ✓ Describe oxidation reactions of aldehydes and ketones. (Applying)
- ✓ Compare the aldehyde and ketone with reference to their laboratory test (tabular form)(Understanding)
- ✓ Enlist the important compounds of Aldehydes and Ketones with their application. (Applying)

INTRODUCTION

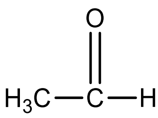
Aldehydes and ketones hold significant importance, with widespread usage in several industries. They are the simplest carbonyl compounds; both contain a carbonyl group, which is a functional group consisting of a carbon atom double-bonded to an oxygen atom.

Aldehyde contain a carbonyl group at the terminal carbon of their carbon chain, whereas ketone have a carbonyl group located on the carbon within their carbon chain. Both types of compounds have unique properties and reactivity due to the presence of the carbonyl group, which makes them useful in a variety of applications.

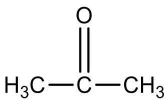
The typical representatives of this class of compounds are formaldehyde, acetone, benzaldehyde and acetophenone. Formaldehyde is exceptional since it carries two hydrogen atoms instead of alkyl substituents.



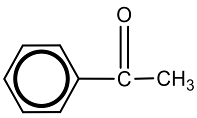
(Formoldehyde)



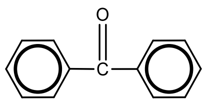
(Acetaldehyde)



(Acetone)



(Acetophenone)



(Benzophenone)

Organic chemistry emphasizes the study of aldehyde and ketones due to their significant applications in various industrial sectors.

For example, formaldehyde is used to produce resins, synthetic plastic and urea formaldehyde. Acetone is used in the preparation of iodoform, chloroform and nail polish remover Benzaldehyde is used in the manufacturing of dyes etc.

8.1 PHYSICAL PROPERTIES

Physical State: Methanal and ethanal are gases; the other lower aldehydes and ketones are colourless liquids at room temperature. The higher aldehydes and ketones (more than C_{20}) are solids at room temperature.

Odour: Lower aldehydes have a pungent smell whereas ketones and higher aldehydes have a pleasant smell.

Boiling Point: Carbonyl compounds have higher boiling points than alkanes of similar molecular weights due to the polar nature of the carbonyl group, enabling intermolecular forces. However, they have lower boiling points compared to alcohols and carboxylic acids due to the absence of intermolecular hydrogen bonding.

Solubility: Carbonyl compounds are generally polar, and they are soluble in polar solvents such as water and ethanol. However, their solubility decreases as the size of the hydrophobic group (hydrocarbon chain) attached to the carbonyl carbon increases.

Self Assessment

Why carbonyl compounds possess low boiling points than alcohols and carboxylic acids?

8.2 STRUCTURE OF ALDEHYDES AND KETONES

In aldehyde and ketone, the carbonyl group comprises a carbon atom that is double bonded to an oxygen atom. The carbon atom in the carbonyl group is sp^2 hybridized, with one of its sp^2 hybrid orbitals participating in sigma bond formation with the oxygen atom, while the other two sp^2 hybrid orbitals form sigma bonds with other atoms. The unhybrid p orbital of the carbon atom in the carbonyl group forms a pi bond with the oxygen atom (Fig.8.1).

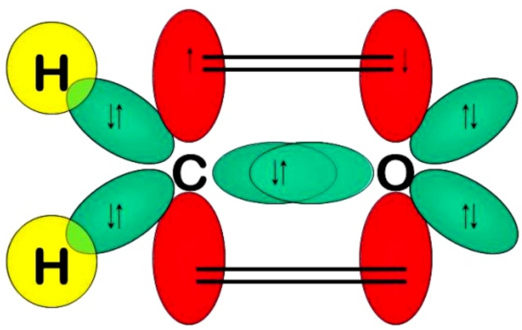
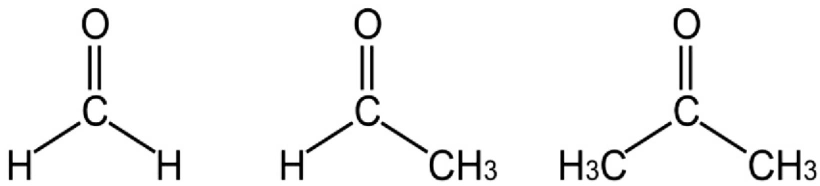


Fig. 8.1: Structure of formaldehyde showing sigma and pi bonding

DO YOU KNOW?

Glucose and fructose are simple sugars, chemically known as aldehydexose and ketohexose. They possess aldehyde and ketone functional groups in the molecular structure respectively.

The sp^2 hybridization of the carbon atom in the carbonyl group allows it to acquire a trigonal planar geometry, with bond angles of approximately 120°.

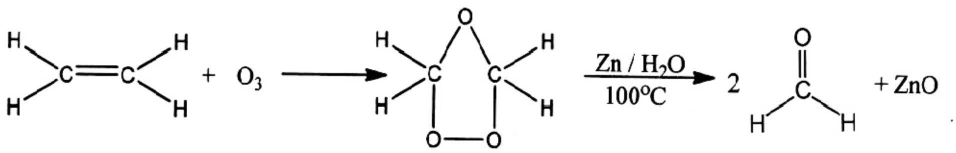


(Formaldehyde) **(Acetaldehyde)** **(Acetone)**

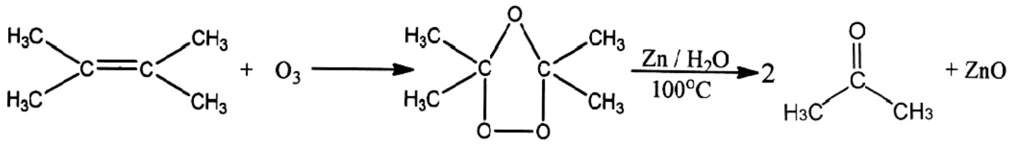
8.3 PREPARATION OF ALDEHYDES AND KETONES

8.3.1 Ozonolysis of Alkenes

Alkenes can be ozonolyzed to yield aldehydes and ketones. This reaction involves the breaking of C=C of alkene by the use of ozone and reducing agent such as zinc.



(Ethene) **(Ozonide)** **(Formaldehyde)**



(2, 3-dimethyl butene) **(Ozonide)** **(Acetone)**

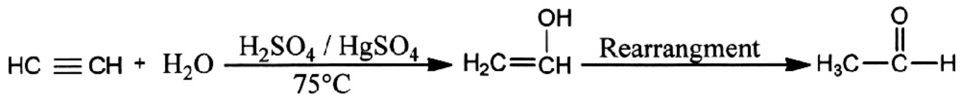
Self Assessment

What is ozonolysis of alkenes and what are the main types of products that can be obtained from this reaction?

8.3.2 Hydration of Alkyne

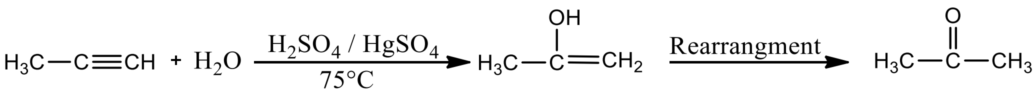
Alkynes when heated with water in the presence of H_2SO_4 and $HgSO_4$, an acid catalysed addition reaction occur on C ≡ C to form an unstable enol which then on tautomerization, gives aldehyde or Ketone.

(i) The hydration of ethyne gives acetaldehyde



(Ethyne) **(Enol)** **(Acetaldehyde)**

(ii) The hydration of propyne gives propanone



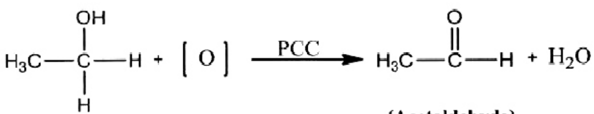
(Propyne) **(Enol)** **(Acetone)**

8.3.3 Oxidation of Alcohol

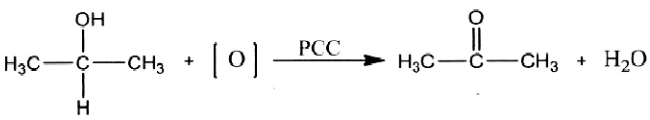
In the oxidation of alcohols, the -OH functional groups are converted to carbonyl groups (C=O). Primary alcohols are oxidized to aldehydes, and secondary alcohols are oxidized to ketones, which can be achieved using pyridinium chlorochromate (PCC) as an oxidizing agent. However, tertiary alcohols do not undergo oxidation. This controlled process is valuable in obtaining specific carbonyl compounds in organic synthesis.

DO YOU KNOW?

Formalin is an aqueous solution of formaldehyde, typically containing 37-40% formaldehyde by weight. It is used as a disinfectant and preservative for biological specimens.
However, it is a known carcinogen and can cause skin and respiratory irritation and should be handled with cautions and appropriate protective measures.



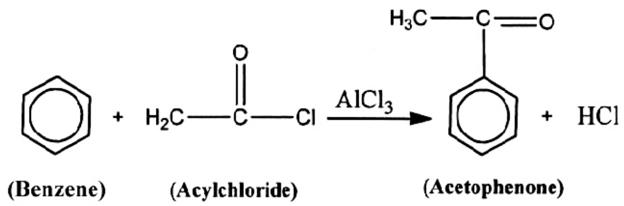
(1°-alcohol) **(Acetaldehyde)**



(2°-alcohol) **(Acetone)**

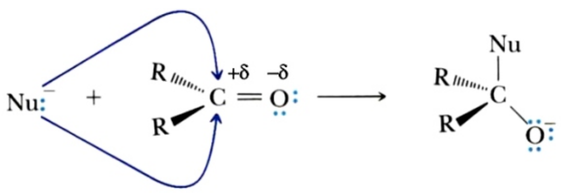
8.3.4 Friedel-Craft Acylation of Aromatic Compounds

Aromatic ketones can be synthesized through the Friedal Craft acylation method. In this reaction, an acyl chloride reacts with benzene or its derivatives in the presence of a Lewis acid catalyst, typically aluminum chloride ($AlCl_3$).



8.4 REACTIVITY OF CARBONYL COMPOUNDS

The carbon-oxygen bond (C=O) in the carbonyl group is highly polar due to the electronegativity difference between carbon and oxygen. It creates partially negative charge on oxygen and partially positive charge on hydrogen, making the carbon and oxygen atoms in aldehydes and ketones act as electrophiles and nucleophiles. Aldehydes are more reactive than ketones due to less steric hindrance (having one alkyl group) and a greater electron-withdrawing effect of the aldehyde's hydrogen, which enhances the electrophilicity of its carbonyl carbon, making it more attractive to nucleophiles.

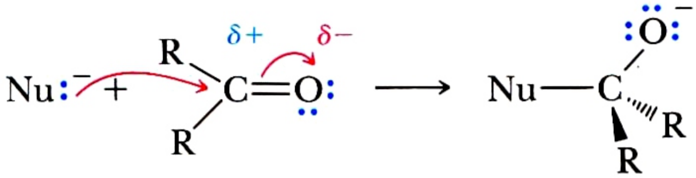


8.5 REACTIONS OF ALDEHYDE AND KETONES

Aldehyde and ketone undergo following types of reactions.
(i) Nucleophilic addition reactions
(ii) Reduction reaction
(iii) Oxidation reaction

8.5.1 Nucleophilic addition reaction

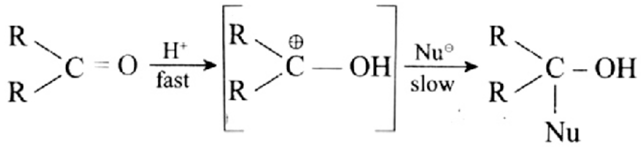
In these reactions, nucleophiles attack the carbonyl carbon of aldehydes and ketones, leading to a change in the hybridization of the carbon atom from sp^2 to sp^3. The pi electron pair of C=O shifts towards the oxygen atom, forming an alkoxide intermediate, which is subsequently protonated to yield the addition product.



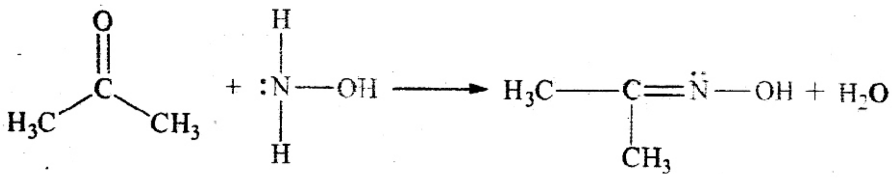
Nucleophilic addition reactions can be either acid-catalyzed or base-catalyzed, depending on the nature of reactants and the reaction conditions.

(i) Acid catalysed Nucleophilic addition reactions

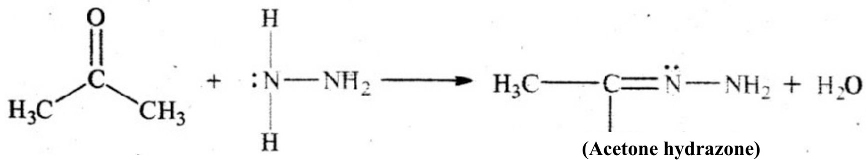
An acid catalyst is employed in a case where a carbonyl compound reacts with weak nucleophile for addition. The acidic proton, attacks the carbonyl atom, resulting in the formation of a protonated carbonyl group. This protonation enhances the electrophilic behavior of the carbonyl carbon making it more responsive to a necleophile. Thus, a weak nucleophile can easily attack on carbonyl carbon and give the addition product. The general mechanism of acid catalysed nucleophilic addition on aldehyde and ketone is written as.



Addition of hydrazine (NH_2-NH_2) and hydroxyl amine (NH_2OH) on aldehyde and ketone is catalysed by an acid.



Propanone **Hydroxyl amine** **Propanone oxime**



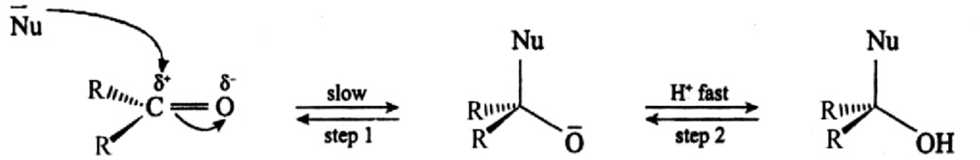
(Acetone hydrazone)

Propanone **Propanone hydrazone**

(ii) Base catalysed Nucleophilic addition reaction

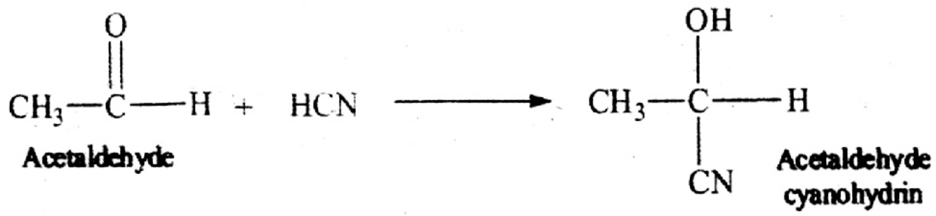
Addition of strong nucleophilic reagents on aldehyde and ketone is catalysed by base. The base first reacts with the reagent to generate a nucleophile. The nucleophile then attacks on carbonyl carbon. The pi electron of C=O is then shifted towards oxygen atom to form tetrahedral alkoxide ion as intermediate. This intermediate captures a proton or the electrophile to give the product.

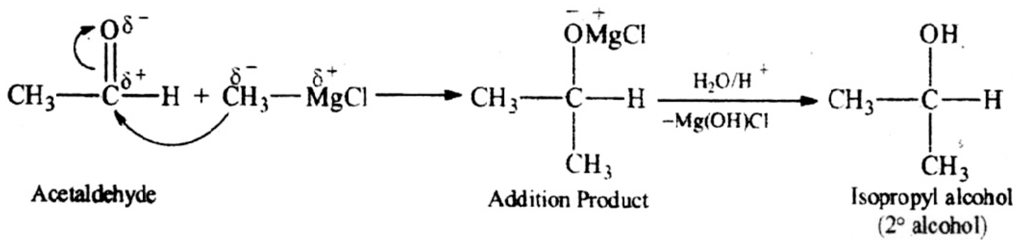
General mechanism of base catalysed Nucleophilic addition reaction is given as.



(Carbonyl compound) (Intermediate) (Addition product)

Addition of HCN and Grignard reagent is catalysed by base.





Self Assessment

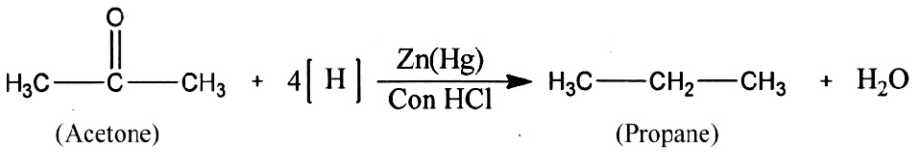
Give equations for the reactions of propanone with the following reagents
(a) Hydrazine (b) Hydroxylamine

8.5.2 Reduction of Aldehyde and Ketone

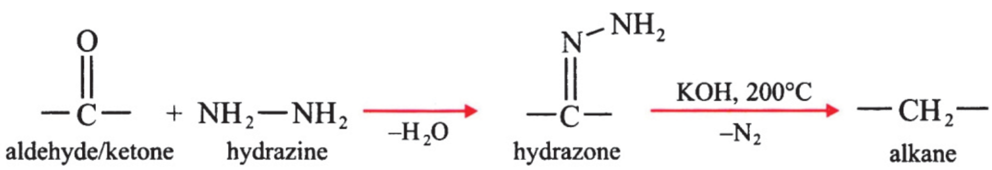
The reduction of aldehydes and ketones involves the addition of hydrogen to the carbonyl group resulting in the formation of an alkane or alcohol depending upon the suitable reducing agent used in the reaction.

8.5.2.1 Reduction to Hydrocarbon

The reduction of aldehyde and ketone into saturated hydrocarbons is carried out if a mixture of zinc amalgam and concentrated HCl is used. This is known as Clemmensen reduction.



Aldehyde and ketone can also be converted into alkane by using hydrazine (NH2-NH2) and postassium hydroxide. This is known as Wolf Kishner reaction.



8.5.2.2 Reduction to Alcohol

Aldehyde and ketone when treated with strong reducing agents such as $NaBH_4$ or $LiAlH_4$, they reduce into primary and secondary alcohols respectively.

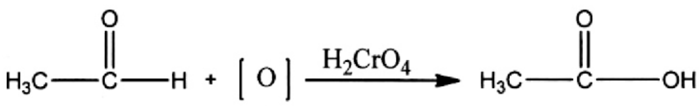
(Acetaldehyde) (Primary alcohol)

(Acetone) (Secondary alcohol)

8.5.3 Oxidation Reaction

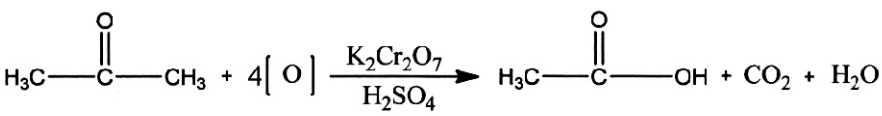
Aldehydes and ketones undergo oxidation with an oxidizing agent to give carboxylic acid. However, the reactivity of aldehyde towards oxidation reaction is quite easy due to the availability of active hydrogen atom at the carbonyl position, thus

i. A variety of mild oxidizing agents such as chromic acid (H_2CrO_4), Tollen's reagent, Fehling reagent and Benedict reagent can be used to convert aldehyde into corresponding carboxylic acid. Aldehydes can also be oxidized by strong oxidizing agents.



(Acetaldehyde) (Acetic acid)

ii. Oxidation of ketone is relatively slow and it involves the breaking of carbon-carbon sigma bond and it happens only in the presence of strong oxidizing agent.



(Acetone) (Acetic acid)

Self Assessment

What reagent can be used to convert an alcohol to aldehydes or ketones without the formation of carboxylic acid?

Laboratory test to distinguish between aldehydes and ketones

(i) Silver mirror test

The reagent used for this test is ammonical silver nitrate (Tollen's reagent). Since this reagent has short shelf life, it should be freshly prepared in laboratory by mixing silver nitrate and ammonium hydroxide.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]OH} \xrightarrow{\text{Heat}} \underset{\text{Ammonium carboxylate}}{RCOO^-NH_4^+} + 3NH_3 + H_2O + \underset{\text{(Silver mirror)}}{2Ag\downarrow}$$

While performing the test, tollens's reagent is mixed with the given carbonyl compound and heated to boiling. If aldehyde is present, a silver mirror will form on the inside of the test tube.

(ii) Fehling test

There are two Fehling solutions available in laboratory. Fehling A is an aqueous copper (II) sulphate solution while Fehling B is an aqueous solution of sodium hydroxide (NaOH) with sodium potassium tartarate.

To carry out the Fehling's test, mix equal volumes of Fehling A and B in a test tube, heat the mixture to boiling and then add a small amount of given carbonyl compound into the test tube. If aldehyde is present, the blue colour of Fehling solution (Cu^{+2}) changes to red precepitates (ppt) of copper (I) oxide.

DO YOU KNOW?

Tollen's reagent, Fehling solution and Benedict solution are three commonly used chemical reagents for a laboratory test to distinguish between an aldehyde and ketones.

- Silver nitrate and ammonium hydroxide are the components of Tollen's reagent.
- Copper sulphate, sodium hydroxide and tartaric acid are the component of Fehling solution.
- Copper sulphate, sodium hydroxide and citric acid are the component of Benedict solution.

$$\underset{\text{(Aldehyde)}}{RCHO} + \underset{\text{(Fehling Solution)}}{2Cu^{+2} + 5\bar{O}H} \longrightarrow RCOO^- + \underset{\text{(Red-brown ppt.)}}{Cu_2O} + 3H_2O$$

8.5.4 Difference between Aldehyde and Ketone

Basic Structure: Both aldehydes and ketones are carbonyl compounds but in aldehydes, the carbonyl carbon is attached with at least one alkyl or aryl group while in ketones, carbonyl carbon is attached with two alkyl or aryl groups.

Physics Properties: The boiling point of ketones is relatively higher than aldehydes since carbonyl group of ketones is more polarized than aldehydes.

Reactivity: The reactivity of aldehydes towards nucleophilic addition is greater than ketones because of less steric hindrance and less electronic effect.

Oxidation into Carboxylic acid: Ketones oxidizes to carboxylic acid with strong oxidizing agent such as potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) while aldehydes can easily be oxidized to carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution and Benedict solution.

Reduction into alcohol: Reduction of aldehydes in the presence of strong reducing agents such as lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) gives primary alcohol while the reduction of ketones gives secondary alcohol.

Table 8.1 Some applications of aldehydes and ketones

Application	Aldehydes	Ketones
Organic Synthesis	Used as key intermediates in various organic reactions.	Important starting materials for creating complex organic compounds.
Flavor and Fragrance	Provide characteristic aroma and taste to many natural and synthetic products, e.g., vanillin and benzaldehyde.	Used as flavoring agents and fragrances in the food, cosmetic, and perfume industries.
Pharmaceuticals	Serve as building blocks for various pharmaceuticals, such as anti-inflammatory drugs and antihistamines.	Some ketones are used as active pharmaceutical ingredients in medicines.
Solvents	Formaldehyde is used as a solvent for certain reactions.	Acetone is a widely used solvent for chemical reactions and as a nail polish remover.

SOCIETY, TECHNOLOGY AND SCIENCE

Role of Ozonolysis in drinking water

Ozone is a powerful oxidizing agent, it is successfully used in the treatment of drinking water in the following manners.
(i) It serves as biocides since it ozonolyses the organic substances present in the cell membrane of microorganisms such as bacteria, viruses and the protozoa and hence killed them.
(ii) It oxidizes certain metals (Cu, Fe, Mn, etc.) which are present in the excess amount in water that can be easily separated by filtration.

SUMMARY

- Aldehydes and ketones are organic compounds that contain carbonyl functional group (>C=O).
- The boiling point of aldehydes and ketones is lower than alcohols since they do not form intermolecular hydrogen bond.
- The boiling point of aldehydes and ketones is higher than alkanes because of molecular polarity and dipole-dipole attractive forces among their molecules.
- The chemical reactivity of aldehydes and ketones is attributed to the polar carbonyl group they contain.
- The geometry of aldehydes and ketones molecules is trigonal planar since carbon atom of carbonyl group (C=O) is sp^2 hybridized.
- Preparation of aldehydes and ketones is mostly carried out by ozonolysis of alkene and hydration of alkyne.
- Reduction of aldehydes and ketones with $LiAlH_4$ or $NaBH_4$ gives primary and secondary alcohol respectively.
- Aldehydes can be oxidized into carboxylic acid with mild oxidizing agent such as chromic acid (H_2CrO_4), Tollen's reagent and Fehling solution etc.

- Ketones can be oxidized into carboxylic acid in presence of strong oxidizing agent.
- Nucleophilic addition reactions of aldehydes and ketones are catalysed by acid or base depending upon the availability of either weak or strong nucleophilic reagent.
- Water, alcohol, and ammonia can undergo nucleophilic addition reactions with aldehydes and ketones, and these reactions are catalyzed by acids.
- Hydrogen cyanide (HCN) and Grignard reagent (RMgX) can react with aldehydes and ketones in the presence of a base catalyst.
- Identification of aldehydes in a laboratory can be carried out by Tollen's reagents or by Fehling solution.

EXERCISE

Multiple Choice Questions

(i) Ketones when treated with $LiAlH_4$, they reduce to:
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) Dihyderic alcohol

(ii) The reagent used to oxidizes ketones into carboxylic acids is:
(a) Ammoniacal silver nitrate (b) Potassium dichromatic
(c) Fehling solution (d) Benedict solution

(iii) The carbonyl carbon of aldehydes and ketones is:
(a) Sp hyrbidized (b) Sp^2 hyrbidized
(c) Sp^3 hyrbidized (d) dsp^3 hyrbidized

(iv) Acetophenone is the member of ketone family, it contains:
(a) Two alkyl groups (b) Two aryl group
(c) One alkyl and one aryl group (d) One aryl and one hydrogen atom

(v) The most reactive molecule towards nucleophilic addition in the following is:
(a) Formaldehyde (b) Acetaldehyde
(c) Diethyl ketone (d) Acetophenone

(vi) Clemmensen reduction is the conversion of aldehydes and ketones into:
(a) Alkanes (b) Alkenes

(c) Alkyl halides (d) Alcohols

(vii) Hydration of propyne in the presence of H_2SO_4 and $HgSO_4$ gives:
(a) Formaldehyde (b) Methyl ethyl ketone
(c) Acetone (d) Acetaldehyde

(viii) Which of the following carbonyl compound is most soluble in water?
(a) Formaldehyde (b) Acetaldehyde
(c) Benzaldehyde (d) Acetophenone

(ix) Which of the following gives silver test with Tollen's reagent?
(a) HCHO (b) CH_3-O-CH_3
(c) C_2H_5OH (d) CH_3COOH

(x) On reduction of a carbonyl compound by Zn-Hg and Conc. HCl, it is converted to an alkane. This reaction is known as;
(a) Dow reduction (b) Cope reduction
(c) Clemmensen reduction (d) Wolf-Kishner reduction

Short Questions

1. Give reasons for the following:
   i. The boiling point of aldehydes and ketones is lower than alcohol.
   ii. Formaldehyde is highly soluble in water as compared to other aldehydes.
   iii. Oxidation of aldehydes is faster than ketones.
2. Write the equation for the reaction of acetaldehyde with the following:
   i. Chromic acid (H_2CrO_4)
   ii. Lithium Aluminum hydride ($LiAlH_4$)
   iii. Zinc mercury amalgam
3. How is formaldehyde prepared by ozonolysis?
4. Why is formaldehyde more reactive towards Nucleophilic addition reactions compared with ketones.
5. How does the oxidation of ketones differ from the oxidation of aldehydes?
6. Why are ethers considered as good solvents in organic reactions?

Descriptive Questions

1. What are aldehydes and ketones? Describe the structure and type of hybridization in them.
2. Explain the acid-catalyzed and base-catalyzed nucleophilic addition reactions in aldehydes and ketones.

3. Describe how aldehydes are distinguished from ketones by the following laboratory test.
   (i) Tollen's reagents (ii) Fehling solution
4. Write the equation and give the name of major product in the following chemical process.
   i. Oxidation of acetone with acidified $K_2Cr_2O_7$.
   ii. Reduction of acetaldehyde with $NaBH_4$.
   iii. Hydration of ethyne in the presence of $H_2SO_4/HgSO_4$
   iv. Acylation of benzene in the presence of $AlCl_3$.
5. Give four differences between aldehydes and ketones.
6. Write the equation for the nucleophilic addition reaction if formaldehyde treated with
   i. Hydrogen cyanide ii. Primary alcohol
   iii. Methyl magnesium bromide iv. Ammonia
7. Explain the factors that influence the reactivity of carbonyl compounds towards nucleophilic addition reaction.