

## Compounds of Carbon Containing Oxygen

### 29.1 INTRODUCTION

In previous lessons you have learnt about a large number of organic compounds such as (i) hydrocarbons eg., alkanes, alkenes, alkynes and arenes (ii) *halogen* containing compounds e.g. haloalkanes and haloarenes. In this lesson you will learn about another class of organic compounds known as "Oxygen" containing compounds 'e.g. alcohols, phenols, aldehydes, ketones and carboxylic acids.

Presence of oxygen along with hydrogen and carbon make their properties very different from those compounds which do not have oxygen at all. The following table will give you an idea of names, general formulae and functional groups of a few oxygen containing compounds :

S. No.	Name	General formula	Functional group
1.	Alcohols	ROH	—OH (hydroxyl group)
2.	Phenols	ArOH	—OH (phenolic group)
3.	Ethers	ROR'	—O— (ethereal group)
4.	Aldehydes	RCHO	—CHO (aldehydic group)
5.	Ketones	RCOR'	—C=O (ketonic group)
6.	Carboxylic acids	RCOOH	—COOH (Carboxylic group)
7.	Esters	RCOOR'	—COO— (ester group)
8.	Carbohydrates		contain aldehydic or ketonic and alcoholic group.

## 29.2 OBJECTIVES

- After reading this lesson, you will be able to:
  - recognize general formulae and functional groups in oxygen containing compounds.
  - reproduce structural formula and write IUPAC & common names of oxygen containing compounds.
  - describe different methods of preparation of Alcohols, phenols, aldehydes, ketones and carboxylic acids.
  - list physical properties of alcohols, phenols, aldehydes, ketones and carboxylic acids.
- describe chemical properties of:
  - (a) Alcohols and phenols.
  - (b) aldehydes and ketones.
  - (c) carboxylic acids.
- differentiate between different types of compounds with the help of chemical tests.

## 29.3 ALCOHOLS AND PHENOLS

In this section you will study the Chemistry of organic compounds, containing hydroxyl group ( $\text{—OH}$ ).

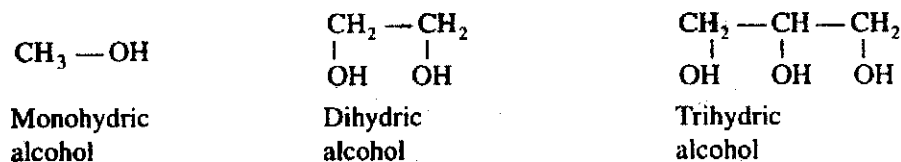
**Alcohols are aliphatic compounds, which contain at least one  $\text{—OH}$  group. The general formula is ROH.**

In phenols  $\text{—OH}$  group is attached directly to an aromatic ring. Their general formula is  $\text{ArOH}$ . Being the functional group,  $\text{—OH}$  determines the properties of alcohols and phenols.

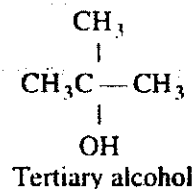
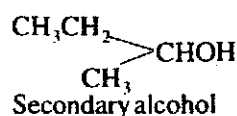
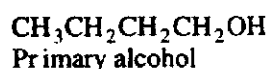
### 29.3.1 Classification of Alcohols:

Alcohols are classified according to number of hydroxyl group present in a molecule.

Alcohols with one hydroxyl group are known as monohydric, alcohols, with two- $\text{OH}$  group dihydric alcohols and when they contain three  $\text{—OH}$  group they are known as trihydric alcohols. When alcohols contain four or more hydroxyl groups, they are called polyhydric alcohols. Few examples are as follows:



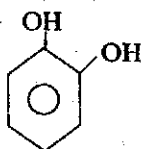
Monohydric alcohols further can be classified as (i) primary  $1^\circ$  (ii) secondary  $2^\circ$  and (iii) tertiary  $3^\circ$  alcohols according to the kind of carbon atom that bears the hydroxyl group. Examples of primary, secondary and tertiary alcohols are as follows:-



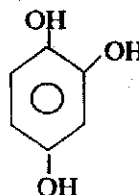
**Classification of phenols:** Phenols are also classified as monohydric, dihydric and trihydric depending upon whether they contain one, two or three hydroxyl group.



Monohydric alcohol



Dihydric alcohol



Trihydric alcohol

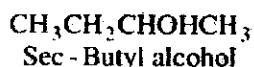
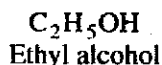
### 29.3.2 Nomenclature of Alcohols

There are two ways to name a monohydric alcohol.

(i) Common system

(ii) IUPAC system.

(i) **Common System:** In this system alcohols are named as alkyl alcohols. As we go higher up in the series, it becomes necessary to indicate whether a particular alcohol is primary, secondary or tertiary. The prefix secondary is abbreviated as *sec-* and prefix tertiary is abbreviated as *tert-*, for example:



(ii) **IUPAC System:-** According to this system alcohols are named as alkanols, ending -e of the parent alkane's name is replaced by -ol (one word name). The position of carbon atom carrying hydroxyl group is specified by a number. The number is attached to the name of longest carbon chain. e.g.

Alkane	Formula	Alcohol	Formula
Ethane	$\text{C}_2\text{H}_6$	Ethanol	$\text{C}_2\text{H}_5\text{OH}$
Butane	$\text{C}_4\text{H}_{10}$	Butan-2-ol	$\text{CH}_3\text{CH}_2\text{CHOHCH}_3$

covers a few more examples to explain the different systems of nomenclature.

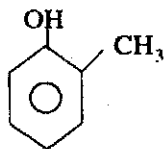
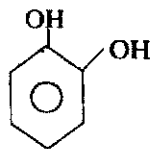
Table 29.1

Formula	Common Name	IUPAC Name
$\text{CH}_3\text{OH}$	Methyl alcohol	Methanol
$\text{C}_2\text{H}_5\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CHOHCH}_3$	Sec-Propyl alcohol	Propan-2-ol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	n-Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{COH} - \text{CH}_2 - \text{CH}_3 \end{array}$	Tert-Pentyl alcohol	2-Methylbutan-2ol

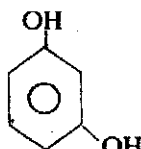
**Nomenclature of phenols:-** Phenols are usually named by the common system or as a derivative of the parent phenol,  $\text{C}_6\text{H}_5\text{OH}$  e.g.:



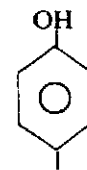
Phenol

O-Cresol  
(2-Methylphenol)

Catechol



Resorcinol

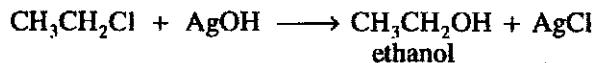
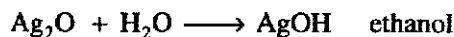
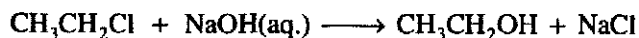


Quinol

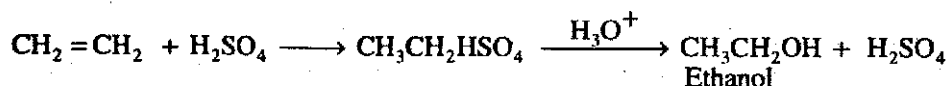
### 29.3.3 General Methods of Preparations of Alcohols

Some of the important methods of preparing alcohols are as follows:

- (i) **Hydrolysis of haloalkanes:** Hydrolysis of an alkyl halide with hot aqueous alkaline solution produces an alcohol. Hydrolysis can also be carried out with moist  $\text{Ag}_2\text{O}$



- (ii) **Hydration of alkene:** The term hydration means addition of water molecule across a double bond. When an alkene is heated with concentrated  $\text{H}_2\text{SO}_4$ , an addition product, alkyl hydrogen sulphate is obtained. This addition product on acid hydrolysis gives alcohol.

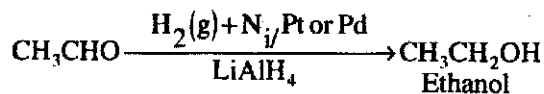


Sulphuric acid is used as a catalyst. This is also an industrial preparation of ethanol

- (iii) **From aldehydes and ketones:** An aldehyde or a ketone can be converted into an alcohol by one of the following methods:

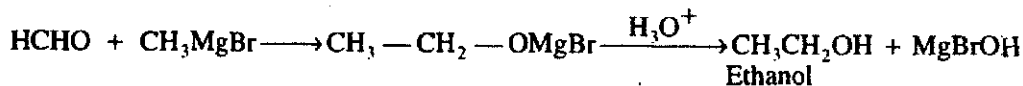
- (a) **Reduction:** Reduction of aldehydes and ketones is carried out by: (i)  $\text{H}_2$  gas in presence of Ni, Pt or Pd as a catalyst, (ii) Lithium aluminum hydride,  $\text{LiAlH}_4$ .

Reactions are as follows:

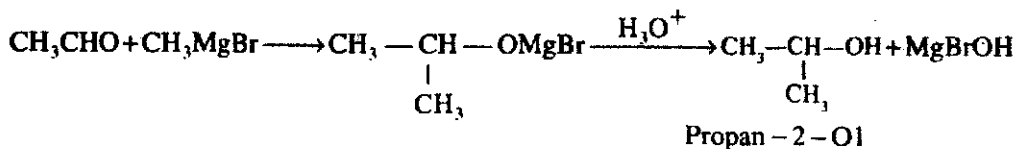


- (b) **From Grignard reagent:** When a Grignard reagent,  $\text{RMgX}$ , reacts with aldehydes or ketones in the presence of dry ether as a solvent, an addition product is obtained. This addition product on hydrolysis produces an alcohol. The reactions are as follows:

On reaction with methanal, a primary alcohol is produced.



reaction with any other aldehyde, secondary alcohol is obtained.



With a ketone, a tertiary alcohol is obtained:



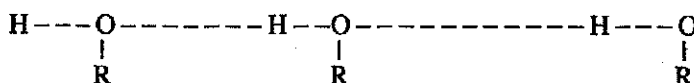
**Solubility in water:** Lower alcohols (upto 4-carbon atoms) are soluble in water, as they are able to make hydrogen bonding with water molecules. But in higher alcohols, as the size of the non polar alkyl group becomes bulkier, its affinity for the polar water molecules decreases, as a result the solubility decreases. Due to presence of bulkier non-polar aryl group, phenol is only slightly soluble in water.

**Boiling points: (i) Comparison of boiling points of alcohol, alkyl halide and an alkane:** Boiling point of an alcohol is much higher than alkanes and alkyl halide with same number of carbon atoms as shown in table 29.2

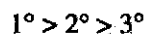
**Table 29.2**

compound	CH <sub>4</sub>	CH <sub>3</sub> Cl	CH <sub>3</sub> OH
b.p/K	111	249	337.5

In alcohols, hydrogen is attached to highly electronegative oxygen atom, in turn this group is able to make hydrogen bonds. Since more energy is needed to break intermolecular hydrogen bonding, the boiling point of an alcohol is much higher.



(ii) **Comparison of b.p. of isomeric alcohols:-** In case of isomeric alcohols the boiling point has the following order :



This can also be seen in the table 29.3

**Table 29.3**

Compounds	Butanol-1	Butanol-2	2-Methylpropanol
b.p/K	391	373	356

This can be explained as follows. As the branching increases from primary to tertiary alcohols, the packing of molecules becomes compact. *Hence the tendency to make intermolecular hydrogen bonding decreases as a result the energy needed to break these forces decreases.*

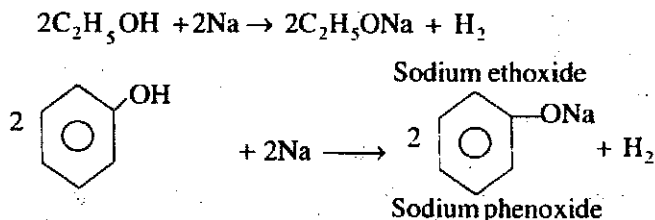
### 29.3.5 Chemical Properties of Alcohols and Phenols

Most of the chemical properties of alcohols and phenols are determined by the functional group, -OH. However up to certain extent the nature of alkyl or aryl group does effect the chemical properties. On the basis of structure, chemical properties can be divided into following categories.

- (i) Reactions due to cleavage of oxygen-hydrogen bond  $\left( \text{C} - \text{O} - \overset{\text{H}}{\underset{|}{\text{H}}} \right)$  bond
- (ii) Reactions due to cleavage of carbon-oxygen bond  $\left( \text{C} - \overset{\text{H}}{\underset{|}{\text{O}}} - \text{H} \right)$
- (iii) Reactions of alcohol molecule as whole
- (iv) Phenols do not undergo carbon-oxygen bond cleavage but instead readily undergo electrophilic substitution reactions of benzene ring.

### (i) Reactions due to Cleavage of Oxygen — Hydrogen Bond (—O—H cleavage):

**Reaction with active metal:** Alcohols and phenols both react readily with sodium metal to liberate a colourless, odourless gas — hydrogen and corresponding salts, sodium alkoxide and sodium phenoxide are formed.



These reactions with sodium metal (a strong base) suggest that alcohols and phenols are acidic in nature. Hence it is necessary to see which one is relatively a stronger acid.

**Comparison of acidic strength of alcohols and phenols:** The stronger acidic character of phenol can be appreciated by looking at the tests given in table 29.4

Table 29.4

Name of tests	Phenol	Alcohol
Reaction on moist blue litmus paper	+ve turns blue litmus paper-red.	-ve
Reaction with NaOH	Phenol readily dissolves	-ve

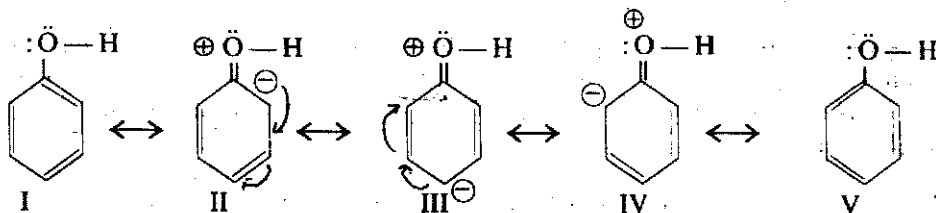
The stronger acidic character of phenol can also be appreciated by looking at their  $K_a$  values.

Methanol  
Phenol

$K_a$  values  
 $1 \times 10^{-16}$   
 $1.3 \times 10^{-10}$

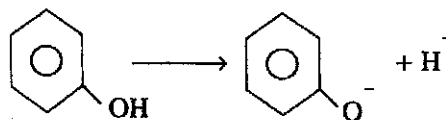
After comparing the observations of the tests and  $K_a$  values, it is obvious that one would like to know, why phenols are more acidic than alcohols. To understand this it is necessary to know more about the structures of an alcohol and phenol molecules and their respective ions.

Phenol is supposed to exist as resonance hybrid of the following resonance structure.

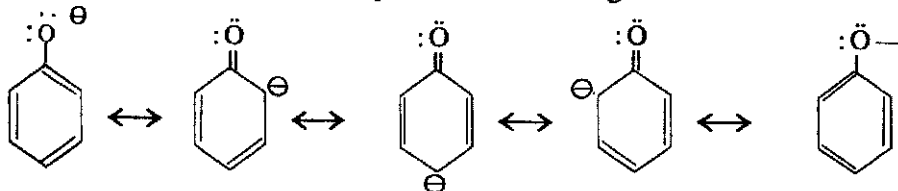


Resonance structure — II, III and IV suggest that oxygen atom of —OH group acquires +ve charge. This weakens the —OH bond which in turn releases the proton ( $\text{H}^+$  ion). As you can see that negative and positive charges develop on two different size sites and thus energy is needed to keep them apart. As a result these structures are less stable.

On ionization a phenol molecule gives phenoxide ion and a  $H^+$  ion as follows:

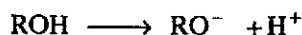


Phenoxide ion is also a resonance hybrid of the following resonance structures:



These structures show that there is only one kind of charge and that is -ve. Which is spread throughout the benzene ring and thereby effectively dispersed. Hence more stable, in turn the affinity for proton decreases greatly.

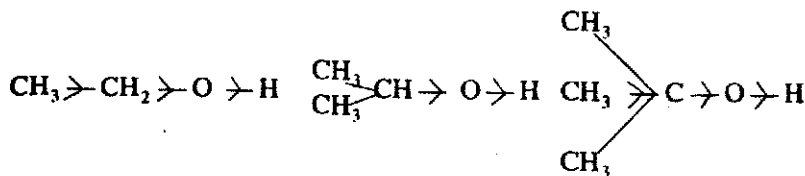
But in case of alcohol molecule (ROH) due to +ve effect of alkyl group, the intensity of -ve charge increases on oxygen atom of OH group. In turn the release of  $H^+$  ions becomes difficult. An alcohol molecule on ionisation gives alkoxide ion and a  $H^+$  ion.



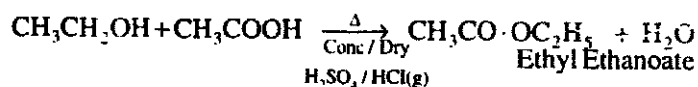
In case of  $\text{RO}^-$  ion, no resonance is possible and negative charge is localized over oxygen atom and hence affinity for  $H^+$  ion increases considerably.

You have already learnt that monohydric alcohols, according to the nature of alkyl group can be divided in  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alcohols. It is interesting to see how the nature of an alkyl group affects the acidity of an alcohol. So let us compare the acidic strength of primary, secondary and tertiary alcohols.

As we move from  $1^\circ$  to  $2^\circ$  to  $3^\circ$  alcohols, the number of alkyl groups attached to carbon atom linked to -OH group increases. With increase in branching there is an increase in +ve inductive effect which in turn increases the electron displacement towards the oxygen atom as shown in the diagrams. Greater the -ve charge on the oxygen atom, more the covalent pair of the hydroxyl bond driven towards the hydrogen atom consequently the release of proton becomes difficult hence  $3^\circ$  alcohol is less acidic than  $2^\circ$  and  $1^\circ$  alcohol.

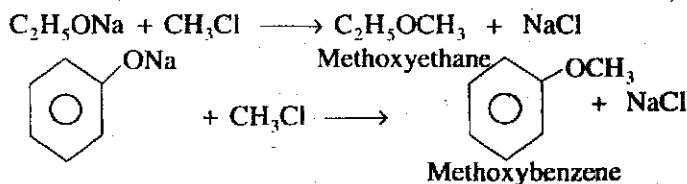


**(b) Reaction with carboxylic acid:** A carboxylic acid is directly converted into an ester when heated with an alcohol in the presence of a little amount of mineral acid, such as conc.  $\text{H}_2\text{SO}_4$  or dry HCl gas. This reaction is slow and reversible and known as *esterification*.



**(c) Reaction with alkyl halide:** When an alkyl halide is allowed to react with sodium alkoxide or sodium phenoxide, an ether is obtained. This is known as *Williamson's*

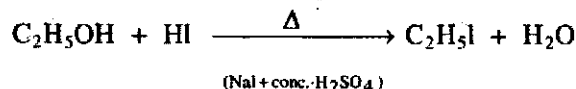
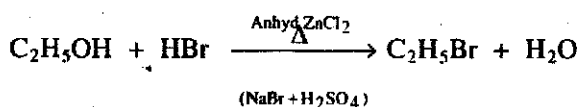
*synthesis.*



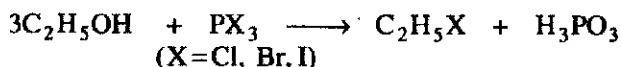
(ii) **Reactions involving cleavage of C—OH bond:** In a number of reactions, alcohols undergo C—OH bond cleavage. However phenols do not undergo this cleavage easily. Due to resonance (refer to resonance structures of phenol) carbon-oxygen bond acquires a double bond character. This makes the bond very strong. More energy is needed to break this bond, which is not available during a chemical reaction under ordinary conditions. Some of the reactions are as follows:

(a) **Preparation of alkyl halide:**

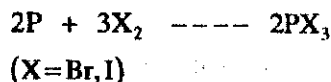
**Reaction with halogen acid:** Alcohols react with hydrogen halides to form haloalkanes and water. The reaction is carried out either by passing the dry hydrogen halide gas into alcohol or by heating the alcohol with conc. aqueous acid. The order of reactivity of hydrogen halide is  $\text{HI} > \text{HBr} > \text{HCl}$ . Being unstable HBr and HI are prepared in situ (during the reaction) by the action of concentrated  $\text{H}_2\text{SO}_4$  on NaBr and NaI respectively. Anhydrous  $\text{ZnCl}_2$  is used as a catalyst for the reaction of conc. HCl with alcohol.



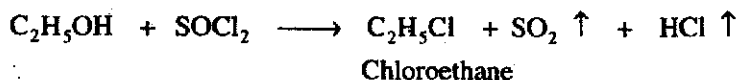
**Reaction with Phosphorous halides:** Alcohols on reaction with phosphorous halides such as  $\text{PX}_3$  and  $\text{PCl}_5$  gives corresponding haloalkanes.



$\text{PBr}_3$  and  $\text{PI}_3$  are unstable, hence prepared in situ as follows:



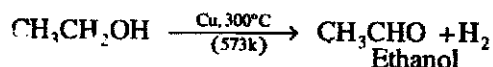
**Reaction with thionyl chloride,  $\text{SOCl}_2$ :** On heating with  $\text{SOCl}_2$  alcohols produce corresponding alkyl chlorides in the presence of pyridine.



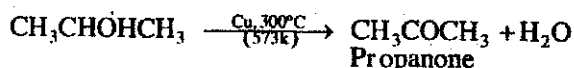
This method is considered as the best method to prepare alkyl halide, because both side products being gases escape and leave behind pure chloroalkane.

(iii) **Reactions involving the alcohol molecule as a whole:** When vapours of alcohols are passed over copper at 300°C following reactions take place.

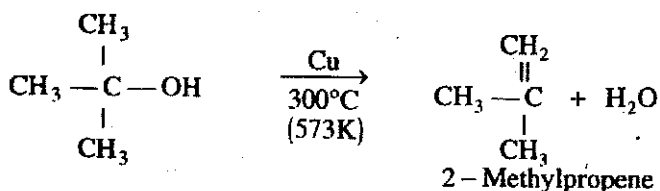
Primary alcohol is dehydrogenated to an aldehyde



Secondary alcohol is dehydrogenated to a ketone

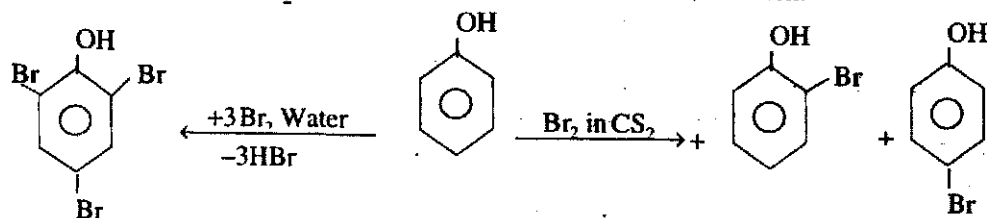


A tertiary alcohol is dehydrated to an alkene:



(iv) **Ring substitution reactions of phenols:** Phenols readily undergo electrophilic substitution in the benzene ring to form ortho- and para-substitution or trisubstituted products depending on the conditions. In an electrophilic substitution, a reaction is initiated by the attack of an electrophile and a stronger electrophile replaces a weaker electrophile. Since an electrophile will attack an electron rich site, it is quite obvious it will attack readily on ortho- and para- positions, rich in electron (refer to resonance structures of phenol).

(a) **Halogenation:** Bromination of phenol gives different products depending on reaction conditions. With bromine water a tri-substituted product is obtained but with solution of bromine in less polar  $\text{CS}_2$ , reaction can be limited to monobromination.

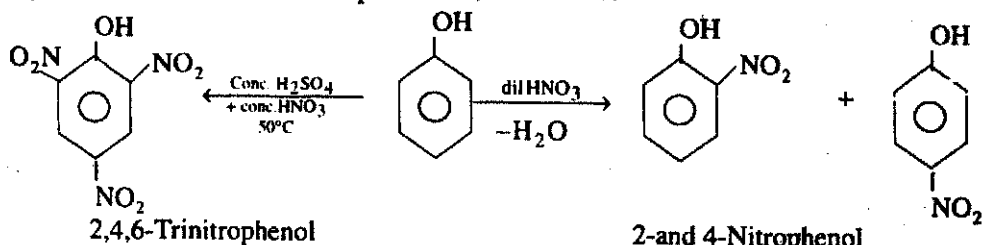


2,4,6-tribromophenol  
White ppt

ortho and para-bromophenol

Para-products are generally more stable because there is less of repulsion between the substituent group and less of steric hindrance.

(b) **Nitration:** Nitration of phenol with dilute nitric acid gives a mixture of 2-nitrophenol and 4-nitrophenol. But on treatment with nitric acid (a mixture of conc.  $\text{H}_2\text{SO}_4$  + conc.  $\text{HNO}_3$ ) at 50°C on long standing, a tribsubstituted product 2,4,6-trinitrophenol, a yellow crystalline solid also known as picric acid, is obtained.

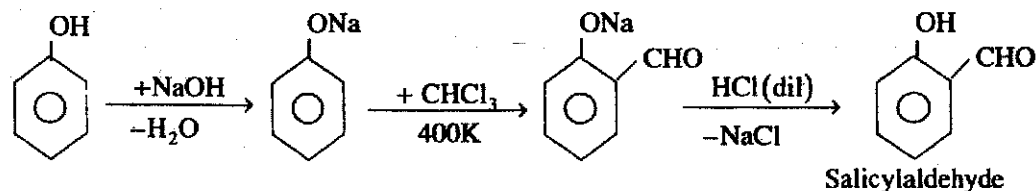


2,4,6-Trinitrophenol  
Yellow crystalline solid (picric acid)

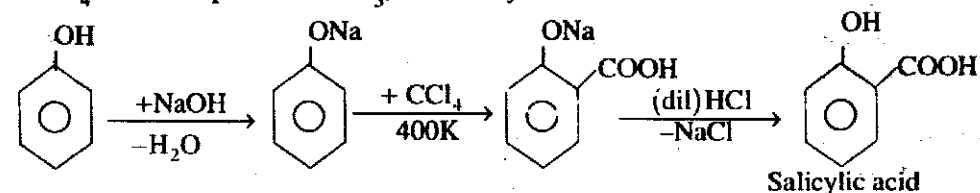
2-and 4-Nitrophenol

Picric acid is a highly explosive chemical.

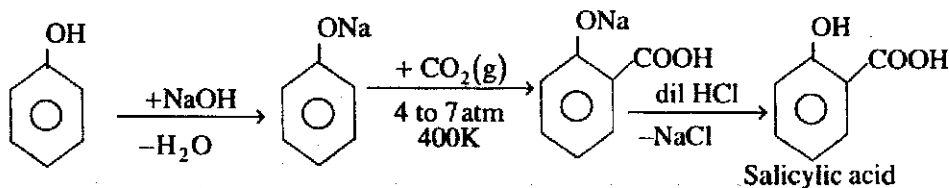
(c) **Riemer Tie Mann Reaction:** This reaction is carried out by refluxing an alkaline solution of phenol with chloroform at 400 K and then acidifying the residual mixture with dilute hydrochloric acid gives salicylaldehyde (an ortho product).



If  $\text{CCl}_4$  is used in place of  $\text{CHCl}_3$ , then salicylic acid is obtained

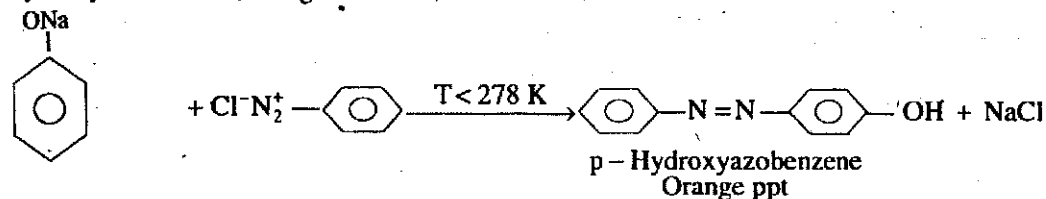


(d) **Kolbe's Synthesis:** When  $\text{CO}_2$  gas is passed through alkaline solution of phenol at  $400^\circ\text{K}$  and 4 to 7 atm pressure, sodium salicylate is obtained, which on reaction with dilute HCl gives salicylic acid (2-Hydroxybenzoic acid).



p-Hydroxybenzoic acid is obtained as an impurity.

(e) **Coupling reaction:** When alkaline solution of phenol is added slowly to phenyldiazonium chloride solution below  $5^\circ\text{C}$  ( $278\text{K}$ ) coupling takes place and a dye, p-hydroxyazobenzene, orange in colour, is obtained.



### 29.3.6 Test to Distinguish Different Types of Alcohols

There are some chemical properties which can be used to distinguish between different types of alcohols, because they behave differently towards these reagents.

**Test to distinguish primary, secondary and tertiary alcohol:** Lucas reagent (a mixture of conc. HCl + anhyd  $\text{ZnCl}_2$ ) can be used to distinguish between primary, secondary and tertiary alcohol. The test is known as **LUCAS TEST**. Refer to table 29.5

Table 29.5

Primary Alcohol	Secondary Alcohol	Tertiary Alcohol
$RCH_2OH$	$R_2CHOH$	$R_3COH$
$\Delta \downarrow$ Lucas reagent No reaction	$\Delta \downarrow$ Lucas reagent $R_2CHCl + H_2O$	$\Delta \downarrow$ Lucas reagent $R_3CCl + H_2O$
No turbidity appears	(Turbidity appears) after 5 mins	(Turbidity appears) immediately

Turbidity is due to formation of insoluble alkyl halide.

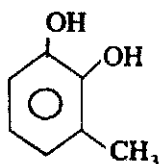
**Test to distinguish phenol and alcohol:** Phenols and alcohols can be distinguished by carrying out the tests given in table 29.6

Table 29.6

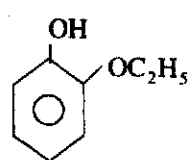
Name of tests	Phenol	Alcohol
(1) Litmus paper test	Turns blue litmus paper red	No Action
(2) Esterification	-ve	+ve
(3) Bromine water	+ve	-ve
(4) Coupling reaction	+ve	+ve

### INTEXT QUESTION 29.1

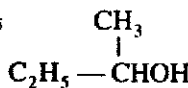
1. Classify the following compounds as monohydric, dihydric, trihydric alcohols or phenols.



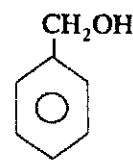
(a)



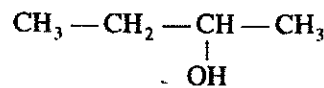
(b)



(c)



(d)



(e)

2. Name the enzymes which are used to convert (i) starch to maltose (ii) glucose to ethanol.
3. Boiling points of chloroethane and ethanol are 285K and 351K respectively. Name the intermolecular forces which are justified by these boiling points.
4. Name two reactions/tests to justify phenols are more acidic in nature than alcohol.

5. Three different bottles contain the following hydroxy compounds., (i) butanol-I, (ii) tertiary butyl alcohol and (iii) phenol. If the bottles were unlabelled, what chemical tests would you carry out to find out the identities of these compounds.

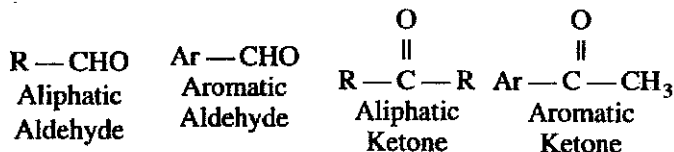
## 29.4 CARBONYL COMPOUND

Carbonyl compounds are those compounds which contain carbonyl group (C=O) as functional group. They are classified as aldehydes and ketones. This group has characteristic properties which are shown by both the classes.

### 29.4.1 Classification

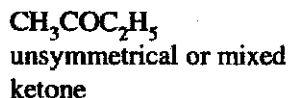
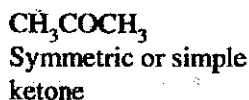
The carbonyl compounds may be aliphatic or aromatic according as carbonyl group is attached to an alkyl group or an aryl group. In aldehydes, the carbon of the carbonyl group is essentially bonded to one hydrogen atom, —CHO group so formed is called *aldehydic* group. In ketones, carbonyl group is called *ketonic* group.

The general formulae are :



The attachment of H-atom to the carbonyl group in an aldehyde gives aldehydes certain properties which ketones do not possess and which enable the two classes of compounds to be distinguished from one another.

If both the groups in a ketone are the same then the ketone is known as a *symmetrical* or *simple ketone* but if the two alkyl groups are different then the ketone is known as *unsymmetrical* or *mixed*, for example :



### 29.4.2 Nomenclature



There are two systems to name carbonyl compounds.

(i) Common System

(ii) IUPAC System

**Nomenclature of aldehydes:**

**Common System:** The common or trivial name of an aldehyde is derived from the name of the corresponding carboxylic acid by replacing —ic acid by word aldehyde. It is a one word name A few examples are:

<i>Formula of acid</i>	<i>Common name of acid</i>	<i>Formula of aldehyde</i>	<i>Common name of aldehyde</i>
HCOOH	Formic acid	HCHO	Formaldehyde
	Benzoic Acid		Benzaldehyde

**IUPAC Name:** According to this system IUPAC name of aldehyde is obtained by replacing ending—e of the name of corresponding alkane (same number of carbon atoms) by—al. IUPAC name is also a one word name. Few examples are:

Formula of alkane/arene	IUPAC Name of alkane	Formula of aldehyde	IUPAC Name of aldehyde
CH <sub>4</sub>	Methane	HCHO	Methanal
C <sub>2</sub> H <sub>6</sub>	Ethane	CH <sub>3</sub> CHO	Ethanal

#### Nomenclature of ketones:

**Common system:** According to this system, the two alkyl groups attached to a ketonic group are named in alphabetical order followed by the word 'ketone'. If the two alkyl groups are the same, then the prefix 'di' is used before the name of alkyl group.

For example:

Formula:	Common name:
CH <sub>3</sub> COCH <sub>3</sub>	Di methyl ketone
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub>	Methyl propyl ketone

The simple ketone di-methyl ketone is popularly known as *Acetone*.

**IUPAC Name:** IUPAC name of a ketone is obtained by replacing -e of the name of corresponding alkane with suffix -one. The chain is then numbered to give the carbonyl carbon the lowest possible number. This number is then used to designate the position of carbonyl group. It is a one word name.

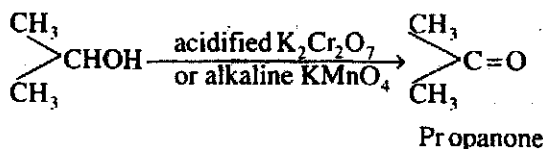
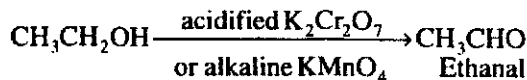
Few examples are as follows:

Formula of alkane	Name of alkane	Formula of ketone	Name of ketone
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Propane	CH <sub>3</sub> COCH <sub>3</sub>	propanone
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub>	Pentan-2-one

### 29.4.3 General Methods of Preparations of Aldehydes and Ketones:

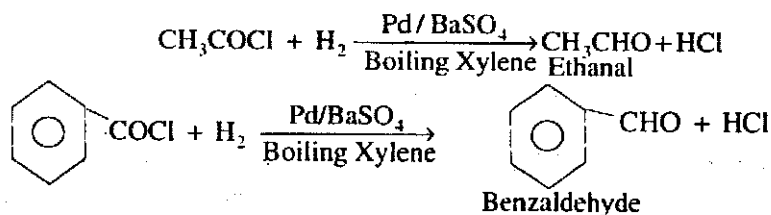
Some of the common methods of preparations of aldehydes and ketones are as follows:

(i) **By oxidation of alcohols:** Aldehydes and ketones are obtained by oxidation of primary and secondary alcohols respectively. Some of the common oxidizing agents are acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or alkaline KMnO<sub>4</sub>.



A difficulty arises in this preparation of aldehyde, because aldehydes easily oxidize further to corresponding acids, if allowed to remain in reaction mixture. In order to prevent this happening, aldehydes are distilled off as soon as they are formed. This is based on the principle that the boiling point of aldehydes is lower than the corresponding alcohol.

(ii) **Reduction of Acid chloride:** This method is only applicable to prepare aldehydes. When an acid chloride is reduced with hydrogen in boiling xylene using palladium, Pd supported on  $\text{BaSO}_4$  as a catalyst. This reaction is known as *Rosemund's reduction*.



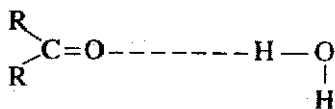
Aldehydes thus obtained readily reduce to alcohol under given conditions. A small amount of sulphur is added to catalyst as prevent reduction of aldehyde to alcohol.

#### 29.4.4 Physical Properties:

Due to presence of polar carbonyl group aldehydes and ketones are polar in nature. Polar carbonyl group effects the physical properties considerably.

**Colour & state:** Methanal and propanone are colourless liquids, however benzaldehyde is slightly yellow in colour. They all have a characteristic smell.

**Solubility:** Lower aldehydes and ketones, containing up to four carbon atoms are soluble in water. This is due to hydrogen bonding between oxygen of polar carbonyl group and hydrogen of water molecules as shown below.



But as the size of non-polar alkyl group increases, the affinity of aldehydes and ketones for polar water molecules decreases, thus solubility decreases.

#### 29.4.5 Chemical Properties of Carbonyl Compounds:

In carbonyl compounds, the carbonyl group is polarised due to the higher electronegativity of oxygen relative to carbon. Thus the electrons between carbon and oxygen are more towards oxygen atom, hence increase the reactivity of carbonyl group. However the presence of H-atom on the carbonyl group of aldehydes makes them slightly more reactive than the ketones. At the same time the presence of H-atom is responsible for many reactions in which aldehydes differ from ketones.

Reactions of carbonyl compounds can be divided into the following categories:-

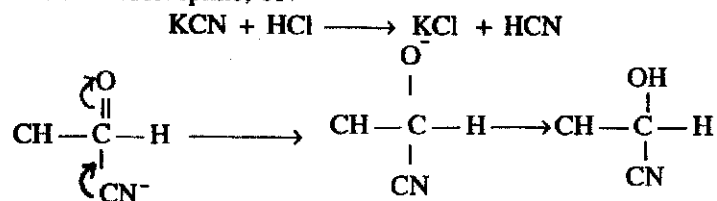
- (i) Reactions due to carbonyl group
- (ii) Oxidation reactions
- (iii) Reactions with alkali

**Reactions of carbonyl group:** These reactions can be subdivided into:

- (a) Nucleophilic addition reactions
- (b) Nucleophilic addition elimination reactions

**Nucleophilic addition reactions:** An addition reaction initiated by a nucleophile is called **nucleophilic addition reaction**. This can be easily understood by addition of HCN across double bond of carbonyl group. Both aldehyde and ketones add a molecule of HCN to form corresponding cyanohydrins. Hydrogen cyanide is produced in the reaction mixture by the action of dilute acid on potassium or sodium cyanide. The reaction proceeds by

attack of nucleophile,  $\text{CN}^-$

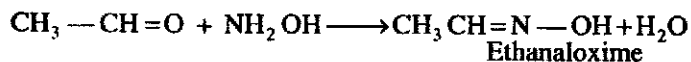


**Addition of Grignard reagent:** Grignard Reagent adds to an aldehyde or a ketone to give an alcohol (details of this reaction can be seen under section preparation of alcohols).

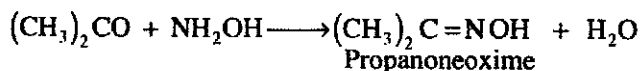
### 29.4.6 Nucleophilic Addition Elimination Reaction:

This reaction is also known as **condensation reaction** in terms of elimination of a water molecule.

Aldehydes and ketones react with compounds which contain  $-\text{NH}_2$  group with the elimination of water. This reaction can be easily understood by studying a reaction with hydroxylamine,  $\text{NH}_2\text{OH}$ . Aldehydes and ketones make corresponding oximes.



Propanone on reaction with hydroxylamine, gives propanone oxime.



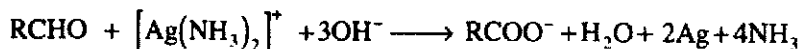
**Oxidation reaction of aldehydes:** Aldehydes are easily oxidized to carboxylic acid containing same number of carbon atom. On the other hand, oxidation of ketones require the breaking of carbon-carbon bond, thus they are difficult to oxidize.

Common oxidizing agents are (a) alkaline  $\text{KMnO}_4$  (b) acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  (c) Tollen's reagent (d) Fehling's solution and (e) sodium hypochlorite,  $\text{NaClO}$  solution.

**Oxidation with alkaline  $\text{KMnO}_4$  or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ :** These oxidising agents readily oxidise an aldehyde to an acid with the same number of carbon atom.

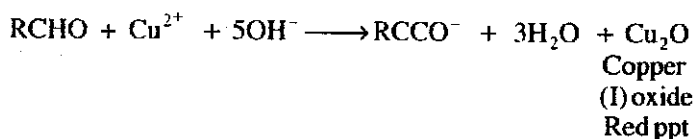


**Oxidation with Tollens' Reagent:** Tollens' reagent is a solution of silver nitrate in an excess of aqueous solution of ammonia, which contains the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$  is reduced by an aldehyde to silver, which deposits on the inner walls of the test tube as an easily recognized **gilder mirror**. The reaction is as follows:



Being a weak oxidising agent, Tollens' Reagent is not able to oxidise a ketone.

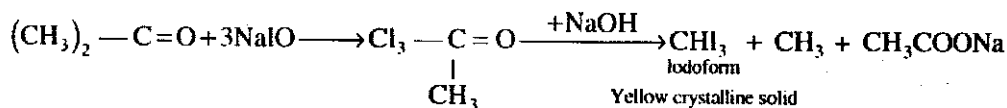
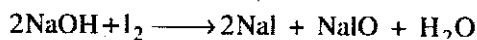
**Oxidation with Fehling's solution:** Fehling's solution which is made by mixing a solution of copper (II) sulphate,  $\text{CuSO}_4$  with an alkaline solution of sodium salt of tartaric acid and which contains a deep blue complex copper (II) ion, is reduced by an aldehyde to copper (I) oxide,  $\text{Cu}_2\text{O}$ , deposits as red ppt.



Fehling's solution is a weaker oxidizing agent hence it is only able to oxidize aliphatic aldehyde but not aromatic aldehydes and ketones.

**Oxidation with a mixture of halogen and NaOH:** The reaction is only applicable to those carbonyl compounds which contain  $\text{CH}_3\text{CO}$ —group. On heating with a mixture of halogen and NaOH, these compounds are able to produce haloform ( $\text{CHX}_3$ ). The reaction is also known as a **haloform test**.

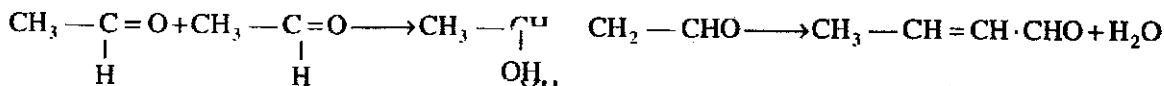
For example on heating a carbonyl compound with a mixture of  $\text{I}_2 + \text{NaOH}$ , a yellow crystalline solid of iodoform  $\text{CHI}_3$ , with characteristic smell is obtained.



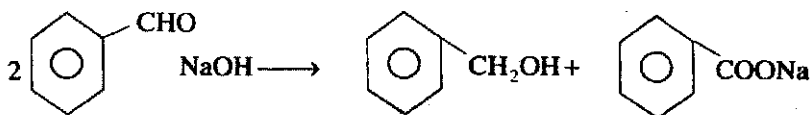
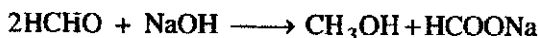
### Reactions with alkaline solution:

**Reactions with dilute alkaline solution :** Aldehydes and ketones which possess at least one hydrogen atom on the carbon atom adjacent to the carbonyl group ( $-\text{CH}-\text{CO}-$ ) undergo condensation reactions in the presence of a base to form hydroxyaldehyde and hydroxy ketone respectively. The aldol thus obtained on warming gives out a water molecule and an unsaturated aldehyde.

The reaction is known as **aldol condensation**.



**Reaction with concentrated alkaline solution:** Aldehydes which do not contain hydrogen atom on the carbon atom adjacent to the carbonyl group do not undergo condensation reaction, as shown above, but instead with conc. alkali such as NaOH, they undergo self oxidation and reduction, that is, one half of the quantity undergoes oxidation to sodium salt of acid and the other half undergoes reduction to corresponding alcohol. The reaction is also known as **Cannizzaro's Reaction**.



### 29.4.7 Test to Distinguish Aliphatic Aldehyde, Aromatic Aldehydes and Ketones :

The table 29.7 will give you an idea that how some of the properties can be used to distinguish different functional groups.

Table: 29.7

Name of the test	Aliphatic Aldehydes	Aromatic Aldehydes	Ketones
Tollen's reagent	+ve	+ve	-ve
Fehling's test	+ve	+ve	-ve
Haloform test	applicable to only ethanal	-ve	applicable to methyl ketones

## INTEXT QUESTION 29.2

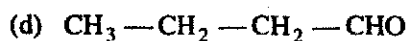
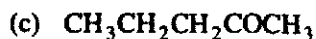
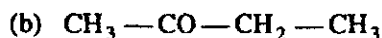
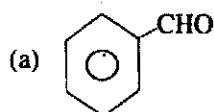
1. Categorise the following compounds

(i) as an aldehyde or a ketone

.....

(ii) as an aliphatic or aromatic compound.

.....



2. Name the products which are obtained:

(a) on heating propanol-2 with alkaline  $\text{KMnO}_4$

.....

(b) on passing  $\text{H}_2$  gas through benzoyl chloride in the presence of a catalyst Pd supported on  $\text{BaSO}_4$  in boiling xylene as a solvent.

.....

3. (a) Name the forces which are responsible for the higher boiling point of aldehydes than corresponding alkanes.

.....

(b) Give reason for solubility of lower carbonyl compounds in water.

.....

4. Write the structural formulae and IUPAC names of compounds containing carbonyl group and having a molecular formula,  $\text{C}_3\text{H}_6\text{O}$ . Name the tests which can be used

to distinguish them.

## 29.5 CARBOXYLIC ACID

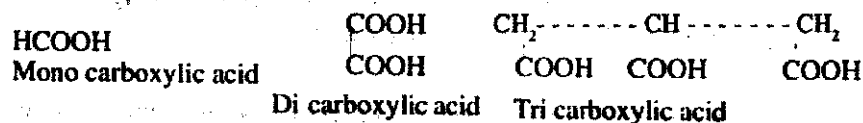
Carboxylic acids are those organic compounds which contain carboxylic group ( $-\text{COOH}$ ) as a functional group. Carboxylic acid may be aliphatic or aromatic according to whether the  $-\text{COOH}$  group is attached to an alkyl group or an aryl group. General formulae are:

$\text{RCOOH}$   
Aliphatic carboxylic acid

$\text{ArCOOH}$   
Aromatic carboxylic acid

### 29.5.1 Classification:

Carboxylic acids can be further classified as mono, di and tri according to the number of carboxylic groups present



In this unit we will discuss the chemistry of only aliphatic monocarboxylic acids.

### 29.5.2 Nomenclature :

There are two different systems to name a carboxylic acid.

(i) Common system

(ii) IUPAC system

(i) **Common System:** The simple carboxylic acids are better known by their common names. The common names are usually derived from the Latin or Greek word, which indicates the original source of the acid. The common name of an acid ends into -ic acid. For example :

In Latin formica means ant, hence acid present in ants is known as formic acid,  $\text{HCOOH}$ . In Latin acetum means vinegar. The acid present in vinegar is called acetic acid. Butyric acid gives a typical smell of rancid butter.

(ii) **IUPAC System :** According to this system the name of an acid is obtained by replacing the ending -e of the name of the corresponding alkane by -oic acid. The longest chain carrying the carboxyl group is considered the parent chain. Carbon of carbonyl group is always considered as number C-1.

For example:

Alkane  
 $\text{C}_4\text{H}_{10}$   
butane

Acid  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
butanoic acid.

The common names and IUPAC names of first four members are given in table 29.8

Table: 29.8

Formulae	Common Name	IUPAC Name
HCOOH	Formic acid	Methanoic acid
CH <sub>3</sub> COOH	Acetic acid	Ethanoic acid
C <sub>2</sub> H <sub>5</sub> COOH	Propionic acid	Propanoic acid
C <sub>3</sub> H <sub>7</sub> COOH	Butyric acid	Butanoic acid

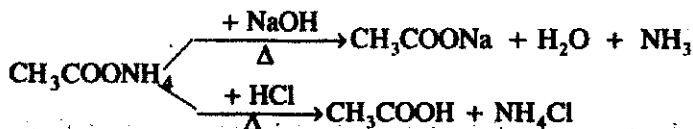
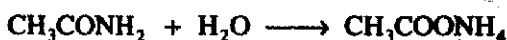
### 29.5.3 General Methods of Preparation

Few common methods of preparation of carboxylic acids are as follows:

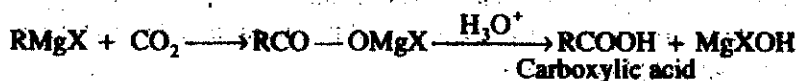
(a) **From oxidation of primary alcohols and aldehydes:** Oxidation of primary alcohol and aldehydes with acidified potassium dichromate or alkaline  $\text{KMnO}_4$  yields corresponding carboxylic acid.



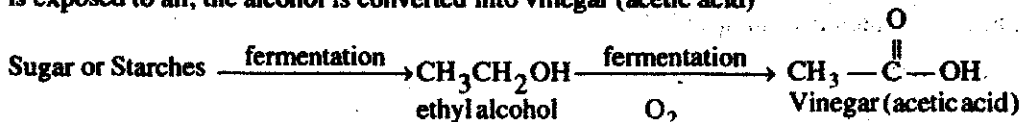
(b) **From hydrolysis of alkyl nitriles:** Hydrolysis of alkyl nitriles with boiling mineral acid or boiling alkali yields corresponding carboxylic acid:



(c) **From Grignard reagent:** By the reaction between a Grignard reagent and carbon dioxide in ethereal solution, an addition product is obtained, which on acid hydrolysis produces an acid:



(d) **Commercial synthesis of Vinegar:** Vinegar is produced by fermentation of sugars and starches. An intermediate in this fermentation is ethyl alcohol. When fermented solution is exposed to air, the alcohol is converted into vinegar (acetic acid)

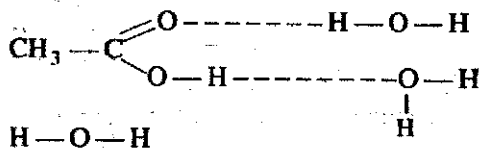


### 29.5.4 Physical properties

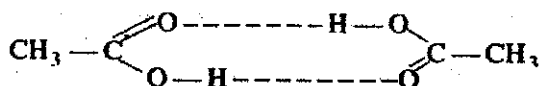
**State and smell:** The lower members are liquids with pungent smell, while higher members are colourless, odourless waxy solids.

As it is expected from the structure, the carboxylic acid molecules are polar like alcohols and are able to make hydrogen bonding with each other.

Carboxylic acids are soluble in water because they are able to make hydrogen bonding with water molecules. This trend is shown by the first four members. But as the size of alkyl group increases the affinity of acid molecule for water molecules decreases, thus solubility decreases.



**Boiling point:** Due to intermolecular hydrogen bonding, two molecules of carboxylic acids are able to make a dimer as shown below:



To break these bonds more energy is required, which is reflected by higher boiling point of carboxylic acids than those of the alkanes and alcohols of comparable masses as shown in the table 29.9

**Table 29.9**

Formula	$C_4H_{10}$	$CH_3CH_2Cl$	$CH_3CH_2OH$	$CH_3COOH$
b.p/K	268	285	371	391

### 29.3.5 Chemical Properties

A molecule of carboxylic acid except methanoic acid is made up of two parts an alkyl group and carboxylic group. Chemical properties of carboxylic acid can be studied under the following headings:

- (i) Reactions due to H-atom of carboxylic group
- (ii) Reactions due to -OH group of carboxylic group
- (iii) Reactions due to -COOH group as a whole.

**(i) Reactions due to H-atom of carboxylic group:** Carboxylic acids are most acidic organic compounds. In aqueous medium a carboxylic acid molecule ionizes to give carboxylate ion and  $H^+$  ion. The release of  $H^+$  ion indicates the acidic nature of carboxylic acid molecule. An equilibrium is established between unionised acid molecule and ionised carboxylate ion as follow:-



At equilibrium the concentration of the components are related by the expression:

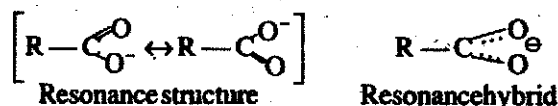
$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$$

The equilibrium constant  $K_a$ , is called acidity or dissociation constant, stronger acids will have higher numerical value or acidity constant.  $K_a$  values for few acids are given in table 29.10

**Table: 29.10**

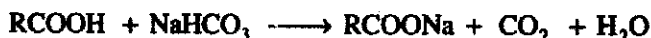
Acids	$K_a$ Values
Methanoic acid	$17.7 \times 10^{-5}$
Ethanoic acid	$1.75 \times 10^{-5}$
Propanoic acid	$1.36 \times 10^{-5}$
Chloroethanoic acid	$136 \times 10^{-5}$

More over the the carboxylate ion thus formed is a hybrid of two resonance structures and can be represented as follows:



The resonance hybrid has more stability than the carboxylic acid molecule. This facilitates release of  $\text{H}^+$  ions.

Reactions with Na, NaOH and  $\text{NaHCO}_3$  also supports acidic character of carboxylic acids.

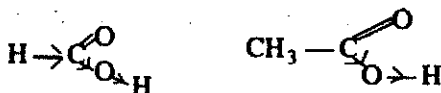


However the acidic character of a carboxylic acid molecule does get effected by the presence of a substituent on the carbon atom adjacent to carboxylic group. There are two such effects.

(i) Effect of electron donating substituent

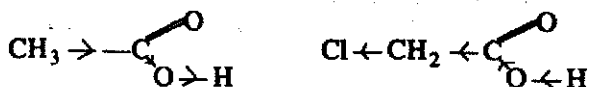
(ii) Effect of electron withdrawing substituent

(i) **Effect of electron donating substituent:** This effect can be readily understood by taking the examples of methanoic acid and ethanoic acid. Methyl group in ethanoic acid has an electron donating effect (+I effect) which in turn increases the -ve charge over the carboxylate ion, thus release of proton becomes difficult. This effect can be seen in the diagram given below:



As the length of the alkyl group increases, positive inductive effect increases, in turn acidic character decreases. This fact is supported by  $K_a$  values of a few acids, as given in the table :

(ii) **Effect of electron withdrawing substituent :** This effect can be understood by comparing the structures of ethanoic acid and chloroacetic acid



The chlorine atom (in general halogen atoms) has electron withdrawing effect (+I), which in turn decreases the negative charge over carboxylate ion and stabilises it. Thus loss of

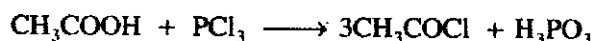
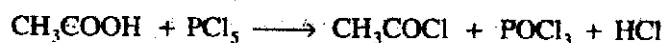
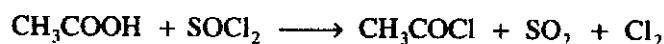
proton becomes relatively easy. Chloroethanoic acid is about 100 times stronger than ethanoic acid.  $K_a$  values can be seen from the table.

**Reactions due to -OH group of carboxylic group:** (i) **Formation of ester:** (reaction with alcohol) (Refer to section-29.3.5, chemical properties of alcohol)

(ii) **Formation of an amide (reaction with ammonia):** On passing ammonia gas through an acid, ammonium salt is obtained, which on heating decomposes to produce an amide.



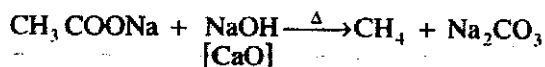
(iii) **Formation of an acid chloride:** Carboxylic acids react with thionyl chloride,  $\text{SOCl}_2$ , phosphorous pentachloride or phosphorous trichloride to form acid chloride,  $\text{RCOCl}$ .



The reaction with  $\text{SOCl}_2$  is considered to be a better method because two side products being gases, escape leaving behind a pure main product, acid chloride.

**Reactions due to -COOH group:** There are some chemical properties of carboxylic acids which are only characteristic of -COOH group.

(i) **Decarboxylation:** The process of elimination of  $\text{CO}_2$  from a carboxylic acid molecule is known as **decarboxylation**. Anhydrous sodium salt of carboxylic acid on heating with soda lime ( $\text{NaOH} + \text{CaO}$  in a ratio of 3:1) liberates an alkane.

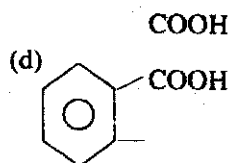
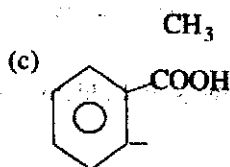


(ii) **Reduction:** When reduction of carboxylic acid is carried out with  $\text{LiAlH}_4$ , they are reduced to an alcohol with the same number of carbon atom.



### INTEXT QUESTIONS 29.3

1. Consider the following acids :  $\text{CH}_2\text{COOH}$  (b)  $\text{CH}_3(\text{CH}_2)_3\text{COOH}$   
 $\text{CH}_2\text{COOH}$



(a) Which one is/are dicarboxylic acids ?

.....

(b) Which one is/are aromatic acid/s ?

.....

(c) Which one is the pentanoic acid ?

.....

2. (a) Which type of bonding is responsible for higher boiling point of carboxylic acid ?
- .....

- (b) Arrange the following acids in their increasing order of solubility in water.



3. (a) How many carbon atoms will be present in carboxylic acid obtained from Grignard reagent, propyl magnesium bromide, and  $CO_2$ .
- .....

- (b) Name the products which are obtained on alkaline hydrolysis of methyl cyanide.
- .....

4. (a) Under what conditions decarboxylation of a sodium salt of carboxylic acid is carried out ?
- .....

- (b) Name the ester which will be obtained by the esterification of formic acid with ethyl alcohol.
- .....

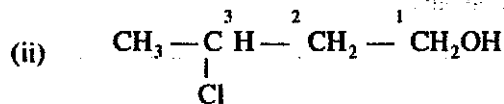
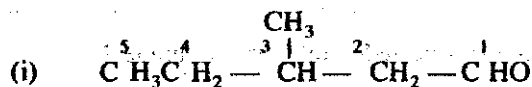
- (c) Write the formula of compound obtained when propanoic acid is heated with  $PCl_5$ .
- .....

## 29.6 WHAT YOU HAVE LEARNT

- The oxygen containing carbon compounds can be classified into alcohols, phenols, aldehydes, ketones and carboxylic acids.
- The oxygen containing carbon compounds can be named according to common system and IUPAC system.
- Alcohols can be prepared from alkyl halides, by hydrolysis of alkenes, by reduction of aldehydes and ketones and by using Grignard reagents.
- Phenols can be prepared from aryl halide and diazonium salts.
- Aldehydes and ketones can be prepared by oxidation of alcohols and by reduction of acid chlorides.
- Carboxylic acids can be prepared by oxidation of alcohols and aldehydes and by hydrolysis.
- The polarity of the functional group and hydrogen bonding in the molecules effects the solubility of alcohols, aldehydes, ketones and carboxylic acids in water and their boiling points.
- The Lucas test can be used to distinguish primary, secondary and tertiary alcohols.
- Bromine water test, litmus paper test and NaOH test are used to distinguish alcohols and phenols.
- Haloform test is used to distinguish aliphatic aldehydes aromatic aldehydes and ketones

**29.7 TERMINAL EXERCISE :**

1. (a) Write the IUPAC names of following compounds :



(b) Write structural formula of the following compounds:

(i) 2-methylpentanol-2, (ii) 3-Methylphenol (iii) 4-Nitrophenol.

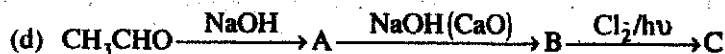
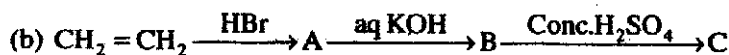
2. Write a complete and balanced equation for the following reactions.

(a) Aqueous NaOH is poured over 2-chloropropane.

(b) Pentanone -3 is reduced by lithium aluminium hydride.

(c) Bromine in  $\text{CS}_2$  is added slowly to phenol.

3. Identify the products A, B and C in the following reactions.



4. What happens when :

(a) A mixture of glacial acetic acid and ethanol is heated in the presence of conc.  $\text{H}_2\text{SO}_4$  ?

- (b) Ammonia gas is bubbled through methanoic acid and the addition product thus obtained heated strongly ?  
.....
- (c) What happens when propanone is heated with hydroxyl amine ?  
.....
- (d) Dilute NaOH is poured over ethanal.  
.....
5. How will you convert :
- (a) Ethanal to 2-Methylpropanol-2.  
.....
- (b) Chlorobenzene to 4-Nitrophenol  
.....
- (c) Acetyl chloride to Ethanoic acid  
.....
6. Give Reasons:
- (a) To liberate hydrogen gas from a tertiary alcohol, a more reactive metal such as potassium is needed.  
.....
- (b) In which type of alcohol the +ve I effect is maximum and why ?  
.....
- (c) Tollens' Reagent can not be used to oxidise an alcohol.  
.....
- (d) Fluoroacetic acid is a stronger acid than acetic acid.  
.....
7. How is iodoform prepared from propanone? Give its reaction sequence.  
.....

---

## CHECK YOUR ANSWERS

### INTEXT QUESTIONS 29.1

1. Monohydric alcohols — c, d Dihydric alcohol — none; Trihydric alcohol — none  
Phenols — a,b.
  2. (i) Diastase (ii) Zymase.
  3. In chloroethane — Van der Waals forces, in ethanol — Hydrogen bonding.
  4. Two tests are (i) blue litmus paper test (ii) solubility in NaOH.
  5. Primary alcohol — Lucas test —ve, Tertiary alcohol — Lucas test —+ve, Phenol —  
Bromine water test —+ve
-

**INTEXT QUESTIONS 29.2**

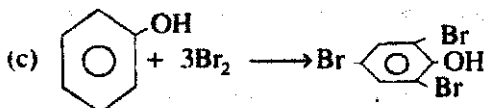
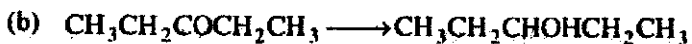
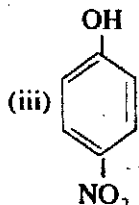
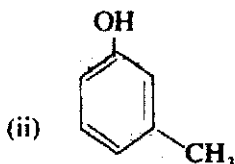
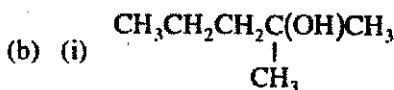
- (i) Aldehydes — (a) & (d), ketones — (b) and c.  
(ii) Aliphatic —(b),(c) & (d), Aromatic — (a)
- (a) Propanone (b) benzaldehyde
- (a) dipole-dipole interaction between carbonyl compounds molecule,  
(b) Oxygen atom of carbonyl group is able to make hydrogen bonding with hydrogen of water molecules.
- (i) Structural formula: (a)  $\text{CH}_3\text{CH}_2\text{CHO}$  (b)  $\text{CH}_3\text{COCH}_3$   
(ii) IUPAC Name : (a) Propanal (b) Propanone  
(iii) Tollens' reagent test or Fehling solution test, both are +ve for propanal. Iodoform test, only +ve for propanone.

**INTEXT QUESTIONS 29.3**

- (i) (a) & (d), (ii) (c) & (d), (iii) (b)
- (a) Intermolecular hydrogen bonding between carboxylic acid molecules.  
(b) Benzoic acid < butanoic acid < ethanoic acid.
- (a) 4, (b) Sodium ethanoate and ammonia.
- (a) Heat in the presence of CaO along with NaOH. (b) ethyl methanoate (c) propanoyl chloride.

**TERMINAL EXERCISE**

- (a) (i) 3-methylpentanal (ii) 3-chlorobutanol



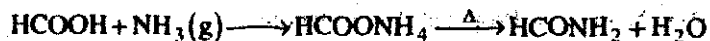
- (a) A:  $\text{CH}_3\text{Cl}$ ; B:  $\text{CH}_3\text{OC}_2\text{H}_5$

- (b) A :  $\text{CH}_3\text{CH}_2\text{Br}$ ; B :  $\text{CH}_3\text{CH}_2\text{OH}$ ; C :  $\text{CH}_2=\text{CH}_2$
- (c) A :  $\text{CH}_3\text{COOH}$ , B :  $\text{CH}_3\text{COCl}$
- (d) A :  $\text{CH}_3\text{COONa}$ ; B :  $\text{CH}_4$ ; C :  $\text{CH}_3\text{Cl}$

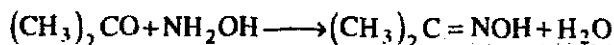
4. (a) An ester ethyl ethanoate is obtained as follows:



(b) On passing  $\text{NH}_3(\text{g})$  through methanoic acid, a salt ammonium methanoate is obtained, which on heating gives methanamide.



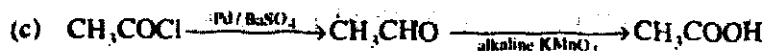
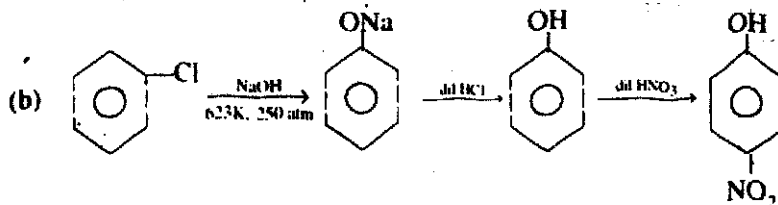
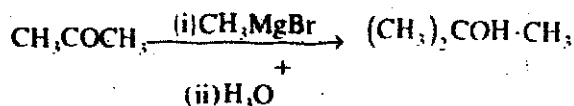
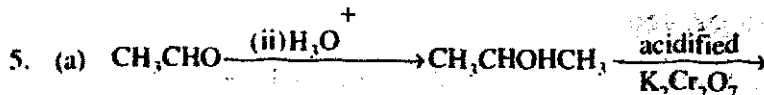
(c) When acetone is heated with hydroxylamine, acetone oxime is obtained.



(d) Aldol condensation takes place. An addition product is obtained, which on heating produces an unsaturated aldehyde.



(i)  $\text{CH}_3\text{MgBr}$



6. (a) Due to strong +I effect on -OH group, release of  $\text{H}^+$  ion as  $\text{H}_2$  becomes difficult, hence to facilitate this, a very reactive metal such as potassium is needed.
- (b) In tertiary alcohol, because it contains maximum number of alkyl group. Alkyl group shows +ve effect.
- (c) Being a weak oxidising agent, Tollens' Reagent is unable to oxidise an alcoholic group.

- (d) Presence of flourine atom (with -ve I effect) on carbon atom adjacent to carboxylic group decreases the -ve charge over the carboxylate ion, in turn stabilises it and hence the release of  $H^+$  ions become easier.

