

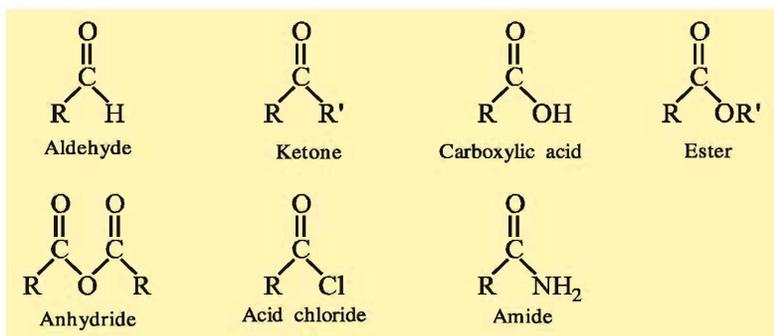
Unit

5

Aldehydes, Ketones and Carboxylic Acids

5.1 Introduction

Organic compounds containing double bond (>C=O) between carbon and oxygen are called carbonyl compounds. In **aldehydes** the carbonyl group is attached to one hydrogen atom and one alkyl or aryl group, while in **ketones** it is attached to one alkyl and one aryl group or to two alkyl or two aryl groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as **carboxylic acids**. In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group, the compounds are known as **esters**, but if it is substituted by acyl group, the compounds are known as **acid anhydrides**. If the carbonyl group is attached to chloro and to amino group, the compounds are known as **acid chlorides** and **amides** respectively. The general formula of these compounds are as below :



Aldehydes and ketones have same general molecular formula $C_nH_{2n}O$, but have different functional groups, therefore, they are called **functional group isomers**. For example compounds having molecular formula C_3H_6O will be CH_3CH_2CHO which is aldehyde (functional group is aldehyde) and CH_3COCH_3 which is ketone (functional group is ketone).

5.2 Structure and Nomenclature of Carbonyl Group

Structure of Carbonyl Group : The $>C=O$ bond of carbonyl group in aldehyde and ketone is made up of one σ -bond and one π -bond. In the formation of carbonyl group compounds, the carbonyl carbon atom is sp^2 hybridised and forms three sp^2 hybrid orbitals. One of the sp^2 hybridised orbitals of carbon overlaps with p-orbital of oxygen atom forming a σ -bond between carbon and oxygen atom. The remaining two hybridised sp^2 orbitals of carbon atom, form additional two σ -bonds, either by overlapping with 1s-orbital of two hydrogen atoms as in formaldehyde or with 1s-orbital of one hydrogen atom and one sp^3 hybrid orbital of an alkyl group carbon in aldehydes other than formaldehyde or with two sp^3 hybrid orbitals of two alkyl groups carbon in ketones. All the three σ -bonds lie in the same plane and are inclined to one another at an angle 120° as shown in figure 5.1. The half-filled $2p_z$ -orbital of carbon atom overlaps sideway with $2p_z$ -orbital of oxygen atom to form a π -bond, and the electron cloud of the π -bond lies both above and below the C–O σ -bond. Thus, the carbonyl carbon and oxygen atoms and two atoms which are directly bonded to the carbonyl carbon lie in the plane as shown in figure. 5.1. This has been also confirmed by **electron diffraction** and **spectroscopic studies**.

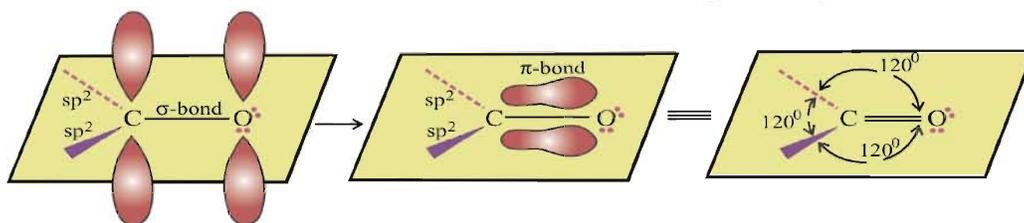


Fig 5.1 Orbital diagram for the formation of carbonyl group

Nature of carbonyl group : In carbonyl group the carbon-oxygen double bond is polarized due to higher electronegativity of oxygen atom relative to that of carbon atom. As a result the oxygen atom tends to attract the electron cloud of the π -bond towards itself as shown in figure 5.2. As a result the carbonyl carbon becomes an electrophile (Lewis acid) and oxygen becomes a nucleophile (Lewis base).

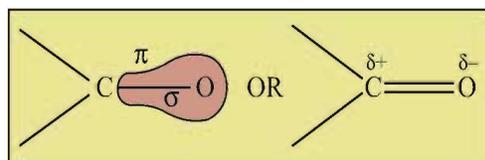
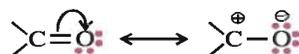


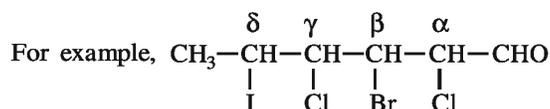
Fig 5.2 Electron cloud gets attracted more towards oxygen atom

Thus the carbonyl group is **polar in nature**. Hence, such compounds have dipole moments. For example, aldehydes and ketones have 2.3-2.8 D dipole moments. The high polarity of the carbonyl group is explained on the basis of resonance structures shown below :



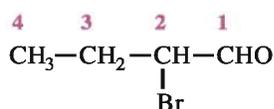
Nomenclature of carbonyl compounds :

Aldehydes and ketones-IUPAC and Common names : The common names of aldehydes are obtained by replacing the terminal **"-ic acid"** by **"aldehyde"** from the common name of the corresponding carboxylic acid. For example, formic acid, acetic acid, benzoic acid; their corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively. In substituted aldehydes the positions of the substituents are indicated by Greek alphabets α , β , γ , δ etc. with the carbon atom next to the $-CHO$ group being designated as α .

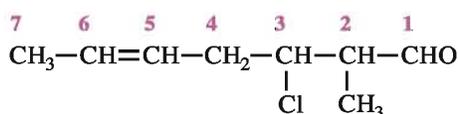


β -Bromo, α - γ dichloro, δ -iodo caproaldehyde

The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet 'e' from its name by '-al'. e.g., methane, a hydrocarbon-its corresponding aldehyde, HCHO and its IUPAC name is methanal. In substituted aldehydes the carbon chain containing aldehyde group, the position of the substituents are indicated by numbers. The numbering of the substituted aldehyde carbon chain is done in such a way so that the aldehyde group at end of the chain gets number 1. For example,

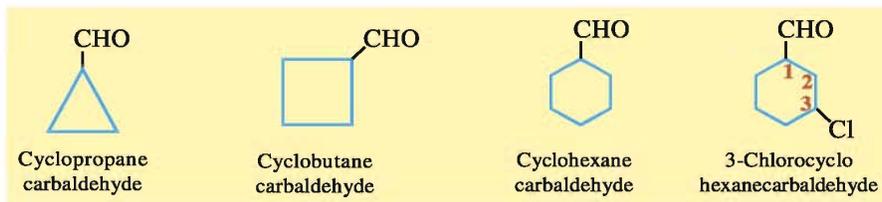


2-Bromobutanal

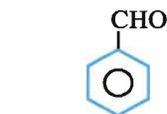


3-Chloro-2-methylhept-5-enal

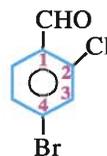
The IUPAC names of aliphatic cyclic aldehydes are given by adding **suffix carbaldehyde** after the full name of the cycloalkane. For example,



The IUPAC names of aromatic aldehyde compounds - like aldehyde group on benzene ring are given by benzenecarbaldehyde (or benzaldehyde) and the position of the substituents are indicated by numbering, starting from the carbon having $-\text{CHO}$ group. For example,

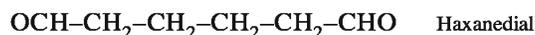


Benzenecarbaldehyde OR
benzaldehyde

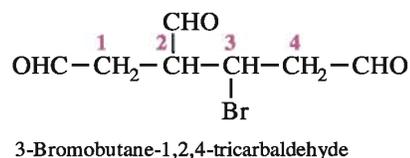
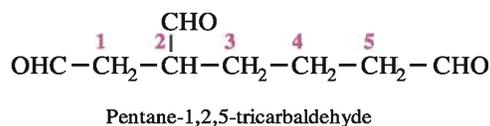


4-Bromo-2-chlorobenzene carbaldehyde
OR 4-bromo-2-chlorobenzaldehyde

When two aldehyde groups are linked to carbon chain then only such aliphatic compounds are named which includes the functional group in calculation of carbon numbers and suffix 'dial' is added. For example,

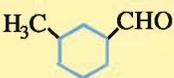
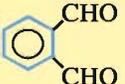
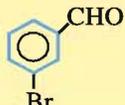


When more than two aldehyde groups are linked to carbon chain then such compounds are named as a derivative of the hydrocarbon which does **not include the carbon atoms of the functional groups**. For example,

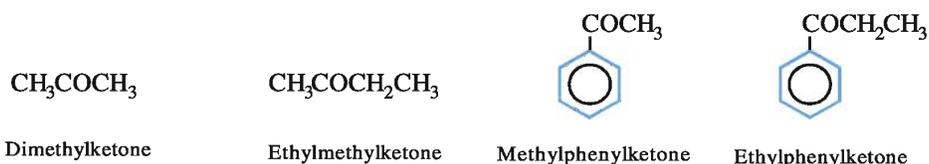


The common and IUPAC names of the aldehydes are given in table 5.1

Table 5.1 Common and IUPAC names of some aldehydes

Structure	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanal	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde

The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl groups (in the alphabetical order) attached to the ketone group as two separate words and adding the suffix ketone. If both the attaching groups are same the **prefix di is used**. For example,



The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet 'e' by the suffix 'one'. For substituted ketones the positions of the substituents are indicated by numbering the chain in such a way that the keto group gets the lowest number. For example,



Propan-2-one

OR

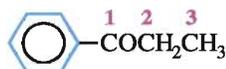
Propanone



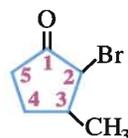
4-Bromopentan-2-one



1-Phenylethan-1-one



1-Phenylpropan-1-one



2-Bromo-3-methylcyclopentanone

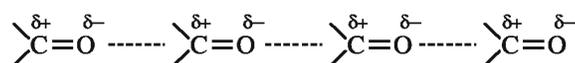
The common and IUPAC names of the ketones are given in table 5.2

Table 5.2 Common and IUPAC names of some ketones

Structure	Common name	IUPAC name
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ketone	Pentan-2-one
$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α -Methylcyclohexanone	2-Methylcyclohexanone
$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	Mesityl oxide	4-Methylpent-3-en-2-one
	Methylphenylketone OR Acetophenone	1-Phenylethan-1-one
	Ethyl phenyl ketone	1-Phenylpropan-1-one
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Biacetyl	Butane-2,3-dione
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Acetyl acetone	Pentane-2,4-dione

5.3 Physical Properties of Aldehydes and Ketones

Aldehydes and ketones possess polar carbonyl group and hence exhibit weak intermolecular association due to **dipole-dipole** interactions between the opposite ends of the >C=O dipoles.



Intermolecular dipole-dipole attraction

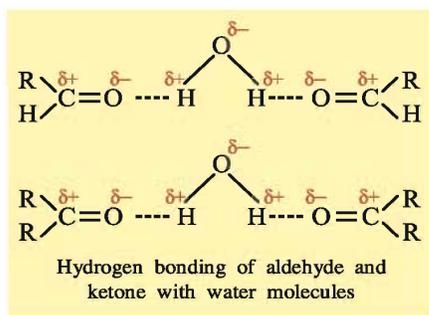
So, the boiling points of aldehydes and ketones are a little higher than non-polar compounds like hydrocarbons and weakly polar compounds like ethers of comparable molecular mass. The boiling points of aldehydes and ketones are lower than those of alcohols and carboxylic acids of comparable molecular mass because in carboxylic acid and alcohol molecules there exists an intermolecular hydrogen bonding which is stronger than dipole-dipole interaction. Among the isomeric aldehydes and ketones, the ketones have slightly higher boiling points. This happens due to the presence of two electron-donating alkyl groups around the carbonyl group which makes them more polar, so the order of boiling points is **carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde > ether > hydrocarbon**.

The boiling points of comparable molecular mass of the following compounds are given in table 5.3.

Table 5.3 Boiling points of some organic compounds

Compound	Boiling point (K)	Molecular mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Propanone	329	58
Propan-1-ol	370	60
Ethanoic acid	391	60

The lower members of aldehydes and ketones upto three carbon atoms such as methanal, ethanal, propanal and propanone are soluble in water due to hydrogen bond formation between the polar carbonyl group and the water molecules.



But the solubility of aldehydes and ketones in water decreases rapidly with the increase in length of alkyl chains. Similarly the solubility of aromatic aldehydes and ketones is much lower than their corresponding aliphatic aldehydes and ketones due to the presence of larger hydrocarbon parts (like benzene ring etc.). However all aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohol, chloroform etc. The lower aldehydes have strong pungent odours, but as the size of the aldehyde molecules increases the odour becomes less pungent and more fragrant. However, the ketones are generally in liquid forms having pleasant smell. A number of naturally occurring aldehydes and ketones are used in the preparation and blending of perfumes and as flavouring agents.

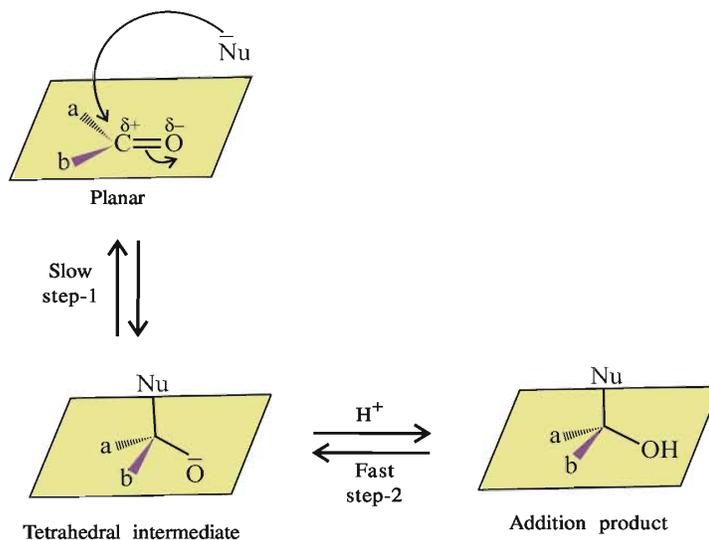
5.4 Chemical Reactions of Aldehydes and Ketones

Aldehydes and ketones have the same functional group i.e. polarized carbonyl group. So they undergo similar chemical reactions. However, the presence of a hydrogen atom on the carbonyl group of aldehydes makes them much **more reactive than ketones**. This hydrogen atom is responsible for many reactions of aldehydes and thus they differ from ketones. Some chemical reactions of aldehydes and ketones are as follows :

(i) Nucleophilic addition reactions : Aldehydes and ketones have the carbonyl group containing double bond and so they can undergo addition reactions. Alkenes have $>C=C<$ and they undergo

electrophilic addition reactions, while the aldehydes and ketones undergo nucleophilic addition reactions because the **carbonyl group is polar and the carbon atom is slightly positively charged which is readily attracted by the nucleophile.**

The mechanism of nucleophilic addition reactions : The structure of carbonyl group is planar and it is polar, so the nucleophile is attracted to the positively charged carbon atom of carbonyl group either from above or below the plane of sp^2 hybridised orbital of carbonyl group. So it results in formation of an anion (tetrahedral alkoxide) by the complete transfer of π -electrons of the carbon-oxygen double bond to the oxygen atom. During this process, the hybridisation of carbon atom changes from sp^2 to sp^3 and hence, the oxygen atom gets pushed out of the plane of the carbonyl group and **form new carbon nucleophile (Nu) bond which is slow step so, it is the rate determining step and it is also reversible.** In the second step the proton (which is obtained from weak acidic medium) gets attracted by oxygen of carbonyl group (tetrahedral alkoxide) and the electrically neutral product is formed. **The second step is also reversible.**



Relative reactivities of aldehydes and ketones : Aldehydes are generally more reactive than corresponding ketones in nucleophilic addition reaction, due to the following reasons.

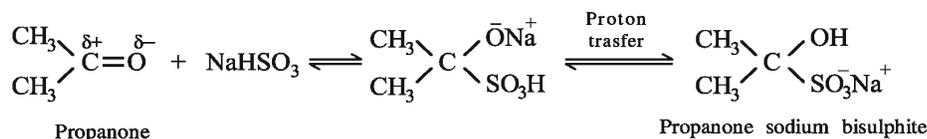
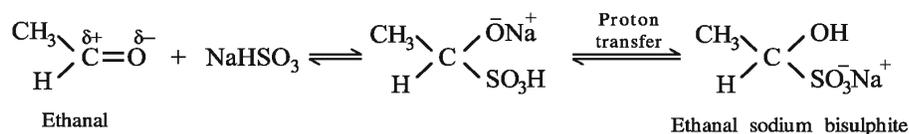
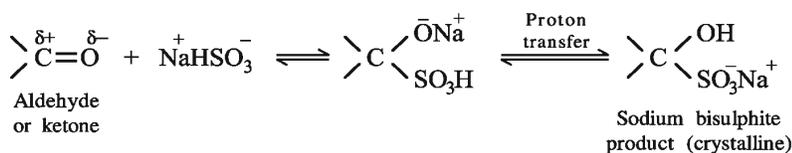
(i) **Steric effects :** As the number and size of the alkyl group attached to the carbonyl group increases, the attachment of nucleophile on the carbonyl group carbon becomes more and more difficult, due to **steric hinderance** (crowding) i.e. **as the crowding increases, the reactivity of carbonyl group compound decreases**, so the reactivity of formaldehyde is more as there is no alkyl group, while the other aldehydes having one alkyl group the reactivity is less compared to formaldehyde while ketones having two alkyl groups, the reactivity is less than the corresponding aldehydes.

(ii) **Inductive effect :** The attachment of nucleophile on the carbonyl group depends upon the magnitude of the positive charge on the carbonyl carbon. The alkyl group **electron donating and hence has inductive effect (+I effect)**. So more the number of alkyl groups on carbonyl carbon, **the magnitude of the positive charge on carbonyl carbon decreases**, which lowers the reactivity towards nucleophilic addition reactions. Therefore formaldehyde is **more reactive** compared to other aldehydes and ketones which are less reactive than aldehydes.

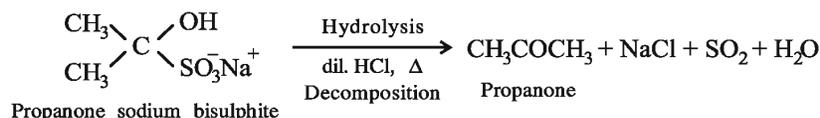
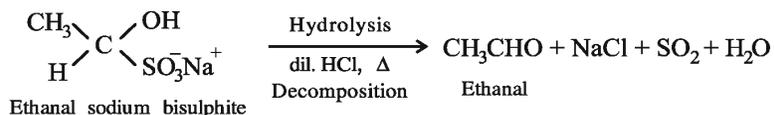
The aromatic aldehydes and ketones are **less reactive** than aliphatic aldehydes and ketones because the electron-donating resonance effect of benzene ring which **increases the electron density on carbonyl carbon**, hence it gets repelled by the nucleophiles. The aromatic aldehyde (like benzaldehyde) is more reactive than alkyl aryl ketone (like acetophenone) while diaryl ketones (like benzophenone) is less reactive than alkyl aryl ketone.

Nucleophilic addition reactions :

(i) **Addition of sodium hydrogen sulphite (NaHSO₃)** : Due to less steric hindrance most of the aldehydes and aliphatic methyl ketones, react with sodium hydrogen sulphite and form additive compounds, while the acetophenone does not react.

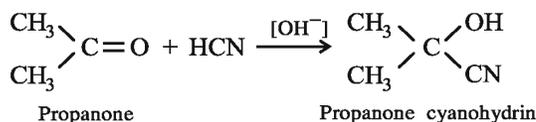
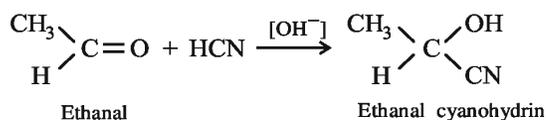
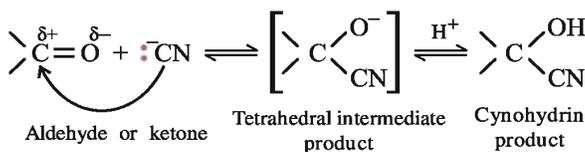


The proton transfer equilibrium lies more towards the **right side for most of the aldehydes and to the left side for most of the ketones**. The bisulphite product obtained, are usually crystalline solids. If they are heated with dilute mineral acids or aqueous alkalies they decompose, due to hydrolysis and regenerate the original aldehyde or ketone.

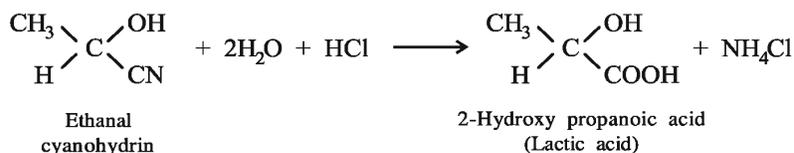


Therefore, this reaction is useful for separation and purification of aldehydes and ketones from non-carbonyl compounds.

(ii) **Addition of Hydrogen cyanide (HCN)** : The aldehydes and ketones react with hydrogen cyanide and give product cyanohydrins. The reaction is extremely slow and so it is carried out in **presence of base which acts as a catalyst**. The reaction occurs very slowly with pure HCN but in presence of base (as a catalyst) the $\text{:}^-\text{CN}$ is generated which is a stronger nucleophile and gets added readily to carbonyl compounds and the product cyanohydrin is obtained. For example,

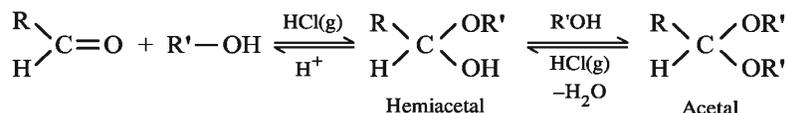


Cyanohydrins are important synthetic substances because they can be readily hydrolysed to give 2-hydroxy acids.

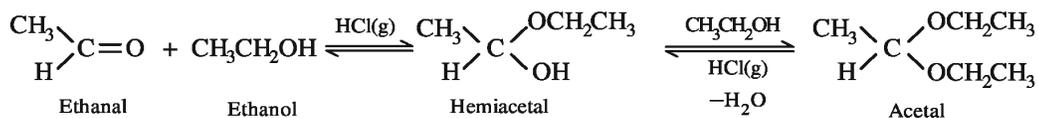


(iii) Addition of Grignard reagent : Aldehydes and ketones react with Grignard reagent to form nucleophilic addition compounds. This intermediate product upon hydrolysis with water or dilute mineral acid gives 1^o, 2^o or 3^o alcohols. This you have studied in unit 7 of Semester III.

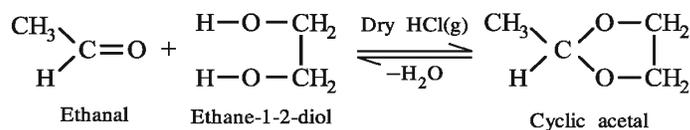
(iv) Addition of alcohols : Aldehyde reacts with one equivalent of monohydric alcohol in presence of dry hydrogen chloride to yield alkoxy alcohol intermediate known as **hemiacetal** (hemi means half). Being unstable it immediately reacts with one more molecule of alcohol to form stable gem-di alkoxy compound known as **acetal**.



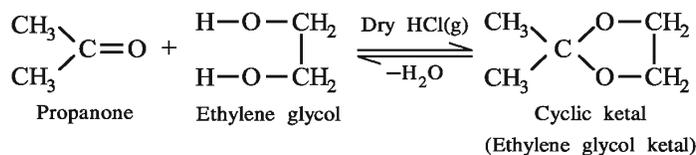
Dry hydrogen chloride protonates the oxygen of aldehyde (carbonyl compound) hence the density of positive charge on carbonyl carbon increases i.e. the electropositivity of carbonyl carbon increases, which **facilitates the nucleophilic attachment**. Dry HCl gas absorbs the water molecules which is produced during acetal formation and shifts the equilibrium in the forward direction. For example,



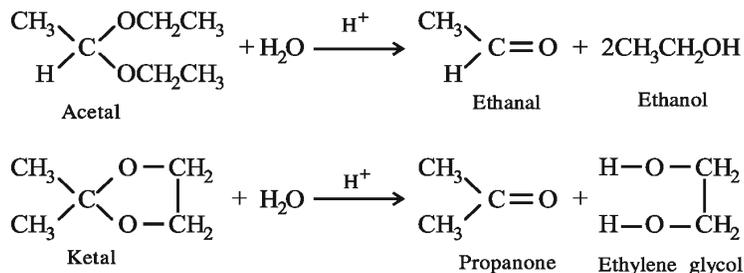
Instead of two molecules of monohydric alcohol in presence of dry hydrogen chloride or paratoluene sulphonic acid (PTS), one molecule of dihydric alcohol such as ethane-1, 2-diol (ethylene glycol) is used, then cyclic acetal (ethylene glycol-acetal) is formed.



Ketones do not react with monohydric alcohols but react with dihydric alcohols in presence of dry hydrogen chloride or PTS and give **cyclic ketals**. For example,

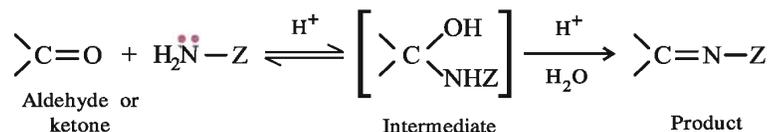


In the formation of acetals and ketals the reactions are reversible; so they are decomposed by dilute acid and the aldehydes and ketones are regenerated. For example,



Nucleophilic addition reactions followed by elimination of a molecule of water :

(v) **Addition of ammonia and its derivatives** : Aldehydes and ketones react with ammonia ($\ddot{\text{N}}\text{H}_3$) and its derivatives ($\text{H}_2\ddot{\text{N}}-\text{Z}$). The reaction is catalysed by acid, hence the carbonyl group gets protonated, so the positive charge on carbonyl carbon is increased and as a result the weak nucleophile like ammonia and its derivatives readily attach to the carbonyl group. For example,



The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z . The $\ddot{\text{N}}\text{H}_3$ and its N-substituted derivatives and product are given in table 5.4

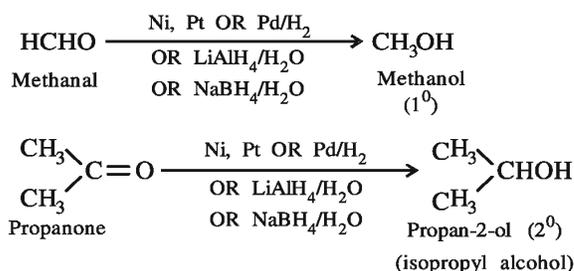
Table 5.4 Some N-Substituted Derivatives of Aldehydes and Ketones

Z	Reagent's name	Carbonyl derivative	Product's name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
-OH	Hydroxylamine	>C=N-OH	Oxime

$-\text{NH}_2$	Hydrazine	$>\text{C}=\text{N}-\text{NH}_2$	Hydrazone
$-\text{HN}-\text{C}_6\text{H}_5$	Phenylhydrazine	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5$	Phenylhydrazone
$-\text{HN}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2,4-Dinitrophenyl hydrazine	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2,4-Dinitrophenyl hydrazone
$-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	Semicarbazide	$>\text{C}=\text{N}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	Semicarbazone

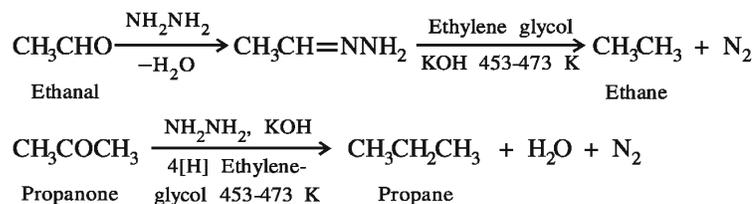
Reduction reactions of aldehydes and ketones :

(i) **Reduction to alcohols** : Aldehydes and ketones on **reduction give 1^o and 2^o alcohols** respectively. Reduction is carried out either catalytically with H_2 in presence of Ni, Pt or Pd or chemically by lithium aluminium hydride (LiAlH_4) or sodium borohydride (NaBH_4). LiAlH_4 is a much more powerful reducing agent than NaBH_4 .

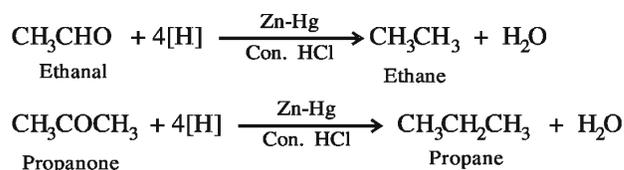


(ii) **Reduction to hydrocarbons** : The carbonyl group of aldehydes or ketones is reduced to **methylene ($-\text{CH}_2-$) group** to form hydrocarbon by using different reducing agents.

(a) **Wolff-Kishner reduction** : Aldehyde or ketone is heated with hydrazine (NH_2NH_2) and KOH in high boiling solvent like ethylene glycol which results **into formation of hydrocarbon**. For example,

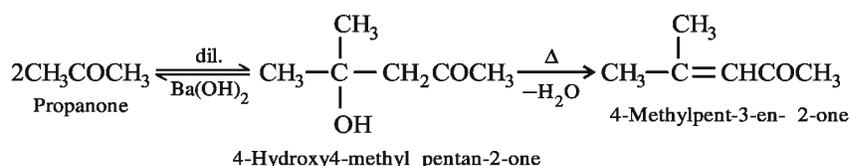
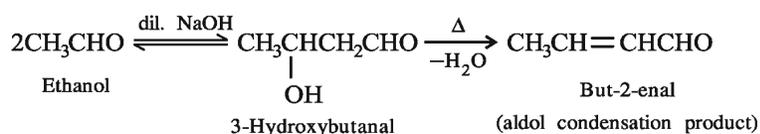


(b) **Clemmensen reduction** : Aldehyde or ketone is **reduced to hydrocarbon**, on treatment with zinc amalgam and concentrated hydrochloric acid. For example,



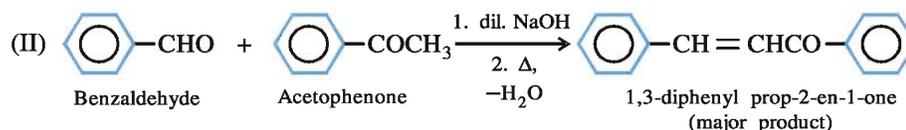
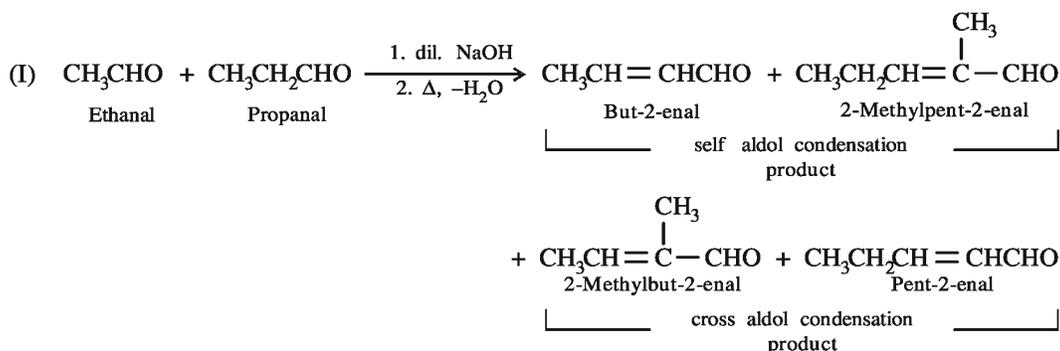
Due to acidity of α -hydrogen of aldehydes and ketones, they undergo a number of reactions such as aldol condensation, cross aldol condensation etc.

(i) Aldol condensation : In this reaction, two same molecules of an aldehyde or ketone, having **at least one α -hydrogen atom** undergo a reaction in presence of dilute alkali (dil. NaOH, Na_2CO_3 , $\text{Ba}(\text{OH})_2$ etc.) to form β -hydroxy aldehyde (Aldol) or β -hydroxy ketone (Ketol) respectively. This reaction is **known as aldol condensation reaction**. The name aldol is derived from the name of two functional groups aldehyde and alcohol present in the product. Same way ketol is derived from two functional groups of ketone and alcohol present in the product. The aldol and ketol readily lose water molecule to give α - β unsaturated carbonyl compounds which are aldol condensation product and the reaction is called aldol condensation. For example,



Formaldehyde, benzaldehyde and benzophenone do not undergo aldol condensation since they do not have an α -hydrogen atom.

(ii) Cross-aldol condensation : An aldol condensation between **two different aldehydes or two different ketones or between one aldehyde and one ketone** is called **cross aldol condensation** and gives mixture of four products which are difficult to separate. So cross aldol condensations are of little synthetic value. However, if one carbonyl compound does not possess α -hydrogen atom then cross aldol condensations are of great synthetic utility. e.g.,



a disinfectant and germicide. Formaldehyde is used in leather industry. Acetaldehyde is used for giving the shining like silver to mirror. Benzaldehyde is used as a flavouring agent in perfume industry and is also used in manufacturing of dye like malachite green. Acetone is used in manufacturing liquid nail polish and also as nail polish remover. Acetone and methylethyl ketone are common industrial solvents. Some aldehydes and ketones for example butyraldehyde, vanillin, acetophenone, camphor etc. are well-known for their odours and flavours.

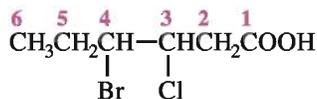
5.6 Carboxylic Acids

Organic compounds containing -COOH as the functional group are called carboxylic acids. The -COOH group is made up of a carbonyl group (>C=O) and hydroxyl group (-OH). So 'Carb' from carbonyl and 'oxyl' from hydroxyl, hence -COOH is called carboxyl group. The -COOH attaches to aliphatic alkyl (or hydrogen atom) or aromatic group, and according to that it may be aliphatic or aromatic carboxylic acid. Aliphatic or aromatic carboxylic acids have one or more than one -COOH groups. A large number of carboxylic acids are found in nature. Higher numbers (C_{12} to C_{18}) of aliphatic acids occur in nature known as **fatty acids**, which occur in natural fats as triesters of glycerol. Carboxylic acid serves as starting material for preparing a number of other important compounds such as acid chloride, acid anhydride, ester, amide etc.

5.7 Common and IUPAC Nomenclature of Carboxylic Acids

The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (Plant or animal product) from which they were first isolated. For example, formic acid was first obtained by distillation of red ants (Latin : formica means red ant). The acetic acid (Latin: acetum means vinegar). The butyric acid (Latin : butyrum means butter) and caprylic, caproic and capric acids (Latin : caper means goat).

The IUPAC names of the saturated monocarboxylic acids are given by replacing the ending alphabet '-e' in the name of the corresponding hydrocarbon with the suffix '**-oic acid**'. For the naming of substituted and branched chain acids, select the -COOH group containing longest chain. The positions of the substituents are indicated by **numbering the carboxylic carbon as number one**. For Example,



4-Bromo-3-chlorohexanoic acid

The IUPAC names of aromatic monocarboxylic acids are derived by benzene carboxylic acid or benzoic acid and the position of the substituents are indicated by **number with carbon atom carrying -COOH group being numbered one**. For example,



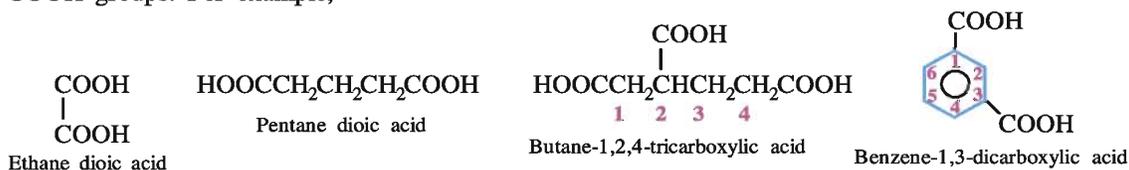
The IUPAC name is 2-Chloro-3-methyl benzene carboxylic acid

OR

2-Chloro-3-methylbenzoic acid

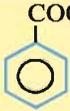
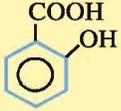
Aliphatic or aromatic carboxylic acid **having more than one -COOH groups** are named as di, tri, tetra... and polycarboxylic acids, according to two, three, four... and many carboxyl groups present in respective molecules. In case of aliphatic dicarboxylic acids the position of -COOH groups are not indicated, but in case of aromatic dicarboxylic acid and other carboxylic acids, the position of

the -COOH groups are indicated by the number and the numbers are indicated before the multiplicative prefix. **The ending '-e' of the hydrocarbon is retained in carboxylic acid having more than one -COOH groups.** For example,



Common and IUPAC names of some carboxylic acids are given in table 5.5.

Table 5.5 Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
$\text{HOOC-CH}_2\text{COOH}$	Malonic acid	Propanedioic acid
$\text{HOOC-(CH}_2)_2\text{-COOH}$	Succinic acid	Butanedioic acid
$\text{HOOC-(CH}_2)_3\text{-COOH}$	Glutaric acid	Pentanedioic acid
$\text{HOOC-(CH}_2)_4\text{-COOH}$	Adipic acid	Hexanedioic acid
$\text{HOOC-CH}_2\text{-CH(COOH)CH}_2\text{COOH}$	–	Propane-1,2,3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid OR Benzoic acid
	Isophthalic acid	Benzene-1,3-dicarboxylic acid
	Salicylic acid	2-Hydroxybenzenecarboxylic acid OR 2-Hydroxybenzoic acid

5.8 Structure of Carboxylic Group

In carboxylic acid compounds the carbon atom of carboxyl group is attached to one oxygen atom by single bond and another by double bond, but **electron and neutron diffraction studies** have proved that -COOH has planar structure having angle of about 120° , so the two oxygen atoms are sp^2

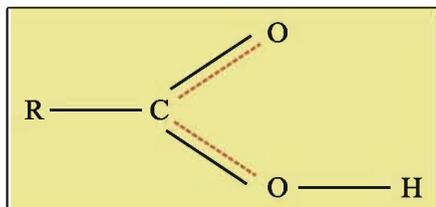


Fig 5.6

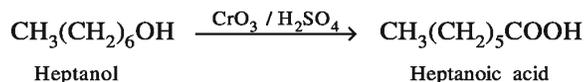
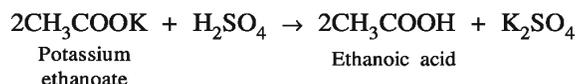
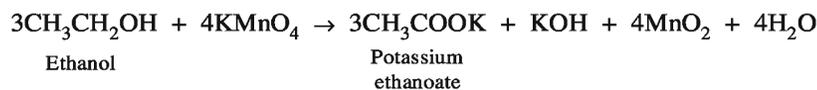
hybridised. The π electrons of double bond are delocalized between carbon and oxygen bond as shown in figure 5.6.

Here, σ and π bond between carbon and oxygen, carbon and both oxygen atoms are sp^2 hybridised R-C-O and O-C-O angle 120° .

5.9 Methods of Preparation of Carboxylic Acids

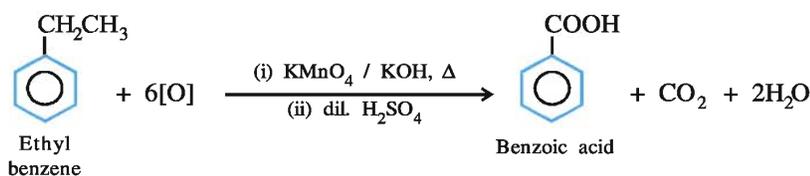
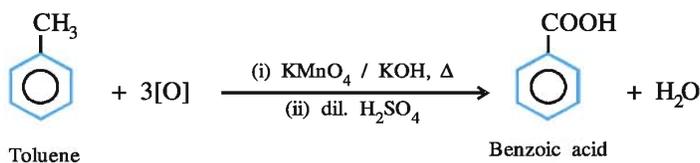
Some important general methods of preparation of carboxylic acid are as follows :

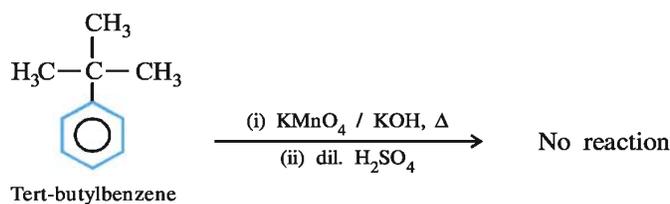
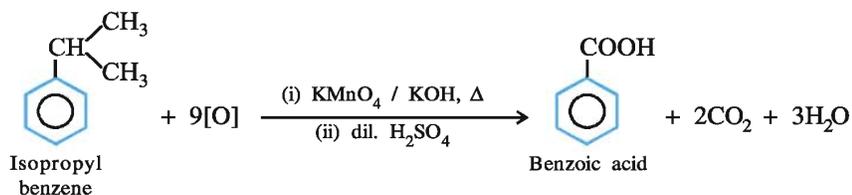
(i) From primary alcohols and aldehydes : The primary alcohols are readily oxidized to the corresponding carboxylic acids with common oxidizing agents such as $KMnO_4$ in **neutral, acidic or alkaline medium** or by $K_2Cr_2O_7$ or CrO_3 (chromium trioxide) in acidic medium. Oxidation with $K_2Cr_2O_7$ or CrO_3 in acidic medium often give some amount of esters. Therefore the oxidation with $KMnO_4$ is preferred. Under these conditions the potassium salts of the carboxylic acid is first obtained, which on treatment with dil H_2SO_4 gives carboxylic acids. For example,



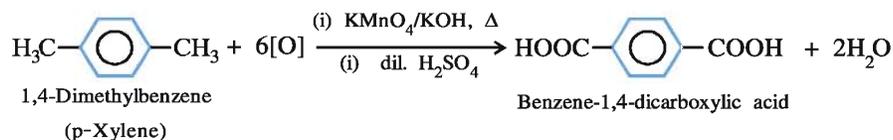
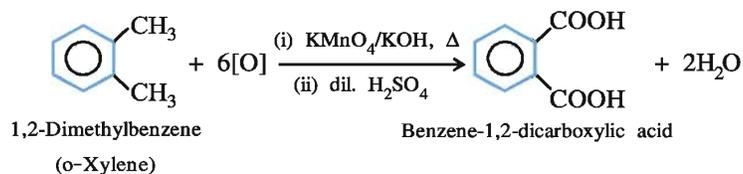
Aldehydes are easily oxidized to corresponding carboxylic acids with $KMnO_4$ in neutral, acidic or alkaline medium or by $K_2Cr_2O_7$ or CrO_3 in acidic medium and also even with mild oxidizing agent such as Tollens' reagent which is discussed in unit 5.4.

(ii) From alkylbenzene and alkenes : Aromatic carboxylic acids are prepared by the vigorous oxidation of alkylbenzene with acidic or alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$ (chromic acid) or dil. HNO_3 . During these oxidation the entire side chain is oxidized to carboxylic acid group irrespective of the length of the side chain. **1° and 2° alkyl groups are oxidized in this manner but the 3° alkyl group is not oxidized and remains unaffected.** For example,

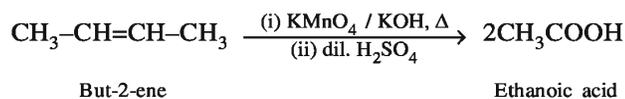




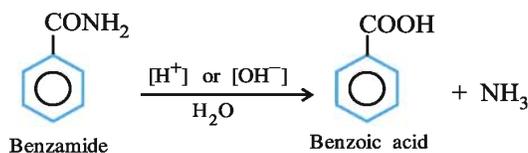
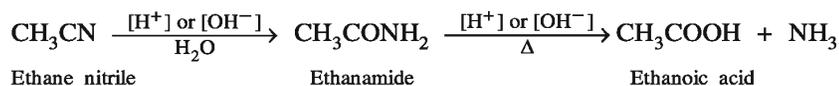
If there are two or more than two alkyl groups in benzene ring, each group is oxidized to -COOH group. For example,



Substituted alkenes are also oxidized to carboxylic acid by acidic $\text{K}_2\text{Cr}_2\text{O}_7$ or alkaline KMnO_4 . For example,

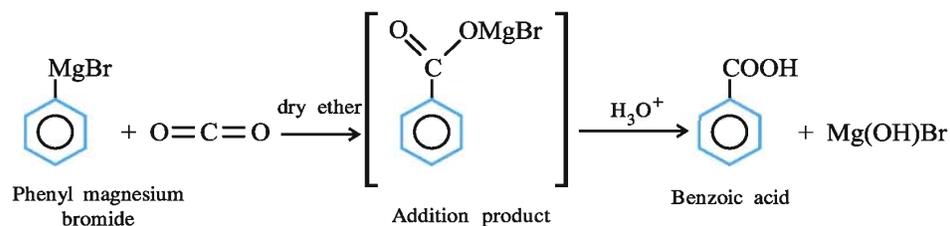
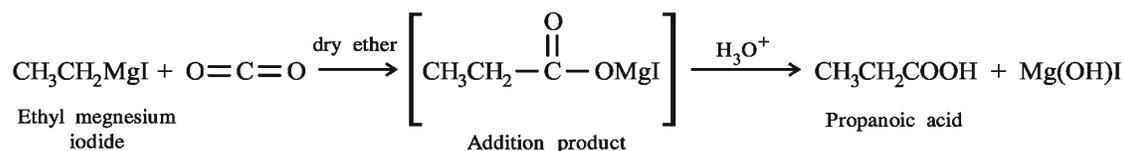
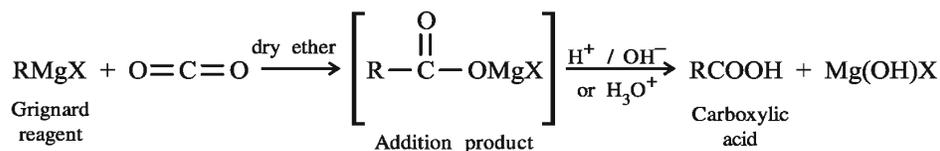


(iii) From nitriles and amides : Nitriles are hydrolysed to amide and then to carboxylic acid on boiling with mineral acids or alkalis as a catalyst. For example,



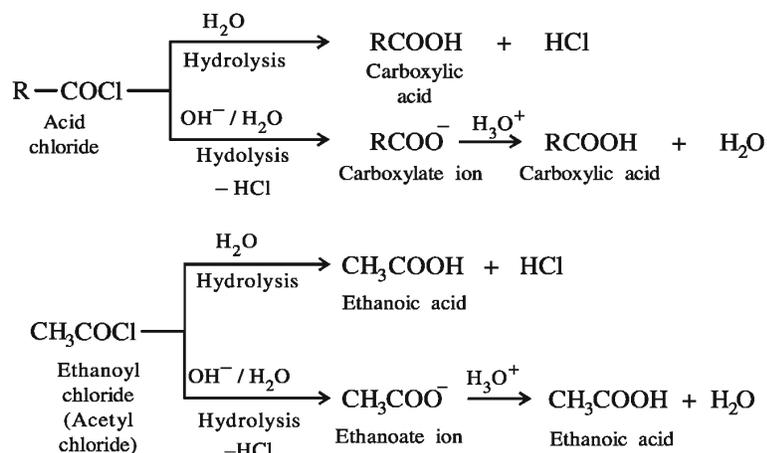
(iv) From Grignard reagent : Carboxylic acids can be prepared by bubbling CO_2 gas into the ethereal solution of a suitable Grignard reagent or by adding the solution of Grignard reagent to

crushed dry ice (solid CO_2) suspended in ether. First the addition product is obtained, which on decomposition with mineral acid gives carboxylic acid. For example,

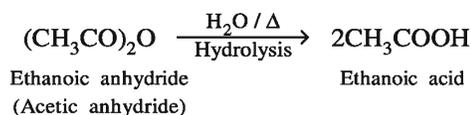


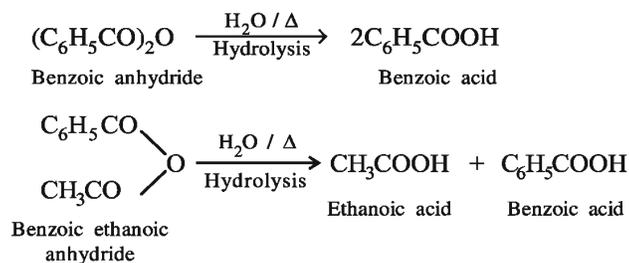
In both the methods-nitriles and Grignard reagent are useful for converting the alkyl halide to the carboxylic acid, having carbon atom or atoms more than that present in alkyl halide.

(v) From acid chloride and anhydrides : Acid chloride when hydrolysed by water gives carboxylic acid, and more readily hydrolysed with aqueous alkali to give carboxylate ions, which on acidification gives corresponding carboxylic acids. For example,

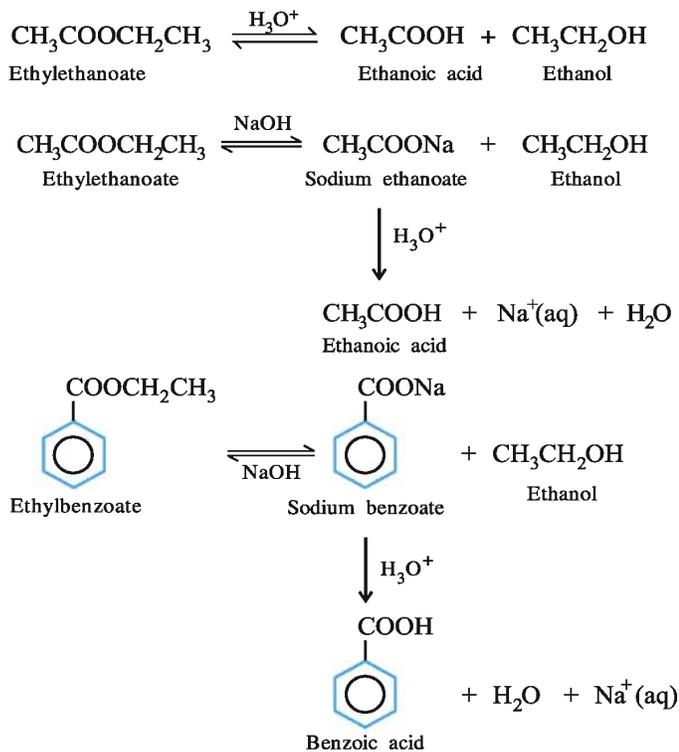


Anhydrides on hydrolysis with water gives carboxylic acids. For example,





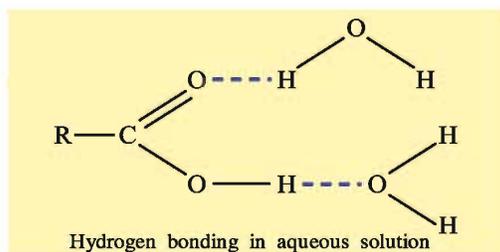
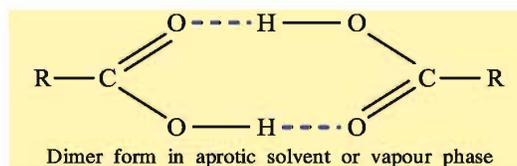
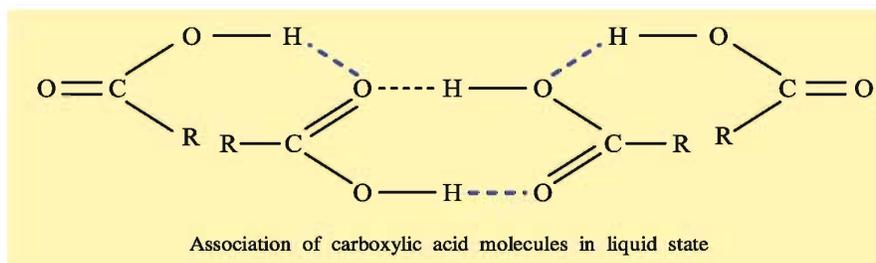
(vi) **From ester** : Hydrolysis of esters in presence of mineral acids give carboxylic acids directly while hydrolysis in presence of alkali gives carboxylates, which on acidification give corresponding carboxylic acid. For example,



5.10 Physical Properties of Carboxylic Acids

The first three aliphatic acids (C_1 to C_3) are colourless liquids with pungent smell. The next three (C_4 to C_6) are colourless oily liquids with unpleasant smell and remaining three (C_7 to C_9) are colourless liquids with unpleasant smell at room temperature, while carboxylic acids with ten or more carbon atoms are colourless, waxy solids with no distinct smell due to low volatility. Aromatic carboxylic acids are solid with no distinct smell. C_1 to C_4 aliphatic carboxylic acids are fairly soluble in water, while C_5 and C_6 are slightly soluble and remaining are insoluble in water. The aromatic acids are almost insoluble in cold water, but soluble in hot water. The solubility of lower members of aliphatic carboxylic acids is due to hydrogen bond formation. The hydrogen bonding of carboxylic acid is stronger than that of alcohol, so the melting points and boiling points of carboxylic acids are more than those of alcohols

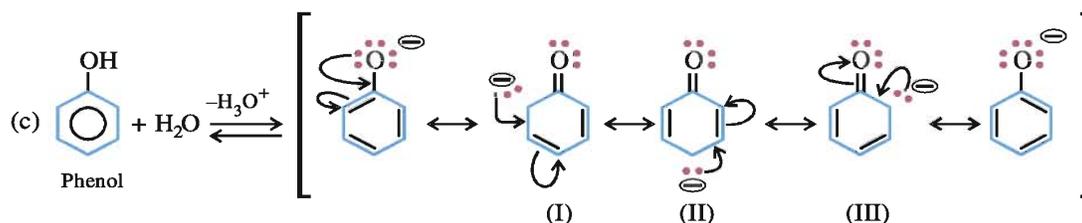
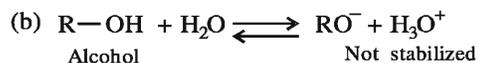
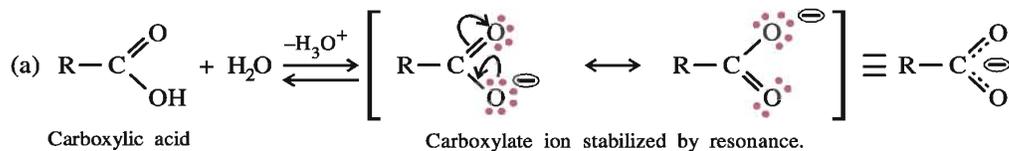
of comparable molecular mass. In liquid state, the carboxylic acid molecules are associated with other carboxylic acid by formation of strong hydrogen bonding. The hydrogen bonding is so strong that they are not broken even in vapour phase. **In vapour phase or in aprotic solvents most of the carboxylic acids exist as cyclic dimers.**



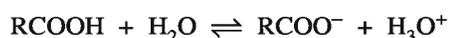
Carboxylic acids in aqueous solution form intermolecular hydrogen bond with water molecules, so the carboxylic acids with lower molecular masses are soluble in water.

5.11 Chemical Reactions of Carboxylic Acids

Acidic nature of carboxylic acid : Alcohols, phenols and carboxylic acids contain an $-OH$ group, but the carboxylic acids are much stronger acid than alcohols and phenols. Comparison of acidic character of alcohols, phenols and carboxylic acids are based on the stability of resonance structure of their negative ions.



As shown in reaction (a) carboxylate anions are stabilized by their resonance structures, so tendency to release proton is more, while the alkoxide ions as shown in reaction (b) are not stabilised by resonance, hence, alcohols have less tendency to release a proton, so the alcohols are much weaker acids than carboxylic acids, though both contain an -OH group. In case of phenoxide ion as shown in reaction (c) having resonating structure I to III, but the structures carry a negative charge on the less electronegative carbon atom. Therefore their contribution towards the resonance stabilization of phenoxide ion is very small, while in carboxylate ion the negative charge on the more electronegative oxygen atom, **so carboxylic acids are stronger acids than alcohols and phenols, but are weaker acids than the mineral acids** (HCl, HNO₃, H₂SO₄) and sulphonic acids. In aqueous solutions, the carboxylic acid ionizes and exist in dynamic equilibrium between carboxylate ion and hydronium ion.



$$\text{So the equilibrium constant can be expressed as } K_{\text{eq}} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]} \quad (5.1)$$

Since water is taken in large excess hence [H₂O] remains constant, so the equation (5.1) can be written as

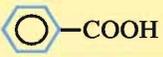
$$K_{\text{eq}} \times [\text{H}_2\text{O}] = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]} = K_{\text{a}} \quad (5.2)$$

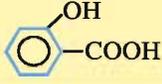
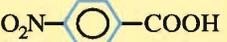
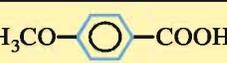
The equilibrium constant K_a is called the dissociation constant of the acid, and it varies with the temperature for a given acid. From equation (5.2) it is clear that at constant temperature, K_a is directly proportional to the [H₃O⁺]. Therefore the value K_a is a measure of the acid strength of an acid, so higher the value of **K_a, greater is the tendency of the acid to ionize and hence stronger is the acid**. For convenience, the strength of an acid is generally indicated by its pK_a value, rather than its K_a value

$$\text{pK}_{\text{a}} = -\log K_{\text{a}}$$

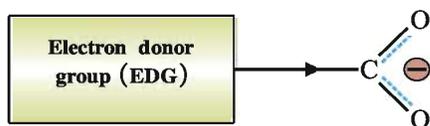
So, if carboxylic acid having smaller numerical value of pK_a, then it is very strong i.e. **better is a proton** donor. Strong acids have **pK_a values < 1**, the acids with pK_a values between **1 and 5** are considered to be moderately strong acids, weak acids have pK_a values between **5 and 15** and extremely weak acids have **pK_a values > 15**. K_a and pK_a values of some acids at 298 K temperature are given in table 5.6.

Table 5.6 K_a and pK_a values of some acids at 298 K (For information only)

Acid	K _a	pK _a	Acid	K _a	pK _a
HCOOH	17.7 × 10 ⁻⁵	3.75	ICH ₂ COOH	67 × 10 ⁻⁵	3.17
CH ₃ COOH	1.75 × 10 ⁻⁵	4.76	CH ₂ =CHCOOH	5.5 × 10 ⁻⁵	4.3
CH ₃ CH ₂ COOH	1.3 × 10 ⁻⁵	4.88		6.3 × 10 ⁻⁵	4.2
ClCH ₂ COOH	136 × 10 ⁻⁵	2.87	CH ₃ -  -COOH	4.2 × 10 ⁻⁵	4.38

Cl_2CHCOOH	5530×10^{-5}	1.26		105×10^{-5}	2.98
Cl_3CCOOH	23200×10^{-5}	0.64		36×10^{-5}	3.44
FCH_2COOH	260×10^{-5}	2.59		3×10^{-5}	4.48
BrCH_2COOH	125×10^{-5}	2.90			

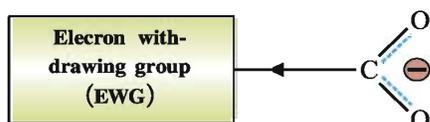
The acid strength of carboxylic acid depends on the effect of various substituents. For example,



(i) Effect of electron donating groups (EDG) :

The alkyl group has electron donating inductive effect (+I effect), hence it will increase the electron density in the -OH bond, so **release of H^+ ions** will be more difficult, hence, the formic acid is stronger acid than acetic acid. Further the +I effect of the alkyl groups increases in the order

$\text{CH}_3- < \text{CH}_3\text{CH}_2- < (\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}-$ Hence the relative strength of carboxylic acid will be as **$\text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C-COOH}$**



(ii) Effect of electron withdrawing group (EWG) :

Electron withdrawing group having -I effect, and it decreases in the order $-\text{F} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{Ph}$. So the strength of the carboxylic acids will be as.

$\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

Further, greater the number of electron withdrawing groups (substituents), stronger will be the acid (strength).

$\text{Cl}_3\text{C COOH} > \text{Cl}_2\text{CH COOH} > \text{Cl CH}_2\text{COOH}$

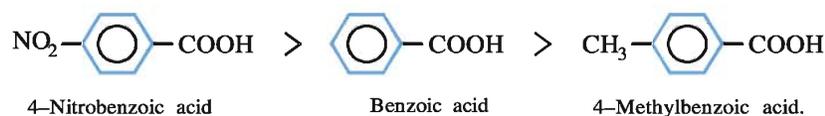
The inductive effect decreases rapidly with distance, so acidic strength order is



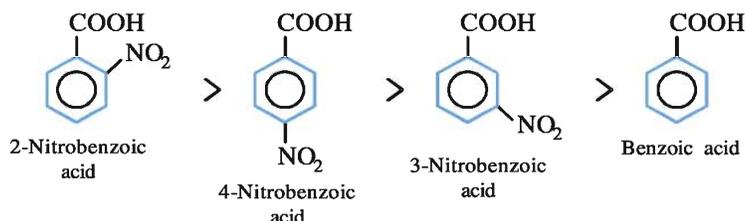
(iii) The phenyl or vinyl group directly attached to carboxyl group have weaker electron donating effect than alkyl group. So unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids, but formic acid does not contain any alkyl group, therefore it is stronger acid than unsubstituted aromatic acid, so the order of acidic strength is

Formic acid > Benzoic acid > Acetic acid.

For substituted aromatic carboxylic acid the presence of electron withdrawing group on the phenyl or aromatic carboxylic acid increases their acidic strength, while electron donating group, decreases their acidic strength. For example,

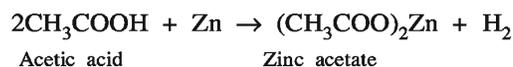
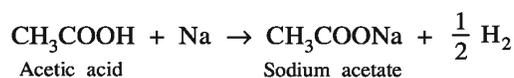


Electron withdrawing or electron donating group effect is more pronounced at 1,2 position (ortho position) than 1,4 position (para position) than 1,3 position (meta position). For example the acid strength is

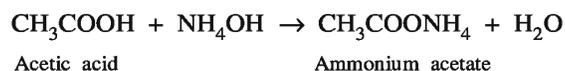
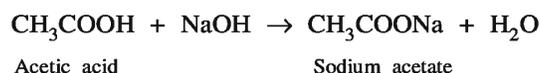


(1) Reactions involving cleavage of O–H bond : The reactions showing the acidic character of the carboxylic acids i.e. cleavage of O–H bond are given below :

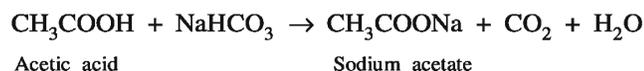
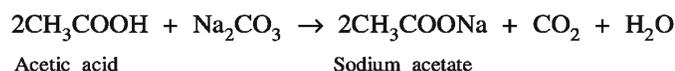
(i) Reaction with metal : Carboxylic acids like alcohols react with electropositive metals such as Na, K, Ca, Mg, Zn etc. to form their respective salts and liberate H_2 gas. For example,



(ii) Reaction with alkalis : Similar to phenols the carboxylic acids neutralize alkalis and form salts. For example,



(iii) Reaction with carbonates and hydrogen carbonates : However unlike phenols the carboxylic acids react with weaker bases such as carbonates and hydrogen carbonates to evolve CO_2 gas. For example,



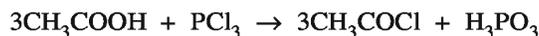
This reaction is used to detect the presence of $-\text{COOH}$ group in organic compounds. As most of the phenols do not produce CO_2 gas with NaHCO_3 . Hence this reaction is **also useful to distinguish phenols from carboxylic acids.**

(2) Reaction involving cleavage of C–OH bond : The hydroxyl group of a carboxylic acid like the hydroxyl group in alcohols, can be replaced (substituted) by group like $-\text{Cl}$, $-\text{OR}'$, $-\text{NH}_2$ and $-\text{OCOR}'$ to form acid chloride, esters, amides, and anhydrides, respectively. These derivatives are known as functional group derivatives of carboxylic acids.

(i) Formation of acid chlorides : Carboxylic acid reacts with SOCl_2 (thionyl chloride) or PCl_5 or PCl_3 to form acid chloride. For example,



Acetic acid Ethanoyl chloride
(Acetyl chloride)



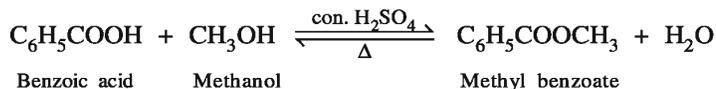
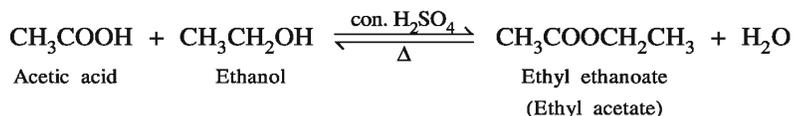
Acetic acid Ethanoyl chloride
(Acetyl chloride)



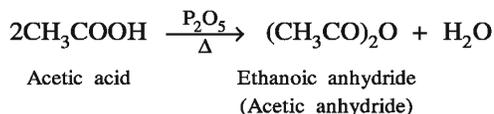
Acetic acid Ethanoyl chloride
(Acetyl chloride)

For the production of acid chloride, the reaction with SOCl_2 is preferred, because in this reaction the other two products SO_2 and HCl both are in gaseous state, so it is very easy to remove them from acid chloride, **hence purification of acid chloride becomes very easy.**

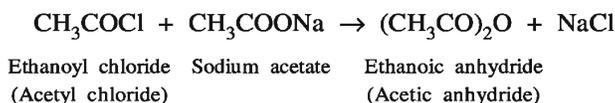
(ii) Formation of esters : When carboxylic acids are heated with alcohols or phenols in presence of con. H_2SO_4 or HCl , esters are formed. The reactions are known as esterifications (**Fischer-Speier esterification**). This reaction is reversible and hence the rate of reaction can be increased by taking excess amount of carboxylic acid or alcohol or by removing water from the reaction mixture.



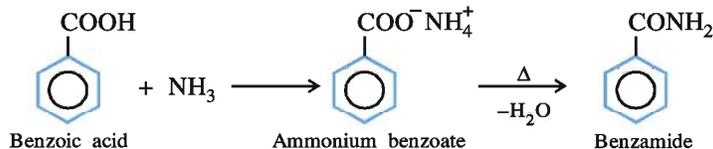
(iii) Formation of anhydrides : Two molecules of carboxylic acids combine in presence of strong dehydrating agent such as P_2O_5 or mineral acid, such as con. H_2SO_4 , on heating gives acid anhydrides. For example,

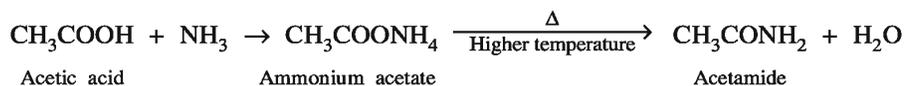
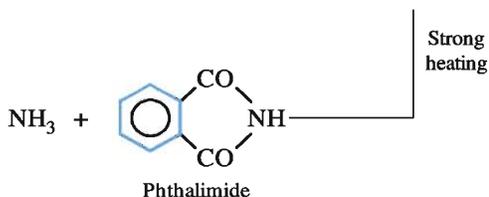


By treating acid chlorides with sodium salts of carboxylic acids, the acid anhydrides are obtained.



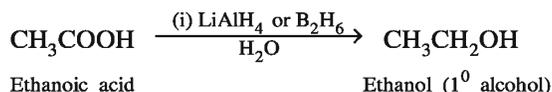
(iv) Formation of Amides : Carboxylic acids react with NH_3 to give ammonium salts, which on further heating at high temperature, lose a molecule of water to form amide. For example,





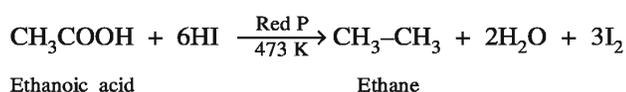
(3) Reactions involving -COOH group as a whole :

(i) Reduction : The reduction of carboxylic acids with Lithium Aluminium hydride (LiAlH_4) or better with diborane (B_2H_6) gives **primary alcohol**. Using this reaction the $-\text{CO}-$ group can be reduced to $-\text{CH}_2-$ group. For example,

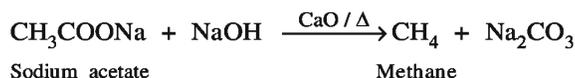


Diborane does not easily reduce functional groups like ester, nitro, halo etc., and sodium borohydride does not reduce the carboxyl group.

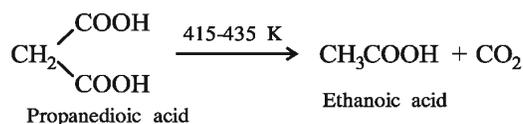
Carboxylic acid on reduction with hydroiodic acid and red phosphorus at 473 K give alkanes. In this reaction the $-\text{COOH}$ group is reduced to $-\text{CH}_3$ group.



(ii) Decarboxylation : Carboxylic acids and their salts lose carbon dioxide to form hydrocarbon and reaction is known as **decarboxylation reaction**. The sodium salts of carboxylic acid are heated with sodalime (NaOH and CaO mixture in the proportion ratio of 3:1) give alkane. e.g.,



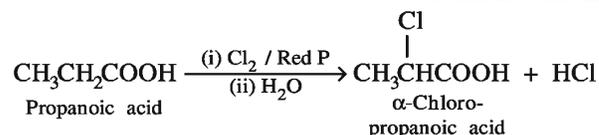
If two carboxylic groups are attached to the same carbon atom called gem-dicarboxylic acid undergo decarboxylation simply on heating at 415-435 K temperature. For example,



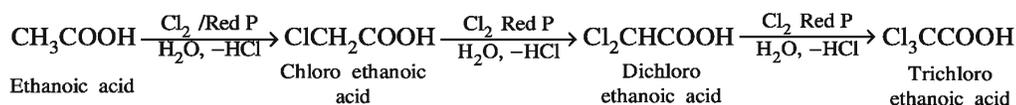
On electrolysis of aqueous solution of sodium or potassium salts of fatty acids at anode due to oxidation, CO_2 is liberated and alkane having double carbon is obtained. At cathode H_2 gas liberated and this process is called **Kolbe's electrolytic reduction or electrolytic decarboxylation**.

(4) Substitution reactions in the hydrocarbon part of carboxylic acids :

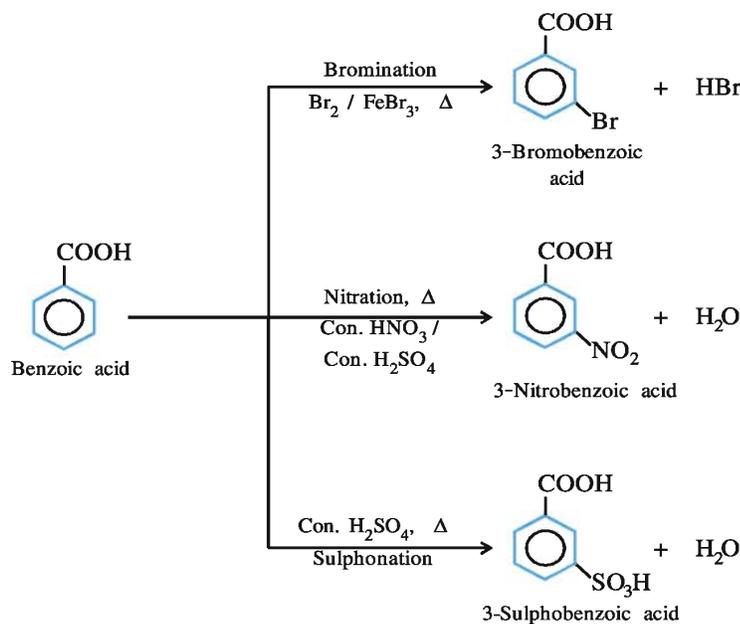
(i) **Halogenation** : Carboxylic acid having an α -hydrogen atoms are halogenated at the α -position on treatment with dichlorine or dibromine in the presence of small amount of red phosphorus to give α -halocarboxylic acid. This reaction is known as **Hell-Volhard-Zelinsky reaction**. For example,



If more than one mole of Cl_2 or Br_2 are used then the 2nd and 3rd α -hydrogen atoms are successively substituted. For example,



(ii) **Ring substitution** : Aromatic carboxylic acids undergo the electrophilic substitution reactions like halogenation, nitration and sulphonation. Since the $-\text{COOH}$ group acts as a deactivating and hence **m-directing group, so the reactions take place only under vigorous conditions**. The $-\text{COOH}$ group deactivates the benzene ring and catalyst aluminium chloride (Lewis acid) gets bonded to the carbonyl group. So they do not undergo Friedel-Crafts reactions.



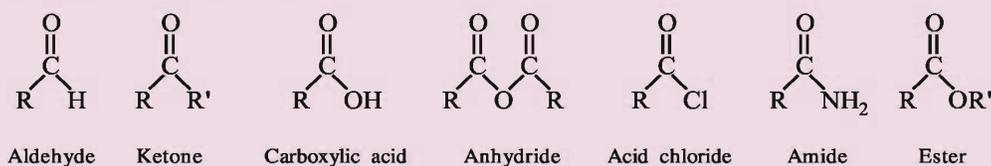
5.12 Uses of Carboxylic Acids

Methanoic acid is used in leather industry, rubber industry, in medicine, in dyeing and electroplating industry, Ethanoic acid is used as coagulant for latex, manufacturing of plastic, rayon and silk. It is also used as a solvent in laboratory and as vinegar in the manufacturing of pickles in food industry. Hexanedioic acid is used in manufacturing of nylon 6,6. Benzoic acid is used in medicine as urinary antiseptic and for making aniline blue in dye industry, and sodium benzoate as food preservatives. Higher

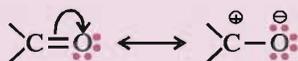
fatty acids are used for manufacturing of soaps and detergents. Benzene-1,2-dicarboxylic acid is used in the manufacturing of resins and benzene-1,4-dicarboxylic acid is used in manufacturing of polyesters.

SUMMARY

Organic compounds containing carbon-oxygen double bond (>C=O) are called carbonyl group or carboxyl group compounds. In aldehydes, the carbonyl group is attached to one hydrogen atom and one alkyl (or aryl or hydrogen atom) group, while in ketones it is attached to one alkyl and one aryl group or to two alkyl (or aryl) groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as carboxylic acids. In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group the compounds are known as esters, but if it is substituted by acyl group, the compounds are known as acid anhydrides. If the carbonyl group is attached to chlorine and to amino group the compounds are known as acid chlorides and amides respectively. The general formula of these compounds are expressed as



- Aldehydes and ketones have same general molecular formula $\text{C}_n\text{H}_{2n}\text{O}$ but different functional groups like aldehydes and ketones. Therefore they are called functional groups isomers. e.g., $\text{C}_3\text{H}_6\text{O}$ can be $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3 i.e. aldehyde and ketone respectively.
- Carbonyl carbon atom is sp^2 hybridised and form three σ bonds and one π bond. All the three σ -bonds lie in same plane having angle 120° . The π -bond lies both above and below the C-O σ bond. Thus the carbonyl carbon and oxygen atoms are directly bonded to the carbonyl carbon which lie in one plane, and is confirmed by electron diffraction and spectroscopic studies.
- Due to higher electronegativity of oxygen atom relative to carbon atom the carbonyl group is polarized and carbonyl carbon becomes electrophile (Lewis acid) and oxygen becomes nucleophile (Lewis base). Carbonyl group is polar in nature and has dipole moments. Aldehydes and ketones have dipole moments 2.3-2.8 D. The resonance structures are as shown below :



- The common names of aldehydes are obtained by replacing the terminal '-ic acid' by 'aldehyde' from the common name of the corresponding carboxylic acid.
- Formic acid, acetic acid and benzoic acid the corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively.
- In the substituted aldehydes, the positions of the substituents are indicated by Greek alphabets α , β , γ , δ etc. with the carbon atom next to the $-\text{CHO}$ group designated as α

- The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet 'e' from its name by '-al' like methanal, ethanal etc.
- The position of substituents are indicated by numbers. The numbering of the substituents are done in such a way that the aldehyde group at the end of the chain gets number 1.
- Names of aliphatic cyclic aldehydes are given by adding suffix carbaldehyde after the full name of the cycloalkane.
- Name of aromatic aldehydes are given as benzene carbaldehyde (or benzaldehyde) and the position is indicated by numbering starting from the carbon having -CHO group.
- More than two -CHO groups are named as derivatives of the hydrocarbon which do not include the carbon atoms of the functional group.
- The common and IUPAC names of aldehydes are given in table 5.1 in the unit.
- The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl group (in the alphabetical order) attached to the ketone group as two separate words and adding suffix ketone.
- If both attaching groups are same the prefix di is used.
- The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet-'e' by the suffix '-one'.
- For substituted ketone the positions of the substituents are indicated by numbering the chain in such a way that the ketone group gets the lowest number.
- The common and IUPAC names of the ketones are given in table 5.2.
- The polar carbonyl groups have dipole-dipole interaction between opposite ends of the >C=O group dipoles and hence due to weak intermolecular attraction the melting points and boiling points of aldehydes and ketones are higher than corresponding non-polar compounds.
- The order of boiling points is carboxylic acid $>$ alcohol $>$ isomeric ketone $>$ isomeric aldehyde $>$ ether $>$ hydrocarbon.
- Due to hydrogen bonding with water molecules the aldehydes and ketones upto three carbon are soluble in water.
- The aromatic aldehydes and ketones due to presence of larger hydrocarbon parts (like benzene ring etc.), are insoluble in water.
- All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohols, chloroform etc.

- Due to presence of hydrogen atom, the carbonyl group of aldehyde is much more reactive than ketone.
- Aldehydes and ketones undergo nucleophilic addition reaction because the carbonyl carbon atom is slightly positively charged.
- In nucleophilic addition reaction the first step is reversible and also slow, so it a rate determining step. The second step is reversible.
- Due to steric effect and inductive effect the aldehydes are more reactive than ketones.
- Most of the aldehydes and aliphatic methyl ketones, due to less steric hindrance are more reactive.
- Aldehydes and ketones react with NaHSO_3 and give bisulphite addition product which are usually crystalline solids. On hydrolysis they give original aldehydes and ketones, so this reaction is useful for separation and purification of aldehydes and ketones.
- Addition of HCN and Grignard reagent to the aldehyde and ketone which give α -hydroxy carboxylic acid and 1° , 2° , 3° alcohols respectively.
- Addition of alcohol to aldehyde give hemiacetal and further acetal, while ketone give the same product.
- Nucleophilic addition reaction of aldehydes and ketones with NH_3 and its derivatives ($\text{H}_2\text{N-Z}$) and reaction catalysed by acids.
- Aldehydes and ketones on reduction give 1° and 2° alcohols respectively.
- Aldehydes and ketones can be reduced to hydrocarbon by using different reactions like Wolff-Kishner reduction, Clemmensen reduction and reagents like red phosphorus and HI and reduction with magnesium amalgam and water give the product-hydrocarbon.
- Oxidation of aldehydes : Tollens' test, Fehling's test and Benedict's test give the product carboxylic acid. Fehling's test and Benedict's test are not given by aromatic aldehydes.
- Oxidation of ketones by strong oxidizing agents like con. HNO_3 , $\text{KMnO}_4 / \text{H}_2\text{SO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ give mixture of carboxylic acids.
- Oxidation of aldehydes and ketones containing CH_3CO -group give iodoform test.
- Aldol condensation and cross aldol condensation are the reactions given by aldehydes and ketones having α -hydrogen atom or atoms using dilute alkali as catalyst.
- Cannizzaro reaction is given by aldehydes and ketones which do not have an α -hydrogen atom by using con. NaOH or 50 % NaOH .
- Electrophilic substitution reactions of aromatic aldehydes and ketones are nitration, sulphonation and halogenation.
- Aldehydes and ketones are used in different fields.

- The carboxylic acids contain -COOH group, contain carbonyl and hydroxyl group so by combining the 'carb' and 'oxyl', the -COOH is called carboxyl group.
- The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (plant or animal products) from which they were first isolated.
- The IUPAC names of monocarboxylic acids are given by replacing the ending alphabet 'e' in the name of corresponding hydrocarbon with suffix “-ioc acid.”
- For naming substituted and branched acids, the longest chain having carboxylic acid group is selected and number one is assigned to carboxylic carbon; then the successive number are assigned to carbon of the chain and the substitution is expressed.
- The IUPAC names of aromatic monocarboxylic acids are derived from benzene carboxylic acid (Benzoic acid) and the position of the substituents are indicated by number with carbon atom carrying -COOH group being number one.
- In aliphatic dicarboxylic acids, the position of -COOH group is not indicated, but in aromatic dicarboxylic acid and other (tri, tetra...poly) carboxylic acid, it is indicated by number before the multiplicative prefix and the ending '-e' of the hydrocarbon is retained.
- The common and IUPAC names of some carboxylic acids are given in table 5.5.
- The -COOH group is represented as a resonance hybrid of the three resonating structures.
- **Carboxylic acids are prepared from :**
 - Primary alcohol and aldehyde
 - Alkyl benzene and alkenes
 - Nitriles and amides.
 - Grignard reagents
 - Acid (chloride) halide and anhydrides
 - Esters
- Carboxylic acid in aqueous solution form intermolecular hydrogen bonding with water molecules.
- Carboxylic acids are cyclic dimer in vapour phase or in aprotic solvents.
- Carboxylic acids are stronger acids than phenol and alcohols.
- For convenience the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

$$\text{pK}_a = -\log \text{K}_a$$
- The acidic strength of carboxylic acids depends on the effect of various substituents like

- effect of electron-donating group
- effect of electron withdrawing group
- attachment of phenyl or vinyl group directly to carbonyl group.
- The reactions of carboxylic acid are
 - Reactions involving cleavage of O–H bond.
 - Reactions involving cleavage of C–OH bond
 - Reaction involving –COOH group
- Substitution reaction in hydrocarbon part of carboxylic acid are halogenation and ring substitution as bromination, nitration and sulphonation.
- Carboxylic acids are used in different fields.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) Which of the following compounds has highest boiling point ?
(A) propanoic acid (B) propanol (C) propanone (D) propanal
- (2) Which of the following compounds has highest solubility in water ?
(A) pentanone (B) butanone (C) formaldehyde (D) propanone
- (3) Which of the following compounds has highest reactivity in nucleophilic addition reaction ?
(A) propanone (B) methanal (C) ethanal (D) butanone
- (4) Propanone + $\text{NH}_2\text{NH}_2 + \text{KOH} \xrightarrow[\Delta]{\text{Ethylene glycol}}$?
(A) propanal (B) propanol (C) propene (D) propane
- (5) Ethanol + $\text{KMnO}_4 \rightarrow ?$
(A) ethanal (B) ethanoic acid
(C) ethane (D) potassium ethanoate
- (6) tert-butyl benzene $\xrightarrow[\text{(ii) dil. H}_2\text{SO}_4]{\text{(i) KMnO}_4 / \text{KOH, } \Delta}$?
(A) tert-butyl benzoic acid (B) benzoic acid
(C) tert-butanol (D) No reaction.
- (7) But-2-ene $\xrightarrow[\text{(ii) dil H}_2\text{SO}_4]{\text{(i) KMnO}_4 / \text{KOH, } \Delta}$?
(A) butanoic acid (B) ethanoic acid (C) butanol (D) ethanol

- (8) Ethane nitrile $\xrightarrow[\Delta]{[H^+] \text{ or } [OH^-]}$?
 (A) ethanol (B) ethanal (C) ethanoic acid (D) ethene
- (9) Ethylbenzoate + NaOH \rightarrow ?
 (A) benzoic acid (B) benzene
 (C) benzaldehyde (D) potassium benzoate
- (10) Which of the following acids has highest relative acid strength ?
 (A) acetic acid (B) propanoic acid
 (C) isopropanoic acid (D) benzoic acid.
- (11) Acetyl chloride + sodium acetate $\xrightarrow{\Delta}$?
 (A) ethyl acetate (B) ethyl chloride
 (C) acetic anhydride (D) ethanol
- (12) Sodium acetate + Sodalime $\xrightarrow{\Delta}$?
 (A) acetic acid (B) ethane (C) methane (D) ethanal
- (13) Propanoic acid $\xrightarrow[H_2O]{Cl_2 / \text{Red P}}$?
 (A) propanal (B) propanol
 (C) propane (D) α -chloro propanoic acid.
- (14) Which substance is used in leather industry ?
 (A) methanoic acid (B) ethanoic acid (C) benzoic acid (D) pentanoic acid.
- (15) Which substance is used in medicine as urinary antiseptic ?
 (A) benzoic acid (B) acetic acid (C) methanoic acid (D) formic acid

2. Write the answers of the following questions in brief :

- (1) Draw general structural formula of anhydride.
- (2) Draw resonance structure of carbonyl group.
- (3) Indicate hydrogen bonding between aldehyde and the water molecules.
- (4) Write equation for reduction of methanal with $LiAlH_4$.
- (5) Write the equation for Wolff-Kishner reduction of ketone.
- (6) Write uses of formaldehyde.
- (7) Write uses of acetaldehyde.
- (8) Write uses of acetone.

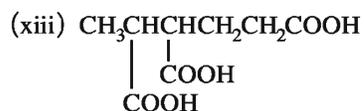
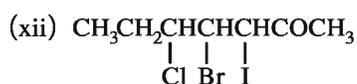
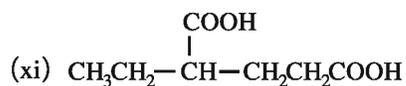
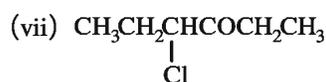
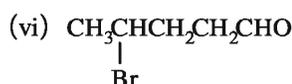
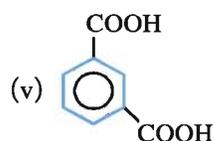
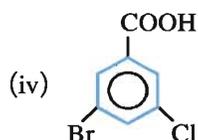
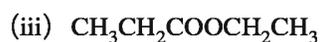
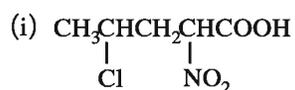
- (9) Draw resonance structures of carboxylate ion.
- (10) Write equation for hydrolysis of ethyl acetate.
- (11) Write the reaction of formation of pinacol.
- (12) Draw structure of association of carboxylic acid in liquid state.
- (13) Draw dimer form of carboxylic acid in vapour state or in aprotic solvent.
- (14) Draw hydrogen bonding between carboxylic acid and water molecules.
- (15) Draw resonance structure of phenoxide ions.
- (16) Explain pK_a in short. What does it indicate ?
- (17) Write equation for reaction of acetic acid with Na_2CO_3 .
- (18) Write equation for acetic acid with $SOCl_2$.
- (19) Write equation for heating acetic acid with P_2O_5 .
- (20) Write equation of nitration of benzoic acid.
- (21) Write uses of methanoic acid.
- (22) Write uses of benzoic acid.
- (23) Write uses of ethanoic acid.
- (24) Write uses of fatty acids ?
- (25) Write equation of halogenation of propanoic acid.

3. Write answers of the following questions :

- (1) Explain nature of carbonyl group.
- (2) Explain addition of $NaHSO_3$ to aldehyde and ketone.
- (3) Explain addition of HCN to aldehyde and ketone.
- (4) Explain acetal formation.
- (5) Explain ketal formation.
- (6) Explain reduction of aldehyde.
- (7) Explain Wolff-Kishner reduction.
- (8) Explain Clemensen reduction.
- (9) Explain Tollens' test.
- (10) Explain Fehling's test.
- (11) Explain Benedict's test.

- (12) Explain Cannizzaro reaction.
- (13) Explain preparation of carboxylic acid from 1^o alcohol.
- (14) Explain acidic nature of carboxylic acid.
- (15) Explain reduction of acetic acid.
- (16) Explain decarboxylation
- (17) Explain halogenation of acetic acid.
- (18) Explain ring substitution in benzoic acid.

(19) Give IUPAC names :



4. Write the answers of the following questions in detail :

- (1) Explain the nucleophilic addition reactions of aldehydes and ketones.
- (2) Explain the relative reactivity of aldehydes and ketones.

- (3) Explain nucleophilic addition reactions followed by elimination of a molecule of water for aldehydes and ketones.
- (4) Explain reduction of aldehydes.
- (5) Explain oxidation of aldehydes.
- (6) Explain oxidation of ketones.
- (7) Explain aldol and cross aldol condensation.
- (8) Explain electrophilic substitution reactions of aromatic aldehyde and ketones.
- (9) Give the different methods of preparation of carboxylic acid.
- (10) Explain the factors that affect the acidic strength of carboxylic acids.
- (11) Explain reaction involving cleavage of C–OH bond in carboxylic acid.
- (12) Explain reaction involving cleavage of O–H bond in carboxylic acid.
- (13) Explain reaction involving of –COOH (as a whole) in carboxylic acid.

