

4 CHAPTER



CARBOXYLIC ACIDS AND DERIVATIVES

- * Carboxylic Acids
- * Preparation, Properties and Uses
- * Derivatives of Carboxylic Acids

CARBOXYLIC ACIDS

4.1.1

Introduction

Higher members of aliphatic carboxylic acids ($C_{12}-C_{18}$) are called fatty acids



IUPAC name of aliphatic acid is alkanoic acid



Carbon compounds which possess a carboxyl functional group, $\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{matrix}$ are called carboxylic acids. Higher members ($C_{12}-C_{18}$) of aliphatic monocarboxylic acids occur in fats as esters of glycerol. Hence they are called fatty acids. The general formula of aliphatic carboxylic acids is $C_nH_{2n}O_2$ and represented by $RCOOH$.

The common names of acids are derived from the source of that particular acid. $HCOOH$ is named as formic acid as it is obtained from red ants (formica means red ant). CH_3COOH is named as acetic acid as it is present in vinegar (acetum means vinegar). $CH_3CH_2CH_2COOH$ is butyric acid as it is present in rancid butter hence the name. $CH_3(CH_2)_3COOH$, valeric acid is present in the root of valerian plant.

In one common system, the acids except formic acid are named as derivatives of acetic acid.

eg : CH_3CH_2COOH is methyl acetic acid,

$(CH_3)_3C-COOH$ is trimethyl acetic acid, etc.

In IUPAC system the secondary suffix -oic acid is included after an appropriate root word and primary suffix. Systematic name of a saturated carboxylic acid is alkanoic acid. The names are listed in Table 4.1 and Table 4.2.

Table 4.1 Aliphatic carboxylic acids

Formula	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$HOOC-COOH$	Oxalic acid	Ethandioic acid
$HOOC-CH_2-COOH$	Malonic acid	Propandioic acid
$HOOC(CH_2)_2COOH$	Succinic acid	Butandioic acid
$HOOC(CH_2)_3COOH$	Glutaric acid	Pentandioic acid
$HOOC(CH_2)_4COOH$	Adipic acid	Hexandioic acid

Table 4.2 Aromatic carboxylic acids

Benzoic acid is named as Benzenecarboxylic acid

Formula	Common name	IUPAC name
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	ortho-Toluic acid	2-Methylbenzenecarboxylic acid
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1,2-dicarboxylic acid

Esters are functional isomers of carboxylic acids

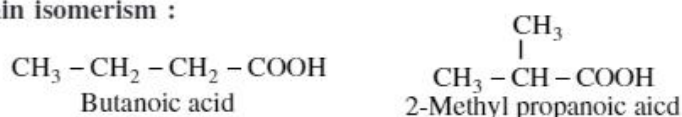
$\begin{matrix} \delta & \gamma & \beta & \alpha \\ \text{CH}_3 & -\text{CH}- & \text{CH}- & \text{CH}_2\text{COOH} \\ 5 & 4 & 3 & 2 \\ & \text{CH}_3 & \text{Cl} & \end{matrix}$ is chlorinated isovaleric acid. It is called β -chloro- γ -methyl valeric acid. Its IUPAC name is 3-chloro-4-methylpentanoic acid.

Some other familiar carboxylic acids are :

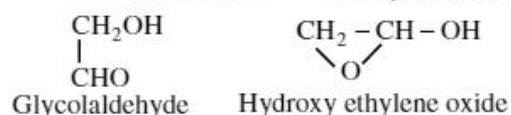
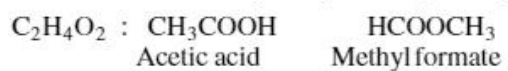
Valeric acid ($\text{C}_4\text{H}_9\text{COOH}$); Caproic acid ($\text{C}_5\text{H}_{11}\text{COOH}$); Caprylic acid ($\text{C}_7\text{H}_{15}\text{COOH}$); Capric acid ($\text{C}_9\text{H}_{19}\text{COOH}$); Lauric acid ($\text{C}_{11}\text{H}_{23}\text{COOH}$); Acrylic acid ($\text{CH}_2=\text{CHCOOH}$); Malic acid ($\text{HOOCCH}(\text{OH})\text{CH}_2\text{COOH}$); Crotonic acid ($\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$); Lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$); Pyruvic acid ($\text{CH}_3\text{COCOCH}_3$) and Anthranilic acid ().

Isomerism : Monocarboxylic acids show chain and functional isomerism. They do not exhibit nutamerism.

Chain isomerism :

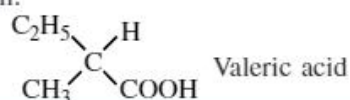


Functional isomerism : Monocarboxylic acids show functional isomerism with the esters of the acids, hydroxy carbonyl compounds and hydroxy oxiranes.



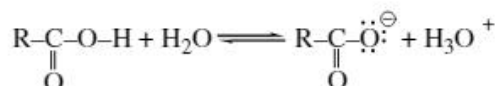
These four are stable, so many other isomers are unstable.

Monocarboxylic acids having at least one chiral carbon atom exhibits optical isomersim.



Acidic nature

Carboxylic acids ionise in water and release H^+ forming a carboxylate ion which is its conjugate base. Proton is accepted by water in aqueous solutions of acid.



It is a reversible reaction and equilibrium is established. The carboxylate anion,



Applying law of mass action, the equilibrium constant is given as,

$$K_{eq} = \frac{[RCOO^{\ominus}][H_3O^+]}{[RCOOH][H_2O]}$$

As water is in large excess and its concentration does not change much, the equilibrium constant is written as,

$$K_a = \frac{[RCOO^{\ominus}][H_3O^+]}{[RCOOH]}$$

K_a is acid dissociation constant. As the value of K_a increases, the strength of the acid also increases. K_a values of some acids are listed in Table 4.3.

Table 4.3 Dissociation constant (K_a) values of some carboxylic acids

Acid	K_a value	Acid	K_a value
HCOOH	1.77×10^{-4}	NCCH ₂ COOH	3.65×10^{-3}
CH ₃ COOH	1.76×10^{-5}	FCH ₂ COOH	2.57×10^{-3}
CH ₃ CH ₂ COOH	1.60×10^{-5}	ClCH ₂ COOH	1.36×10^{-3}
(CH ₃) ₂ CHCOOH	1.38×10^{-5}	Cl ₂ CHCOOH	5.33×10^{-2}
(CH ₃) ₃ CCOOH	8.91×10^{-6}	Cl ₃ CCOOH	2.32×10^{-1}
C ₆ H ₅ COOH	6.35×10^{-5}	HOOC-COOH	5.4×10^{-2}
$\begin{array}{c} \text{COOH} \\ \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \\ \text{COOH} \end{array}$	4.21×10^{-5}	$\begin{array}{c} \text{COOH} \\ \diagup \\ \text{CH}_2 \\ \diagdown \\ \text{COOH} \end{array}$	1.7×10^{-3}

Acidic strength increases with an increase in K_a value

Trifluoroacetic acid is the strongest carboxylic acid

The negative logarithm of K_a is denoted as pK_a ; $pK_a = -\log K_a$.

As the value of pK_a decreases, strength of acid increases. So strength of a carboxylic acid increases with increase in K_a and decreases with increase in pK_a . The pK_a of HCl is -7 and of strongest carboxylic acid, CF_3COOH is 0.23 .

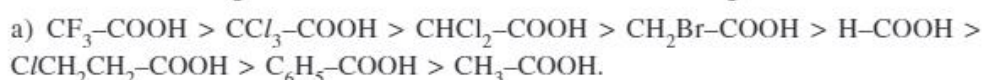
Effect of substituents on the strength of acids : The strength of an acid depends on the stability of its conjugate base $RCOO^{\ominus}$. Greater the stability of the conjugate base, stronger is the acid. Stability of the conjugate base depends on spreading of charge. Greater the charge spreading, more is the stability of the conjugate base. Correspondingly the parent acid becomes stronger acid.

Charge spreading can take place by resonance or inductive effect

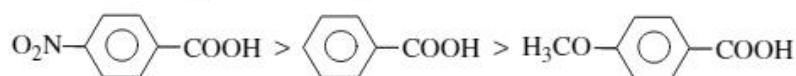
Charge spreading can take place by resonance or inductive effect. Groups with $-I$ or $-M$ effects increase the strength of an acid and $+I$ or $+M$ effects decrease the acidic strength.

Presence of electron withdrawing groups increases the strength of the acid and electron releasing groups decreases the strength of the acid.

The acidic strength of some of the acids is in the following order :



b) The $-\text{NO}_2$ group increases strength by exerting $-M$ and $-I$ effects. The $-\text{OCH}_3$ group decreases strength by exerting $+M$ effect.



c) The sp and sp^2 carbon atoms are more electronegative and they increase the acidic strength by $-I$ effect.



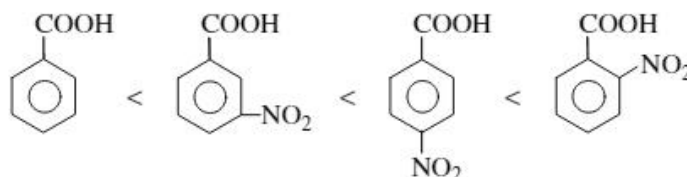
d) Acidic strength due to $-I$ effect depends on positions : $\alpha- > \beta- > \gamma-$.



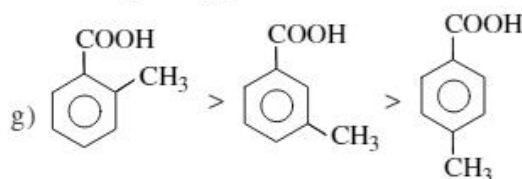
e) Acidic strength due to $-I$ effect also depends on the nature of the group.



f) $-M$ effect is more pronounced at ortho and para positions.



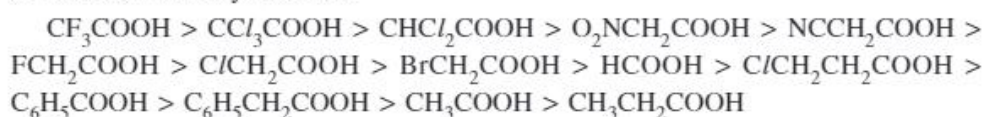
The ortho-substituted isomer of every substituted benzoic acid (whether the substituent is electron releasing or electron withdrawing) is relatively stronger than the corresponding para and meta isomer. This is called **ortho effect**.



The effect of the following groups in increasing acidity order is :



Based on the pK_a values, the following is the decreasing order of acidic nature of different carboxylic acids :



Benzoic acid with substituent at ortho position is stronger

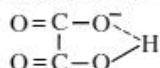
P.4.1 Attachment of vinyl group or phenyl group directly to carboxylic acid group has effect on the acidic character of that carboxylic acid. Explain.

Solution Direct attachment of phenyl group or vinyl group to carboxylic acid increases the acidic character due to greater electronegativity of sp^2 carbon and also due to resonance.



P.4.2 Why oxalic acid is a stronger acid than acetic acid?

Solution The mono oxalate ion is stabilised by intramolecular hydrogen bonding and becomes a weak base. So oxalic acid is a stronger acid than acetic acid. Mono oxalate ion has also chelation.

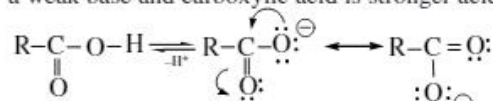


P.4.3 Why benzoic acid is a stronger acid than acetic acid?

Solution The $-\text{COOH}$ group in benzoic acid is connected to sp^2 hybridised carbon of the benzene ring which is more electronegative than sp^3 carbon of $-\text{CH}_3$ to which $-\text{COOH}$ is connected in acetic acid. Hence benzoic acid is stronger acid.

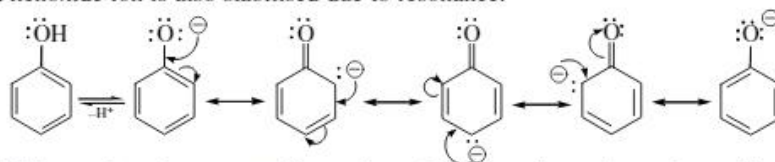
P.4.4 Explain why carboxylic acids are stronger acids than phenols?

Solution Carboxylate ion is more stable due to symmetrical resonating structures. So carboxylate ion is a weak base and carboxylic acid is stronger acid.



Correspondingly the acid becomes a strong acid. $\text{C}(=\text{O})-\text{O}^- \longleftrightarrow \text{C}(\text{O}^-)=\text{O}$

Phenoxide ion is also stabilised due to resonance.



With negative charge spreading to less electronegative carbon, phenoxide ion is less stable than carboxylate ion.

P.4.5 Chloroacetic acid is stronger acid than acetic acid. Explain.

Solution Carbon atom of $-\text{CH}_2\text{Cl}$ group acquires partial positive charge which spreads to oxygen of chloroacetate ion, when H^+ is released.

So the negative charge of this oxygen is stabilised and anion becomes a weak base.

EXERCISE - 4.1.1

1. Write examples and names of carboxylic acids.
2. Write on the dissociation equilibrium of carboxylic acids.
3. Carboxylic acids are weak organic acids. Discuss the relative acidic strength of carboxylic acids based on K_a values.
4. Draw the structures of Hex-2-en-4-ynoic acid and 3-chloro-4-phenylpentanoic acid.
5. Write IUPAC names of $\text{CH}_3\text{COCH}_2\text{COCH}_3$ and $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$.

PREPARATION, PROPERTIES AND USES

4.2.1

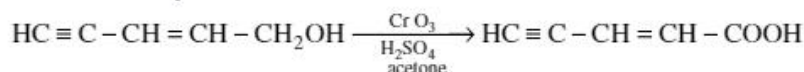
Preparation

*Oxidation of
primary alcohols
or aldehydes gives
carboxylic acids*

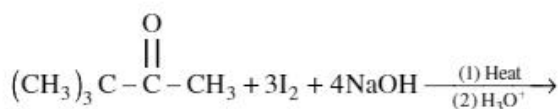
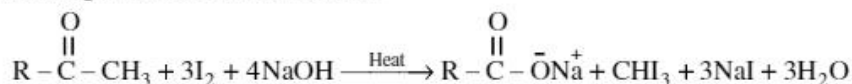
(i) **From primary alcohols and aldehydes :** Carboxylic acids are prepared by the oxidation of primary alcohols or aldehydes, using acidic, alkaline or neutral potassium permanganate or potassium dichromate and chromium trioxide in acidic media.



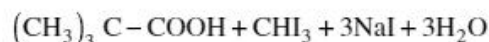
Aldehydes can be oxidised to corresponding carboxylic acids even with mild oxidants like ammoniacal silver nitrate solution (Tollens reagent). This reagent does not affect carbon-carbon double bond and triple bond. Even CrO_3 , H_2SO_4 in acetone or MnO_2 in acetone does not affect double or triple bond but can oxidise unsaturated alcohols to carboxylic acids.



Oxidation of methyl ketones : Methyl ketones can be converted to carboxylic acids through the haloform reaction.



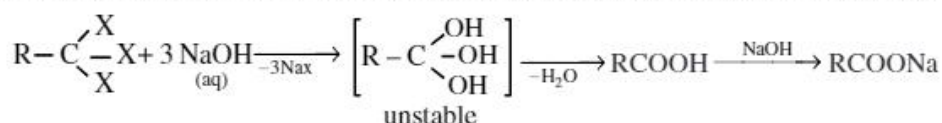
t-Butyl methyl ketone



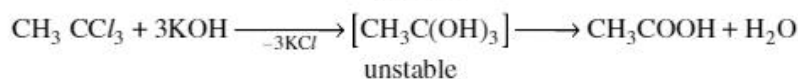
Trimethyl acetic acid
(pivalic acid)

*Hydrolysis of
1,1,1-trihalides
yields salts of
carboxylic acids*

Hydrolysis of 1,1,1-trihalides : Hydrolysis of 1,1,1-trihalides with aqueous alkali yields carboxylate salts which give carboxylic acids with dilute mineral acids.

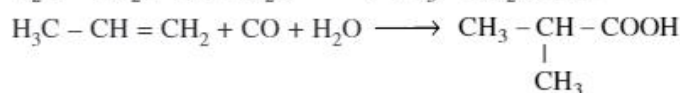
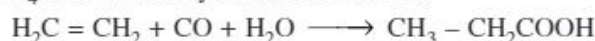


unstable



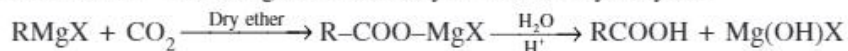
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Hydrocarboxylation of alkenes : When a mixture of an alkene, carbon monoxide and steam is heated under pressure at 300-400°C in the presence of H_3PO_4 , monocarboxylic acid is formed.



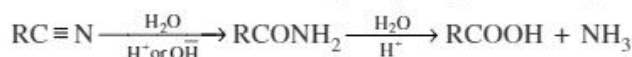
This is a recent method and is known as **Koch reaction**.

(ii) **From Grignard reagents :** Grignard reagents combine with carbon dioxide and form a salt. The salt gives a carboxylic acid on hydrolysis.

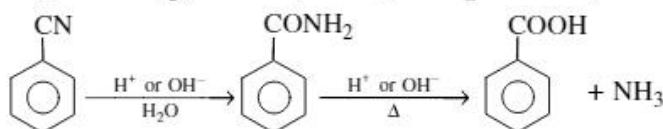
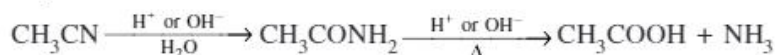


The acid formed has one carbon atom more than the alkyl group present in the Grignard reagent.

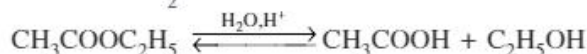
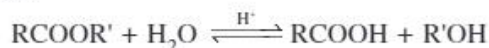
(iii) **From cyanides and esters :** Alkyl and aryl nitriles on acid or alkaline hydrolysis give amides which on further hydrolysis give carboxylic acids.



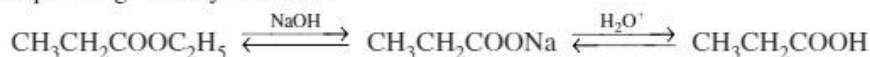
This method serves as a very good synthetic method for the preparation of carboxylic acids.



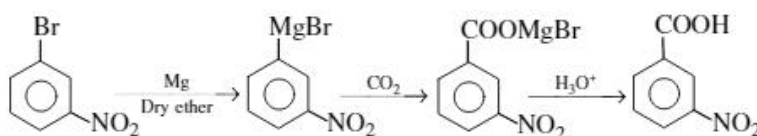
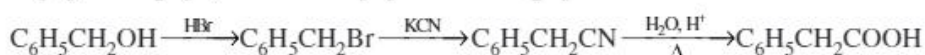
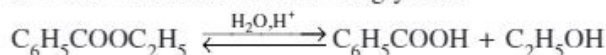
Esters also give carboxylic acids on hydrolysis in the presence of dilute mineral acids.



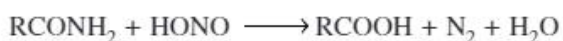
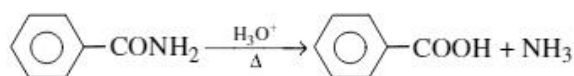
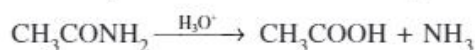
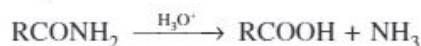
During base hydrolysis, carboxylates are formed which on acidification give corresponding carboxylic acids.



This method is particularly useful for the preparation of higher fatty acids from oils and fats which are triesters of glycerol.



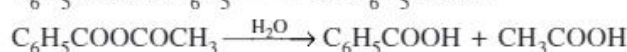
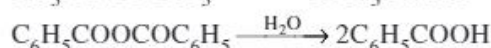
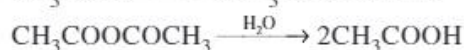
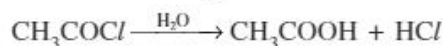
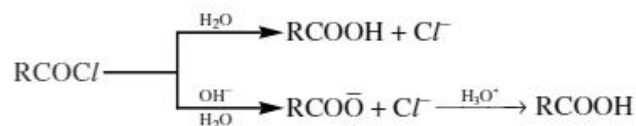
(iv) **From amides :** Amides on hydrolysis or on treatment with nitrous acid give carboxylic acids.



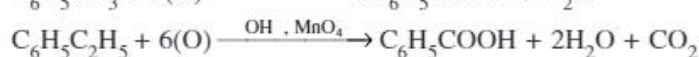
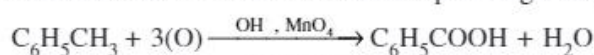
Acetic acid is obtained by the hydrolysis of acetonitrile or ethyl acetate

Amides or acid halides on hydrolysis give carboxylic acids

(v) **From acid halides and anhydrides** : Acid chlorides on hydrolysis give carboxylic acids. They are more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides are hydrolysed to corresponding acids.

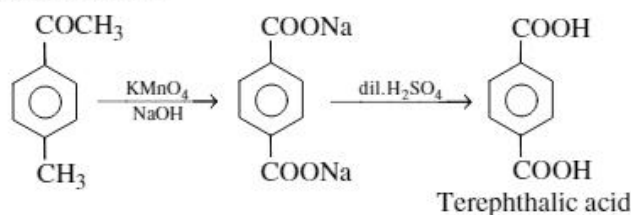


(vi) **Oxidation** : Aromatic compounds with a side chain ($\text{C}_6\text{H}_5\text{-CH-}$) on oxidation with chromic acid or acidic or alkaline permanganate produce benzoic acid.

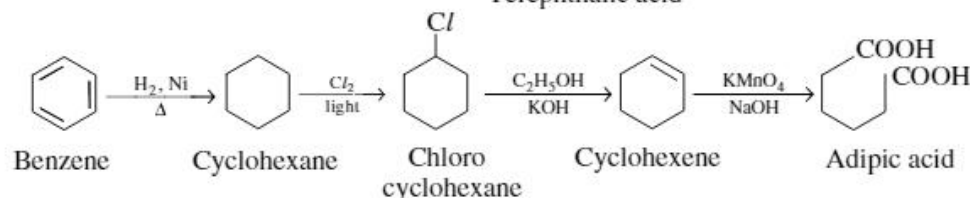


The alkyl side chain gets oxidised to $-\text{COOH}$ group irrespective of the length of the side chain.

Oxidation of 4-methylacetophenone gives terephthalic acid

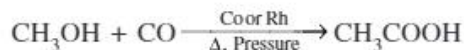


Oxidation of cyclohexene gives adipic acid

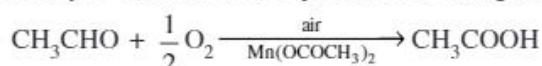


Acetic acid is prepared by the following methods :

From methyl alcohol and carbon monoxide : In presence of rhodium or cobalt, methanol combines with carbon monoxide and forms acetic acid.



From acetaldehyde : Acetic acid is commercially prepared by the oxidation of acetaldehyde with air in the presence of manganese acetate catalyst.



From ethyl alcohol : Vinegar is 6–10% aqueous solution of acetic acid. It is obtained by fermentation of liquors containing 12 to 15% ethyl alcohol. Fermentation is done by *Bacterium mycoderma aceti* in presence of air at 30–35°C. This process is termed acetous fermentation.



Commercially acetic acid is prepared by the atmospheric oxidation of acetaldehyde



P.4.6 How is formic acid prepared ?

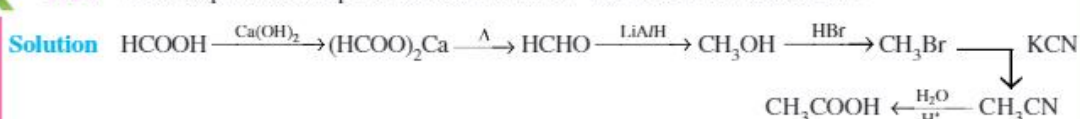
Solution a) Formic acid is prepared by the oxidation of methyl alcohol.



b) It is also prepared by heating a mixture of carbon monoxide and sodium hydroxide at 210°C under pressure.

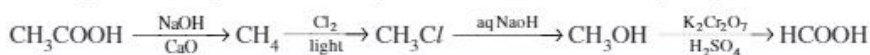


P.4.7 Write sequence of steps for the conversion of formic acid to acetic acid ?



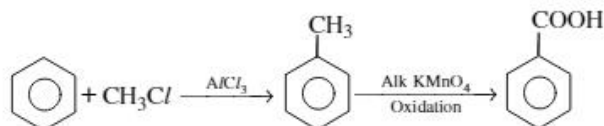
P.4.8 How is acetic acid converted to formic acid ?

Solution The sequence of steps are decarboxylation, chlorination, base hydrolysis and oxidation.



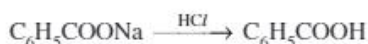
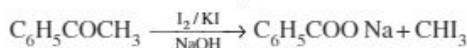
P.4.9 How is benzoic acid prepared from benzene ?

Solution Benzene is converted to benzoic acid in the following sequence of steps.

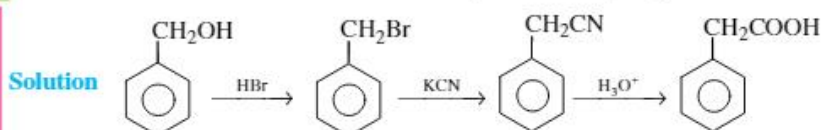


P.4.10 Explain how acetophenone can be converted to benzoic acid ?

Solution Acetophenone on oxidation with iodine and alkali gives iodoform and sodium benzoate. The latter on acidification gives benzoic acid.

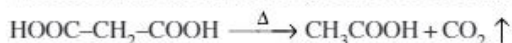


P.4.11 How is the transformation of benzyl alcohol to phenylethanoic acid affected ?



P.4.12 What happens when malonic acid is heated ?

Solution When malonic acid is heated, acetic acid is formed with the liberation of carbon dioxide.



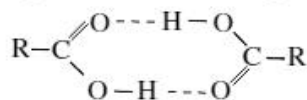
4.2.2

Physical properties

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odour. The higher acids are wax like solids. Carboxylic acids are higher boiling liquids than aldehydes, ketones, alkyl halides, ethers, alkanes and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular

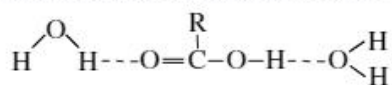
Carboxylic acids are polymeric in liquid state, but dimeric in gaseous state

hydrogen bonding. Even in vapour state, the hydrogen bonds are not broken completely. In liquid state, carboxylic acids are polymeric. In the vapour state or in non-aqueous solutions, they are dimeric.



Carboxylic acids are highly soluble in water due to the formation of hydrogen bonds with water. Solubility of acid decreases with an increase in the size of hydrophobic alkyl group.

Carboxylic acids are also soluble in less polar organic solvents like benzene, carbondisulphide, chloroform, ether, etc.



Acetic acid is a colourless pungent liquid with a boiling point of 118°C . It is sour to taste and miscible with water in all proportions.

4.2.3

Chemical properties

1. Reactions due to the fission of O-H bond

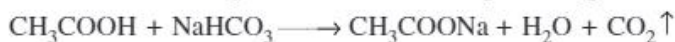
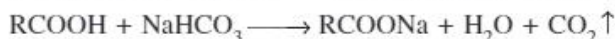
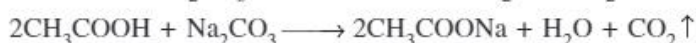
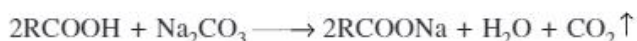
Carboxylic acids release hydrogen with active metals like sodium.



Carboxylic acids form salts with alkalis like sodium hydroxide, calcium hydroxide, etc.



Unlike phenols, carboxylic acids react with weaker bases like carbonates and bicarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.



Acids stronger than carbonic acid release carbon dioxide from carbonates or bicarbonates. This reaction is characteristic of carboxylic acids and they can be distinguished from other compounds. Carboxylic acids can be separated from other compounds by dissolving in NaHCO_3 or Na_2CO_3 . The sodium salt of acid formed regenerates acid on adding HCl .

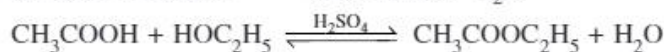
2. Reactions due to the fission of C-O bond

Formation of esters : Carboxylic acids react with alcohols in presence of conc. H_2SO_4 and form esters. This is called **Fischer's esterification**. It is a reversible reaction. Esters have pleasant smell.

*Carboxylic acids
liberate CO_2 with
bicarbonates
and carbonates*

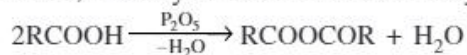
Esterification of acetic acid with ethyl alcohol gives ethyl acetate

Carboxylic acid
on dehydration
gives
corresponding
anhydride

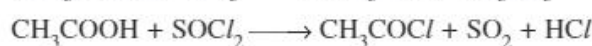
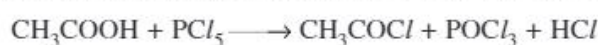


Ester of amylalcohol with acetic acid is called amyl acetate, which has the odour of banana fruits.

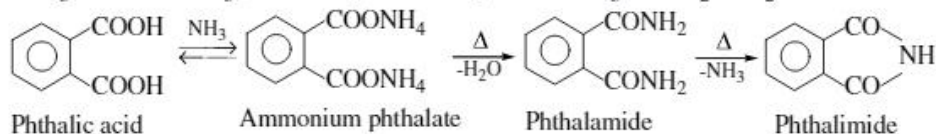
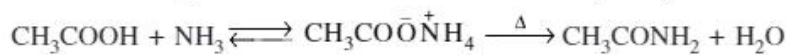
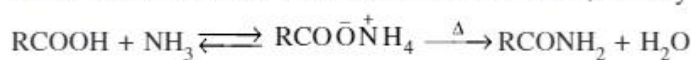
Formation of anhydrides : On heating with a dehydrating agent like phosphorus pentoxide, carboxylic acids form acid anhydrides.



Formation of acid chlorides : Carboxylic acids form acid chlorides with thionyl chloride or phosphorus pentachloride or phosphorus trichloride.

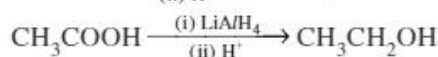
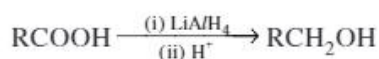


Formation of amides : When heated with ammonia, carboxylic acids form amides.

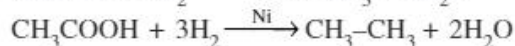
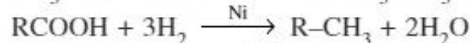
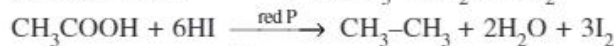
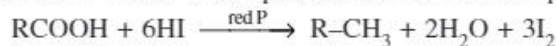


3. Reactions involving -COOH group

Reduction : On reduction with lithium aluminium hydride or diborane or hydrogen in presence of copper chromate or H_2/Ru , carboxylic acids form primary alcohols.

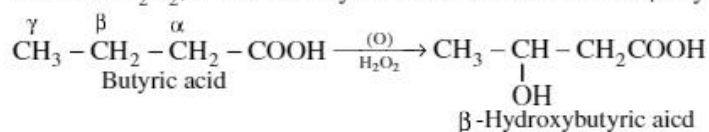


When carboxylic acids are reduced with hydrogen iodide and red phosphorus, alkanes are formed. For this reduction of carboxylic acids to alkanes, hydrogen in presence of nickel under pressure at elevated temperature may also be used.



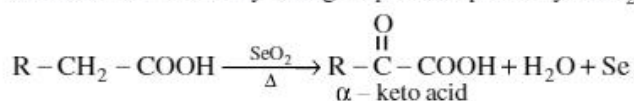
Oxidation : Acetic acid is highly resistant to oxidation, but on prolonged heating with oxidising agents finally produces carbon dioxide and water.

With 3% H_2O_2 ; monocarboxylic acids are oxidised to β -hydroxy acids.



Reduction of
acetic acid with
 LiAlH_4 gives
ethyl alcohol
and with
 HI gives ethane

Oxidation of α -methylene group takes place by SeO_2 to give α -keto acid.

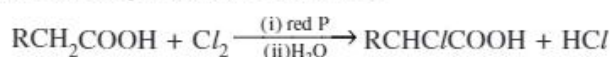


α -Halocarboxylic acids are formed in HVZ reaction

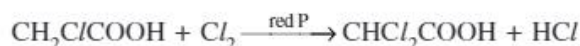
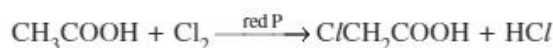
4. Reactions involving alkyl group of acid

The α -hydrogens of a carboxylic acid are substituted by atoms of chlorine or bromine when the acid reacts with chlorine or bromine in presence of red phosphorus.

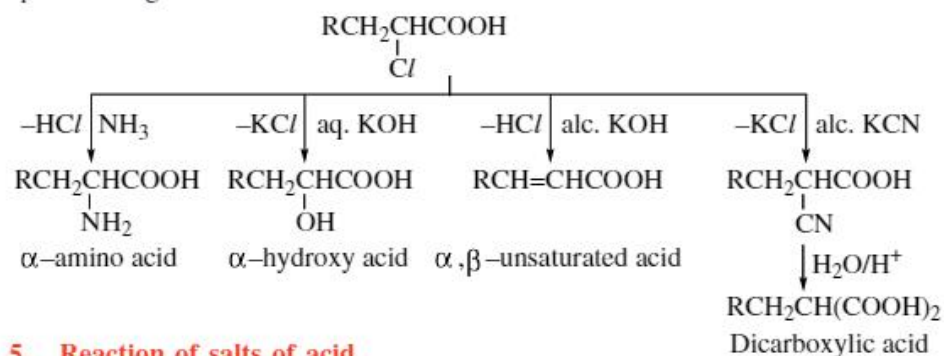
This reaction is called Hell-Volhard-Zelinsky (HVZ) reaction. In this reaction, α -halocarboxylic acids are formed.



Acetic acid reacts with chlorine in the presence of red phosphorus to give monochloro, dichloro and trichloro acetic acid.

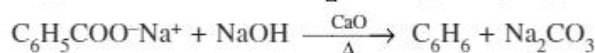
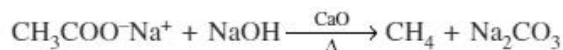


The halo acids can be converted to many other compounds based on the use of specific reagents.

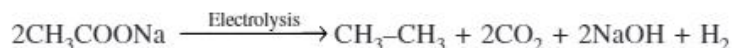


5. Reaction of salts of acid

Decarboxylation : Carboxylic acids undergo decarboxylation when their sodium salts are heated with soda lime, and form hydrocarbons. The hydrocarbon formed will have one carbon less than the acid from which it is formed.

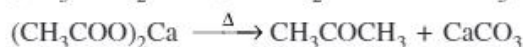
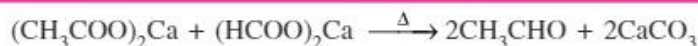


Kolbe's electrolysis : When the aqueous solution of sodium salt of an acid is subjected to electrolysis, a hydrocarbon having twice the number of carbon atoms present in the alkyl group of the acid is formed.



Formation of aldehydes and ketones : The calcium salt of acetic acid on heating with calcium formate produces acetaldehyde and calcium salt of acetic acid alone is heated, acetone is formed. If the calcium salt of formic acid alone is heated, formaldehyde is formed.

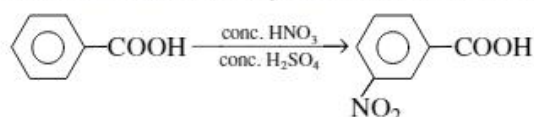
Sodium acetate on decarboxylation gives methane and on electrolysis gives ethane



6. Ring Substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions. Carboxyl group is meta directing and deactivating. Aromatic carboxylic acids, however, do not undergo Friedel-Craft's reaction because the carboxyl group is deactivating and the catalyst aluminium chloride, Lewis acid gets bonded to the carboxyl group.

With nitration mixture, benzoic acid forms m-nitrobenzoic acid.



With chlorine, in presence of ferric chloride, benzoic acid forms m-chlorobenzoic acid as main product.

4.2.4

Uses

1. Acetic acid is used as a solvent and to provide non-aqueous medium.
2. Acetic acid is used to prepare acetic anhydride, acetone, ethyl acetate, acetamide, etc.
3. Acetic acid is used in the preparation of perfumes, dyes and drugs.
4. Acetic acid is used to cure fish and meat.
5. About 6–10% acetic acid is used as vinegar in cooking.
6. Formic acid is used in rubber, textile, dyeing, leather and in the electroplating process.
7. Hexanedioic acid is used in the manufacture of nylon-6,6, a polymer.
8. Esters of benzoic acid are used in the preparation of perfumes.
9. Sodium benzoate is used as food preservative.
10. Higher fatty acids are used for the manufacture of soaps and also for preparing synthetic detergents.

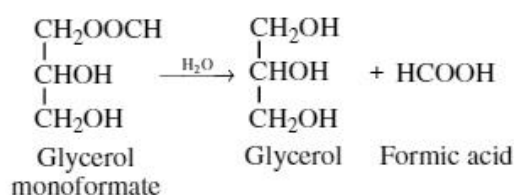
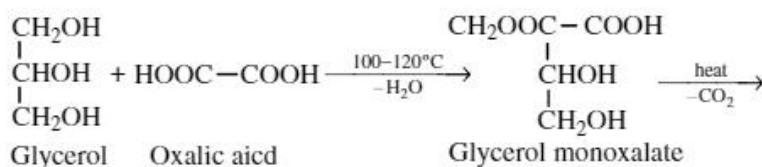
Vinegar is 6-10% aqueous acetic acid

4.2.5

Formic acid

Preparation : Formic acid is prepared in the laboratory by heating oxalic acid with glycerol at 100–120°C.

Formic acid is prepared from oxalic acid using glycerol at 120°C



Formic acid is industrially obtained from NaOH and CO

Formic acid is prepared industrially by heating sodium hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.



Sodium formate thus formed is distilled with sodium hydrogensulphate.



Physical properties : It is colourless pungent smelling liquid. In aqueous solution, it exists as dimer. It is miscible with water, alcohol and ether.

Chemical properties : Formic acid is the strongest acid among all the members of the homologous series. It exhibits some characteristics which are not shown by other members. This unique nature is due to the fact that it contains both aldehyde and carbonyl groups.

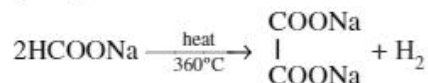
- a) When heated above 160°C; formic acid decomposes to give carbondioxide and oxygen.



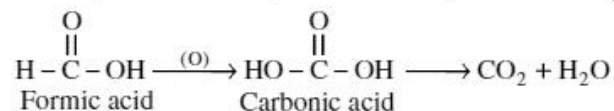
- b) When formic acid is heated with conc. H_2SO_4 , it decomposes to give carbon monoxide and water.



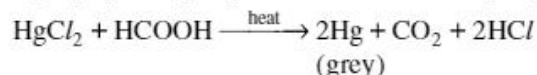
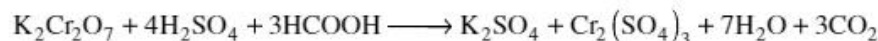
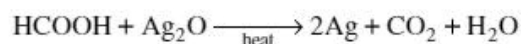
- c) When sodium formate is heated to 360°C, it decomposes to form sodium oxalate and hydrogen.



- d) Like aldehydes, formic acid behaves as a reducing agent. It is oxidised to an unstable acid, carbonic acid, which decomposes into CO_2 and H_2O .



Thus, like the aldehydes, formic acid reduces Tollens reagent, Fehling's solution, acidified KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. It also reduces mercuric chloride. Other carboxylic acids do not possess such reducing properties since they are oxidised only with difficulty.



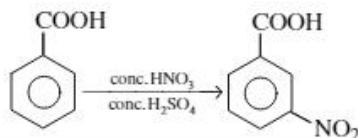
Formic acid is coagulating agent for rubber latex

Uses : Formic acid used in the preparation of carbon monoxide in the laboratory. It is used for dyeing cloth in textile industry and coagulating agent for rubber latex.

In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.

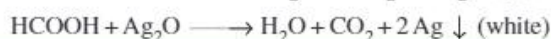
P.4.13 Explain the orientation of $-\text{COOH}$ group, when present on benzene ring.

Solution The $-\text{COOH}$ group is electron withdrawing and is meta-orienting.



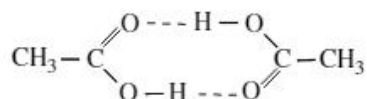
P.4.14 How is formic acid distinguished from acetic acid ?

Solution The only carboxylic acid that has $-\text{CHO}$ group is formic acid. Formic acid reduces Fehling's solution and Tollen's reagent, but not acetic acid



P.4.15 Acetic acid has a molecular mass of 120 when dissolved in benzene. Why ?

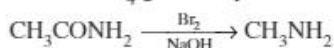
Solution Due to its existence in the form of a dimer, acetic acid has a molecular weight of 120 in non-aqueous solutions, a solvent like benzene.



P.4.16 How is acetic acid converted separately to methyl amine and ethyl amine ?

Solution On heating with ammonia, acetic acid gives acetamide.

Acetamide on heating with bromine in presence of NaOH gives methyl amine and on reduction with LiAlH_4 gives ethyl amine.

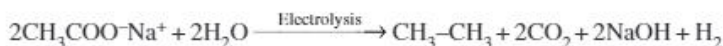


P.4.17 Explain the conversion of acetic acid into methane and ethane in separate steps.

Solution Sodium acetate on decarboxylation gives methane.



Electrolysis of aqueous conc. sodium acetate gives ethane.



EXERCISE - 4.1.2

- How is acetic acid prepared? Explain the properties of acetic acid.
- How is acetic acid obtained from: (a) ethanol, (b) acetonitrile and (c) Grignard reagent.
- Write equations for the reaction of acetic acid with the following reagents : (a) Na , (b) NaOH , (c) NaHCO_3 , (d) NH_3 and (e) $\text{Cl}_2/\text{red P}$.
- How is acetic acid converted to (a) acetone, (b) ethane and (c) ethyl amine.
- How the strength of an acid changes with inductive and mesomeric effects exerted by various groups present in it.

- What happens when acetic acid is (a) heated with P_2O_5 , (b) treated with $LiAlH_4$ and (c) treated with $SOCl_2$?
- Write the equations for the following reactions : (a) Calcium acetate $\xrightarrow{\Delta}$
(b) Sodium acetate $\xrightarrow[CaO]{NaOH}$ and (c) Acetic acid $\xrightarrow[Red\ P]{HI}$
- Write short notes on : (a) HVZ reaction and (b) Esterification.
- Explain why the boiling point of acetic acid is higher than that of aldehydes and alcohols having same molar mass.
- Write the important uses of acetic acid.
- Write the conversions $C_2H_5OH \rightarrow CH_3COOH$ and $CH_3OH \rightarrow CH_3COOH$
- Complete the reactions :
(a) $CH_3COOH \xrightarrow[\Delta]{P_2O_5}$; (b) $CH_3COOH \xrightarrow{LiAlH_4}$
- Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

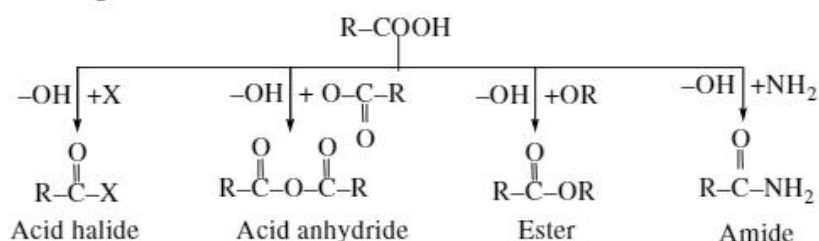
DERIVATIVES OF CARBOXYLIC ACIDS

4.3.1

Introduction

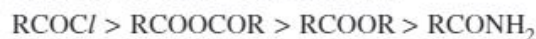
Acid chlorides, anhydrides, esters and amides are called acid derivatives. These are formed by the displacement of $-OH$ group of $-COOH$ by $-Cl$, $-O-C(=O)-R$, $-O-R$, and $-NH_2$ groups respectively.

Carboxylic acid derivatives are four types



All these acid derivatives on hydrolysis give back the parent acid from which they are formed.

A nucleophile can displace the $-Cl$, $-OCOR$, $-OR$ or $-NH_2$ groups present in these compounds by connecting to the carboxylic carbon. The reactivity depends on the rate of attack of nucleophile on carboxylic carbon and the ability of $-Cl$, $-OCOR$, $-OR$ or $-NH_2$ to leave. A weak base is a better leaving group. So the order of reactivity of these compounds is :



Boiling points however follow a different order, based on the hydrogen bonding ability and van der Waals forces.

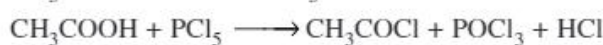


The common derivatives of acetic acid are : acetyl chloride, acetic anhydride, ethyl acetate and acetamide. Their preparation and properties are briefly discussed.

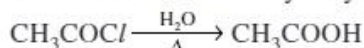
4.3.2

Acid chlorides

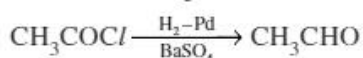
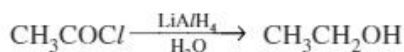
Preparation : Acetyl chloride is prepared from the acetic acid by reaction with thionyl chloride or phosphorus chlorides.

**Properties**

a) **Formation of acid** : Hydrolysis of acid chloride gives carboxylic acid.



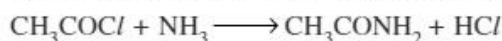
b) **Formation of alcohol and aldehyde** : Reduction of acid chloride with lithium aluminium hydride gives alcohol, but aldehyde is obtained in Rosenmund's reduction.



c) **Formation of ester** : Acid chlorides react, with alcohols or ethers to form esters.



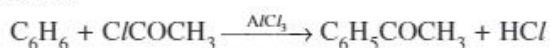
d) **Formation of amide** : On heating with ammonia, acid chlorides form amides.



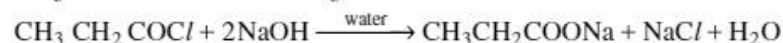
e) **Formation of anhydride** : With metal acetates, acid chlorides react to give acid anhydrides.



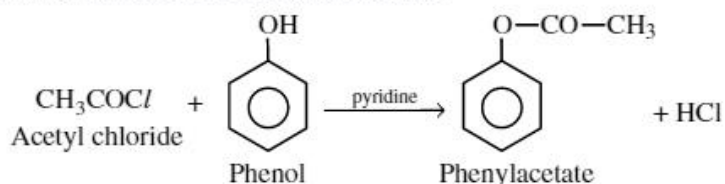
f) **Friedel - Crafts reaction** : In the Friedel-Crafts reaction, acid chlorides react with benzene in the presence of anhydrous aluminium chloride to give aromatic ketones.



g) **Hydrolysis** : Acid chlorides are readily hydrolysed by water to give the corresponding carboxylic acids. They react with NaOH or KOH to form carboxylate salts.



h) **Reaction with phenols** : Acid chlorides react with phenols to form phenyl esters. The reactions of aromatic acid chlorides with alcohols and phenols can be carried out in presence of dilute NaOH (to neutralise the liberated HCl). This procedure is known as Schotten-Baumann reaction.

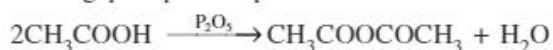


*Rosenmund's
reduction of acid
halide gives
aldehyde*

*Benzene reacts
with acid halides
to give aromatic
ketones*

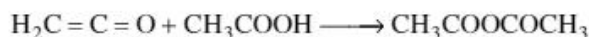
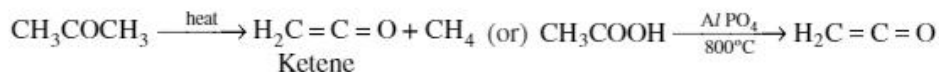
4.3.3**Acid anhydrides**

Preparation : Acetic anhydride is commonly prepared by dehydration of acetic acid using phosphorus pentoxide.



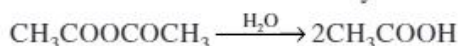
Acid halides, anhydrides, esters and amides on hydrolysis give carboxylic acids

From Ketenes : Ketene is obtained from acetone or acetic acid. The ketene then passed through glacial acetic acid when formation of acetic anhydride takes place. This is the modern method.



Properties

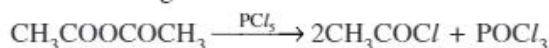
a) **Formation of acids :** Acid anhydrides on treating with water give carboxylic acids.



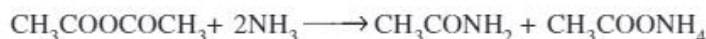
b) **Formation of esters :** Acid anhydrides react with alcohol or ether to give esters.



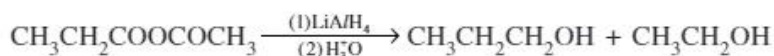
c) **Formation of acid chloride :** Acid anhydrides react with phosphorus pentachloride to give acid chlorides.



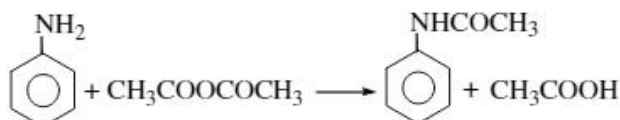
d) **Formation of amides :** On treating with ammonia, acid anhydrides give amides and carboxylic acids.



e) **Formation of alcohols :** Reduction of acid anhydride with lithium aluminium hydride gives alcohol.



f) **Acetylation :** Acetylation of aniline with acetic anhydride gives acetanilide and with salicylic acid gives acetyl salicylic acid called aspirin.

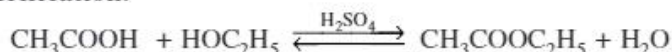


Aspirin is prepared from aniline and acetic anhydride

4.3.4

Esters

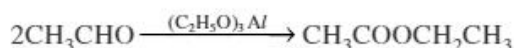
Preparation : Ethyl acetate is formed in the reaction between acetic acid and ethyl alcohol in the presence of conc. sulphuric acid. This is called **Fischer's esterification**.



Esters are also formed by the reaction of alcohols or ethers with acid chlorides or acid anhydrides. A silver salt of carboxylic acid on treating with an alkyl halide gives an ester.



Esters are also formed by the Tischenko reaction of aldehydes in the presence of aluminium ethoxide catalyst.



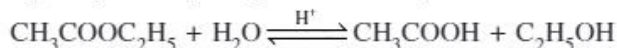
Tischenko reaction of acetaldehyde gives ethylacetate

Methyl esters of carboxylic acids can be prepared by the reaction of carboxylic acids with diazomethane in ether solution.



Properties

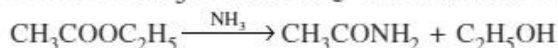
a) **Hydrolysis** : Hydrolysis of esters give alcohol and acids.



b) **Reduction** : Esters on treating with lithium aluminium hydride or sodium in ethanol gives alcohols.



c) **Action of NH_3** : On treating with ammonia, esters form amides.



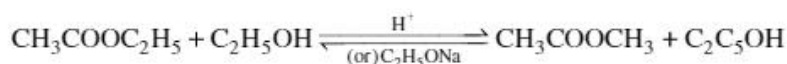
d) **Action of PCl_5** : Esters on treating with phosphorus pentachloride give a mixture of acid halide and alkyl halide.



e) **Claisen condensation** : In the presence of sodium ethoxide, ethyl acetate gives ethyl acetoacetate.



f) **Alcoholysis** : When an ester, RCOOR' is heated with an excess of another alcohol, $\text{R}''\text{OH}$ in presence of an acid or a base as a catalyst a new ester is formed. This is transformation of an ester into a new ester by the action of an alcohol is called as **transesterification** reaction.

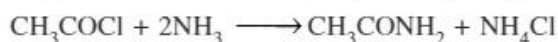
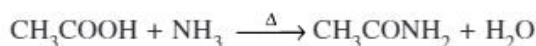


*Ethyl acetoacetate
is formed by
Claisen
condensation*

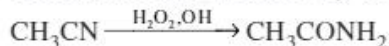
4.3.5

Amides

Preparation : Acetamide is prepared by heating acetic acid or acid halide or acid anhydride or ester with ammonia.

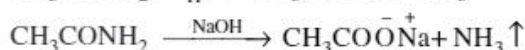
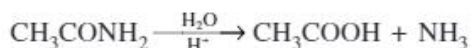


Amides are also obtained by the oxidative hydrolysis alkyl cyanides.

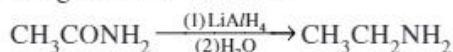


Properties

a) **Hydrolysis** : Amides on acid hydrolysis give carboxylic acids. However on treating with alkali solution, salt of carboxylic acid is formed.



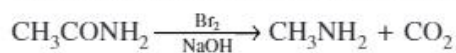
b) **Reduction** : Reduction of amides with lithium aluminium hydride or sodium in alcohol gives aminoalkane.



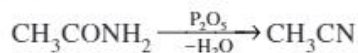
*Reduction of
amides with
 LiAlH_4 gives
alkylamine*

Amide gives amine by the degradation

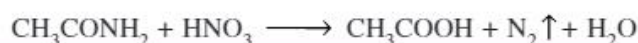
c) **Hofmann hypobromite reaction** : This is also called degradation reaction. Amides are converted to amines on treating with bromine and alkali.



d) **Dehydration** : Amides on heating with phosphorus pentoxide at 500°C give cyanides.



e) **Action of HNO_2** : On treating with sodium nitrite and hydrochloric acid, amides give carboxylic acid and liberate nitrogen.



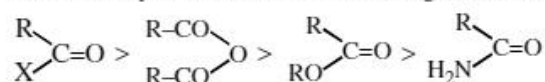
P.4.18 Hydrolysis of an ester in presence of NaOH is called saponification. Explain.

Solution If the ester is the ester of higher acid, the hydrolysis of an ester with NaOH gives sodium salt of higher acid. Sodium salt of higher fatty acid is soap, so the reaction is saponification.



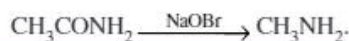
P.4.19 Give the order of reactivity of various acid derivatives towards nucleophilic substitution.

Solution The reactivity of the acid derivatives, in general, follows the order :

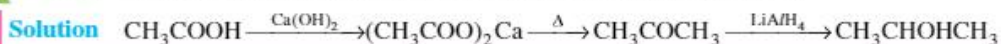


P.4.20 How is acetamide converted to methamine ?

Solution Amides can be converted to amines by Hofmann hypobromite reaction. This conversion is also called degradation reaction



P.4.21 Write sequence of reactions to convert acetic acid into 2-propanol.



EXERCISE - 4.1.3

1. Explain how ethyl acetate is prepared? Discuss its properties.
2. How is acetamide prepared? What are its properties?
3. How is acetyl chloride prepared? Discuss its properties.
4. Discuss the methods of preparation and properties of acetic anhydride.
5. Write short notes on the Hofmann hypobromite reaction with mechanism.



1. Carboxylic acids are compounds which contain $-\text{COOH}$ group as functional group with general formula RCOOH .
2. Carboxylic acids release H^+ ions in aqueous solution and so are acidic in nature.
3. Carboxylic acids are prepared by the oxidation of primary alcohols and aldehydes.

4. The hydrolysis of RCN , RCOCl , $(\text{RCO})_2\text{O}$, RCOOR' or RCONH_2 gives the corresponding carboxylic acids.
5. Carboxylic acids are also prepared by the action of CO_2 on Grignard reagent followed by hydrolysis.
6. Aromatic carboxylic acids are prepared by the oxidation of alkyl benzenes.
7. Carboxylic acids release H_2 with Na , release CO_2 with NaHCO_3 or Na_2CO_3 .
8. Carboxylic acids dissolve in NaOH and are regenerated by HCl (not by CO_2).
9. Carboxylic acids form esters with alcohols, acid chlorides with PCl_5 and amides with ammonia.
10. On heating with P_2O_5 , they give anhydrides, on reduction with LiAlH_4 , they give primary alcohols.
11. Carboxylic acids give aldehydes and ketones when their calcium salts are heated with calcium formate and alone respectively.
12. Decarboxylation of carboxylic acids gives hydrocarbons in the presence of soda lime.
13. Carboxylic acids form α -chloro acids with Cl_2 in the presence of red phosphorus. This is called HVZ reaction.
14. A 6-10% dilute aqueous acetic acid is called vinegar. It is used in cooking.
15. Acid chlorides, anhydrides, esters and amides are acid derivatives. Boiling points of acid derivatives are in the order : $\text{RCONH}_2 > (\text{RCO})_2\text{O} > \text{RCOOH} > \text{RCOOR}' > \text{RCOCl}$.
16. Reduction of amides with lithium aluminium hydride gives alkanamines.

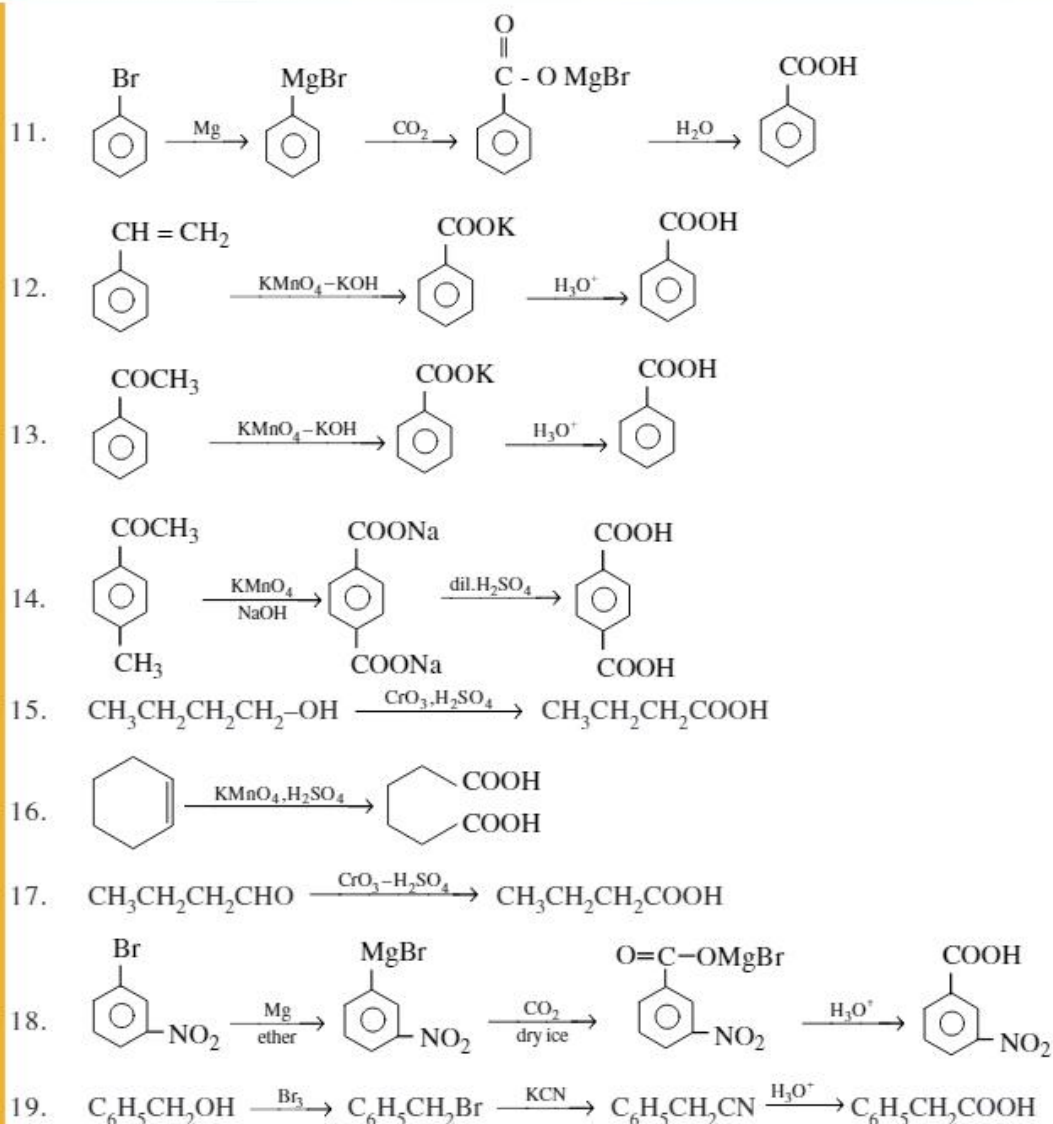
CONVERSIONS

1. Methanol to acetic acid
2. Ethanoic acid to propanoic acid
3. Benzene to methylbenzoate
4. Propanoic acid to acetic acid
5. Nitrobenzene to benzoic acid
6. Benzene to phenylacetic acid
7. Benzene to p-nitrobenzoic acid
8. Benzene to m-nitrobenzoic acid
9. Benzene to m-nitroacetophenone
10. Ethylbenzene to benzoic acid
11. Bromobenzene to benzoic acid
12. Styrene to benzoic acid
13. Acetophenone to benzoic acid
14. 4-Methylacetophenone to benzene-1, 4-dicarboxylic acid
15. Butanol-1 to butanoic acid

16. Cyclohexene to hexane-1, 6-dioic acid
17. Butanal to butanoic acid
18. 3-Nitrobromobenzene to 3-nitrobenzoic acid
19. Benzyl alcohol to phenylethanoic acid

ANSWERS to CONVERSIONS

1. $\text{CH}_3 - \text{OH} + \text{CO} \xrightarrow[\Delta, \text{pressure}]{\text{Co(or)Rh}} \text{CH}_3 - \text{COOH}$
2. $\text{CH}_3 - \text{COOH} \xrightarrow{\text{Ca(OH)}_2} (\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\Delta} \text{CH}_3\text{COCH}_3 \xrightarrow{\text{LiAlH}_4} \text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow{\text{PBr}_3} \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{KCN}} \text{CH}_3\text{CH}_2\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3\text{CH}_2\text{COOH}$
3. $\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}} \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{(O)}]{\text{Alkaline KMnO}_4} \text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{CH}_3\text{OH}} \text{C}_6\text{H}_5\text{COOCH}_3$
4. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}_2\text{COONa} \xrightarrow[\text{CaO}]{\text{NaOH}} \text{C}_2\text{H}_6 \xrightarrow{\text{Cl}_2/\text{h}\nu} \text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{AgOH}} \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{KMnO}_4/\text{H}^+]{\text{(O)}} \text{CH}_3\text{COOH}$
5. $\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{HCl}]{\text{NaNO}_2} \text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow{\text{CuCN}} \text{C}_6\text{H}_5\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{COOH}$
6. $\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}} \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{Cl}_2/\text{h}\nu} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{C}_6\text{H}_5\text{CH}_2\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
7. $\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}} \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2 \xrightarrow{\text{CrO}_2\text{Cl}_2} \text{C}_6\text{H}_4(\text{CHO})\text{NO}_2 \xrightarrow[\text{H}^+]{\text{KMnO}_4} \text{C}_6\text{H}_4(\text{COOH})\text{NO}_2$
8. $\text{C}_6\text{H}_6 \xrightarrow[\text{AlBr}_3]{\text{CH}_3\text{Br}} \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{H}_3\text{O}^+]{\text{Alc. KMnO}_4} \text{C}_6\text{H}_5\text{COOH} \xrightarrow[\text{Conc. H}_2\text{SO}_4]{\text{conc. HNO}_3} \text{C}_6\text{H}_4(\text{COOH})\text{NO}_2$
9. $\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}} \text{C}_6\text{H}_5\text{COCH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{C}_6\text{H}_4(\text{COCH}_3)\text{NO}_2$
10. $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \xrightarrow{\text{KMnO}_4 - \text{KOH}} \text{C}_6\text{H}_5\text{COOK} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{COOH}$

**EXERCISE - 4.2**

1. What is Etard reaction?
2. Explain Gattermann-Koch reaction?
3. Carboxylic acids are more acidic than phenol. Explain.
4. How is inductive effect useful to explain the relative strength of aliphatic carboxylic acids? Explain with suitable examples.
5. Acetic acid is stronger acid than peroxyacetic acid? Why?
6. How is benzoic acid prepared? What are its properties?
7. How is lactic acid prepared? Write two reactions of lactic acid.
8. Explain the optical isomerism exhibited by lactic acid and tartaric acid.
9. Write the mechanism of Claisen condensation.

10. Explain the differences between acetic acid and formic acid.
11. Discuss the geometrical isomerism exhibited by maleic and fumaric acids. How they differ in properties?
12. Write the order of acidic strengths of benzoic acid and isomeric chlorobenzoic acids.
13. Cyanides on alkaline hydrolysis liberate ammonia while acidic hydrolysis doesnot. Explain?
14. Explain how succinic acid is prepared.
15. Discuss the preparation and properties of phthalic acid.
16. Explain how salicylic acid is prepared? Write important properties of salicylic acid.
17. Explain the mechanism of Hofmann hypobromite reaction.
18. Write the mechanism of acid and alkaline hydrolysis of esters.
19. The boiling points of carboxylic acids are higher than those of alcohols. Explain with suitable examples.
20. Give equations for the reaction of acetic acid with (i) PCl_3 (ii) PCl_5 (iii) SOCl_2
21. Predict the order of reactivity of acid derivatives towards nucleophilic displacement reactions.
22. Write sequence of reactions to convert benzene into benzoic acid. Give two methods.
23. Predict the order of acidic nature of (i) p-nitrobenzoic acid (ii) p-methylbenzoic acid (iii) p-chlorobenzoic acid (iv) p-methoxybenzoic acid
24. The first ionisation constant of oxalic acid is much greater than its second ionisation constant. Justify.
25. "Salts of acetic acid are useful in the preparation of several organic compounds". Account for the observation with suitable examples.
26. Explain how acetic acid can be converted to : glycine and lactic acid.
27. Acid halides undergo esterification at a faster rate than acids. Explain?
28. $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{dil. NaOH}} \text{A} \xrightarrow[\text{CaO}]{\text{NaOH}} \text{B} \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}} \text{C}$. Name the reaction in the formation of C from B. (Ans : Friedel–Craft's alkylation)
29. $\text{C}_6\text{H}_6 + \text{Br}_2 \xrightarrow{\text{AlCl}_3} \text{A} \xrightarrow{\text{Mg, ether}} \text{B} \xrightarrow{\text{CO}_2} \text{C} \xrightarrow{\text{H}_3\text{O}^+} \text{D}$. Write the organic products A, B, C and D. Discuss these conversions. (Ans : D = $\text{C}_6\text{H}_5\text{COOH}$)
30. $\text{CH}_3\text{COOH} \xrightarrow{\text{Cl}_2, \text{P}} \text{A} \xrightarrow[\text{C}_2\text{H}_5\text{OH}/\text{H}^+]{\text{esterification}} \text{B} \xrightarrow{\text{alc. KCN}} \text{C} \xrightarrow[\text{H}_2\text{O}/\text{H}^+]{\text{hydrolysis}} \text{D} \xrightarrow[\text{-CO}_2]{\text{heat } 150^\circ\text{C}} \text{E}$. Name the functional isomer of compound E in the above sequence. (Ans : methyl formate)

