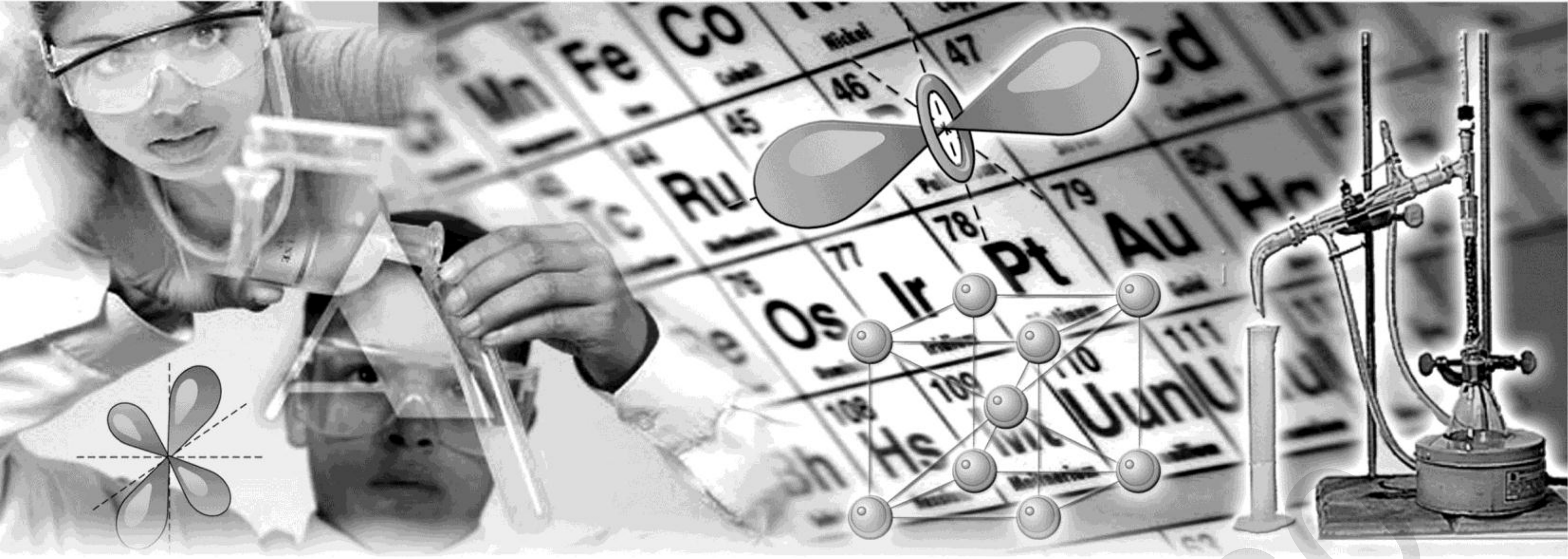


Chapter
28
Carboxylic acids and Their derivatives

Carboxylic Acids

Carboxylic acids are the compounds containing the carboxyl functional group $\left(-\underset{\underset{O}{||}}{C}-OH \right)$

The carboxyl group is made up of carbonyl (>C=O) and hydroxyl (–OH) group.

Classification

(1) Carboxylic acids are classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids etc. depending on the number of $-COOH$ groups present in the molecule.

$$\underset{\text{Monocarboxylic acid}}{CH_3COOH} \qquad \underset{\text{Dicarboxylic acid}}{\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}} \qquad \underset{\text{Tricarboxylic acid}}{\begin{array}{l} CH_2COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{array}}$$

(2) Monocarboxylic acids of aliphatic series are commonly known as fatty acids such as palmitic acid $(C_{15}H_{31}COOH)$ and stearic acid $(C_{17}H_{35}COOH)$.

(3) The general formula for monocarboxylic acids is $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. Where n = number of carbon atoms.

(4) The carboxylic acids may be aliphatic or aromatic depending upon whether $-COOH$ group is attached to aliphatic alkyl chain or aryl group respectively.

Methods of preparation of monocarboxylic acid

(1) **By oxidation of alcohols, aldehydes and ketones**

$$\underset{\text{alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7]{[O]} RCHO \xrightarrow[K_2Cr_2O_7]{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{monocarboxylic acid}}{RCOOH}$$

❑ Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammonical silver nitrate solution $[Ag_2O \text{ or } Ag(NH_3)_2^+OH^-]$

❑ Methanoic acid can not be prepared by oxidation method.

❑ Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.

❑ Methyl ketones can also be converted to carboxylic acid through the haloform reaction.

$$R-\underset{\underset{O}{||}}{C}-CH_3 + 3I_2 + 3NaOH \xrightarrow[H_2O]{\Delta}$$

$$R-\underset{\underset{O}{||}}{C}-OH + CHI_3 + 3NaI + 3H_2O$$

(2) **By Hydrolysis of nitriles, ester, anhydrides and acid chloride**

(i) ***Hydrolysis of nitriles***

$$R-C\equiv N + HOH \xrightarrow[\text{or } NaOH]{HCl} \left[R-C\begin{matrix} \diagup OH \\ \diagdown\!\!\diagdown NH \end{matrix} \right] \xrightarrow{\text{Rearrangement}}$$

$$R-C\begin{matrix} \diagup\!\!\diagup O \\ \diagdown NH_2 \end{matrix} \xrightarrow[HCl]{H_2O} RCOOH + NH_4Cl$$

(ii) ***Hydrolysis of Esters***

$$\underset{\text{Ester}}{RCOOR'} + HOH \xrightarrow[OH^-]{HCl} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

(iii) ***Hydrolysis of Anhydrides***

$$\underset{\text{Ethanoic anhydride}}{\begin{matrix} CH_3-\overset{\overset{O}{||}}{C} \\ CH_3-\underset{\underset{O}{||}}{C} \end{matrix}\!\!>O} + HOH \xrightarrow{H^+/OH^-} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

(iv) ***Hydrolysis of acid chloride and nitro alkane***

$$R-\underset{\underset{O}{||}}{C}-Cl + HOH \xrightarrow{H^+/OH^-} RCOOH + HCl$$

$$R-CH_2-NO_2 \xrightarrow{85\% H_2SO_4} RCOOH$$

(v) ***Hydrolysis of Trihalogen*** **:**

$$R-C\begin{smallmatrix}X\\X\\X\end{smallmatrix} + 3NaOH \rightarrow \left[R-C\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}\right] \xrightarrow{-H_2O}$$

$$R-C\begin{smallmatrix}=O\\ \diagdown OH\end{smallmatrix} + 3NaX$$

(3) **From Grignard Reagent**

$$\underset{\text{Carbon dioxide}}{O=C=O} + \underset{\text{Grignard reagent}}{\overset{\delta- \; \delta+}{RMgX}} \xrightarrow{\text{Dry ether}} R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H^+/H_2O} RCOOH + Mg(OH)X$$

(4) **From Alkene or Hydro-carboxy-addition (koch reaction)**

$$CH_2=CH_2+CO+H_2O \xrightarrow[\substack{500-1000 atm\\ \& 350°C}]{H_3PO_4} CH_3CH_2COOH$$

(5) **Special methods**

(i) ***Carboxylation of sodium alkoxide***

$$\underset{\text{Sod. alkoxide}}{RONa} + CO \rightarrow \underset{\text{Sod. salt}}{RCOONa} \xrightarrow{HCl} \underset{\text{Acid}}{RCOOH}$$

(ii) ***Action of heat on dicarboxylic acid***

$$\underset{\text{Substituted malonic acid}}{R-CH\begin{smallmatrix}COOH\\COOH\end{smallmatrix}} \xrightarrow[\text{heat}]{-CO_2} \underset{\text{Monocarboxylic acid}}{R-CH_2COOH}$$

(iii) ***From acetoacetic ester***

$$\begin{matrix}CH_3CO & \vdots & CHRCO & \vdots & OC_2H_5\\ OH & \vdots & H \quad OH & \vdots & H\end{matrix} \xrightarrow{\text{Hydrolysis}} \begin{matrix}CH_3COOH\\ +RCH_2COOH+C_2H_5OH\end{matrix}$$

(iv) ***Oxidation of alkene and alkyne***

$$\underset{\text{Alkene}}{RCH=CHR'} \xrightarrow[\substack{\text{Hot alkaline}\\ KMnO_4}]{[O]} RCOOH + R'COOH$$

$$\underset{\text{Alkyne}}{R-C\equiv C-R'} \xrightarrow[(ii) H_2O]{(i) O_3} R-COOH+R'COOH$$

(v) ***The Arndt-Eistert synthesis***

$$R-\underset{\underset{O}{\|}}{C}-Cl + CH_2N_2 \rightarrow R-\underset{\underset{O}{\|}}{C}-CHN_2 \xrightarrow[Ag_2O]{H_2O}$$

$$R-CH_2-COOH$$

(vi) ***From acid amides***

$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow[\text{or } Alkali]{\text{Acid}} \underset{\text{Acid}}{RCOOH} + NH_3$$

$$\underset{\text{Amide}}{RCONH_2} + \underset{\text{Nitrous acid}}{HNO_2} \rightarrow RCOOH + N_2 + H_2O$$

Physical properties of monocarboxylic acids

(1) **Physical state :** The first three members (upto 3 carbon atoms) are colourless, pungent smelling liquids. The next six members are oily liquids having unpleasant smell. The higher members are colourless and odourless waxy solids.

(2) **Solubility :** The lower members of the aliphatic carboxylic acid family (upto C_4) are highly soluble in water. The solubility decreases with the increase in the size of the alkyl group. All carboxylic acids are soluble in alcohol, ether and benzene etc.

❑ The solubility of lower members of carboxylic acids is due to the formation of hydrogen bonds between the $-COOH$ group and water molecules.

❑ Acetic acid exists in the solution in dimer form due to intermolecular hydrogen bonding. The observed molecular mass of acetic acid is 120 instead of 60.

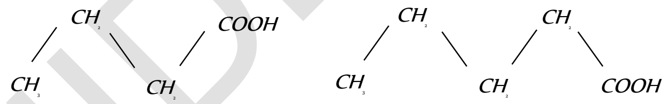
(3) **Melting point**

(i) The melting points of carboxylic acids donot vary smoothly from one member to another.

(ii) The melting point of the acids having even number of carbon atoms are higher than those containing an odd number immediately above and below them.

(iii) The acids with even number of carbon atoms have the $-COOH$ group and the terminal $-CH_3$ group on the opposite side of the carbon chain.

(iv) In the case of odd numbers, the two groups lie on the same side of the chain.



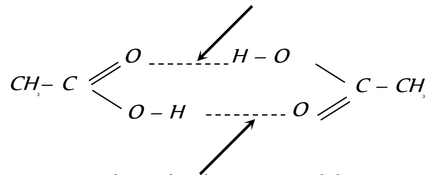
the two terminal groups lie on the opposite sides of the chain

the two terminal groups lie on the same side of the chain

When the terminal groups lie on the opposite sides the molecules fit into each other more closely. More effective packing of the molecule in the lattice. Therefore, results into higher melting point.

(4) **Boiling point :** Boiling point of carboxylic acids increase regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular hydrogen bonding between two acid molecules.

Hydrogen bonding

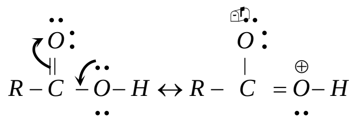


Hydrogen bonding Acetic acid dimer

Acidic nature of monocarboxylic acids

(1) **Cause of acidic nature**

(i) A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.



(I) (II)

(ii) Due to electron deficiency on oxygen atom of the hydroxyl group (Structure II), their is a displacement of electron pair of $O–H$ bond toward the oxygen atom. This facilitate the release of hydrogen as proton (H^+).

$$R-C\overset{O^-}{\diagup}\!\!=\overset{\oplus}{O}\leftarrow H \leftrightarrow \left[R-C\begin{smallmatrix}\nearrow O\\ \searrow O^-\end{smallmatrix} \leftrightarrow R-C\begin{smallmatrix}\nearrow O^-\\ \searrow O\end{smallmatrix} \equiv R-C\begin{smallmatrix}\nearrow O\ 1.27A^\circ\\ \searrow O\ 1.27A^\circ\end{smallmatrix}\right]$$

Resonance hybrid

(iii) The resulting carboxylate ion also stabilized by resonance (As negative charge is dispersed on both the oxygen atom). This enhance the stability of carboxylate anion and make it weaker base or strong acid.

(2) **Effect of substituent on acidic nature**

(i) An electron withdrawing substituent ($-I$ effect) stabilizes the anion by dispersing the negative charge and therefore increases the acidity.

$$\left.G\leftarrow C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}\right]^- \qquad \left.G\rightarrow C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}\right]^-$$

(I) (II)

(ii) An electron releasing substituent ($+I$ effect) stabilizes negative charge on the anion resulting in the decrease of stability and thus decreased the acidity of acid.

Electron with drawing nature of halogen : $F > Cl > Br > I$

Thus, the acidic strength decreases in the order :

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$$

similarly :

$$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$$

(iii) Inductive effect is stronger at α-position than β-position similarly at β-position it is more stronger than at γ -position

Example:

$$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}H-COOH > CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_2-COOH$$

$$> \underset{\displaystyle Cl}{\underset{|}{C}}H_2-CH_2-CH_2-COOH$$

(iv) Relative acid strength in different compounds

$$RCOOH > HOH > ROH > HC\equiv CH > NH_3 > RH$$

❑ *Greater the value of K_a or lesser the value of pK_a stronger is the acid, i.e.* $pK_a = -\log K_a$

❑ Acidic nature (K_a) α 1/molecular weight

	$HCOOH$	>	$CH_3COOH > C_2H_5COOH$
K_a Value	17.7×10^{-5}	1.75×10^{-5}	1.3×10^{-5}

❑ The formic acid is strongest of all fatty acids.

❑ Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

Chemical properties of monocarboxylic acids

(1) **Reaction involving removal of proton from $-OH$ group**

(i) ***Action with blue litmus*** : All carboxylic acids turn blue litmus red.

(ii) ***Reaction with metals***

$$2CH_3COOH + 2Na \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + H_2$$

$$2CH_3COOH + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

(iii) ***Action with alkalies***

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

(iv) ***Action with carbonates and bicarbonates***

$$2CH_3COOH + Na_2CO_3 \rightarrow \underset{\text{Sod. acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \rightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + CO_2 + H_2O$$

❑ Reaction of carboxylic acid with aqueous sodium carbonates solution produces bricks effervescence. However most phenols do not produce effervescence. Therefore, this reaction may be used to distinguish between carboxylic acids and phenols.

(2) **Reaction involving replacement of $-OH$ group** (i) ***Formation of acid chloride***

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \rightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$

(ii) ***Formation of esters*** (***Esterification***)

$$\underset{\text{Acetic acid}}{CH_3CO\boxed{OH+H}}\underset{\text{Ethyl alcohol}}{OC_2H_5} \underset{\Delta}{\overset{\text{Conc.}H_2SO_4}{\rightleftharpoons}} \underset{\substack{\text{Ethyl acetate}\\ \text{(Fruity smelling)}}}{CH_3COOC_2H_5} + H_2O$$

(a) The reaction is shifted to the right by using excess of alcohol or removal of water by distillation.

(b) The reactivity of alcohol towards esterification.

tert-alcohol < *sec*-alcohol < *pri*-alcohol < methyl alcohol

(c) The acidic strength of carboxylic acid plays only a minor role.

$$R_3CCOOH < R_2CHCOOH < RCH_2COOH < CH_3COOH < HCOOH$$

When **methanol** is taken in place of **ethanol**. then reaction is called **trans esterification.**

(iv) ***Formation of amides***

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \xrightarrow{\text{heat}} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(v) ***Formation of acid anhydrides***

$$\begin{matrix} CH_3COO\boxed{H} \\ + \\ \underset{\text{Acetic acid}}{CH_3CO\boxed{OH}} \end{matrix} \underset{P_2O_5}{\xrightarrow{\text{Heat}}} \underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\!\!>O} + H_2O$$

(vi) ***Reaction with organo-metallic reagents***

$$R'CH_2MgBr + RCOOH \xrightarrow{\text{ether}} \underset{\text{Alkane}}{R'CH_3} + RCOOMgBr$$

(3) **Reaction involving carbonyl ($>C=O$) group:**

Reduction : $R-\underset{\displaystyle O}{\underset{||}{C}}-OH \xrightarrow{LiAlH_4} R-CH_2-OH$

Carboxylic acid are difficult to reduce either by catalytic hydrogenation or Na/C_2H_5OH

(4) **Reaction involving attack of carboxylic group ($-COOH$)**

(i) ***Decarboxylation*** : $R-\overset{\overset{\displaystyle O}{||}}{C}-OH \xrightarrow{(-CO_2)} R-H$

When anhydrous alkali salt of fatty acid is heated with sodalime then :

$$\underset{\text{Sodium salt}}{RCOONa} + NaOH \xrightarrow[\text{heat}]{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

❑ When sodium formate is heated with sodalim*e* H_2 is evolved. (Exception)

$$HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$$

(ii) ***Heating of calcium salts***

$$\underset{\text{Sodium salt}}{(RCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Ketone}}{RCOR} + CaCO_3$$

(iii) ***Electrolysis*** : **(Kolbe's synthesis)**

$$RCOONa \rightleftharpoons RCOO^- + Na^+$$

At anode $2RCOO^- \to R-R+2CO_2+2e^-$

At cathode $2Na^+ + 2e^- \to 2Na \xrightarrow{2H_2O} 2NaOH + H_2$

$$\underset{\text{Potassium acetate}}{2CH_3COOK} + 2H_2O \xrightarrow{\text{Electrolysis}}$$

$$\underset{\text{Ethane}}{CH_3-CH_3} + 2CO_2 + 2KOH + H_2$$

(iv) ***Formation of Alkyl halide*** (Hunsdiecker's reaction)

$$\underset{\text{Silver acetate}}{CH_3COOAg} + Br_2 \xrightarrow[CCl_4]{\text{heat}} \underset{\text{Methyl bromide}}{CH_3Br} + AgBr + CO_2$$

❑ In Hunsdiecker reaction, one carbon atom less alkyl halide is formed from acid salt.

(v) ***Formation of amines*** (Schmidt reaction)

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{H_2SO_4(conc.)} \underset{\text{Primary amine}}{RNH_2} + CO_2 + N_2$$

In Schmidt reaction, one carbon less product is formed.

(vi) ***Complete reduction***

$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow{P} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$$

In the above reaction, the $-COOH$ group is reduced to a CH_3 group.

(5) **Reaction involving hydrogen of α-carbon**

Halogenation

(i) ***In presence of U.V. light***

$$-\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}-COOH + Cl_2 \xrightarrow{U.V.\Delta} \underset{\alpha\text{-chloro acid}}{-\overset{\overset{\displaystyle Cl}{|}}{\underset{|}{C}}-COOH} + HCl$$

(ii) ***In presence of Red P and diffused light [Hell Volhard-zelinsky reaction]***

Carboxylic acid having an α-hydrogen react with Cl_2 or Br_2 in the presence of a small amount of red phosphorus to give chloro acetic acid. The reaction is known as **Hell Volhard-zelinsky reaction.**

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{Cl_2,\text{red } P_4} \underset{\text{Chloro acetic acid}}{ClCH_2COOH} \xrightarrow[-HCl]{Cl_2,\text{red } P_4}$$

$$\underset{\text{Dichloro acetic acid}}{Cl_2CHCOOH} \xrightarrow[-HCl]{Cl_2,\text{ red } P_4} \underset{\text{Trichloro acetic acid}}{Cl_3CCOOH}$$

Individual members of monocarboxylic acids

Formic Acid or Methanoic acid ($HCOOH$)

Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and fruits. In traces it is present in perspiration, urine, blood and in caterpillar's.

(1) **Methods of preparation**

(i) ***Oxidation of methyl alcohol or formaldehyde***

$$CH_3OH + O_2 \xrightarrow{Pt} \underset{\text{Formic acid}}{HCOOH} + H_2O$$

(ii) ***Hydrolysis of hydrocyanic acid :*** Formic acid is formed by the hydrolysis of HCN with acids or alkalies.

$$HCN + 2H_2O \xrightarrow{HCl} HCOOH + NH_3;$$

$$HCN + H_2O \xrightarrow{NaOH} HCOONa + NH_3$$

(iii) ***Laboratory preparation***

$$\underset{\text{Glycerol}}{\begin{array}{l} CH_2O\boxed{H+HO}OC-COOH \\ | \qquad\qquad\quad \text{Oxalic acid} \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow[100-120^oC]{-H_2O} \underset{\text{Glycerol monoxalate}}{\begin{array}{l} CH_2OOC\boxed{COO}H \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow[110°C]{-CO_2}$$

$$\underset{\text{Glycerol monoformate}}{\begin{array}{l} CH_2OOCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow{(COOH)_2\, 2H_2O} \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

The following procedure is applied for obtaining anhydrous formic acid.

$$2HCOOH + PbCO_3 \to \underset{\text{Lead formate}}{(HCOO)_2Pb} + CO_2 + H_2O;$$

$$(HCOO)_2Pb + H_2S \to \underset{\text{ppt.}}{PbS} + \underset{\text{Formic acid}}{2HCOOH}$$

(iv) ***Industrial preparation*** : Formic acid is prepared on industrial scale by heating sodium hydroxide with carbon monoxide at 210°C under a pressure of about 10 atmospheres.

$$CO + NaOH \xrightarrow[210^oC,10\,\text{atm}]{\Delta} \underset{\text{Sodium formate}}{HCOONa}$$

Sodium formate thus formed is distilled with sodium hydrogen sulphate, when anhydrous formic acid distils over.

$$HCOONa + NaHSO_4 \to HCOOH + Na_2SO_4$$

(2) **Physical properties**

(i) It is a colourless pungent smelling liquid.

(ii) It melts at 8.4°C and boils at 100.5°C.

(iii) It is miscible with water, alcohol and ether. It forms azeotropic mixture with water.

(iv) It is strongly corrosive and cause blisters on skin.

(v) It exists in aqueous solution as a dimer involving hydrogen bonding.

(3) **Uses :** Formic acid is used.

(i) In the laboratory for preparation of carbon monoxide.

(ii) In the preservation of fruits.

(iii) In textile dyeing and finishing.

(iv) In leather tanning.

(v) As coagulating agent for rubber latex.

(vi) As an antiseptic and in the treatment of gout.

(vii) In the manufacture of plastics, water proofing compounds.

(viii) In electroplating to give proper deposit of metals.

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

(x) As a reducing agent.

(xi) In the manufacture of oxalic acid.

Acetic Acid (Ethanoic Acid) (CH_3COOH)

Acetic acid is the oldest known fatty acid. It is the chief constituent of vinegar and hence its name (Latin acetum = vinegar)

(1) **Preparation**

(i) ***By oxidation of acetaldehyde (Laboratory-preparation)***

$$CH_3CHO \xrightarrow[H_2SO_4(O)]{Na_2Cr_2O_7} CH_3COOH$$

(ii) ***By hydrolysis of methyl cyanide with acid***

$$CH_3CN + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3$$

(iii) ***By Grignard reagent***

$$CH_3MgBr + CO_2 \rightarrow CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - OMgBr \xrightarrow{H_2O/H^+}$$

$$\left(CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - OH \right)$$

(iv) By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester

(a) $\underset{\text{Ester}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H_2SO_4(\text{conc.})}$

$$CH_3COOH + C_2H_5OH$$

(b) $\underset{\text{acetylchloride}}{CH_3COCl} + H_2O \xrightarrow{\text{dil.}HCl} CH_3COOH + HCl$

(c) $(CH_3CO)_2O + H_2O \xrightarrow{\text{dil.}HCl} 2CH_3COOH$

(v) ***Manufacture of acetic acid***

(a) *From ethyl alcohol (Quick vinegar process)* : 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*. The process is termed **acetous fermentation.**

$$\underset{\text{Ethylalcohol}}{CH_3CH_2OH} + O_2 \xrightarrow[\text{Bacteria}]{\text{Mycoderma aceti}} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

It is a slow process and takes about 8 to 10 days for completion.

In this process, the following precautions are necessary:

• The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.

• The supply of air should be regulated. With less air the oxidation takes place only upto acetaldehyde stage while with excess of air, the acid is oxidised to CO_2 and water.

• The flow of alcohol is so regulated that temperature does not exceed 35°*C*, which is the optimum temperature for bacterial growth.

Acetic acid can be obtained from vinegar with the help of lime. The calcium acetate crystallised from the solution is distilled with concentrated sulphuric acid when pure acetic acid distils over.

(b) *From acetylene* : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°*C* in presence of 1% $HgSO_4$ (catalyst).

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4(\text{dil.})} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

The acetaldehyde is oxidised to acetic acid by passing a mixture of acetaldehyde vapour and air over manganous acetate at 70°*C*.

$$2CH_3CHO + O_2 \xrightarrow[70°C]{\text{Manganous acetate}} 2CH_3COOH$$

❑ Acetylene required for this purpose is obtained by action of water on calcium carbide.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

The yield is very good and the strength of acid prepared is 97%. The method is also quite cheap.

(c) *By the action of CO on methyl alcohol* : Methyl alcohol and carbon monoxide react together under a pressure of 30 atmospheres and 200°*C* in presence of a catalyst cobalt octacarbonyl, $Co_2(CO)_8$ to form acetic acid.

$$\underset{\text{Methylalcohol}}{CH_3OH} + CO \xrightarrow[30atm\,200°C]{Co_2(CO)_8} \underset{\text{Acetic acid}}{CH_3COOH}$$

(2) **Physical properties**

(i) At ordinary temperature, acetic acid is a colourless, corrosive liquid with a sharp pungent odour of vinegar. It has a sour taste.

(ii) Below 16.5°*C*, it solidifies as an icy mass, hence it is named glacial acetic acid.

(iii) It boils at 118°*C*. The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same molecular masses is due to more stronger hydrogen bonding between acid molecules. This also explains dimer formation of acetic acid in vapour state.

(iv) It is miscible with water, alcohol and ether in all proportions.

(v) It is good solvent for phosphorus, sulphur, iodine and many organic compounds.

(3) **Uses :** It is used,

(i) As a solvent and a laboratory reagent.

(ii) As vinegar for table purpose and for manufacturing pickles.

(iii) In coagulation of rubber latex.

(iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.

(v) For making various useful metallic acetates, such as:

(a) Basic copper acetate which is used for making green paints.

(b) *Al*, *Fe* and *Cr* acetates which are used as mordants in dyeing.

(c) Lead tetra-acetate which is a good oxidising agent.

(d) Basic lead acetate which is used in the manufacture of white lead.

(e) Aluminium acetate which is used in the manufacture of water-proof fabrics.

(f) Alkali acetates which are used as diuretics.

Table : 28.1 Comparison of Formic Acid and Acetic Acid

Property	Formic acid	Acetic acid
1. Acidic nature,		

(i) With electro-positive metals	Forms salts, Hydrogen is evolved. $HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$	Forms salts. Hydrogen is evolved. $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$
(ii) With bases	Forms salts. $HCOOH + NaOH \rightarrow HCOONa + H_2O$	Forms salts. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii) With carbonates and bicarbonates	Forms salts. Carbon dioxide is evolved. $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$	Forms salts. Carbon dioxide is evolved. $CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2$
2. Ester formation	Forms esters when treated with alcohols. $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	Forms esters when treated with alcohols. $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4(conc.)}$ $CH_3COOC_2H_5 + H_2O$
3. Reaction with PCl_5	Forms formyl chloride which decomposes into CO and HCl. $HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	Forms acetyl chloride which is a stable compound. $CH_3COOH + PCl_5 \rightarrow$ $CH_3COCl + POCl_3 + HCl$
4. Heating of ammonium salt	Forms formamide. $HCOONH_4 \rightarrow HCONH_2 + H_2O$	Forms acetamide. $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5. Heating alone	it decomposes into CO_2 and H_2 $HCOOH \rightarrow CO_2 + H_2$	Unaffected
6. Heating with conc. H_2SO_4	Decomposed into CO and H_2O $HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$	Unaffected
7. Reaction with Cl_2 in presence of red P	Unaffected	Forms mono, *di* or trichloro acetic acids.
8. Action of heat on salts, (i) Calcium salt	Forms formaldehyde. $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	Forms acetone. $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii) Sodium salt	Forms sodium oxalate. $2HCOONa \xrightarrow{\text{heat}} \begin{matrix} COONa \\ \vert \\ COONa \end{matrix} + H_2$	Unaffected.
(iii) Sodium salt with soda-lime	Forms sodium carbonate and H_2. $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	Forms sodium carbonate and methane. $CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9. Electrolysis of sodium or potassium salt	It evolves hydrogen.	It forms ethane.
10. On heating with P_2O_5	Unaffected	Forms acetic anhydride. $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11. Reducing nature, (i) Tollen's reagent	Gives silver mirror or black precipitate. $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected.
(ii) Fehling's solution	Gives red precipitate $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected.
(iii) Mercuric chloride	Forms a white ppt. which changes to greyish black. $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$	Unaffected.
(iv) Acidified $KMnO_4$	Decolourises	Unaffected.
12. Acid (neutral solution) + $NaHSO_3$ + Sodium nitroprusside.	Greenish blue colour.	Unaffected.

13. Acid (neutral solution) + neutral ferric chloride	Red colour which changes to brown ppt. on heating.	Wine red colour.

Interconversions

(1) **Ascent of series :** Conversion of formic acid into acetic acid.

(i) $$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{CH_3MgBr} \underset{\text{Addition product}}{CH_3CH_2OMgBr}$$

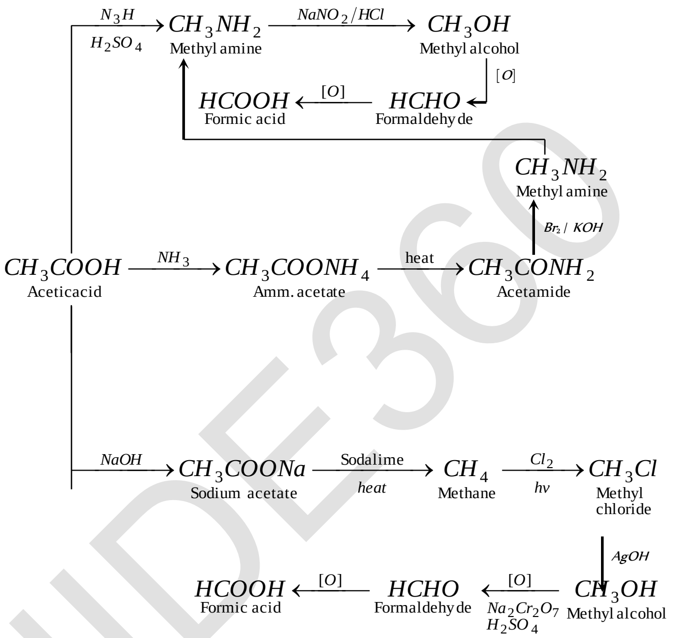
$$\underset{\text{Addition product}}{CH_3CH_2OMgBr} \xrightarrow[H^+]{H_2O} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Aceticacid}}{CH_3COOH}$$

(ii) $$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{HI} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN(Alc.)} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[H^+]{H_2O} \underset{\text{Aciticacid}}{CH_3COOH}$$

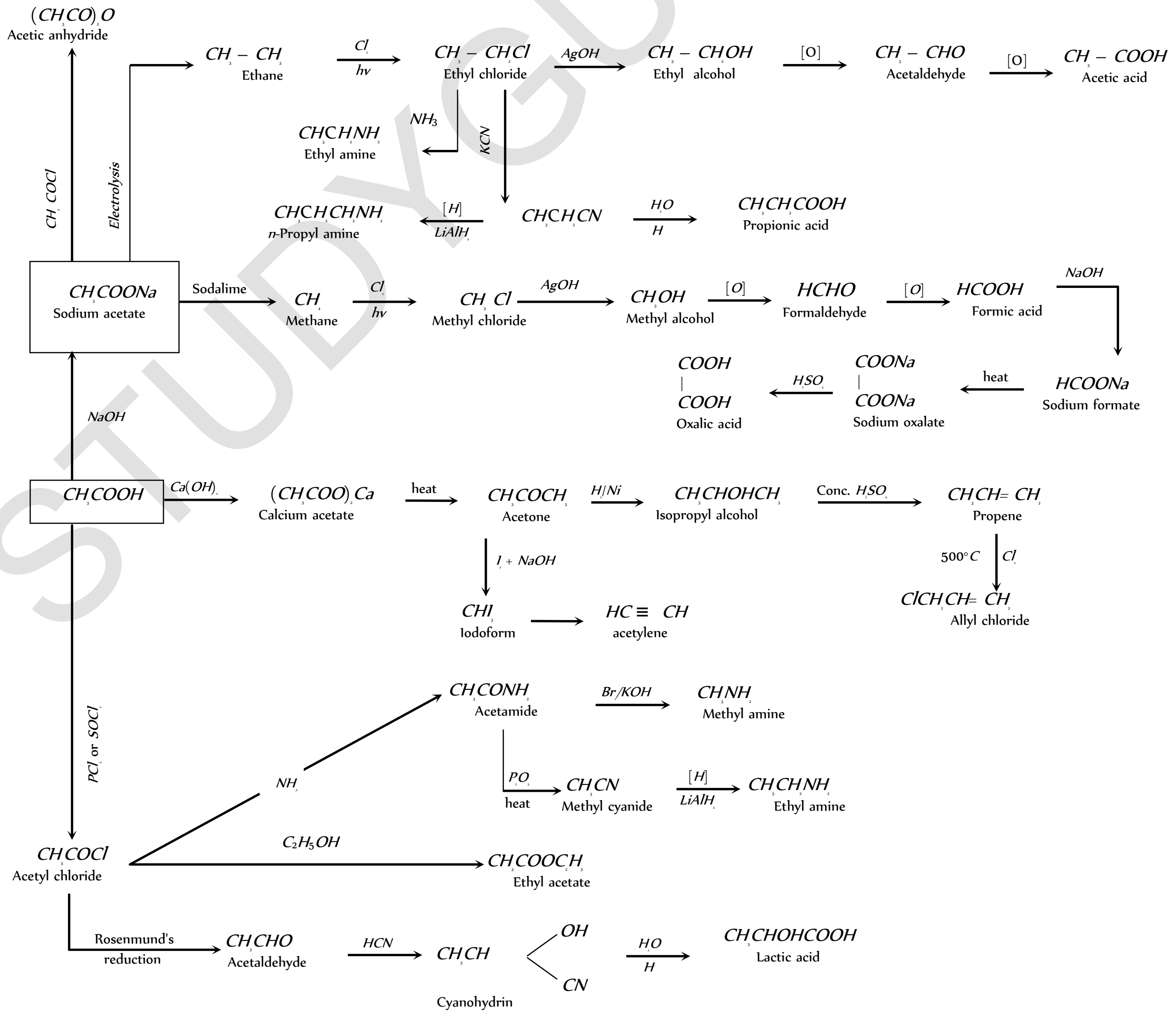
Arndt-Eistert homologation : This is a convenient method of converting an acid, $RCOOH$ to RCH_2COOH.

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[Ag_2O]{EtOH} RCH_2COOC_2H_5 \xrightarrow{\text{Hydrolysis}} RCH_2COOH$$

(2) **Descent of series :** Conversion of acetic acid into formic acid.



Conversion of Acetic acid into other organic compound



Dicarboxylic acids

The acids containing two carboxylic groups are called dicarboxylic acids.

The saturated dicarboxylic acid are represented by the general formula $C_nH_{2n}(COOH)_2$ where n = 0, 1, 2, 3 etc.

$$HO-\underset{\underset{O}{||}}{C}-(CH_2)_n-\underset{\underset{O}{||}}{C}-OH \quad \text{or} \quad HOOC(CH_2)_nCOOH$$

According to IUPAC system, the suffix-dioic acid is added to the name of parent alkane, *i.e.* Alkane dioxic acid.

Table : 28.2

Formula	Common name	IUPAC name
$HOOCCOOH$	Oxalic acid	Ethanedioic acid
$HOOCCH_2COOH$	Malonic acid	1-3 Propanedioic acid
$HOOCCH_2CH_2\ COOH$	Succinic acid	1,4-Butanedioic acid
$HOOC(CH_2)_3COOH$	Glutaric acid	1,5-Pentanedioic acid
$HOOC(CH_2)_4\ COOH$	Adipic acid	1,6-Hexanedioic acid

Oxalic Acid or Ethanedioic Acid

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \quad \text{or } (COOH)_2 \text{ or } (C_2H_2O_4)$$

Oxalic acid is first member of dicarboxylic series.

It occurs as potassium hydrogen oxalate in the wood sorel, rhubarb and other plants of oxalis group and as calcium oxalate in plants of rumex family.

It is found in the form of calcium oxalate in stony deposits in kidneys and bladdar in human body.

Oxalic acid present in tomatoes.

(1) **Methods of Preparation**

(i) ***By oxidation of ethylene glycol with acidified potassium dichromate***

$$\underset{\text{Glycol}}{\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}} + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2H_2O$$

(ii) ***By hydrolysis of cyanogen with conc. hydrochloric acid*** :

$$\begin{array}{c} CN \\ | \\ CN \end{array} + 4H_2O \xrightarrow{2(HCl)} \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2NH_4Cl$$

(iii) ***By heating sodium or potassium in a current of carbon dioxide at 360°C***

$$2Na + 2CO_2 \xrightarrow{\text{heat}} \underset{\text{Sodium oxalate}}{\begin{array}{c} COONa \\ | \\ COONa \end{array}}$$

(iv) ***Laboratory preparation***

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 18[O] \xrightarrow[V_2O_5]{HNO_3} 6\underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + 5H_2O$$

(v) ***Industrial method***

$$\underset{\text{Sod. formate}}{2HCOONa} \xrightarrow{360°C} \underset{\text{Sod. oxalate}}{\begin{array}{c} COONa \\ | \\ COONa \end{array}} + H_2$$

Sodium formate is obtained by passing carbon monoxide over fine powdered of sodium hydroxide.

$$CO + NaOH \xrightarrow[8-10\,atm]{200°C} HCOONa$$

The sodium oxalate thus formed is dissolved in water and calcium hydroxide is added. The precipitate of calcium oxalate is formed which is separated by filtration. It is decomposed with calculated quantity of dilute sulphuric acid.

$$\begin{array}{c} COONa \\ | \\ COONa \end{array} + Ca(OH)_2 \rightarrow \underset{\text{Calcium oxalate}}{\begin{array}{c} COO \\ | \\ COO \end{array}\!\!>\! Ca} + 2NaOH$$

$$\begin{array}{c} COO \\ | \\ COO \end{array}\!\!>\! Ca + H_2SO_4(\text{dil}) \rightarrow \underset{\substack{\text{Oxalic acid} \\ \text{(soluble)}}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + \underset{\substack{\text{Calcium sulphate} \\ \text{(insoluble)}}}{CaSO_4}$$

(2) **Physical Properties**

(i) It is a colourless crystalline solid. It consists of two molecules of water as water of crystallisation.

(ii) The hydrated form has the melting point 101.5°C while the anhydrous form melts at 190°C.

(iii) It is soluble in water and alcohol but insoluble in ether.

(iv) It is poisonous in nature. It affects the central nervous system.

(3) **Chemical Properties**

(i) ***Action of heat*** **:** It becomes anhydrous.

$$\underset{\text{Hydrated oxalic acid}}{(COOH)_2 2H_2O} \xrightarrow{100-105°C} \underset{\text{Anhydrous oxalic acid}}{(COOH)_2} + 2H_2O$$

(a) At 200°C, $(COOH)_2 \longrightarrow \underset{\text{Formic acid}}{HCOOH} + CO_2$

On further heating, formic acid also decomposes.

$$HCOOH \rightarrow CO_2 + H_2$$

(b) *Heating with conc.* H_2SO_4

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow[(conc.)]{H_2SO_4} CO + CO_2 + H_2O$$

(ii) ***Acidic nature***

Salt formation

$$\underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + KOH \rightarrow \underset{\text{Acid pot. oxalate}}{\begin{array}{c} COOK \\ | \\ COOK \end{array}} \xrightarrow{KOH} \underset{\text{Pot. oxalate}}{\begin{array}{c} COOK \\ | \\ COOK \end{array}}$$

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + 2NaHCO_3 \rightarrow \underset{\text{Sod. oxalate}}{\begin{array}{c} COONa \\ | \\ COONa \end{array}} + 2CO_2 + 2H_2O$$

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + Na_2CO_3 \rightarrow \begin{array}{c} COONa \\ | \\ COONa \end{array} + H_2O + CO_2$$

(iii) ***Esterification***

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \xrightarrow{C_2H_5OH} \underset{\text{Ethyl hydrogen oxalate}}{\begin{array}{c} COOC_2H_5 \\ | \\ COOH \end{array}} \xrightarrow{C_2H_5OH} \underset{\text{Ethyl oxalate}}{\begin{array}{c} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}}$$

(iv) ***Reaction with*** PCl_5 **:**

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2PCl_5 \rightarrow \underset{\text{Oxalyl chloride}}{\begin{matrix} COCl \\ | \\ COCl \end{matrix}} + 2POCl_3 + 2HCl$$

(v) ***Reaction with ammonia***

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + NH_3 \rightarrow \underset{\text{Acid ammonium oxalate}}{\begin{matrix} COONH_4 \\ | \\ COOH \end{matrix}} \xrightarrow{NH_3} \underset{\text{Amm. oxalate}}{\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix}}$$

$$\underset{\text{Acid ammonium oxalate}}{\begin{matrix} COONH_4 \\ | \\ COOH \end{matrix}} \xrightarrow[-H_2O]{heat} \underset{\text{Oxamic acid}}{\begin{matrix} CONH_2 \\ | \\ COOH \end{matrix}} \qquad \underset{\text{Amm. oxalate}}{\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix}} \xrightarrow[-2H_2O]{heat} \underset{\text{Oxamide}}{\begin{matrix} CONH_2 \\ | \\ CONH_2 \end{matrix}}$$

(vi) ***Oxidation*** **:** When oxalic acid is warmed with acidified $KMnO_4$.

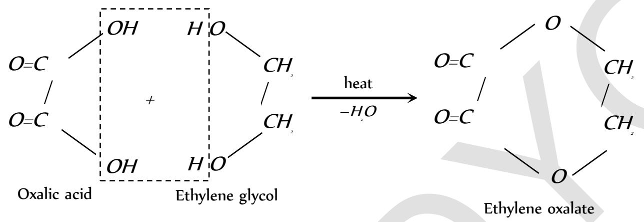
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\left[\begin{matrix} COOH \\ | \\ COOH \end{matrix} + [O] \rightarrow 2CO_2 + H_2O\right] \times 5$$

$$\underset{\substack{\text{Pot. permanganate} \\ \text{(Purple)}}}{2KMnO_4} + 3H_2SO_4 + 5\underset{\text{Oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} \rightarrow \underbrace{K_2SO_4 + 2MnSO_4}_{\text{Colourless}} + 10CO_2 + 8H_2O$$

❑ *Oxalic acid decolourises the acidic* $KMnO_4$ *solution.*

(vii) ***Reaction with ethylene glycol***



(viii) ***Reduction*** **:** $\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 4H \xrightarrow[H_2SO_4]{Zn} \underset{\text{Glycolic acid}}{\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}} + H_2O$

$$2\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[6[H]]{\text{Electrolytic reduction}} \underset{\text{Glycolic acid}}{\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}} + \underset{\text{Glyoxalic acid}}{\begin{matrix} COOH \\ | \\ CHO \end{matrix}} + 2H_2O$$

(ix) ***Reaction with Glycerol*** **:** At 100° – 110°*C*, formic acid is formed. At 260°, allyl alcohol is formed.

(4) **Uses :** Oxalic acid (Polyprotic acid) is used,

(i) In the manufacture of carbon monoxide, formic acid and allyl alcohol.

(ii) As a laboratory reagent and as a standard substance in volumetric analysis.

(iii) In the form of antimony salt as a mordant in dyeing and calico printing.

(iv) In the manufacture of inks.

(v) For removing ink stains and rust stains and for bleaching straw, wood and leather.

(vi) In the form of ferrous potassium oxalate as developer in photography.

(5) **Analytical test**

(i) The aqueous solution turns blue litmus red.

(ii) The aqueous solution evolves effervescences with $NaHCO_3$.

(iii) The neutral solution gives a white precipitate with calcium chloride solution. It is insoluble in acetic acid.

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} \xrightarrow{NH_4OH} \underset{\text{Amm. oxalate}}{(NH_4)_2C_2O_4} \xrightarrow{CaCl_2} \underset{\text{Calcium oxalate}}{CaC_2O_4}$$

(iv) Oxalic acid decolourises hot potassium permanganate solution having dilute sulphuric acid.

(v) With hot conc. H_2SO_4, it evolves carbon monoxide which burns with blue flame.

Malonic Acid or Propane-1,3-Dioic Acid $CH_2\begin{matrix} COOH \\ COOH \end{matrix}$ **or** $CH_2(COOH)_2$ **or** $(C_3H_4O_4)$

The acid occurs as calcium salt in sugar beet. It was so named because it was first obtained from malic acid (hydroxy succinic acid) by oxidation.

(1) **Methods of Preparation :** From acetic acid

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[P]{Cl_2} \underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow{KCN(Aq.)}$$

$$\underset{\text{Cyano acetic acid}}{CH_2CNCOOH} \xrightarrow{H_2O/H^+} \underset{\text{Malonic acid}}{CH_2\begin{matrix} COOH \\ COOH \end{matrix}}$$

(2) **Physical Properties**

(i) It is a white crystalline solid.

(ii) It's melting point is 135°*C*.

(iii) It is soluble in water and alcohol but sparingly soluble in ether.

(3) **Chemical Properties**

(i) ***Action of heat***

(a) *Heating at 150°C :*

$$CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2$$

(b) *Heating with* P_2O_5 *:*

$$O = \begin{matrix} \\ C \\ | \\ OH \end{matrix} - \begin{matrix} H \\ | \\ C \\ | \\ H \end{matrix} - \begin{matrix} OH \\ | \\ C \\ \\ \end{matrix} = O \xrightarrow[heat]{P_2O_5} \underset{\text{Carbon suboxide}}{O = C = C = C = O} + 2H_2O$$

(ii) ***Reaction with aldehyde*** **:** With aldehydes, α-β unsaturated acids are formed.

$$\underset{\text{Aldehyde}}{RCH = O} + H_2C\begin{matrix} COOH \\ COOH \end{matrix} \xrightarrow[heat]{\text{Pyridine}}$$

$$\underset{\alpha\text{-}\beta\text{ unsaturated acid}}{RCH = CHCOOH} + H_2O + CO_2$$

(4) **Uses :** Its diethyl ester (malonic ester) is a valuable synthetic reagent for preparation of a variety of carboxylic acids.

Succinic Acid or Butane-1,4-Dioic Acid :

$$\begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix} \textbf{ or } (CH_2)_2(COOH)_2 \textbf{ or } (C_4H_6O_4)$$

It was first obtained by the distillation of yellow fossil, resin, amber and hence its name (Latin, *Succinum* = amber).

It is also formed in small amount during the fermentation of sugar.

(1) **Methods of Preparation**

(i) ***From ethylene***

$$\underset{\text{Ethylene}}{\begin{array}{l}CH_2\\ ||\\ CH_2\end{array}} \xrightarrow{Br_2} \underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}} \xrightarrow{NaCN} \underset{\text{Ethylene cyanide}}{\begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array}} \xrightarrow{H_2O/HCl} \underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}}$$

(ii) ***From maleic acid [catalytic reduction]***

$$\begin{array}{l}CHCOOH\\ ||\\ CHCOOH\end{array} + H_2 \xrightarrow[\text{heat}]{Ni} \begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$$

❑ This is an industrial method.

(iii) ***Reduction of tartaric acid or malic acid***

$$\underset{\text{Tartaric acid}}{\begin{array}{l}CHOHCOOH\\ |\\ CHOHCOOH\end{array}} \xrightarrow[P]{HI} \underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}} \xleftarrow[P]{HI} \underset{\text{Malic acid}}{\begin{array}{l}CHOHCOOH\\ |\\ CH_2COOH\end{array}}$$

(2) **Physical properties**

(i) It is a white crystalline solid. It melts at 188^oC

(ii) It is less soluble in water. It is comparatively more soluble in alcohol.

(3) **Chemical Properties :** Succinic acid gives the usual reactions of dicarboxylic acid, some important reactions are :

(i) ***Action of heat*** **:** At 300°*C*

$$\underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}} \xrightarrow[(-H_2O)]{300°C} \underset{\text{Succinic anhydride}}{\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>O}$$

(ii) ***With ammonia***

$$\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array} \xrightarrow{NH_3} \underset{\text{Ammonium succinate}}{\begin{array}{l}CH_2COONH_4\\ |\\ CH_2COONH_4\end{array}} \xrightarrow[-H_2O]{\text{heat}}$$

$$\underset{\text{Succinamide}}{\begin{array}{l}CH_2CONH_2\\ |\\ CH_2CONH_2\end{array}} \xrightarrow[-NH_3]{\text{heat}} \underset{\text{Succinimide}}{\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>NH}$$

(iii) ***Reaction with*** Br_2

$$\underset{\text{Succinimide}}{\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NH} + Br_2 \xrightarrow[0°C]{NaOH} \underset{N\text{-bromosuccinimide (N.B.S)}}{\begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>N-Br} + HBr$$

(iv) ***Reaction with ethylene glycol***

$$HOOC-(CH_2)_2-CO\boxed{OH+H}OCH_2-$$
$$CH_2O\boxed{H+HO}OC-(CH_2)_2-CO\ OH+.......$$
$$\Big\downarrow -H_2O$$
$$HOOC-(CH_2)_2-CO-[-OCH_2-CH_2O-OC$$
$$\underset{\text{Polyester}}{-(CH_2)_2-CO-]_n}-OH+H_2O$$

When sodium or potassium salt in aqueous solution is electrolysed, ethylene is obtained at anode.

(4) **Uses :** It finds use in volumetric analysis, medicine and in the manufacture of dyes, perfumes and polyester resins.

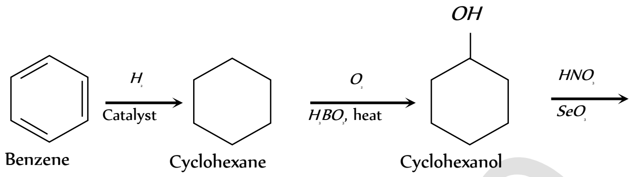
Adipic Acid or Hexane-1,6 –Dioic Acid

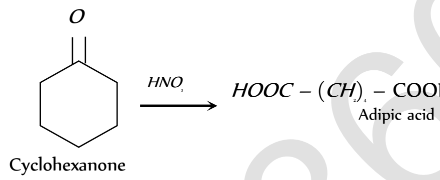
$$\begin{array}{l}\boldsymbol{CH_2-CH_2-COOH}\\ |\\ \boldsymbol{CH_2-CH_2-COOH}\end{array} \textbf{ or } \boldsymbol{(CH_2)_4(COOH)_2} \textbf{ or } \boldsymbol{(C_6H_{10}O_4)}$$

It was first obtained by the oxidation of fats (Latin, adeps = fat.)

(1) **Methods of Preparation**

(i) ***From benzene*** **(In industries)**





❑ It is an industrial method.

(ii) ***From tetrahydrofuran*** **(*THF*)**

$$\underset{\text{THF}}{\begin{array}{l}CH_2-CH_2\\ |\qquad |\\ CH_2\ \ CH_2\\ \ \ \diagdown\ \diagup\\ \ \ \ \ O\end{array}} + 2CO + HOH \rightarrow \underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH}$$

(2) **Physical Properties**

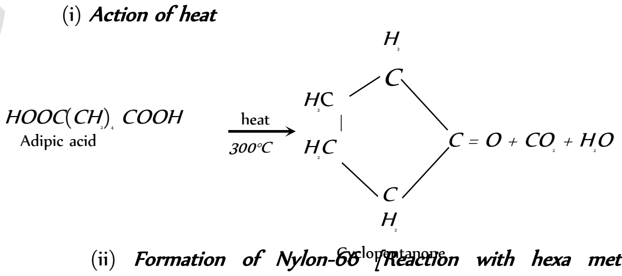
(i) It is a white crystalline solid. Its melting point is 150°*C*.

(ii) It is fairly soluble in alcohol and ether but less soluble in water.

(3) **Chemical Properties**

It shows all the general reaction of dicarboxylic acids.

(i) ***Action of heat***



(ii) ***Formation of Nylon-66 [Reaction with hexa methylene diamine]***

$$\underset{\text{hexamethylene diamine}}{nH_2N(CH_2)_6NH_2} + nHO-\underset{\underset{O}{||}}{C}-(CH_2)_4-\underset{\underset{O}{||}}{C}-OH$$
$$\text{adipic acid}$$
$$\Big\downarrow -nH_2O$$
$$\underset{\text{nylon-66}}{-(-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C}-)_n-}$$

(4) **Uses :** It is used in the manufacture of several polymers.

Unsaturated Acids : When the double bond presents in the carbon chain of an acid is called unsaturated acid.

Example: $\underset{\text{Acrylic acid}}{CH_2=CH-COOH}$ + $\underset{\text{Maleic acid}}{\begin{array}{l}H-C-COOH\\ \quad\ ||\\ H-C-COOH\end{array}}$

Acrylic Acid or Prop-2-Enoic Acid

$\boldsymbol{CH_2=CH-COOH}$ **or** $\boldsymbol{(C_3H_4O_2)}$

(1) **Methods of Preparation**

(i) ***From allyl alcohol***

$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2} \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array} \xrightarrow[{[O]}]{HNO_3} \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ COOH \end{array} \xrightarrow[\text{heat}]{Zn} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

(ii) ***By oxidation of acrolein***

$$CH_2 = CHCHO + [O] \xrightarrow[NH_4OH]{AgNO_3} CH_2 = CHCOOH$$

(iii) ***From propionic acid*** : $\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{HVZ reaction}]{Br_2/P}$

$$\underset{\alpha\text{-Bromopropionic acid}}{CH_3CHBrCOOH} \xrightarrow{Alc.KOH} CH_2 = CHCOOH$$

(iv) ***By heating β-hydroxy propionic acid***

$$\underset{\beta\text{-hydroxypropionic acid}}{\begin{array}{l} CH_2 - CH_2 - COOH \\ | \\ OH \end{array}} \xrightarrow[\text{heat}, -H_2O]{ZnCl_2} CH_2 = CH - COOH$$

(v) ***From vinyl cyanide***

$$\underset{\text{Acetylene}}{HC \equiv CH} + HCN \xrightarrow[90°C]{Cu_2Cl_2/HCl} \underset{\text{Vinylcyanide}}{CH_2 = CH - CN}$$

$$\xrightarrow{H^+/H_2O} CH_2 = CH - COOH$$

(vi) ***From ethylene cyanohydrin***

$$\underset{\text{Ethylene oxide}}{\begin{array}{c} CH_2 - CH_2 \\ \diagdown \ \diagup \\ O \end{array}} \xrightarrow{+HCN} \underset{\text{Ethylene cyanohydrin}}{\begin{array}{l} CH_2 - CH_2 - CN \\ | \\ OH \end{array}} \xrightarrow[\text{heat } -H_2O]{\text{Conc.}H_2SO_4}$$

$$\underset{\substack{\text{Vinylcyanide} \\ \text{(acrylonitrile)}}}{CH_2 = CH - CN} \xrightarrow{H^+/H_2O} CH_2 = CHCOOH$$

Industrial method : This is a new method of its manufacture.

$$CH \equiv CH + CO + H_2O \xrightarrow{Ni(CO)_4} CH_2 = CHCOOH$$

(2) **Physical Properties**

- ❑ It is colourless pungent smelling liquid. Its boiling point is 141°C.
- ❑ It is miscible with water, alcohol and ether.
- ❑ It shows properties of an alkene as well as of an acid.

(3) **Chemical Properties**

(i) ***With nascent hydrogen (Na and C_2H_5OH)***

$$CH_2 = CHCOOH + 2[H] \xrightarrow{Ni} CH_3CH_2COOH$$

(ii) ***With halogens and halogen acids*** **:** Markownikoff's rule is not followed.

$$CH_2 = CHCOOH + Br_2 \xrightarrow{CCl_4} \underset{\alpha,\beta\text{-Dibromopropionic acid}}{CH_2Br - CHBrCOOH}$$

$$CH_2 = CHCOOH + HBr \rightarrow \underset{\beta\text{-Bromopropionic acid}}{BrCH_2 - CH_2COOH}$$

(iii) ***Oxidation*** **:** In presence of dilute alkaline $KMnO_4$.

$$CH_2 = CHCOOH + [O] + H_2O \rightarrow \underset{\text{Glyceric acid}}{CH_2OHCHOHCOOH}$$

- ❑ On vigorous oxidation, oxalic acid is formed.

(iv) ***Salt formation***

$$CH_2 = CHCOOH + KOH \rightarrow CH_2 = CHCO\overline{O}K^+ + H_2O$$

$$2CH_2 = CHCOOH + Na_2CO_3 \rightarrow$$

$$\underset{\text{Sodium acrylate}}{2CH_2 = CHCO\overline{O}Na^+} + H_2O + CO_2$$

(v) ***Ester formation***

$$CH_2 = CHCOOH + HOC_2H_5 \xrightarrow[-H_2O]{\text{Conc.}H_2SO_4}$$

$$\underset{\text{Ethyl acrylate}}{CH_2 = CH - COOC_2H_5}$$

(vi) ***With PCl_5***

$$CH_2 = CHCOOH + PCl_5 \rightarrow \underset{\text{Acryl chloride}}{CH_2 = CH - COCl}$$

(4) **Uses :** Its ester are used for making plastics such as Lucite and plexiglass.

Unsaturated dicarboxylic acids

The molecular formula of the simplest unsaturated dicarboxylic acid is $HOOC.CH = CH.COOH$ This formula, however represents two chemical compounds, maleic acid and fumaric acid, which are geometrical isomers.

$$\underset{\textit{Cis}\text{-form (Maleic acid)}}{\begin{array}{c} H - C - COOH \\ \| \\ H - C - COOH \end{array}} \qquad \underset{\textit{Trans}\text{-form (Fumaric acid)}}{\begin{array}{c} HOOC - C - H \\ \| \\ H - C - COOH \end{array}}$$

(1) **Methods of Preparation of Maleic Acid**

(i) ***By catalytic oxidation of 2-butene or benzene***

$$\underset{2\text{–Butene}}{\begin{array}{l} CH - CH_3 \\ \| \\ CH - CH_3 \end{array}} + 3O_2 \xrightarrow[400°C]{V_2O_5} \underset{\text{Maleic acid}}{\begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array}} + 2H_2O$$

$$\underset{\text{Benzene}}{C_6H_6} + \frac{9}{2}O_2 \xrightarrow[400^oC]{V_2O_5} \underset{\text{Maleic anhydride}}{\begin{array}{l} CH - CO \\ \| \qquad \quad \rangle O \\ CH - CO \end{array}} \xrightarrow{H_2O/H^+} \begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array}$$

(ii) ***From malic acid*** :

$$\underset{\substack{\text{Malic acid} \\ \text{(Hydroxy succinic acid)}}}{\begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}} \xrightarrow[-H_2O]{\text{heat}} \underset{\substack{\text{Maleic acid} \\ \text{(intermediate)}}}{\begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array}} \xrightarrow[-H_2O]{\text{heat}} \underset{\text{Maleic anhydride}}{\begin{array}{l} CH - CO \\ \| \qquad \quad \rangle O \\ CH - CO \end{array}}$$

$$\xrightarrow[\text{boil}]{NaOH} \underset{\text{Sodium salt}}{\begin{array}{l} CH - COONa \\ \| \\ CH - COONa \end{array}} \xrightarrow{H^+/H_2O} \underset{\text{Maleic acid}}{\begin{array}{l} CH - COOH \\ \| \\ CH - COOH \end{array}}$$

(2) **Methods of Preparation of Fumaric Acid**

(i) ***From maleic acid*** :

$$\underset{\text{Maleic acid}}{\begin{array}{c} H - C - COOH \\ \| \\ H - C - COOH \end{array}} \xrightarrow[\text{boil}]{HCl} \begin{array}{c} HOOC - C - H \\ \| \\ H - C - COOH \end{array}$$

(ii) ***By oxidation of furfural with sodium chlorate***

$$\begin{array}{l} HC \text{———} CH \\ \| \qquad\quad \| \\ HC \qquad C - CHO \\ \ \diagdown \quad \diagup \\ \quad\ O \end{array} + 4[O] \xrightarrow{NaClO_3} \begin{array}{c} HOOC - C - H \\ \| \\ H - C - COOH \end{array} + CO_2$$

(iii) ***By heating malic acid at about 150°C for long time***

$$\underset{\text{Malic acid}}{\begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}} \xrightarrow[150°C, -H_2O]{\text{heat}} \begin{array}{c} HOOC - C - H \\ \| \\ H - C - COOH \end{array}$$

(iv) ***By heating bromosuccinic acid with alcoholic potash*** **:** By heating bromosuccinic acid with alcoholic potash.

$$\begin{array}{l} CH_2COOH \\ | \\ CH.(Br)COOH \end{array} \xrightarrow{\text{Alc.}KOH} \begin{array}{c} HOOC-C-H \\ || \\ H-C-COOH \end{array} + KBr + H_2O$$

(3) **Physical Properties**

(i) Both are colourless crystalline solids. Both are soluble in water.

(ii) The melting point of maleic acid (130.5°C) is lower than the melting point of fumaric acid (287°C).

(4) **Chemical Properties**

Chemically, both the acids give the reactions of alkenes and dibasic acids except that the maleic acid on heating forms an anhydride while fumaric acid does not give anhydride.

$$\underset{\text{Maleic acid}}{\begin{array}{l} CHCOOH \\ || \\ CHCOOH \end{array}} \xrightarrow{\text{heat}} \underset{\text{Maleic anhydride}}{\begin{array}{l} CHCO \\ || \\ CHCO \end{array} \!\!> O} + H_2O$$

Both form succinic acid on reduction with sodium amalgam. They undergo addition reactions with bromine, hydrobromic acid, water, etc. and form salts, esters and acid chlorides as usual. With alkaline $KMnO_4$ solution, they get oxidised to tartaric acid.

$$\underset{\substack{\text{Tartaric acid} \\ \text{(Meso)}}}{\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ COOH \end{array}} \xleftarrow[\text{(Syn-addition)}]{\text{Alk}KMnO_4} \underset{\substack{\text{Maleic acid} \\ (Cis)}}{\begin{array}{c} H-C-COOH \\ || \\ H-C-COOH \end{array}} \xrightarrow[\text{(anti-addition)}]{Br_2\text{ water}} \underset{\text{(Racemic mixture)}}{\begin{array}{c} COOH \\ | \\ H-C-Br \\ | \\ Br-C-H \\ | \\ COOH \end{array}}$$

$$\underset{\substack{\text{Tartaric acid} \\ \text{(Racemic mixture)}}}{\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ COOH \end{array}} \xleftarrow[\text{(Syn-addition)}]{\text{Alk.}KMnO_4} \underset{\text{Fumaric acid } (Trans)}{\begin{array}{c} H-C-COOH \\ || \\ HOOC-C-H \end{array}} \xrightarrow[\text{(anti-addition)}]{Br_2\text{water}} \underset{\text{((Meso)}}{\begin{array}{c} COOH \\ | \\ H-C-Br \\ | \\ H-C-Br \\ | \\ COOH \end{array}}$$

Higher fatty acids

Palmitic, stearic and **oleic acids** are found in natural fats and oils as glyceryl esters.

They have derived their names from the natural source from which they are prepared by hydrolysis with alkali.

Table : 28.3

Name of acids	Source	Molecular formula
Palmitic acid	Palm oil	$CH_3(CH_2)_{14}COOH$
Stearic acid	Stear (meaning tallow)	$CH_3(CH_2)_{16}COOH$
Oleic acid	Olive oil.	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

Palmitic and stearic acids are waxy colourless solids with melting points 64°C and 72°C, respectively. They are insoluble in water but soluble in ethanol and ether. They find use in the manufacture of soaps and candles. Soaps contain sodium or potassium salts of these higher fatty acids.

Oleic acid has low melting point, *i.e.*, 16°C. It is insoluble in water but soluble in alcohol and ether. Besides the reactions of acids, it also gives reactions of alkenes. Two aldehydes are formed on ozonolysis.

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH \xrightarrow[(ii)Zn+H_2O]{(i)O_3} CH_3(CH_2)_7CHO + HOOC(CH_2)_7CHO$$

It is used for making soaps, lubricants and detergents.

(1) **Difference between oils and fats :** Oils and fats belong to the same chemical group, yet they are different in their physical state.

(i) Oils are liquids at ordinary temperature (below 20°C) while fats are semi solids or solids (their melting points are more than 20°C). A substance may be classed as fat in one season and oil in another season or the same glyceride may be solid at a hill station and liquid in plains. Thus, this distinction is not well founded as the physical state depends on climate and weather.

(ii) The difference in oils and fats is actually dependent on the nature of monocarboxylic acid present in the glyceride. Oils contain large proportion of the glycerides of lower carboxylic acids, (*e.g.*, butyric acid, caprylic acid and caproic acid) and unsaturated fatty acids, (*e.g.*, oleic, linoleic and linolenic acids) while fats contain a large proportion of glycerides of higher saturated carboxylic acids, (*e.g.*, palmitic, stearic acids).

Lard (fat of hogs) is a solid fat and its composition in terms of fatty acids produced on hydrolysis is approximately 32% palmitic acid, 18% stearic acid, 45% oleic acid and 5% linolenic acid. Olive oil on the other hand, contains 84% oleic acid, 4% linoleic acid, 9% palmitic acid and 3% stearic acid.

(2) **Physical Properties of oils and Fats**

(i) Fats are solids, whereas oils are liquids.

(ii) They are insoluble in water but soluble in ether, chloroform and benzene.

(iii) They have less specific gravity than water and consequently float on the surface when mixed with it.

(iv) Pure fats and oils are colourless, odourless and tasteless but natural fats and oils possess a characteristic odour due to presence of other substances.

(v) They have specific melting points, specific gravity and refractive index hence they can be identified by these oil constants.

(vi) Animal fats contain cholesterol, an unsaturated alcohol, whereas vegetable fats contains phytosterol.

(3) **Chemical Properties :** They give reactions of carbon-carbon double bonds and ester groups.

(i) ***Hydrolysis***

(a) *By superheated steam*

$$\underset{\text{Tristearin}}{\begin{array}{l} CH_2O \vdots COC_{17}H_{35} \\ | \\ CHO \vdots COC_{17}H_{35} \\ | \\ CH_2O \vdots COC_{17}H_{35} \end{array}} \xrightarrow{+3H_2O} \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH}$$

(b) *Base hydrolysis [Saponification]*

$$\underset{\text{Fat or oil}}{\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array}} + 3NaOH \rightarrow \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\substack{\text{Salt fatty acid} \\ \text{(Soap)}}}{3RCOONa}$$

(c) *Enzyme hydrolysis* : Enzyme like lipase, when added to an emulsion of fat in water, hydrolyses it into acid and glycerol in about two or three days.

(ii) ***Hydrogenation*** **:** In the presence of finally divided nickel, at low pressure the hydrogenation process is called hardening of oils.

$$\begin{array}{l} \overset{O}{\overset{\|}{CH_2O\,C}}(CH_2)_7CH=CH(CH_2)_7CH_3 \\ | \\ \overset{O}{\overset{\|}{CHO\,C}}(CH_2)_7CH=CH(CH_2)_7CH_3 \\ | \\ \overset{O}{\overset{\|}{CH_2O\,C}}(CH_2)_7CH=CH(CH_2)_7CH_3 \\ \text{Glyceryl tioleateor triolein (Liquid oil)} \end{array} \xrightarrow[Ni,\text{Heat}]{+3H_2} \begin{array}{l} \overset{O}{\overset{\|}{CH_2O\,C}}C_{17}H_{35} \\ | \\ \overset{O}{\overset{\|}{CHO\,C}}C_{17}H_{35} \\ | \\ \overset{O}{\overset{\|}{CH_2O\,C}}C_{17}H_{35} \\ \text{Tristearin (A solid fat)} \end{array}$$

(iii) ***Hydrogenolysis [Reduction to alcohol]***

$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ \text{Tristearin} \end{array} \xrightarrow[200\,atm]{6H_2} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{Octadecyl alcohol}}{3C_{17}H_{35}CH_2OH}$$

(iv) ***Drying*** **:** Certain oils, containing glycerides of unsaturated fatty acids having two or three double bonds have the tendency of slowly absorbing oxygen from atmosphere and undergoing polymerisation to form hard transparent coating. This process is known as drying and such oils are called drying oils. Unsaturated oils such as linseed oil are, therefore, used as medium of paints and varnishes.

(v) ***Rancidification*** **:** On long storage in contact with air and moisture, oils and fats develop unpleasant smell. The process is known as rancidification. It is believed that rancidification occurs due to hydrolysis-oxidation.

(4) **Analysis of oils and fats**

(i) *Acid value* : It indicates the amount of free acid present in the oil or fat**.** *It is defined as the number of milligrams of KOH required to neutralize the free acid present in one gram of the oil or fat.* It is determined by dissolving a weighed amount of oil or fat in alcohol and titrating it against a standard solution of *KOH* using phenolphthalein as an indicator.

(ii) ***Saponification value*** **:** It is a measure of fatty acids present as esters in oils and fats. It is defined as the number of milligrams of *KOH* required to saponify one gram of the oil or fat or number of milligrams of *KOH* required to neutralize the free acids resulting from the hydrolysis of one gram of an oil or fat. It is determined by refluxing a Saponification number of fat or oil

$$= \frac{168,000}{M}, \quad \text{Where } M = \text{molecular mass}$$

(iii) ***Iodine value*** **:** Iodine value of a fat or oil is a measure of its degree of unsaturation. *It is defined as the number of grams of iodine taken up by 100 grams of fat or oil for saturation.* For a saturated acid glyceride, the iodine value is zero. Thus, the iodine value for a fat is low whereas for oil, it is high. As iodine does not react readily, in actual practice, iodine monochloride is used. Iodine monochloride is known as Wij's reagent.

(iv) ***Reichert-Meissl value, (R/M value)*** **:** It indicates the amount of steam volatile fatty acids present in the oil or fat. *It is defined as the number of millilitres of 0.1 N KOH solution required to neutralize the distillate of 5 grams of hydrolysed fat.* It is determined by hydrolysing a known weighed amount (5 grams) of the fat with alkali solution and the mixture is acidified with dilute sulphuric acid and steam distilled. The distillate is cooled, filtered and titrated against 0.1 *N KOH.*

(5) **Uses**

(i) Many oils and fats are used as food material.

(ii) Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc.

(iii) Oils like linseed oil, tung oil, etc., are used for the manufacture of paints, varnish, etc.

(iv) Castor oil is used as purgative and codliver oil as a source of vitamins *A* and *D.* Almond oil is used in pharmacy. Olive oil is also used as medicine.

(v) Oils are also used as lubricants and illuminants.

Table : 28.4 Difference between vegetable oils and Mineral oils

Property	Vegetable oils	Minerals oils
1. Composition	These are triesters of glycerol with higher fatty acids.	These are hydrocarbons (saturated). Kerosene oil–Alkanes from C_{12} to C_{16}.
2. Source	Seeds root and fruits of plants.	These occur inside earth in the form of petroleum.
3. Hydrolysis	Undergo hydrolysis with alkali. Form soap and glycerol.	No hydrolysis occurs.
4. On adding *NaOH* and phenolphthalein	Decolourisation of pink colour occurs.	No effect.
5. Burning	Burns slowly	Burn very readily.
6. Hydrogenation	Hydrogenation occurs in presence of nickel catalyst. Solid glycerides (fats) are formed.	No hydrogenation occurs.

(6) **Soaps :** Soaps are the metallic salts of higher fatty acids such as palmitic, stearic, oleic, etc. The sodium and potassium salts are the common soaps which are soluble in water and used for cleansing purposes. Soaps of other metals such as calcium, magnesium, zinc, chromium, lead, etc., are insoluble in water. These are not used for cleansing purposes but for other purposes (lubricants, driers, adhesives, etc.)

Ordinary soaps (sodium and potassium) are the products of hydrolysis of oils and fats with sodium hydroxide or potassium hydroxide. The oils and fats are mixed glycerides and thus *soaps are mixtures of salts of saturated and unsaturated long chain carboxylic acids containing 12 to 18 carbon atoms.* This process always yields glycerol as a byproduct.

$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \\ \text{Triglyceride} \end{array} + 3NaOH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} \; \begin{array}{l} R_1COONa \\ + \\ R_2COONa \\ + \\ R_3COONa \\ \text{Soap} \end{array}$$

There are three methods for manufacture of soaps :

(i) The cold process

(ii) The hot process

(iii) Modern process

(7) **Synthetic Detergents :** The synthetic detergents or **Syndets** are substitutes of soaps. They have cleansing power as good or better than ordinary soaps. Like soap, they contain both hydrophilic (water soluble) and hydrophobic (oil-soluble) parts in the molecule.

$$\underbrace{\boxed{C_{12}H_{25}}}_{\text{Hydrophobic part}}\underbrace{\boxed{OSO_3Na}}_{\text{Hydrophilic part}}$$
Sodium lauryl sulphate (Detergent)

$$\underbrace{\boxed{C_{15}H_{31}}}_{\text{Hydrophobic part}}\underbrace{\boxed{COONa}}_{\text{Hydrophilic part}}$$
Sodium palmitate (Soap)

Some of the detergents used these days are given below:

(i) ***Sodium alkyl sulphates* :** These are sodium salts of sulphuric acid esters of long chain aliphatic alcohols containing usually 10 to 15 carbon atoms. The alcohols are obtained from oils or fats by hydrogenolysis.

$$\underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} + \underset{\text{Sulphuric acid}}{HOSO_3H} \rightarrow \underset{\text{Lauryl hydrogen sulphate}}{CH_3(CH_2)_{10}CH_2OSO_2OH} \xrightarrow{NaOH} \underset{\text{Sodium lauryl sulphate (Detergent)}}{CH_3(CH_2)_{10}CH_2OSO_2ONa}$$

The other examples are sodium cetyl sulphate, $C_{16}H_{33}OSO_2ONa$ and sodium stearyl sulphate, $CH_3(CH_2)_{16}CH_2OSO_3Na$. Unlike ordinary soaps, they do not produce OH ions on hydrolysis and thus can be safely used for woollen garments.

(ii) ***Sodium alkyl benzene sulphonates* :** Sodium *p*-dodecyl benzene sulphonate (S.D.S.) acts as a good detergent. It is most widely used since 1975.

$$\underset{\text{1-Dodecene}}{CH_3(CH_2)_9CH=CH_2} + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{2-Dodecyl benzene}}{CH_3(CH_2)_9\overset{\overset{CH_3}{|}}{C}H-C_6H_5}$$

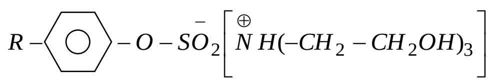
$$\xrightarrow[(ii)NaOH]{(i)H_2SO_4} \underset{\text{(S.D.S.)}}{CH_3-(CH_2)_9-\overset{\overset{CH_3}{|}}{C}H-C_6H_4-SO_3Na}$$

These long chain alkyl benzene sulphonate (L.A.S.) are most widely used syndets.

(iii) ***Quaternary ammonium salts* :** Quaternary ammonium salts with long chain alkyl group have been used as detergents, *e.g.*, trimethyl stearyl ammonium bromide.

$$(CH_3)_3N{<}{\begin{matrix} Br \\ C_{18}H_{37}\end{matrix}}$$

(iv) Sulphonates with triethanol ammonium ion in place of sodium serve as highly soluble materials for liquid detergents.



(v) Partially esterified polyhydroxy compounds also acts as detergents.

$$C_{17}H_{35}COOCH_2-\overset{\overset{CH_2OH}{|}}{\underset{\underset{CH_2OH}{|}}{C}}-CH_2OH$$
Pentaerythritol monostearate

Detergents are superior cleansing agents due to following properties.

(i) These can be used both in soft and hard waters as the calcium and magnesium ions present in hard water form soluble salts with detergents. Ordinary soap cannot be used in hard water.

(ii) The aqueous solution of detergents are neutral. Hence these can be used for washing all types of fabrics without any damage. The solution or ordinary soap is alkaline and thus cannot be used to wash delicate fabrics.

(8) **Waxes :** Waxes are the esters of higher fatty acids with higher monohydric alcohols. The acids and alcohols commonly found in waxes are palmitic, cerotic acid $(C_{25}H_{51}COOH)$, melissic acid $(C_{30}H_{61}COOH)$ and cetyl alcohol $(C_{16}H_{33}OH)$, ceryl alcohol $(C_{26}H_{53}OH)$, myricyl alcohol $(C_{30}H_{61}OH)$, etc.

Waxes are insoluble in water but are readily soluble in benzene, petroleum, carbon disulphide etc. Waxes on hydrolysis with water yields higher fatty acids and higher monohydric alcohols.

$$\underset{\text{Cetyl palmitate}}{C_{15}H_{31}COOC_{16}H_{33}} + H_2O \rightarrow \underset{\text{Palmitic acid}}{C_{15}H_{31}COOH} + \underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH}$$

When hydrolysis is carried with caustic alkalies, soap and higher monohydric alcohols are formed.

$$C_{15}H_{31}COOC_{16}H_{33} + NaOH \rightarrow C_{16}H_{33}OH + \underset{\text{Sodium palmitate (Soap)}}{C_{15}H_{31}COONa}$$

The common waxes are:

(i) **Bees wax,** Myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$

(ii) **Spermaceti wax**, Cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$

(iii) **Carnauba wax**, Myricyl cerotate, $C_{25}H_{51}COOC_{30}H_{61}$

Waxes are used in the manufacture of candles, polishes, inks, water proof coating and cosmetic preparations.

Waxes obtained from plants and animals are different than **paraffin wax** which is a petroleum product and a mixture of higher hydrocarbons (20 to 30 carbon atoms). So paraffin wax is not an ester.

Candles are prepared by mixing paraffin wax (90%) with higher fatty acids like stearic and palmitic. The fatty acids are added to paraffin wax as to give strength to candles. The mixture is melted and poured into metal tubes containing streched threads. On cooling candles are obtained.

Substituted carboxylic acids

The compounds formed by the replacement of one or more hydrogen atoms of the hydrocarbon chain part of the carboxylic acids by atoms or groups such as X (halogen), OH or NH_2 are referred to as substituted acids. For example,

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH}\ ;\quad \underset{\text{Hydroxyacetic acid}}{CH_2OHCOOH}\ ;\quad \underset{\text{Aminoacetic acid}}{CH_2NH_2COOH}$$

The position of the substituents on the carbon chain are indicated by Greek letters or numbers.

$$\underset{\varepsilon}{\overset{6}{C}}-\underset{\delta}{\overset{5}{C}}-\underset{\gamma}{\overset{4}{C}}-\underset{\beta}{\overset{3}{C}}-\underset{\alpha}{\overset{2}{C}}-\overset{1}{C}OOH$$

For example,

$$\underset{\substack{\alpha\text{-Hydroxypropionic acid}\\ \text{2-Hydroxypropanoic acid}}}{CH_3CHOHCOOH}\ ;\qquad \underset{\substack{\beta\text{-Hydroxybutyric acid}\\ \text{3-Hydroxybutanoic acid}}}{CH_3CHOHCH_2COOH}$$

Lactic Acid or α-hydroxy propionic acid or 2-hydroxy propanoic acid

It is the main constituent of sour milk. It is manufactured by fermentation of molasses by the micro-organism (*Bacterium acidi lactici*-sour milk) in presence of $CaCO_3$.

(1) **Method of Preparation**

From acetaldehyde :

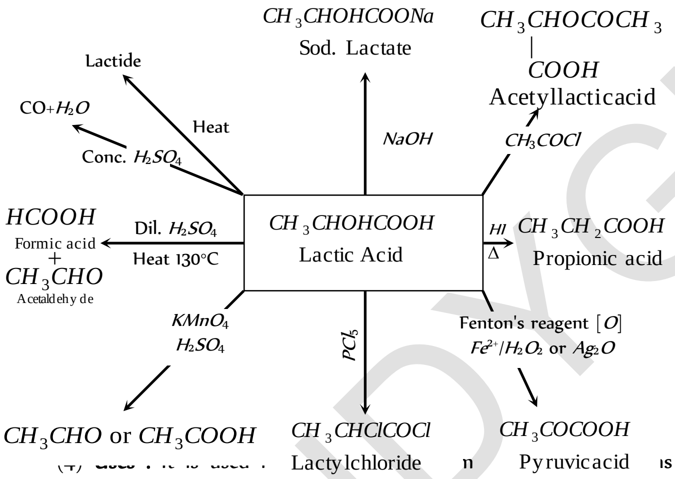
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN \rightarrow \underset{\text{Cyanohydrin}}{CH_3CH(OH)CN} \xrightarrow{H_2O/H^+} \underset{\text{Lactic acid}}{CH_3CHOHCOOH}$$

(2) **Physical Properties**

It is a colourless syrupy liquid having a sour taste and smell.

It is hygroscopic and very soluble in water. It is optically active and exists in three distinct forms.

(3) **Chemical Properties :** It gives reactions of secondary alcoholic group and a carboxylic group.



(4) **Uses :** It is used ... as mordant in dyeing, as acidulant in beverages and **candies**, as a solvent (ethyl and butyl lactates) for cellulose nitrate.

Tartaric Acid. Or α,α'-Dihydroxy succinic acid or 2,3-Dihydroxy-Butane-1,4-Dioic acid

$$\begin{matrix} HO-CH-COOH \\ | \\ HO-CH-COOH \end{matrix}$$

It is found as free or potassium salt in grapes, tamarind, and berries.

(1) **Methods of Preparation**

(i) **Argol** which separates as a crust during fermentation of grape juice is impure potassium hydrogen tartrate. Argol is boiled with limewater. Calcium tartrate is precipitated which is filtered. The solution contains potassium tartrate which is also precipitated by addition of $CaCl_2$. The calcium salt is then decomposed with calculated quantity of dilute H_2SO_4. The precipitate ($CaSO_4$) is filtered and the filtrate on concentration gives the crystals of tartaric acid.

$$2\underset{\text{Pot.hydrogen tartrate}}{\begin{matrix} CH(OH)COOK \\ | \\ CH(OH)COOH \end{matrix}} + Ca(OH)_2 \rightarrow \underset{\text{Pot.tartrate (Filtrate)}}{\begin{matrix} CH(OH)COOK \\ | \\ CH(OH)COOK \end{matrix}} + \underset{\text{Calcium tartrate (ppt.)}}{\begin{matrix} CH(OH)COO \\ | \\ CH(OH)COO \end{matrix} > Ca}$$

$$\xrightarrow[-2KCl]{CaCl_2}$$

$$\begin{matrix} CH(OH)COO \\ | \\ CH(OH)COO \end{matrix} > Ca + H_2SO_4 \rightarrow CaSO_4 + \underset{\text{Tartaric acid}}{\begin{matrix} CH(OH)COOH \\ | \\ CH(OH)COOH \end{matrix}}$$

(ii) ***Synthetic method***

$$C + H_2 \xrightarrow[arc]{\text{Electric}} \underset{\text{Acetylene}}{CH \equiv CH} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{Br_2}$$

$$\underset{\text{Ethylene bromide}}{(CH_2Br)_2} \xrightarrow{2KCN} \begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} \xrightarrow{H_2O/H^+} \underset{\text{Succinic acid}}{\begin{matrix} CH_2CO_2H \\ | \\ CH_2CO_2H \end{matrix}}$$

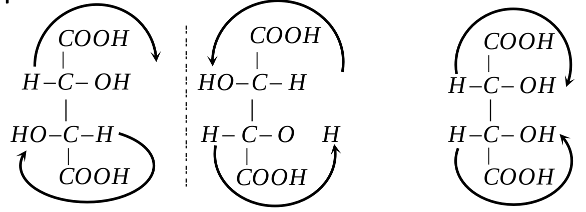
$$\xrightarrow[Br_2]{\text{Red } P} \underset{\alpha,\alpha'\text{-Dibromo succinic acid}}{\begin{matrix} CHBrCOOH \\ | \\ CHBrCOOH \end{matrix}} \xrightarrow{AgOH} \underset{\text{Tartaric acid}}{\begin{matrix} CHOHCOOH \\ | \\ CHOHCOOH \end{matrix}}$$

(iii) ***From glyoxal cyanohydrin :***

$$\underset{\text{Glyoxal}}{\begin{matrix} CHO \\ | \\ CHO \end{matrix}} \xrightarrow{HCN} \underset{\text{Glyoxal cyanohydrin}}{\begin{matrix} CH(OH)CN \\ | \\ CH(OH)CN \end{matrix}} \xrightarrow{H_2O/H^+} \underset{\text{Tartaric acid}}{\begin{matrix} CH(OH)COOH \\ | \\ CH(OH)COOH \end{matrix}}$$

(2) **Physical Properties :** It is a colourless crystalline compound. It is soluble in water and alcohol but insoluble in ether. It contains two asymmetric carbon atoms and thus shows optical isomerism (four forms). Natural tartaric acid is the dextro variety. It contains two secondary alcoholic groups and two carboxylic groups.

Optical Isomerism in tartaric acid



d+ Dextrorotatory Tartaric acid

l-(Leavorotatory acid)

Meso-Tartaric acid (Optical inactive)

Optical active

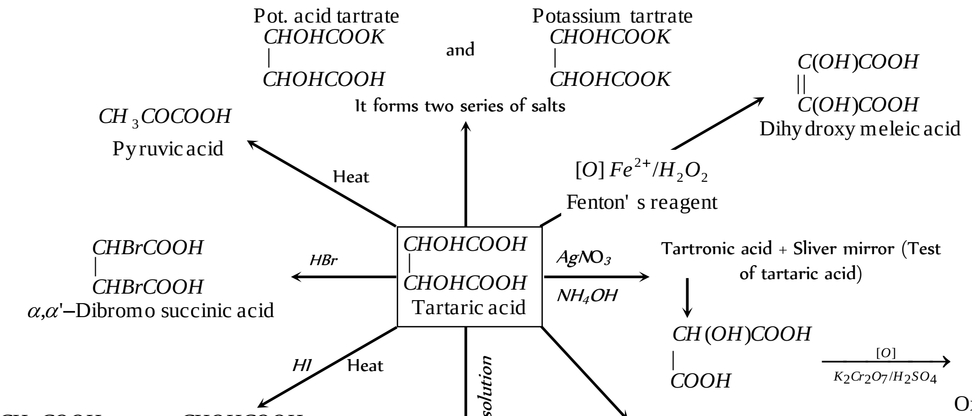
(i) $d+$ Tartaric acid-Dextro-rotatory

(ii) l –Tartaric acid-Leavorotatory

Optical active

(iii) Meso tartaric acid-optically inactive due to internal compensation.

(3) **Chemical Properties**



(4) **Uses :** It is used in carbonated beverages and effervescent tablets, in making baking powder (cream of tartar) and mordant in dyeing (potassium hydrogen tartrate), in preparing Fehling's solution (sodium potassium tartrate–Rochelle salt), in medicine as emetic, dyeing and calico-printing (tartar emetic-potassium antimonyl tartrate) and silver mirroring.

(5) **Tests**

(i) When heated strongly, tartaric acid chars readily giving a smell of burnt sugar to produce free carbon and pyruvic acid.

(ii) ***With $AgNO_3$* :** A neutral solution of tartaric acid gives a white ppt. which is soluble in ammonia. A silver mirror is obtained on warming the ammonical silver nitrate solution (Tollen's reagent).

(iii) ***With Fenton's reagent* :** (H_2O_2 containing a little of ferrous salt) and caustic soda, It gives a violet colour.

(iv) ***With Resorcinol and conc. H_2SO_4* :** It gives blue colour.

Citric Acid Or 2-Hydroxypropane Or 1,2,3-Tri Carboxylic Acid Or β-Hydroxy Tricarballylic Acid

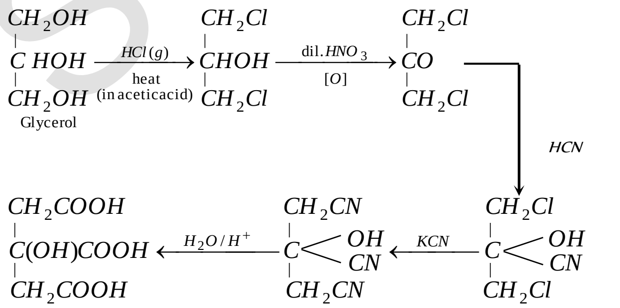
It occurs in the juice of citrus fruits such as lemon, galgal, orange, lime, etc. Lemon juice contains 6-10% of citric acid.

(1) **Methods of Preparation**

(i) ***By Fermentation* :** Citric acid is obtained by carrying fermentation of dilute solution of molasses with micro-organism, *Aspergillus nigar*, at 26-28°C for 7 to 10 days. The resulting solution is neutralised with $Ca(OH)_2$ to form insoluble precipitate, calcium citrate. It is decomposed by dilute H_2SO_4. The $CaSO_4$ is filtered off and the solution is concentrated under vacuum to get crystals of citric acid.

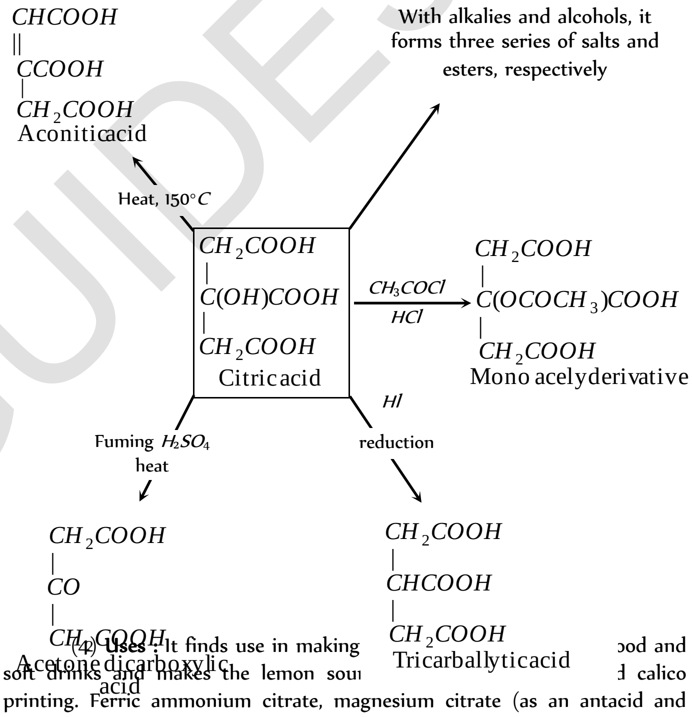
(ii) ***By Lemon juice* :** It is also obtained from lemon juice. The juice is boiled to coagulate proteins. From clear solution, citric acid is obtained as calcium salt with $Ca(OH)_2$.

(iii) ***By synthetic method***



(2) **Physical Properties :** It is a colourless crystalline compound. It possesses one water molecule as water of crystallisation. It is soluble in water and alcohol but less soluble in ether. It is not optically active compound. It is nontoxic in nature. It behaves as an alcohol and tribasic acid.

(3) **Chemical properties**

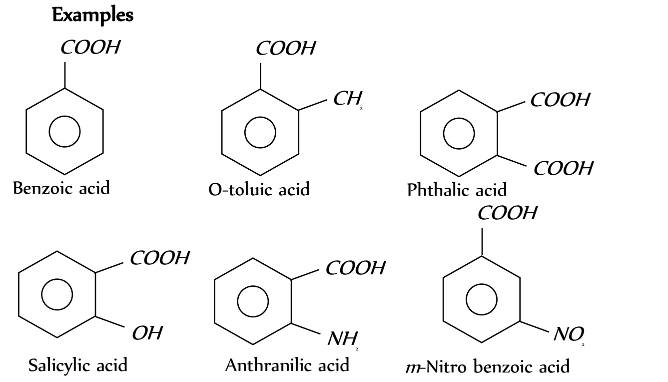


(4) **Uses :** It finds use in making ... ood and soft drinks and makes the lemon sou... d calico printing. Ferric ammonium citrate, magnesium citrate (as an antacid and laxative), sodium or potassium citrate are used in medicine. Ferric ammonium citrate finds use in making blue prints.

Aromatic Carboxylic Acids

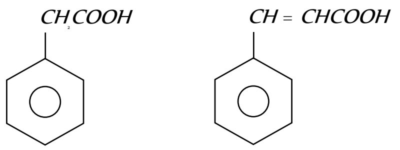
Aromatic acid contain one or more carboxyl group ($COOH$) attached directly to aromatic nucleus.

Examples



Aromatic acid containing-*COOH* group in the side chain, they are considered as aryl substituted aliphatic acid.

Examples

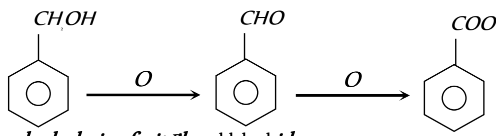


Phenyl acetic acid   Cinnamic acid

Benzoic Acid

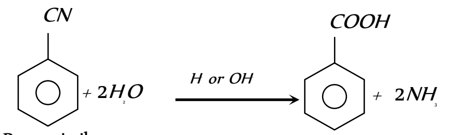
(1) **Methods of Preparation**

(i) ***From oxidation of Benzyl alcohol [Laboratory method]***



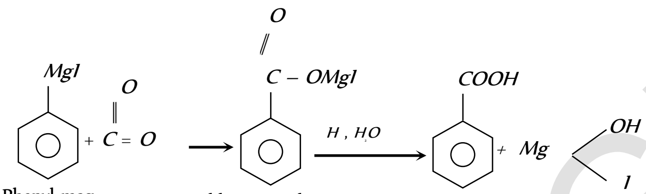
Benzyl alcohol   Benzaldehyde   Benzoic acid

(ii) ***From hydrolysis of nitriles or cyanides***



Benzonitrile   Benzoic acid

(iii) ***From Grignard reagent***

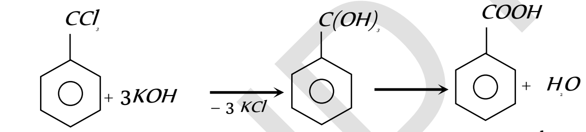


Phenyl mag. iodide   Addition product   Benzoic acid

(iv) ***By hydrolysis of esters***

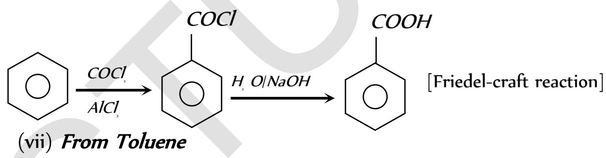
$$\underset{\text{Methyl benzoate}}{C_6H_5COOCH_3} + H_2O \xrightarrow{H^+ or OH^-} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Methanol}}{CH_3OH}$$

(v) ***From trihalogen derivatives of hydrocarbons***

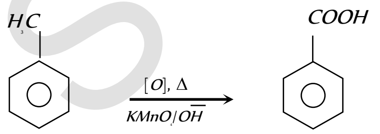


Benzotrichloride   Unstable   Benzoic acid

(vi) ***From benzene***

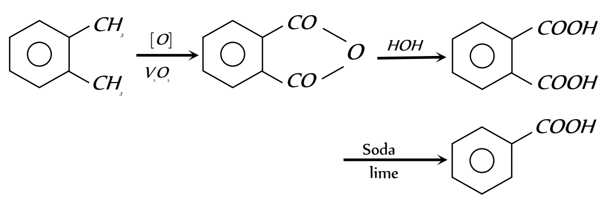


(vii) ***From Toluene***

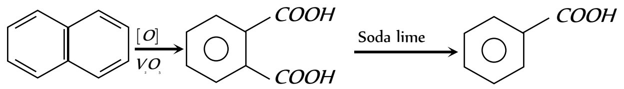


❑ Chromic trioxide in glacial acetic acid or Co-Mn acetate can also be taken in place of alkaline $KMnO_4$.

(viii) ***From o-xylene*** [*Industrial method*]



(ix) ***From naphthalene*** [*Industrial method*]



(2) **Physical Properties**

(i) It is a white crystalline solid.

(ii) It has m.p. 394 K.

(iii) It is sparingly soluble in cold water but fairly soluble in hot water, alcohol and ether.

(iv) It has a faint aromatic odour and readily sublimes and is volatile in steam.

(3) **Acidity of Aromatic Carboxylic Acid :** Aromatic acid dissociates to give a carboxylate anion and proton.

$$C_6H_5COOH \rightleftharpoons C_6H_5CO\bar{O} + H^+$$

Since the carboxylate anion $(ArCO\bar{O})$ is resonance stabilised to a greater extent than the carboxylic acid (*ArCOOH*).

$$\underset{\substack{\text{Resonance in carboxylic acid} \\ \left[\text{Non-equivalent structure and hence less stable}\right]}}{Ar-\overset{\overset{O}{\|}}{C}-OH \leftrightarrow Ar-\overset{\overset{O^-}{|}}{C}=\overset{+}{O}H} \qquad \underset{\substack{\text{Resonance in carboxylate anion} \\ \left[\text{Equivalent structure and hence more stable}\right]}}{Ar-\overset{\overset{O}{\|}}{C}-O^- \leftrightarrow Ar-\overset{\overset{O^-}{|}}{C}=O}$$

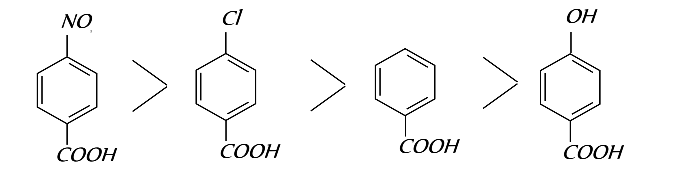
Effect of Substituents on Acidity : The overall influence of a substituent on acidity of substituted benzoic acids is due to two factors.

(i) ***Inductive effect*** **:** If the substituent exerts–*I* effect, it increases the acidity of carboxylic acids, while if it exerts + *I* effect it decreases the acidity. Inductive effect affects all positions, *i.e.*, *o*–, *m*– and *p*–.

(ii) ***Resonance effect*** **:** Like inductive effect, if the resonance producing group exerts minus effect *i.e.,* if it withdraws electrons, it increases the strength of the benzoic acid. Similarly, if the group causes +*R* effect it decreases the acidity of benzoic acid. However, remember that resonance effect affects only *o*- and *p*- positions. Thus if resonance producing group is present in the *m*-position it will not exert its effect.

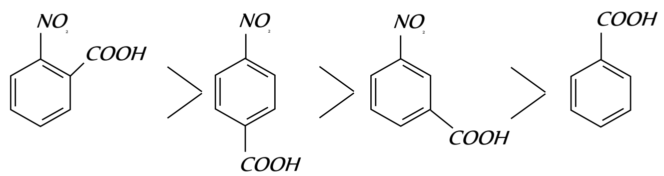
In case resonance and inductive effects both operate in the molecule, resonance effect being stronger overpowers the inductive effect.

Thus on the above basis, the following order of acidity can be explained.



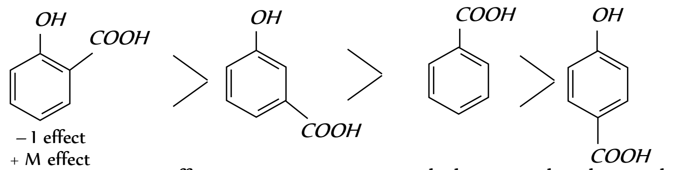
p-Nitrobenzoic acid – *NO₂* group exerts – *R* and – *I* effects   *p*-Chlorobenzoic acid – *Cl* group exerts – *I* effects, + R   Benzoic acid No other group   *p*-Hydroxybenzoic acid – *OH* group exerts + *R* and – *I* effects

Similarly :



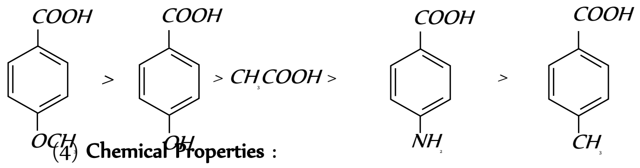
Acidity is only due to electron withdrawing inductive effect of the $-NO_2$ group (resonance does not affect the *m*-position) while in the *p*-isomer acidity is due to electron withdrawing inductive as well as resonance effect.

The acidity of the three isomers of hydroxybenzoic acids follows the following order.



Resonance effect cannot operate and hence only the acid-strengthening –I effect takes part with the result *m*-hydroxybenzoic acid is stronger acid than benzoic acid. Like other substituted benzoic acid.

Acidic character among benzoic acids having different electron releasing group.



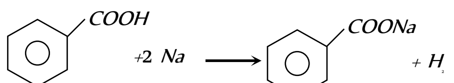
(4) **Chemical Properties** :

(i) Reactions of carboxylic group

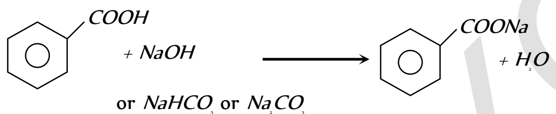
(ii) Reactions of aromatic ring

(i) ***Reactions of Carboxylic Group***

(a) *Reaction with metals*



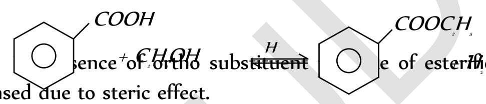
(b) *Reaction with Alkalies Or $NaHCO_3$ Or Na_2CO_3* :



or $NaHCO_3$ or Na_2CO_3

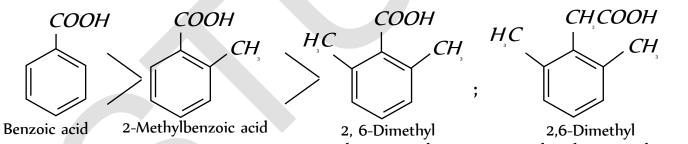
(c) *Formation of Esters* :

Aromatic acid (benzoic acid) having no group in its ortho positions can be readily esterified with alcohol in presence of a mineral acid.



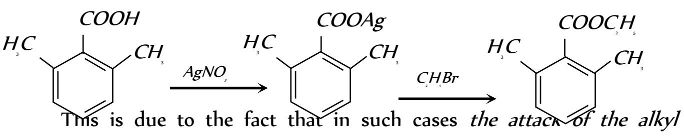
In presence of ortho substituent the rate of esterification is greatly decreased due to steric effect.

The esterification of the various benzoic acids :



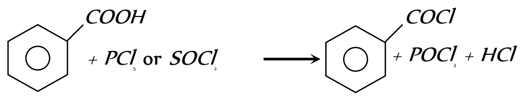
The substituted phenylacetic acid is easily esterified because $-COOH$ group is separated from benzene ring by $-CH_2-$ part.

The *ortho*-substituted benzoic acids can be easily esterified by treating the silver salt of the acid with alkyl halides, *i.e.,*



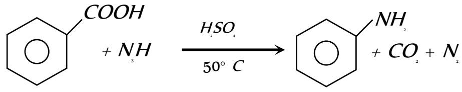
This is due to the fact that in such cases *the attack of the alkyl group of the alkyl halides is on the oxygen atom of the $-COOH$ group but not on the sterically hindered carbon atom.*

(d) *Formation of acid chloride*



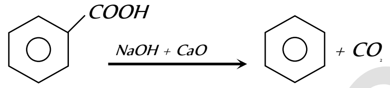
Benzoyl Chloride

(e) *Reaction with N_3H [Schmidt reaction]*



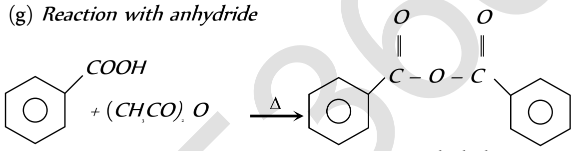
Aniline

(f) *Reaction with sodalime*



Benzene

(g) *Reaction with anhydride*

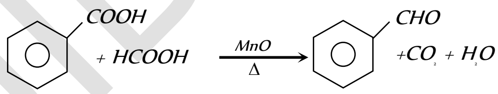


Benzoic anhydride

(h) *Reduction*

Benzyl alcohol

(i) *Decarboxylation*

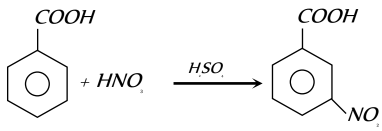


(j) *Hunsdiecker reaction* :

$$\underset{\text{Silver benzoate}}{C_6H_5COOAg} + \underset{(Br_2 \text{ or } Cl_2)}{X_2} \xrightarrow[\text{heat}]{\text{in } CCl_4} \underset{\text{Phenyl halide}}{C_6H_5-X} + CO_2\uparrow + AgX$$

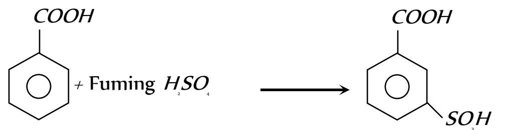
(ii) ***Reactions of Aromatic Ring***

(a) *Nitration*



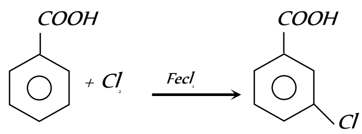
m-nitrobenzoic acid

(b) *Sulphonation*



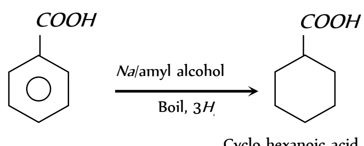
m-sulpho benzoic acid

(c) *Chlorination*



m-chloro benzoic acid

(d) *Reduction*



Cyclo hexanoic acid

(5) **Uses :** Benzoic acid is used,

(i) in medicine in the form of its salts especially as urinary antiseptic.

(ii) As sodium benzoate for preservation of food such as fruit juices, tomato ketchup, pickles etc.

(iii) In the preparation of aniline blue.

(iv) In treatment of skin diseases like eczema.

(6) **General Tests**

(i) Benzoic acid dissolves in hot water but separates out in the form of white shining flakes on cooling.

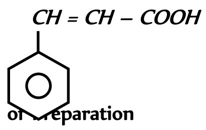
(ii) It evolves CO_2 with sodium bicarbonate, *i.e.*, it gives effervescence with sodium carbonate.

(iii) Neutral ferric chloride gives a buff coloured precipitate.

(iv) When warmed with ethyl alcohol and a little conc. H_2SO_4 a fragrant odour of ethyl benzoate is obtained.

(v) When heated strongly with soda lime, benzene vapours are evolved which are inflammable.

Cinnamic Acid [β-Phenyl acrylic acid]



(1) **Methods of preparation**

(i) ***By Perkin's reaction***

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[180°C]{CH_3COONa} C_6H_5CH = CHCOOH + CH_3COOH$$

(ii) ***By Claisen condensation***

$$C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa'} \underset{\text{Ester}}{C_6H_5CH = CHCOOC_2H_5} \xrightarrow[H^+]{H_2O} C_6H_5CH = CHCOOH + C_2H_5OH$$

(iii) ***By knoevenagel reaction***

$$C_6H_5CHO + CH_2(COOH)_2 \xrightarrow[\text{heat}]{NH_3} C_6H_5CH = CHCOOH + CO_2 + H_2O$$

(iv) ***Industrial method***

$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + \underset{\text{Sodium acetate}}{H_2CHCOONa} \xrightarrow{200°C} C_6H_5CH = CHCOOH + NaCl + HCl$$

(2) **Physical Properties**

(i) It is a white crystalline solid and its melting point 133°*C*.

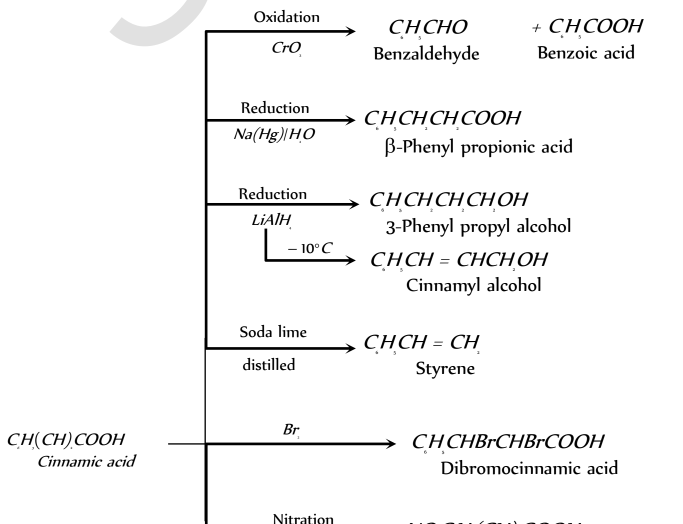
(ii) It is sparingly soluble in water.

(iii) It exhibits geometrical isomerism.

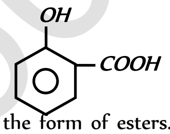
$$\underset{\substack{\text{Trans-form}\\ \text{(Cinnamic acid)}}}{\begin{matrix} C_6H_5-C-H \\ \| \\ H-C-COOH \end{matrix}} \qquad \underset{\substack{\textit{Cis}\text{-form}\\ \text{(Allocinnamic acid)}}}{\begin{matrix} C_6H_5-C-H \\ \| \\ HOOC-C-H \end{matrix}}$$

Cinnamic acid (stable form) occurs in nature both free and as esters in balsams and resins.

(3) **Chemical properties**



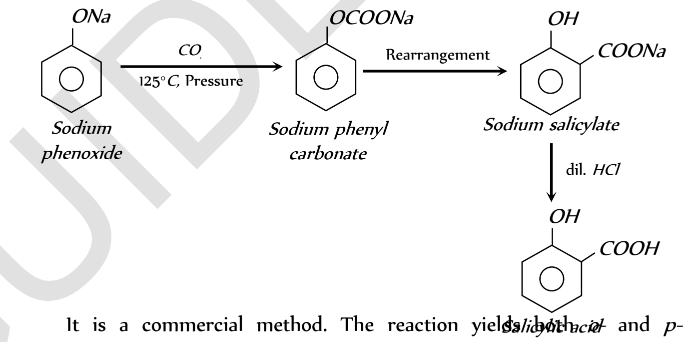
Salicylic acid [O-Hydroxy benzoic acid];



Salicylic acid is present in many essential oils in the form of esters. Oil of winter green is a methyl ester of salicylic acid.

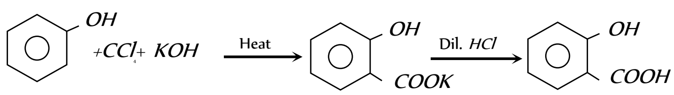
(1) **Methods of preparation**

(i) ***Kolbe Schmidt reaction***

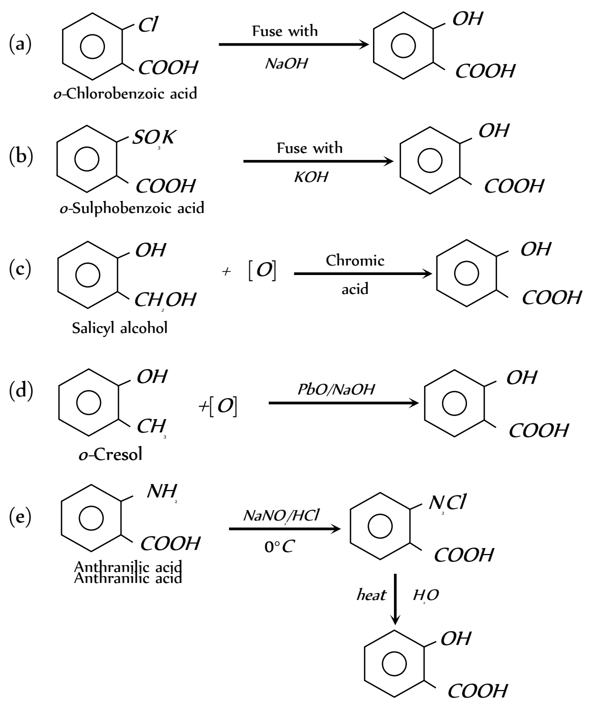


It is a commercial method. The reaction yields both *o*- and *p*- isomers. Salicylic acid is more volatile and separated by steam distillation.

(ii) ***Reimer-Tiemann reaction***



(iii) ***From benzene derivatives***



(2) **Physical properties**

(i) It is a colourless needle shaped crystalline compound.

(ii) Its *m.p.* is 156°*C*.

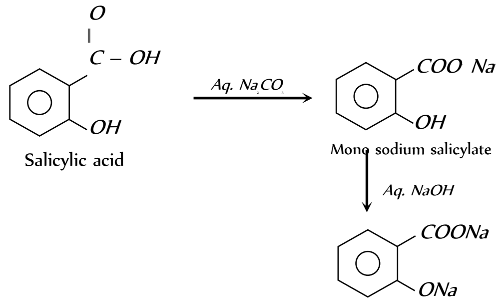
(iii) It is sparingly soluble in cold water but readily soluble in hot water, alcohol, ether and chloroform.

(iv) It is steam volatile.

(v) It is poisonous in nature. However, its derivative used in medicine internally and externally as antipyretic and antiseptic.

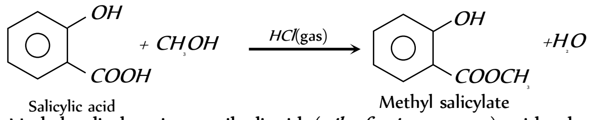
(3) **Chemical properties**

(i) ***Reaction with Na_2CO_3, $NaHCO_3$ or NaOH***

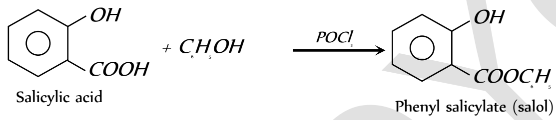


Disodium salicylate

(ii) ***Reaction with alcohols or phenols***

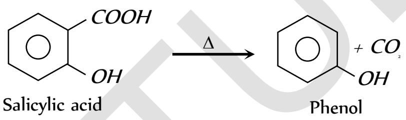


Methyl salicylate is an oily liquid (*oil of winter green*) with pleasant material. It is also used in medicine in the treatment of rheumatic pain and as a remedy for aches, sprains and bruises. It is used in perfumery and as a flavouring. It is used for making of iodex.

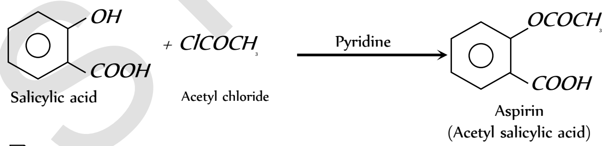


Salol is a white solid *m.pt.* 43°*C*. It is a good internal antiseptic. It is used in making of toothpastes. Salol absorbs ultraviolet light and its main use now is sun-screening agent and stabiliser of plastics.

(iii) ***Decarboxylation***

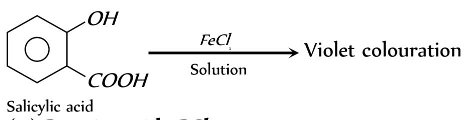


(iv) ***Acetylation***

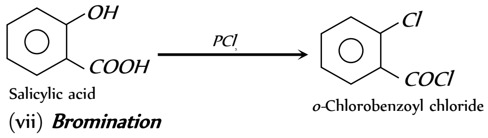


❑ Aspirin is a white solid, melting point 135°*C*. It is used as antipyretic and pain killer (analgesic action).

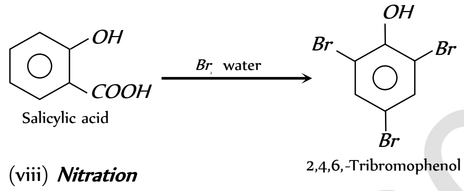
(v) ***Reaction with ferric chloride solution***



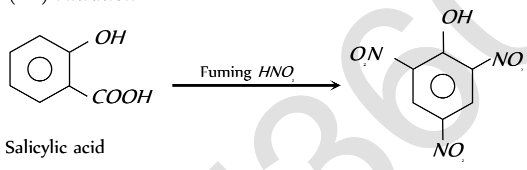
(vi) **Reaction with** PCl_5



(vii) ***Bromination***

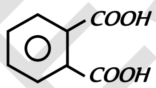


(viii) ***Nitration***

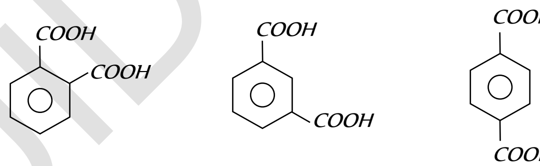


2,4,6,-Trinitrophenol

Phthalic acid [1,2,-Benzene dicarboxylic acid]



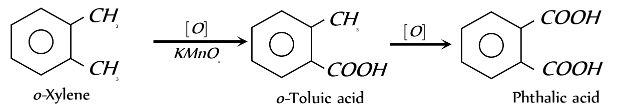
There are three isomer (ortho, meta, para) of benzene dicarboxylic acid.



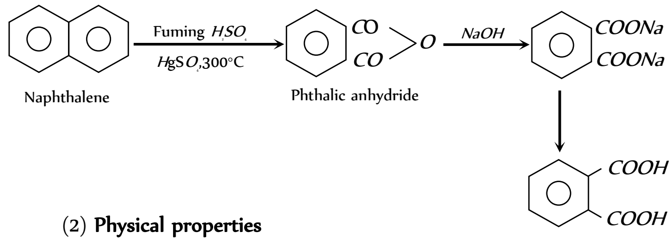
Benzene-1,2-dicarboxylic acid (Phthalic acid)   Benzene-1,3-dicarboxylic acid (Isophthalic acid)   Benzene-1,4-dicarboxylic acid (Terphthalic acid)

(1) **Methods of preparation**

(i) ***By the oxidation of o-xylene*** **:**



(ii) ***From naphthalene*** (Industrial method) **:** It is known as aerial oxidation.



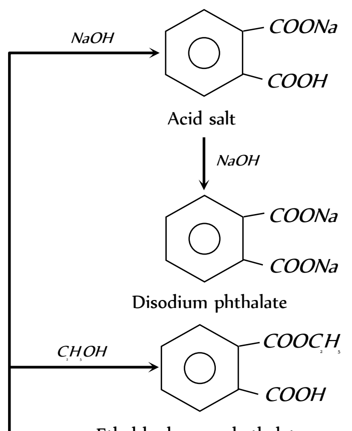
(2) **Physical properties**

(i) It is colourless crystalline compound.

(ii) Its melting point is not sharp (195–213°*C*).

(iii) It is sparingly soluble in cold water but soluble in hot water, alcohol, ether, benzene etc.

(3) **Chemical properties**



(4) **Uses :** It is used in the manufacture of plastics, dyes and other compounds such as phthalic anhydride, phthalimide, anthraquinone and fluorescein etc.

Acid derivatives

The compounds which are obtained by replacing the $-OH$ of the carboxylic group by other atoms or groups such as $X^-, -NH_2, -OR$ and $O-\underset{\underset{O}{\|}}{C}-R$ are known as acid derivatives.

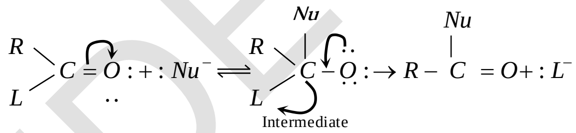
- $R-\underset{\underset{O}{\|}}{C}-$ group is common to all the derivatives and is known as acyl group and these derivatives are termed as acyl compound.

- The important derivatives are given below :

Group replacing $-OH$	Name	Structure
$(X = F, Cl, Br, I)$	Acyl halide	$R-\overset{\overset{O}{\|}}{C}-X$
$-NH_2$	Amide	$R-\overset{\overset{O}{\|}}{C}-NH_2$
$-OR'$	ester	$R-\overset{\overset{O}{\|}}{C}-OR'$ (R' may be R)
$-OOCR$	anhydride	$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.



$$(L = X, NH_2, O-\overset{\overset{O}{\|}}{C}-R \text{ or } OR)$$

The relative reactivities of various acyl compounds have been found to be in the following order:

$$\begin{matrix}R\\X\end{matrix}\!\!>C=O > R-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R > R-C\begin{matrix}{=}O\\ {-}OR\end{matrix} > R-C\begin{matrix}{=}O\\ {-}NH_2\end{matrix}$$

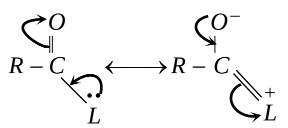
Out of acid halides, the acid chlorides are more important ones.

The overall order of reactivity can be accounted for in terms of the following three factors:

(i) Basicity of the leaving group (ii) Resonance effects and (iii) Inductive effects.

(i) ***Basicity of the leaving group*** : Weaker bases are good leaving groups. Hence, the acyl derivatives with weaker bases as leaving groups are more reactive. Chloride ion is the weakest base while $-NH_2$ is the strongest base. Thus, acyl chlorides are most reactive and amides are least reactive.

(ii) ***Resonance effect*** : The leaving group in each case has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.



This makes the molecule more stable. The greater the stabilization, the smaller is the reactivity of the acyl compound.

However, acyl chlorides are least affected by resonance. Due to lower stabilization, the acid chlorides are more reactive as the loss of $-Cl$ is easier. Greater stabilization is achieved by resonance in esters and amides and thus, they are less reactive.

(iii) ***Inductive effect*** : Higher the $-I$ effect, more reactive is the acyl compound. Inductive effect of oxygen in ester is greater than nitrogen in amide, hence ester is more reactive than an amide.

Acyl Halides $R-C\begin{matrix} \nearrow O \\ \searrow Cl \end{matrix}$

where R may be alkyl or aryl group.

(1) **Methods of Preparation**

(i) ***From carboxylic acid*** :

$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

(ii) ***Industrial method*** : By distilling anhydrous sodium acetate

$$3CH_3COONa + PCl_3 \xrightarrow{\text{heat}} 3CH_3COCl + Na_3PO_3$$

$$\underset{\text{Sodium acetate}}{2CH_3COONa} + POCl_3 \xrightarrow{\text{heat}} \underset{\text{Acetyl chloride}}{2CH_3COCl} + NaPO_3 + NaCl$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Sulphuryl chloride}}{SO_2Cl_2} \xrightarrow{\text{heat}} \underset{\text{Acetyl chloride}}{2CH_3COCl} + CaSO_4$$

(iii) ***With thionyl chloride*** :

$$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

This is the best method because SO_2 and *HCl* are gases and easily escape leaving behind acyl chloride.

(2) **Physical properties** : The lower acyl chloride are mobile, colourless liquid while the higher members are coloured solids.

Acyl chloride have very pungent, irritating order and are strong lachrymators (tears gases)

They fume in air due to the formation of hydrochloric acid by hydrolysis.

They are readily soluble in most of the organic solvent. Acyl chloride don't form intermolecular hydrogen bonding. Therefore, their boiling points are lower than those of their parent acids.

(3) **Chemical properties**

$$R-\overset{\overset{O}{\|}}{C}-Cl + :Nu^- \rightarrow R-\underset{\underset{Nu}{|}}{\overset{\overset{O^-}{|}}{C}}-Cl \rightarrow R-\underset{\underset{Nu}{|}}{\overset{\overset{O}{\|}}{C}} + Cl^-$$

$$Cl^- + H^+ \rightarrow HCl$$

(i) ***Hydrolysis*** : $\underset{\text{Acetyl chloride}}{CH_3COCl} + HOH \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2O \rightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

(ii) ***Reaction with alcohols (alcoholysis)***

$$CH_3COCl + CH_3CH_2OH \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3} + HCl$$

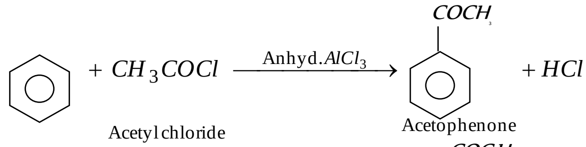
$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[\text{Pyridine}]{\text{aq } NaOH \text{ or}} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + HCl$$

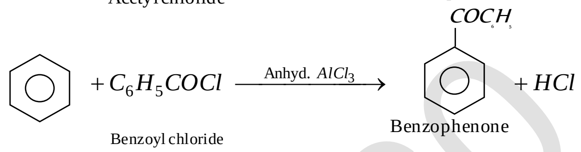
This reaction is called **Schotten Baumann reaction**.

(iii) ***Reaction with salts of carboxylic acid***

$$CH_3COCl + CH_3COO^-Na^+ \xrightarrow{\text{Pyridine}} \underset{\text{Acetic anhydride}}{CH_3\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3}$$

(iv) ***Reaction with benzene*** **(acylation)** : This reaction is called friedel craft reaction.





(v) ***Reaction with ammonia or amines*** :

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 2NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + NH_4Cl$$

$$C_6H_5COCl + 2NH_3 \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + NH_4Cl$$

However, acyl chlorides react with amines to form substituted amides.

$$CH_3COCl + H_2NC_2H_5 \rightarrow \underset{\text{N-Ethyl acetamide}}{CH_3\overset{\overset{O}{\|}}{C}-NH-C_2H_5}$$

$$CH_3COCl + (C_2H_5)_2NH \rightarrow \underset{\text{N, N-Diethyl acetamide}}{CH_3CON(C_2H_5)_2} + HCl$$

(vi) ***Reduction*** :

$$CH_3COCl \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} \underset{\text{Ethanol (Primary alcohol)}}{CH_3CH_2OH}$$

$$CH_3COCl + H_2 \xrightarrow{Pd / BaSO_4} CH_3CHO + HCl$$

This reaction is called **Rosenmund reaction**.

(vii) ***Reaction with organocadmium compounds*** **(formation of ketones)**

$$2CH_3COCl + \underset{\text{Dimethyl Cadmium}}{(CH_3)_2Cd} \rightarrow \underset{\text{Acetone}}{2CH_3COCH_3} + CdCl_2$$

$$2C_6H_5COCl + (CH_3)_2Cd \rightarrow \underset{\text{Acetophenone}}{2C_6H_5COCH_3} + CdCl_2$$

(viii) ***Reaction with diazomethane***

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + \underset{\text{Diazomethane}}{2\bar{C}H_2-\overset{+}{N}\equiv N} \rightarrow \underset{\text{Diazoacetone}}{CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{C}H-\overset{+}{N}\equiv N}$$

$$\xrightarrow[(-N_2)]{H_2O} CH_3CH_2\overset{\overset{O}{\|}}{C}-OH$$

(ix) ***Reaction with water***

$$CH_3COCl \xrightarrow{AgNO_3 / H_2O} CH_3COOH + AgCl + HNO_3$$

(x) ***Reaction with chlorine***

$$CH_3COCl + Cl_2 \xrightarrow{\text{Red } P} \underset{\text{Mono-}\alpha\text{-chloroacetyl chloride}}{Cl-CH_2-CO-Cl} + HCl$$

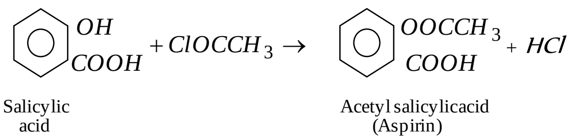
(xi) ***Reaction with Grignard reagent***

$$\underset{\text{Methyl magnesium iodide}}{CH_3CO\boxed{Cl + IMg}CH_3} \rightarrow \underset{\text{Acetone}}{CH_3COCH_3} + Mg\begin{matrix} I \\ Cl \end{matrix}$$

(xii) ***Reaction with KCN***

$$CH_3COCl + KCN \rightarrow \underset{\text{Acetyl cyanide}}{CH_3COCN} \xrightarrow{H_2O} \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

(xiii) ***Reaction with Salicylic acid***



(xiv) ***Reaction with ether***

$$CH_3COCl + \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow[\text{anhy.}]{ZnCl_2}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

(xv) ***Reaction with sodium peroxide*** **(Peroxide formation)**

$$\underset{\text{Acetyl chloride}}{2CH_3 - \overset{\overset{O}{\|}}{C} - Cl} + \overset{+}{Na}\overset{-}{O} - \overset{-}{O}\overset{+}{Na} \rightarrow \underset{\text{Acetyl peroxide}}{CH_3\overset{\overset{O}{\|}}{C} - O - O - \overset{\overset{O}{\|}}{C} - CH_3} + 2NaCl$$

(xvi) ***Reaction with hydroxylamine and hydrazine***

$$CH_3COCl + \underset{\text{Hydroxyl amine}}{H_2NOH} \rightarrow \underset{\substack{\text{Acetyl hydroxylamine} \\ \text{(hydroxamic acid)}}}{CH_3CONHOH} + HCl$$

$$CH_3COCl + \underset{\text{Hydrazine}}{H_2NNH_2} \rightarrow \underset{\text{Acetyl hydrazine}}{CH_3CONHNH_2} + HCl$$

(4) **Uses**

(i) As an acetylating agent.

(ii) In the estimation and determination of number of hydroxyl and amino groups.

(iii) In the preparation of acetaldehyde, acetic anhydride, acetamide, acetanilide, aspirin, acetophenone etc.

Acid Amides $\mathbf{R - C}\begin{matrix} \mathbf{\nearrow O} \\ \mathbf{\searrow NH_2} \end{matrix}$

where, $R = -CH_3, -CH_2CH_3, -C_6H_5$

(1) **Methods of preparation**

(i) ***Ammonolysis of acid derivatives***

$$CH_3COCl + 2NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + NH_4Cl$$

$$(CH_3CO)_2O + 2NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Amm. acetate}}{CH_3COONH_4}$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + NH_3 \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$$

(ii) ***From ammonium salts of carboxylic acids*** **(Laboratory Method)**

$$CH_3COONH_4 \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

❑ Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product (CH_3COOH).

(iii) ***By partial hydrolysis of alkyl cyanide*** :

$$CH_3C \equiv N \xrightarrow[H_2O/OH^-]{\text{Conc. } HCl} \underset{\text{Acetamide}}{CH_3CONH_2}$$

(iv) ***By heating carboxylic acid and urea***

$$H_2N - \underset{\underset{O}{\|}}{C} - NH_2 + R - \underset{\underset{O}{\|}}{C} - OH \xrightarrow{\text{heat}} \underset{\text{Amide}}{R - \underset{\underset{O}{\|}}{C} - NH_2} + CO_2 + NH_3$$

(2) **Physical properties**

(i) ***Physical state*** **:** Formamide is a liquid while all other amides are solids.

(ii) ***Boiling points*** **:** Amides have high boiling points than the corresponding acids.

Acetamide	Boiling points 494 K
Acetic Acid	Boiling points 391 K
Benzamide	Boiling points 563 K
Benzoic acid	Boiling points 522 K

The higher boiling points of amides is because of intermolecular hydrogen bonding

$$\ldots\ldots\ldots\; H - \overset{\overset{H}{|}}{N} - \overset{\overset{R}{|}}{C} = O \ldots\ldots\ldots\; H - \overset{\overset{H}{|}}{N} - \overset{\overset{R}{|}}{C} = O \ldots\ldots\ldots\; H - \overset{\overset{H}{|}}{N} - \overset{\overset{R}{|}}{C} = O$$

(iii) ***Solubility*** **:** The lower members of amide family are soluble in water due to the formation of hydrogen bonds with water.

(3) **Chemical properties**

(i) ***Hydrolysis***

$$CH_3CONH_2 + H_2O \xrightarrow{\text{Slowly}} CH_3COOH + NH_3$$

$$CH_3CONH_2 + H_2O + HCl \xrightarrow{\text{Rapidly}} CH_3COOH + NH_4Cl$$

$$CH_3CONH_2 + NaOH \xrightarrow{\text{Far more rapidly}} CH_3COONa + NH_3$$

(ii) ***Amphoteric nature*** **(Salt formation)**

It shows feebly acidic as well as basic nature.

$$CH_3CONH_2 + HCl(\text{conc.}) \rightarrow \underset{\substack{\text{Acetamide hydrochloride} \\ \text{(only stable in aqueous solution)}}}{CH_3CONH_2.HCl}$$

$$\underset{\text{Acetamide}}{2CH_3CONH_2} + \underset{\text{Mercuric Oxide}}{HgO} \rightarrow \underset{\text{Mercuric acetamide}}{(CH_3CONH)_2Hg} + H_2O$$

$$CH_3CONH_2 + Na \xrightarrow{\text{Ether}} \underset{\text{Sodium acetamide}}{CH_3CONHNa} + \frac{1}{2}H_2$$

(iii) ***Reduction***

$$\underset{\text{Acetamide}}{CH_3CONH_2} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + H_2O$$

(iv) ***Dehydration***

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{heat}]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3C \equiv N} + H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[\text{heat}]{P_2O_5} \underset{\text{Phenyl cyanide}}{C_6H_5C \equiv N} + H_2O$$

$$C_6H_5CONH_2 \xrightarrow{SOCl_2} \underset{\text{Phenyl cyanide}}{C_6H_5C \equiv N}$$

(v) ***Reaction with nitrous acid***

$$CH_3CONH_2 + HONO \xrightarrow{NaNO_2 / HCl} \underset{\text{Aceticacid}}{CH_3COOH} + N_2 + H_2O$$

$$C_6H_5CONH_2 + HONO \xrightarrow{NaNO_2 / HCl} \underset{\text{Benzoic acid}}{C_6H_5COOH} + N_2 + H_2O$$

(vi) ***Hofmann bromamide reaction or Hofmann degradation*** **:** This is an important reaction for reducing a carbon atom from a compound, *i.e.,* $-CONH_2$ is changed to $-NH_2$ group.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[NaOH \text{ or } KOH]{Br_2} \underset{\text{Methylamine (p-)}}{CH_3NH_2}$$

This reaction occurs is three steps:

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + KOH \rightarrow \underset{\text{Acetobromamide}}{CH_3CONHBr} + KBr + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-NHBr + KOH \rightarrow \underset{\text{Methyl isocyanate}}{CH_3NCO} + KBr + H_2O$$

$$CH_3NCO + 2KOH \rightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + K_2CO_3$$

$$CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

❑ In this reaction a number of intermediates have been isolated; *N*-bromamides, $RCONHBr$; salts of these bromamides $[RCONBr^-]\ K^+$; Isocyanates, *RNCO*.

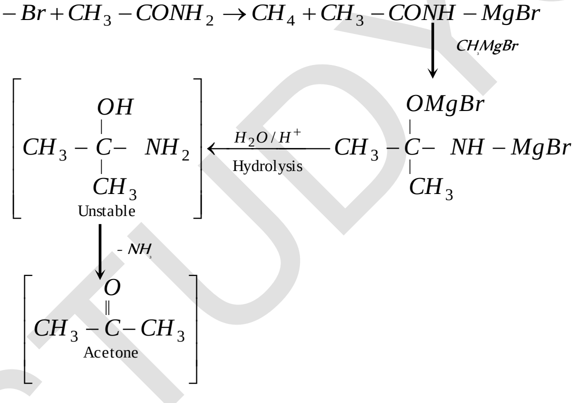
❑ Nitrene rearranges to form isocyanate.

(vii) ***Action with alcohol*** **:**

$$CH_3CONH_2 + CH_3OH \xrightarrow[70^o C]{HCl} \underset{\text{methyl acetate}}{CH_3COOCH_3} + NH_4Cl$$

(viii) **Reaction with grignard reagent**

$$CH_3-Mg-Br + CH_3-CONH_2 \rightarrow CH_4 + CH_3-CONH-MgBr$$



(4) **Uses**

(i) In organic synthesis. The compounds like methyl cyanide, Methylamine and ethylamine can be prepared.

(ii) In leather tanning and paper industry.

(iii) As a wetting agent and as soldering flux.

Amides such as dimethyl formamide (DMF), dimethyl acetamide (DMA) are used as solvents for organic and inorganic compounds.

Esters, $R-\underset{\underset{O}{\|}}{C}-OR$

These are the most important class of acid derivatives and are widely distributed in nature in plants, fruits and flowers.

(1) **Methods of preparation**

(i) ***From carboxylic acid*** [**Esterification**] **:** Laboratory method.

$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH+H}OR' \overset{H}{\rightleftharpoons} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{\text{Ether}} \underset{\text{Methyl acetate}}{CH_3COOCH_3} + N_2$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{\text{Ether}} \underset{\text{Methyl benzoate}}{C_6H_5COOCH_3} + N_2$$

❑ With diazomethane is the best method.

(ii) ***From acid chloride or acid anhydrides***

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl+H}}\underset{\text{Ethyl alcohol}}{OC_2H_5} \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

$$\underset{\text{Acetic anhydride}}{\begin{matrix} CH_3CO \\ CH_3CO \end{matrix} > O} + \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3} + CH_3COOH$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5CO\boxed{Cl\ +\ H}}\underset{\text{Ethyl alcohol}}{OC_2H_5} \rightarrow \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + HCl$$

(iii) ***From alkyl halide :***

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Silver acetate}}{CH_3COOAg} \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgBr$$

(iv) ***From ether*** **:**

$$\underset{\text{Methoxy methane}}{CH_3-O-CH_3} + CO \xrightarrow[350K]{BF_3} \underset{\text{Methyl acetate}}{CH_3COOCH_3}$$

(v) ***From Tischenko reaction :***

$$CH_3-\underset{\underset{O}{\|}}{C}-H + O=\underset{\underset{H}{|}}{C}-CH_3 \xrightarrow{Al(OC_2H_5)_3} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5$$

(2) **Physical properties**

(i) ***Physical state and smell*** **:** Esters are colourless liquids (or solids) with characteristic fruity smell. Flavours of some of the esters are listed below :

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octyl acetate	Orange

(ii) ***Solubility*** **:** They are sparingly soluble in water but readily soluble in organic solvents such as alcohol, ether etc.

(iii) ***Boiling points*** **:** Their boiling points are lower than the corresponding acids because of the absence of hydrogen bonding. *i.e.,* ethyl acetate = $77.5^{\circ}C$.

(3) **Chemical properties**

(i) ***Hydrolysis*** **:**

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \overset{\text{dil. acid}}{\rightleftharpoons} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Hydrolysis of ester by alkalies (*NaOH*) is known as saponification and leads to the formation of soaps

❑ This reaction (saponification) is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

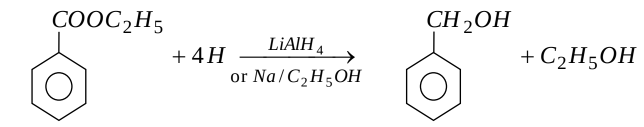
❑ The acid hydrolysis of esters is reversible.

(ii) ***Reaction with ammonia*** (**ammonolysis**) **:**

$$\underset{\text{Ethyl acetate}}{CH_3CO\boxed{OC_2H_5+H}}NH_2 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + C_2H_5OH$$

(iii) ***Reduction***

$$CH_3COOC_2H_5 + 4[H] \xrightarrow[\text{or } Na / C_2H_5OH]{LiAlH_4} 2C_2H_5OH$$



Ethyl benzoate Benzyl alcohol

❑ Reduction in presence of Na/C_2H_5OH is known as Bouveault Blanc reduction.

❑ The catalytic hydrogenation of ester is not easy and requires high temperature and pressure. The catalyst most commonly used is a mixture of oxides known as copper chromate $(CuO.CuCr_2O_4)$.

$$R-\overset{\overset{O}{\|}}{C}-OR'+2H_2 \xrightarrow[525\,K,\,200-300\,\text{atm}]{CuO.CuCr_2O_4} RCH_2OH+R'OH$$

(iv) ***Reaction with PCl_5 or $SOCl_2$***

$$CH_3COOC_2H_5+PCl_5 \rightarrow CH_3COCl+C_2H_5Cl+POCl_3$$

$$CH_3COOC_2H_5+SOCl_2 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl}+\underset{\text{Ethyl chloride}}{C_2H_5Cl}+SO_2$$

$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}+PCl_5 \rightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl}+POCl_3+C_2H_5Cl$$

(v) ***Reaction with alcohols*** **:** On refluxing ester undergoes exchange of alcohols residues.

$$R-C\begin{matrix}\nearrow O\\ \searrow OR'\end{matrix}+\underset{\text{(Excess)}}{R''OH} \overset{H^+}{\rightleftharpoons} R-C\begin{matrix}\nearrow O\\ \searrow OR''\end{matrix}+R'OH$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}+CH_3OH \rightarrow \underset{\text{Methyl acetate}}{CH_3COOCH_3}+C_2H_5OH$$

❑ This reaction is known as alcoholysis or trans esterification.

(vi) ***Reaction with Grignard reagents***

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5}+CH_3MgBr \rightarrow \left[CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-OC_2H_5\right] \xrightarrow{-C_2H_5OMgBr} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H^+/H_2O} \underset{3^o\ \text{alcohol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

(vii) ***Claisen condensation***

$$\underset{\text{Ethyl acetate(2 molecules)}}{CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OC_2H_5+H}-CH_2COOC_2H_5} \xrightarrow{C_2H_5O^-Na^+}$$

$$\underset{\text{Ethyl acetoacetate }(\beta\text{-ketoester})}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5}+C_2H_5OH$$

(viii) ***Reaction with hydroxyl amine***

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OC_2H_5+H}}\underset{\text{Hydroxyl amine}}{NHOH} \xrightarrow{\text{base}} \underset{\text{Hydroxamic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-NHOH}+C_2H_5OH$$

(ix) ***Reaction with hydrazine***

$$CH_3COOC_2H_5+\underset{\text{Hydrazine}}{H_2NNH_2} \rightarrow \underset{\text{Acid hydrazide}}{CH_3CONHNH_2}+C_2H_5OH$$

(x) ***Halogenation***

$$CH_3COOC_2H_5+Br_2 \xrightarrow{\text{Red P}} \underset{\alpha-\text{Bromoethyl acetate}}{CH_2BrCOOC_2H_5}+HBr$$

(xi) ***Reaction with HI***

$$CH_3COOC_2H_5+HI \rightarrow \underset{\text{Acetic acid}}{CH_3COOH}+\underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(4) **Uses**

(i) As a solvent for oils, fats, cellulose, resins etc.

(ii) In making artificial flavours and essences.

(iii) In the preparation of ethyl acetoacetate.

(5) **General Tests**

(i) It has sweet smell

(ii) It is neutral towards litmus

(iii) A pink colour is developed when one or two drops of phenolphthalein are added to dilute sodium hydroxide solution. The pink colour is discharged when shaken or warmed with ethyl acetate.

(iv) Ethyl acetate on hydrolysis with caustic soda solution forms two compounds, sodium acetate and ethyl alcohol.

$$CH_3COOC_2H_5+NaOH \rightarrow CH_3COONa+C_2H_5OH$$

Acid Anhydride $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!\!>O$ or $(CH_3CO)_2O$

(1) **Method of preparation**

(i) ***From carboxylic acid***

$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH+H}O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[\text{Porcelain chips }1073\,K]{\text{Quartz tube}} \underset{\text{Acid anhydride}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R}+H_2O$$

$$C_6H_5CO\boxed{OH+H}OOCC_6H_5 \xrightarrow[\text{heat}]{P_4O_{10}}$$

$$\underset{\text{Benzoic anhydride}}{C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_6H_5}+H_2O$$

(ii) ***From carboxylic acid salt and acyl chloride*** [Laboratory method]

$$CH_3COONa+CH_3COCl \xrightarrow{Py} \underset{\text{Acetic anhydride}}{CH_3COOCOCH_3}+NaCl$$

$$C_6H_5COONa+C_6H_5COCl \xrightarrow{Py} \underset{\text{Benzoic anhydride}}{C_6H_5COOCOC_6H_5}$$

$$+NaCl$$

(iii) ***From acetylene***

$$\begin{matrix}CH\\ |||\\ CH\end{matrix}+2CH_3COOH \xrightarrow{HgSO_4} \begin{matrix}CH_3\\ |\\ CH(OOCCH_3)_2\end{matrix} \xrightarrow[\text{heat}]{\text{Distill}}$$

$$CH_3CHO + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O$$
Aceticanhydride

(iv) ***From acetaldehyde*** :

$$CH_3CHO + O_2 \xrightarrow[\text{acetate}]{\text{Cobalt}} 2CH_3 - \underset{\underset{O}{\|}}{C} - O - O - H$$

$$\rightarrow (CH_3CO)_2O + H_2O$$

(2) **Physical properties**

(i) ***Physical state*** **:** Lower aliphatic anhydrides are colourless liquids with sharp irritating smell. The higher members of the family as well as the aromatic acid anhydrides are solids in nature.

(ii) ***Solubility*** **:** They are generally insoluble in water but are soluble in the organic solvents such as ether, acetone, alcohol, etc.

(iii) ***Boiling points*** **:** The boiling points of acid anhydrides are higher than those of carboxylic acids because of the greater molecular size.

(3) **Chemical Properties**

(i) ***Hydrolysis*** **:**

$$\underset{\text{Aceticanhydride}}{CH_3 - \overset{\overset{O}{\|}}{C} - O - \overset{\overset{O}{\|}}{C} - CH_3} + H_2O \rightarrow \underset{\text{Aceticacid}}{2CH_3COOH}$$

(ii) ***Action with ammonia***

$$(CH_3CO)_2O + 2NH_3 \rightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Amm. acetate}}{CH_3COONH_4}$$

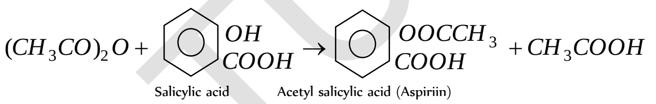
(iii) ***Acetylation*** **:** Acetic anhydride react with compound having active hydrogen.

$$(CH_3CO)_2O + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Ethylamine}}{H_2NC_2H_5} \rightarrow \underset{N-\text{Ethylacetamide}}{CH_3CONHC_2H_5} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Diethylamine}}{HN(C_2H_5)_2} \rightarrow \underset{N,N-\text{Diethyl acetamide}}{CH_3CON(C_2H_5)_2} + CH_3COOH$$

$$(CH_3CO)_2O + \underset{\text{Aniline}}{H_2NC_6H_5} \rightarrow \underset{\text{Acetanilide}}{CH_3CONHC_6H_5} + CH_3COOH$$



(iv) ***Action of dry HCl***

$$(CH_3CO)_2O + HCl \rightarrow CH_3COCl + CH_3COOH$$

(v) ***Reaction with chlorine***

$$(CH_3CO)_2O + Cl_2 \rightarrow \underset{\text{Acetylchloride}}{CH_3COCl} + \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH}$$

(vi) ***Reaction with PCl₅***

$$(CH_3CO)_2O + PCl_5 \rightarrow 2CH_3COCl + POCl_3$$

(vii) ***Friedel craft's reaction***

$$(CH_3CO)_2O + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + CH_3COOH$$

(viii) ***Reaction with acetaldehyde***

$$(CH_3CO)_2O + \underset{\text{Acetaldehyde}}{CH_3CHO} \rightarrow \underset{\text{Ethylidene acetate}}{CH_3CH(OOCCH_3)_2}$$

(ix) ***Reduction***

$$(CH_3CO)_2O \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(x) ***Action with ether*** **:**

$$CH_3CO\boxed{O.COCH_3 + C_2H_5}\!-O-\underset{\text{Diethyl ether}}{C_2H_5} \rightarrow \underset{\text{Ethyl acetate}}{2CH_3COOC_2H_5}$$

(xi) ***Action with N_2O_5***

$$CH_3COOCOCH_3 + N_2O_5 \rightarrow CH_3 - \underset{\underset{O}{\|}}{C} - O - N\begin{matrix} \nearrow O \\ \searrow O \end{matrix}$$

(4) **Uses :** Acetic anhydride is used

(i) as an acetylating agent.

(ii) For the detection and estimation of hydroxyl and amino group.

(iii) in the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, acetophenone, etc.

Urea or Carbamide $O = C\begin{matrix} NH_2 \\ NH_2 \end{matrix}$

Urea may be considered as diamide of an unstable and dibasic carbonic acid from which both the hydroxyl groups have been replaced by $-NH_2$ groups.

$$\underset{\text{Carbonic acid}}{O = C\begin{matrix} OH \\ OH \end{matrix}} \xrightarrow[+NH_2]{-OH} \underset{\text{Carbamic acid, (Monoamide)}}{O = C\begin{matrix} NH_2 \\ OH \end{matrix}} \xrightarrow[+NH_2]{-OH} \underset{\text{Urea, diamide of carbonic acid or carbamide}}{O = C\begin{matrix} NH_2 \\ NH_2 \end{matrix}}$$

❑ First time isolated from urine in 1773 by Roulle and hence the name urea was given.

❑ It was the first organic compound synthesised in the laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.

❑ This preparation gave a death blow to Vital force theory.

❑ It is the final decomposition product of protein's metabolism in man and mammals and is excreted along with urine.

❑ Adults excrete about 30 grams of urea per day in the urine.

(1) **Method of preparation**

(i) ***From urine*** : Urine is treated with conc. nitric acid where crystals of urea nitrate $CO(NH_2)_2.HNO_3$ are obtained.

$$\underset{\text{Urea nitrate}}{2CO(NH_2)_2.HNO_3} + BaCO_3 \rightarrow \underset{\text{Urea}}{2CO(NH_2)_2} + Ba(NO_3)_2 + H_2O + CO_2$$

(ii) ***Laboratory preparation***

(a) Wohler synthesis

$$\underset{\text{Potassium cyanate}}{2KCNO} + \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} \rightarrow \underset{\text{Ammonium cyanate}}{2NH_4CNO} + K_2SO_4$$

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow[\text{On heating}]{\text{Isomeric change}} \underset{\text{Urea}}{NH_2CONH_2}$$

❑ The solid residue is extracted with alcohol and the extract evaporated when the crystals of urea are obtained. It can be recrystalised from water.

(b) From phosgene or alkyl carbonate

$$\underset{\substack{\text{Carbonyl chloride}\\\text{(Phosgene)}}}{O=C\begin{matrix}Cl\\Cl\end{matrix}} + 2NH_3 \rightarrow \underset{\text{Urea}}{O=C\begin{matrix}NH_2\\NH_2\end{matrix}} + 2HCl$$

$$\underset{\text{Ethyl carbonate (urethane)}}{O=C\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} + 2NH_3 \rightarrow \underset{\text{Urea}}{O=C\begin{matrix}NH_2\\NH_2\end{matrix}} + 2C_2H_5OH$$

(iii) ***Industrial method***

(a) By partial hydrolysis of calcium cyanide

$$\underset{\substack{\text{Calcium}\\\text{Carbide}}}{CaC_2} + N_2 \xrightarrow{\text{heat}} \underset{\substack{\text{Calcium}\\\text{cyanamide}}}{CaCN_2} + C$$

The cyanamide is treated with dilute sulphuric acid at 40^oC where partial hydrolysis occurs with the formation of urea.

$$CaCN_2 \xrightarrow[-CaSO_4]{H_2SO_4} \underset{\text{Cyanamide}}{H_2NCN} \xrightarrow[(H_2O_2)]{H_2O} \underset{\text{(Urea)}}{H_2NCONH_2}$$

or

$$CaCN_2 + H_2O + H_2SO_4 \xrightarrow{40^oC} NH_2CONH_2 + CaSO_4$$

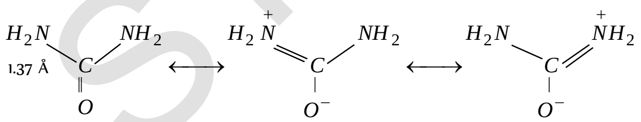
(b) From carbon dioxide and ammonia

$$CO_2 + 2NH_3 \xrightarrow{150-200^oC} \underset{\text{Ammonium carbamate}}{NH_2COONH_4}$$

$$\xrightarrow[-H_2O]{\text{heat }(140^o\text{C})} \underset{\text{Urea}}{NH_2CONH_2}$$

(2) **Physical properties** : Urea is a colourless, odourless crystalline solid. It melts at 132^oC. It is very soluble in water, less soluble in alcohol but insoluble in ether, chloroform and benzene.

Crystal structure: In solid urea, both nitrogen atoms are identical.



This indicates that $C-N$ bond in urea has some double bond character.

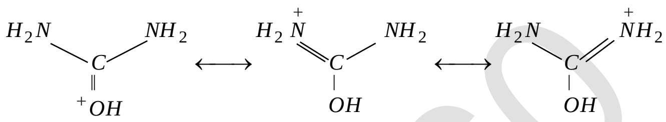
(3) **Chemical Properties**

(i) ***Basic nature (Salt formation)***: It behaves as a weak monoacid base $(K_b = 1.5\times10^{-14})$. It forms solt with strong acid.

$$NH_2CONH_2 + HNO_3(\text{conc.}) \rightarrow \underset{\text{Urea nitrate}}{NH_2CONH_2.HNO_3}$$

$$2NH_2CONH_2 + \underset{\text{Oxalic acid}}{H_2C_2O_4} \rightarrow \underset{\text{Urea oxalate}}{(NH_2CONH_2)_2H_2C_2O_4}$$

Urea is a stronger base than ordinary amide. It is due to the resonance stabilization of cation, the negatively charged oxygen atom is capable of coordination with one proton.



❑ An aqueous solution of urea is neutral.

(ii) ***Hydrolysis***

$$\underset{\text{Urea}}{O=C\begin{matrix}\boxed{NH_2+H}OH\\\boxed{NH_2+H}OH\end{matrix}} \xrightarrow[\text{acid}]{\text{Aq. alkali or}} \underset{\text{Carbonic acid}}{O=C\begin{matrix}OH\\OH\end{matrix}} + \underset{\text{Ammonia}}{2NH_3}$$

$$\downarrow$$

$$CO_2 + H_2O$$

$$NH_2CONH_2 + 2NaOH \rightarrow 2NH_3 + Na_2CO_3$$

An enzyme, urease, present in soyabean and soil also brings hydrolysis .

$$NH_2CONH_2 + 2H_2O \rightarrow \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3} \rightarrow 2NH_3 + CO_2 + H_2O$$

(iii) ***Action of heat***

$$\underset{\text{(Two molecules of urea)}}{NH_2CO\boxed{NH_2+H}HNCONH_2} \xrightarrow{\text{heat}} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3$$

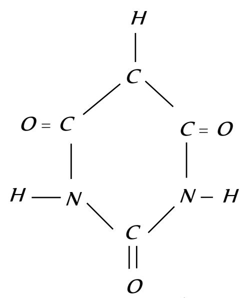
Urea is identified by the test known as biuret test. The biuret residue is dissolved in water and made alkaline with a few drops of *NaOH.* When a drop of copper sulphate solution is added to the alkaline solution of biuret, a violet colouration is produced.

when heated rapidly at 170^oC, polymerisation takes place:

$$NH_2CONH_2 \xrightarrow{\text{heat}} NH_3 + \underset{\text{Cyanic acid}}{HOCN}\,(H-N=C=O)$$

$$3HOCN \xrightarrow{\text{Polymerisation}} (HOCN)_3 \text{ or } (H_3N_3C_3O_3)$$

or



Cyanuric acid

(iv) ***Reaction with nitrous acid***

$$\begin{matrix} O & N & OH & & \\ H_2 & N\,+\,CO & + & N & H_2 \end{matrix} + 2HNO_2 \xrightarrow{NaNO_2+HCl}$$

$$HO \quad N \quad O$$

$$\underset{\text{Carbonic acid}}{H_2CO_3} + 2N_2 + 2H_2O$$
$$\downarrow$$
$$H_2O + CO_2$$

(v) ***Reaction with alkaline hypohalides***

$$NaOH + Br_2 \rightarrow NaOBr + HBr$$

$$NH_2CONH_2 + 3NaBrO \rightarrow N_2 + 2H_2O + CO_2 + 3NaBr$$

(vi) ***Reaction with acetyl chloride or acetic anhydrides***

$$NH_2CONH_2 + \underset{\text{Acetyl chloride}}{CH_3COCl} \rightarrow \underset{\text{Acetyl urea (Ureide)}}{NH_2CONHCOCH_3} + HCl$$

$$NH_2CONH_2 + (CH_3CO)_2O \rightarrow \underset{\text{Acetylurea}}{NH_2CONHCOCH_3} + \underset{\text{Aceticacid}}{CH_3COOH}$$

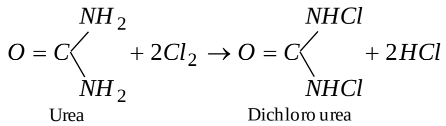
(vii) ***Reaction with hydrazine***

$$\underset{\text{Urea}}{NH_2CONH_2} + \underset{\text{Hydrazine}}{H_2N.NH_2} \xrightarrow{100^oC} \underset{\text{Semicarbazide}}{NH_2CONH.NH_2} + NH_3$$

(viii) ***Reaction with ethanol***

$$H_2NCO\boxed{NH_2 + H}\underset{\text{Ethanol}}{OC_2H_5} \xrightarrow{\text{heat}} \underset{\text{Urethane}}{H_2NCOOC_2H_5} + NH_3$$

(ix) ***Reaction with chlorine water***



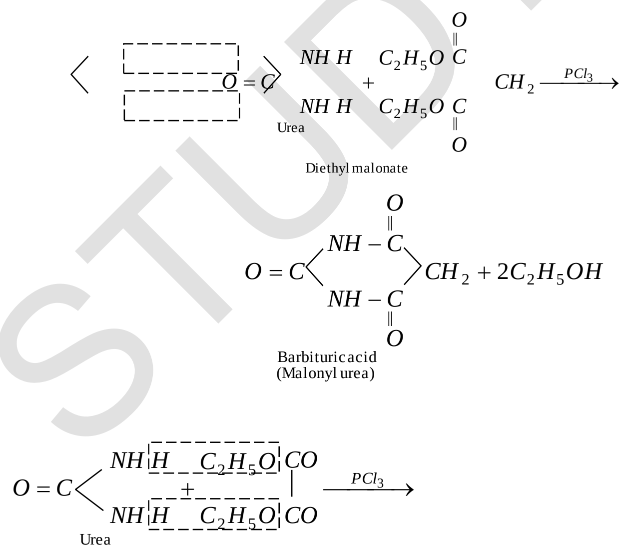
(x) ***Dehydration***

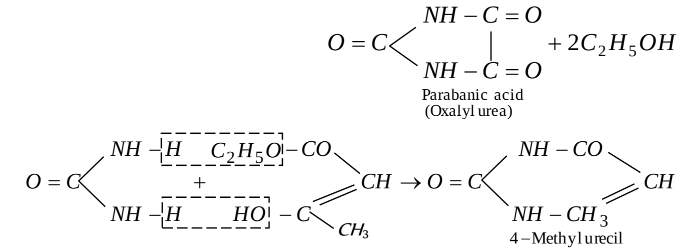
$$NH_2CONH_2 + SOCl_2 \rightarrow H_2N - C \equiv N + SO_2 + 2HCl + H_2O$$

(xi) ***Reaction with fuming sulphuric acid***

$$NH_2CONH_2 + \underbrace{H_2SO_4 + SO_3}_{\text{Oleum}} \rightarrow \underset{\text{sulphamic acid}}{2NH_2SO_3H} + CO_2$$

(xii) ***Formation of cyclic ureides***





(xiii) ***Reaction with formaldehyde***

$$\underset{\text{Fomaldehyde}}{CH_2 = O} + NH_2CONH_2 \xrightarrow{HCl} \underset{\text{Monomethylol urea}}{CH_2(OH)NHCONH_2} \xrightarrow{CH_2=O}$$

$$\underset{\text{Dimethylol urea}}{CH_2(OH)NHCONH(OH)CH_2} \xrightarrow{heat} \underset{\text{(Urea -Fomaldehyde)}}{\text{Resin}}$$

(4) **Uses**

(i) Mainly as a nitrogen fertilizer. It has 46.4% nitrogen.

(ii) In the manufacture of formaldehyde-urea plastic and semicarbazide.

(iii) As animal feed.

(iv) For making barbiturates and other drugs.

(v) As a stabilizer for nitrocellulose explosives.

(5) **General Tests**

(i) When heated with sodium hydroxide, ammonia is evolved.

(ii) When heated gently, it forms biuret which gives violet colouration with sodium hydroxide and a drop of copper sulphate solution.

(iii) Its aqueous solution with concentrated nitric acid gives a white precipitate.

(iv) On adding sodium nitrite solution and dil. HCl (*i.e.,* HNO_2) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.

Tips & Tricks

✍ Oxidation of 1° alcohols and aldehyde cannot be carried out with alkaline $K_2Cr_2O_7$ since under these condition K_2CrO_4 is formed which does not act as an oxidising agent.

✍ During oxidation of alkyl benzenes with alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$, the aromatic nucleus remain intact but each side chain oxidised to $-COOH$ group irrespective of its length. The ease of oxidation of alkyl benzenes follows the order.

Toluene > Ethyl benzene > Isopropyl benzene.

Tert butyl benzene however does not undergo oxidation to give benzoic acid since it does not have any benzylic *H*-atom.

✍ Carboxylic acids are stronger acids than phenols since carboxylate ion is better stabilized by resonance than phenoxide ion.

✍ The melting points of carboxylic acids show oscillation or alternation effect, *i.e.* melting point of an acid containing even number of carbon atom is higher than the next lower or higher homologue containing odd number of carbon atom, due to greater symmetry and close packing of molecules in the crystal lattice.

✍ Carboxylic acid do not give the characteristic reaction of the carbonyl group. The reason being that due to resonance, the double bond character of the $C=O$ bond in carboxylic acid is greatly reduced as compared to that in aldehyde and ketone.

✍ The boiling point of acid derivatives follow the order.

$RCONH_2 > (RCO)_2O > RCOOH > RCOOR' > RCOCl$.

✍ The boiling point of acid chloride and ester are lower than those of their parent acid due to absence of *H*-bonding in their molecule.

✍ The boiling points of acid anhydrides are higher than those of the acids from which they are derived because of stronger Vander Waal's forces of attraction owing to the larger size of their molecules.

✍ The melting points and boiling points of acid amide are much higher than those of the acids from which they are derived due to strong intermolecular *H*-bonding even though their molecular masses are almost identical.

✍ Aromatic acid chlorides are less reactive than aliphatic acid chlorides primarily due to greater electron donating effect of the benzene ring over alkyl group which tends to reduce the electron deficiency of aromatic acyl carbon.

✍ Phthalimide and succinimide on treatment with Br_2-KOH undergo Hofmann bromamide reaction to form anthranilic acid and β-aminopropionic acid respectively.

✍ Urea acts as a monoacidic base.

✍ Malonic acid on heating with P_2O_5 gives carbon suboxide (C_3O_2).

✍ Tamarind contain tartaric acid which does not exist in nature.

✍ Baking powder is a mixture of sodium bicarbonate and cream of tartar *i.e.* acid potassium hydrogen sulphate.

✍ Smell of ammonia in public urinals is due to hydrolysis of urea present in urine by the enzyme urease present in atmosphere.

✍ Tartar emetic (*i.e.* potassium antimony $D(+)$ tartrate is used to cause nausea and vomiting during treatment of poisoning.

✍ Magnesium citrate is used as an antacid.

✍ Succinic acid was prepared by the distillation of amber.

✍ Malic acid is found in apples, grapes etc.