

Carboxylic acids and Their derivatives Chapter 28

Carboxylic Acids

Carboxylic acids are the compounds containing the carboxyl

All the contract of the contr \overline{a}

 $\sqrt{2}$

functional group $\left(\begin{array}{cc} & & \\ & & \end{array} \right)$ *OH* – *C*– ||

The carboxyl group is made up of carbonyl $(\ge C=O)$ 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.

> [|] ² | 2^{c $_2$ *COOH CH₂COOH — — — — — О* | \overline{CHCOOH} | \overline{CHCOOH} (2) By Hy 3 *CH COOH C H COOH*

Tricarboxylic acid Dicarboxylic acid Monocarboxylic acid

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

(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**

$$
RCH_2OH \xrightarrow{[Q]} RCHO \xrightarrow{[Q]} RCHO \xrightarrow{[Q]} RCOOH
$$
\n
$$
H_2C_2O_7 \xrightarrow{CH_2C_2O_7} Carboxylic acid
$$
\n
$$
CH_3-C
$$
\n
$$
D
$$
\n
$$
Chanoicanlydride
$$

$$
RCHO \xrightarrow{[O]} RCOOH
$$

Aldehyde monocatoxylic acid
(iv) **Hudrolysis of a**

 Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammonical silver nitrate solution $[Ag_2$ *O* or $Ag(MH_3)_2^+$ *OH*⁻]

 \Box Methanoic acid can not be prepared by oxidation method.

 O \Box Ketones can be oxidized under drastic conditions using strong oxidising agent like $K_2Cr_2O_7$.

> \Box Methyl ketones can also be converted to carboxylic acid through the haloform reaction*.*

$$
R - C - CH_3 + 3I_2 + 3NaOH \xrightarrow{A}{H_2O}
$$

\n
$$
R - C - OH + CHI_3 + 3NaI + 3H_2O
$$

\n
$$
U
$$

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

(i) *Hydrolysis of nitriles*

$$
R-C \equiv N + HOH \frac{HCl}{\text{or NaOH}} \left[R - C \right] \longrightarrow \frac{OH}{NH} \frac{\text{Rearrangement}}{H + C \longrightarrow \text{RCOOH} + NH_4 \text{Cl}}
$$

2 HCI

 $\overline{0}$

(ii) *Hydrolysis of Esters*

$$
RCOOR + HOH \xrightarrow{\text{HCl}} \text{PCl} \rightarrow RCOOH + ROH
$$
\n
$$
RCH \xrightarrow{\text{Bcl}} \text{Acl} \xrightarrow{\text{Acl}} \text{Acl}
$$

(iii) *Hydrolysis of Anhydrides*

paration of monocarboxylic acid	O			
On of alcohols, aldehydes and ketones	CH ₃ - C	OH	CH ₁₀ - H ⁺ + OH	2CH ₃ COOH
$\frac{[Q]}{K_2C_2O_1}$ <i>RCHO</i> - H ⁺ + OH	CH ₃ - C	CH ₃ - C	Ethanoicacid	
Chag (Hg) - C ₂₀ O + HOH	CH ₃ - C	U	Ethanoicacid	
Chanoicanhydride	U	Ethanoicanhydride		

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

$$
R-C-CI+HOH \xrightarrow{H^+ + OH^-} RCOOH + HCl
$$
acid

$$
O
$$

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

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

$$
R-C \xrightarrow{\times} X + 3NaOH \rightarrow \begin{bmatrix} OH \\ R-C \xrightarrow{OH} \\ AH \end{bmatrix} \xrightarrow{-H_2O} \begin{bmatrix} H_2O \xrightarrow{H_2O} \\ OH \end{bmatrix}
$$
\nwater molecules.
\n
$$
R-C \xrightarrow{O} H
$$
\n
$$
R-C \xrightarrow{O} H_2O + 3NaX
$$
\n
$$
R-C \xrightarrow{O} H_2O + 3NaX
$$
\n
$$
R = C \xrightarrow{O} H_2O + 3NaX
$$
\n
$$
= C \xrightarrow{O} H_2O + 3NaX
$$
\n
$$
(3) Melting point
$$

(3) **From Grignard Reagent**

$$
O = C = Q + RMgX \xrightarrow{S - \delta + \text{Ory either}} R - C - OMgX
$$

Carbon dioxide \t $\text{Grignard reagent} \xrightarrow{H^+ + H_2O} R \text{C} + OH + MAOH$

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

$$
CH_2 = CH_2 + CO + H_2O \xrightarrow[500-1000 atm]{H_3PQ_4} CH_2COOH
$$

\n ${}^{2}CH_2 = CH_2 + CO + H_2O \xrightarrow[500-1000 atm]{H_3PQ_4} CH_2COOH$
\n ${}^{2}CH_2 = CH_2 + CO + H_2O \xrightarrow[500-1000 atm]{H_3PQ_4} CH_2COOH$
\n ${}^{2}CH_2 = CH_2 + CO + H_2O \xrightarrow[500-1000 atm]{H_2PQ_4} CH_2COOH$

(5) **Special methods**

(i) *Carboxylation of sodium alkoxide*

$$
RONa + CO → RCOONa → RCOOH
$$

\nSod.alkoxide
\nSod.alkoxide
\nSod.alk

(ii) *Action of heat on dicarboxylic acid*

$$
R-CH \xrightarrow{COOH} \xrightarrow{COOH} R-CH_2COOH
$$
\n
$$
R-H \xrightarrow{COOH} R-CH_2COOH
$$
\n
$$
Substituted malonic acid
$$
\nSubstituted malonic acid\n
$$
Monocarboxylic acid
$$
\n
$$
When the terminal groups lie on the
$$

(iii) *From acetoacetic ester*

$$
CH_3CO
$$
 $CHRCO$ OC_2H_5 $Hydrolysis$ CH_3COOH lattice. Therefore, results into higher melting point.
\n OH OH H OH H

(iv) *Oxidation of alkene and alkyne*

$$
RCH = CHR \xrightarrow{\text{[O]}} \text{RCOOH} + R \text{COOH}
$$

Alkene

$$
KMnO_4
$$

KMnO₄

$$
R-C \equiv C-R \xrightarrow{\text{(i)O_3}} R-COOH + RCOOH
$$

Alkyne

$$
\text{(ii)H}_2O
$$

(v) *The Arndt-Eistert synthesis*

$$
R-C-C1 + CH_2N_2 \rightarrow R-C-CHN_2 \xrightarrow{\text{H}_2O} \text{CH}_3-C \xrightarrow{\text{CH}_3-C} \text{CH}_3-C \xrightarrow{\text{CH}_3-C} \text{C}-CH_3
$$

(vi) *From acid amides*

$RCONH_2 + H_2O \xrightarrow{\text{Acid}} RCOOH + NH_3$	(1) Cause of acidic nature
$RCONH_2 + HNO_2 \rightarrow RCOOH + N_2 + H_2O$	(i) A molecule of carboxylic acid can Amide
$AMide$	Nitrous acid

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.

 $Cl + HOH \xrightarrow{H^+ \, l \, OH^-} RCOOH + HCl$ (2) **Solubility** : The lower members of the aliphatic carboxylic $- C - C l + HOH \xrightarrow{l} BCOOH + HCl$

acid family (upto C_4) are highly soluble in water. The solubility $R - CH_2 - NO_2 \xrightarrow{85\% H_2SO_4} RCOOH$ carboxylic acids are soluble in alcohol, ether and benzene etc. decreases with the increase in the size of the alkyl group. All

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OH water molecules. \Box The solubility of lower members of carboxylic acids is due to the formation of hydrogen bonds between the – *COOH* group and

 OH intermolecular hydrogen bonding. The observed molecular mass of *O* acetic acid is 120 instead of 60.

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

 $O = C = O + RMgX$ *O* $H = O + H$ $H = O$ $H = O$ $H^+ + H_2O \rightarrow RCOOH + Mg(OH)X$ immediately above and below them. (ii) The melting point of the acids having even number of

> *H PO COOH* group and the terminal – *CH*³ group on the opposite side of the (iii) The acids with even number of carbon atoms have the –

> > (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 same side of the chain

CH COOH lattice. Therefore, results into higher melting point. 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

 $RCH = CHR$ $\frac{[0]}{[0]}$ *RCOOH RCOOH* mass. This is due to intermolecular hydrogen bonding between two mass. This is due to intermolecular hydrogen bonding between two regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular acid molecules.

 $R - CH_2 - COOH$ Hydrogen bonding Acetic acid dimer

Acidic nature of monocarboxylic acids

(i) A molecule of carboxylic acid can be represented as a

$$
\begin{array}{ccc}\n\cdots & \cdots & \cdots \\
\bigvee_{||} C & O & \cdots & \cdots \\
R-C & O & H \leftrightarrow R & C = O-H \\
& \cdots & & \cdots & \\
& & & \cdots & \\
& & & & \cdots & \\
& & & & & \cdots\n\end{array}
$$
\n(1)

(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^+) .

$$
R-C \stackrel{\overbrace{O}_{\oplus}}{=} O \leftarrow H \leftrightarrow \left[R-C \stackrel{\overbrace{O}_{\oplus}}{=} R-C \stackrel{\overbrace{O}_{\oplus}}{=} R-C \stackrel{\overbrace{O}_{\oplus}}{=} 1.27 \stackrel{\overbrace{O}_{\oplus}}{=} 1.27 \stackrel{\overbrace{O}_{\oplus}}{=} 2CH_3COOH + Zn \rightarrow (CH_3CO) \stackrel{\overbrace{O}_{\oplus}}{Zincace}
$$

(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 $(-I \text{ effect})$ stabilizes the anion by dispersing the negative charge and therefore increases the acidity.

$$
G \leftarrow C \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad \qquad G \rightarrow C \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad \qquad \begin{array}{c} (2) \text{ Re } \\ (1) \text{ Form } \\ \text{CH}_3 \text{ CC} \\ \text{Acetica} \end{array}
$$

(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 ²*COOH ClCH* ²*COOH BrCH* ²*COOH ICH* ²*COOH*

similarly :

$$
CCI3COOH > CHCl2COOH > CH2ClCOOH > CH3COOH
$$
 (F)

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

Example:

$$
CH_3 - CH_2 - CH - COOH > CH_3 - CH - CH_2 - COOH
$$

\n Cl
\n $CH_3 - CH_2 - CH - CH_2 - COOH$
\n Cl
\n Cl

(iv) Relative acid strength in different compounds

 $RCOOH > HOH > ROH > HC \equiv CH > NH₃ > RH$

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

 \Box Acidic nature (K_a) α 1/molecular weight

$$
HCOOH \rightarrow CH_3COOH > C_2H_5COOH
$$
\n
$$
CH_3CO_4 \rightarrow CH_3CO_5 O/H
$$
\n
$$
CH_3CO_4 \rightarrow CH_3CO O/H
$$
\n
$$
CH_3CO_4 \rightarrow CH_3CO O/H
$$
\n
$$
CH_3CO_4 \rightarrow CH_3CO O/H
$$
\n
$$
H_3CO \rightarrow CH_3CO O/H
$$

□ 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.

te the release of hydrogen
\n
$$
2CH_3COOH + 2Na \rightarrow 2CH_3COONa+ H_2
$$
\nSodium acetate
\n
$$
O = R-C \left(\frac{Q}{2O} \cdot 1.27A^{\circ}\right)
$$
\n2CH₃COOH + Zn \rightarrow (CH₃COO₂ Zn+ H₂
\n
$$
O = R-C \left(\frac{Q}{2O} \cdot 1.27A^{\circ}\right)
$$
\n2CH₃COOH + Zn \rightarrow (CH₃COO₂ Zn+ H₂
\n
$$
O = R-C \left(\frac{Q}{2O} \cdot 1.27A^{\circ}\right)
$$
\n2CH₃COOH + Zn \rightarrow CH₃COONa+ H₂O

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Aceticacid Sodium acetate (iv) *Action with carbonates and bicarbonates* $2CH_{3}COOH + N$ a $_2CO_{3} \rightarrow 2CH_{3}CO$ ONa+ $CO_{2} + H_{2}O$
Sod.acetate $\mathit{CH}_{3}\mathit{COOH} + \mathit{NaHCO}_{3} \rightarrow \mathit{CH}_{3}\mathit{COON}$ a+ $\mathit{CO}_{2} + \mathit{H}_{2}\mathit{O}$ Sod.acetate

 \Box 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.

$$
G \rightarrow C \begin{matrix} O \\ O \end{matrix}
$$
 (2) Reaction involving replacement of $-OH$ group
(i) *formation of acid chloride*

O	$CH_3COOH + PCl_5 \rightarrow 3CH_3COCH + POC_3 + HCl$
<i>l</i> effect) stabilizes	$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$
<i>l</i> effect) stabilizes	$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$
<i>l</i> detection	$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$
$2CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$	
$2CH_3COOH + OCl_2 \rightarrow CH_3COCl + SO_2 + HCl$	
<i>l</i> coefficient	$CH_3CO \overline{OH + H} \overline{O} \overline{O} \overline{O} \overline{H_3}$
$2CH_3CO \overline{O} \overline{O} \overline{H_3} \overline{O} \overline{O} \overline{H_3}$	
<i>l</i> t	$CH_3COOCl + H_3O$

(Fruity smelling) Ethyl acetate

(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

 $CH_3 - CH_2 - CH - COOH > CH_3 - CH - CH_2 - COOH$ (c) The acidic strength of carboxylic acid plays only a minor role.

*^R*3*CCOOH ^R*2*CHCOOH RCH*2*COOH CH* ³*COOH HCOOH*

 \geq *CH*₂ – *CH*₂ – *COOH* When **methanol** is taken in place of **ethanol**. then reaction is called **trans esterification.**

(iv) *Formation of amides*

$$
CH_3COOH + NH_3 \xrightarrow{\text{heat}} CH_3COONH_4 \xrightarrow{\Delta} \text{Amm. acetate}
$$
\n
$$
CH_3CONH_2 + H_2O
$$

Acetamide

(v) *Formation of acid anhydrides CH COO H*

$$
CH_3COO/H_1
$$
 Heat
 CH_3CO OH_2O
 Al_3CO OH_3CO OH_2O
 Al_3CO OH_3CO

(vi) *Reaction with organo-metallic reagents*

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

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

Dichloro aceticacid ^{-HCl} Trichloro aceticacid

Reduction:
$$
R-C-OH \xrightarrow{\text{LialH}_4} R-CH_2-OH
$$

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*:
$$
R-C-OH \xrightarrow{(-CO_2)} R-H
$$

\n*Individual members of monocarboxylic acids*

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

$$
RCOONa+ NaOH \xrightarrow{CoO} R-H + Na2CO3
$$

 \Box When sodium formate is heated with sodalime H_2 is evolved. (Exception)

$$
HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3
$$
\n
$$
CH_2OH + O_2 \xrightarrow{Pt} HCC
$$

(ii) *Heating of calcium salts*

$$
\begin{array}{ccc}\n(RCOO_2 Ca & \stackrel{\text{heat}}{\longrightarrow} RCOR & CaCO_3 \\
\text{Sodium salt} & \stackrel{\text{Ketone}}{\longrightarrow}\n\end{array}\n\quad \text{the h}
$$

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

$$
RCOONa \rightleftharpoons RCOO + Na^{+}
$$

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

At cathode
$$
2Na^{+} + 2e^{-} \rightarrow 2Na \xrightarrow{2H_{2}O} 2NaOH + H_{2}
$$

CHOH

Electrolysis

$$
\begin{array}{c} \mathit{CH}_3-\mathit{CH}_3+2\mathit{CO}_2+2\mathit{KOH}+\mathit{H}_2\\ \mathit{Ethane} \end{array}
$$

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

$$
CH_3COOAg + Br_2 \xrightarrow{\text{heat}} CH_3Br + AgBr + CO_2
$$

\nSilveracetate\n
\n $Cl_3COOAg + Br_2 \xrightarrow{CCl_4}$ \n CH_3OH \n CH_2OH \n Cl_3CO

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

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

$$
\begin{array}{ccc}\nRCOOH+&N_3H & \xrightarrow{H_2SO_4(\text{conc})} RNH_2 + CO_2 + N_2 & & 2HCOOH + PbCO_3 \rightarrow (HCOO)_2\,PL \\
\text{Acid} & Hydrazoic & \xrightarrow{Primary} & \text{lead formate} \\
\text{acid} & \text{amine} & & \xrightarrow{(1)QO_2 \rightarrow P} H \rightarrow (1)Q_2 \rightarrow (1)Q_2
$$

In Schmidt reaction, one carbon less product is formed. (vi) *Complete reduction*

$$
CH_3COOH + 6HI \xrightarrow{P} CH_3CH_3 + 2H_2O + 3I_2
$$
ir
Aceticacid
Ethane 2

In the above reaction, the – *COOH* group is reduced to a CH_3

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

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

group.

H
\n
$$
- C - COOH + Cl_2 \xrightarrow{U.V. \Delta} - C - COOH + HCl
$$
\n(2) Physical properties
\n(i) It is a colourless pungent smelling liquid.
\n(ii) It melts at 8.4°C and boils at 100.5°C.

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

Reduction **:** $R - C - OH - \frac{LiA H_4}{\sqrt{2}} \rightarrow R - CH_2 - OH$ Carboxylic acid having an α -hydrogen react with Cl_2 or Br_2 in *O* acid. The reaction is known as **Hell Volhard-zelinsky reaction.** $- C$ - $OH \xrightarrow{L/4H/T_4}$ R - CH_2 - OH
 \parallel the presence of a small amount of red phosphorus to give chloro acetic

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$$
CH_3COOH \xrightarrow{Cl_2, \text{red } P_4} CICH_2COOH \xrightarrow{Cl_2, \text{red } P_4} \rightarrow
$$
\n
$$
\xrightarrow{A
$$
\n
$$
CICHCOOH \xrightarrow{Cl_2, \text{red } P_4} CIGHCOOH
$$
\n
$$
Cl_2CHCOOH \xrightarrow{Cl_2, \text{red } P_4} CIGCOOH
$$
\n
$$
\xrightarrow{CIGMron\,
$$
\n
$$
Tichloro\,
$$

Formic Acid or Methanoic acid (*HCOOH*)

RCOONa+ NaOH Card and R- H+ Na₂CO₃ is the community of the community of the main of the context Formic acid is the first member of monocarboxylic acids series. It occurs in the sting of bees, wasps, red ants, stinging nettles. and caterpillar's.

(1) **Methods of preparation**

(i) *Oxidation of methyl alcohol or formaldehyde*

$$
CH_3OH + Q_2 \xrightarrow{PI} HCOOH + H_2O
$$
\n
$$
Fomicacid
$$

 $(RCOO₂ Ca$ ^{- read} $RCOR₁ CaCO₃$ the hydrolysis of *HCN* with acids or alkalies. (ii) *Hydrolysis of hydrocyanic acid :* Formic acid is formed by

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

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

The following procedure is applied for obtaining anhydrous formic acid.

$$
P_2 + N_2
$$

2*HCOOH + PbCO₃ \rightarrow (HCOO)₂ Pb+ CO₂ + H₂O;
lead formate
(*HCOO*)₂ Pb+ H₂ S \rightarrow PbS+ 2*HCOOH*
Formic acid
Formic acid*

 $CH_3COOH + 6HI \xrightarrow{P} CH_3CH_3 + 2H_2O + 3I_2$ industrial scale by heating sodium hydroxide with carbon monoxide at (iv) *Industrial preparation* : Formic acid is prepared on 210°*C* under a pressure of about 10 atmospheres.

$$
CO + NaOH \xrightarrow{\Delta} HCOONa
$$

210^o C, 10 atm Sodium formate

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

*HCOONa NaHSO*⁴ *HCOOH Na*2*SO*⁴

(2) **Physical properties**

(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*3*COOH*)

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)*

 $CH_3CHO \xrightarrow{Nq_2 \cup Nq_1} CH_3COOH$ (c) By the action

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

 $CH_3CN + 2H_2O \xrightarrow{HCl} CH_3COOH + NH_3$ form acetic acid.

(iii) *By Grignard reagent*

$$
CH_3MgBr + CO_2 \rightarrow CH_3 - C - OMgBr \xrightarrow{H_2O/H^+}
$$
 (2) Physical properties
\n(i) At ordinary temperature, acetic acid is a colourless,
\n $CH_3 - C - OH$ (ii) Below 16.5°C, it solidifies as an icy mass, hence it is named

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

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

$$
CH_3COOH + C_2H_5OH
$$

(b)
$$
CH_3COCl + H_2O \xrightarrow{\text{dil. } HCl} CH_3COOH + HCl
$$
 proportions.
acetylchlvide\n(v) It is good solvent for phosphory

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

(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**.

$$
CH_3CH_2OH + O_2 \xrightarrow{\text{Mycodermaaceti}} CH_3COOH + H_2O
$$

\n $Brthyl alcohol$ \n $Brthylalcohol$ \n $Brthylalcohol$ \n $Brthylalcohol$ \n $Brthylalcohol$

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.

 Carboxylic acids and Their derivatives 1310

 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 $CO₂$ 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).

$$
CH \equiv CH + H_2O \xrightarrow{H_2SO_4(\text{dil.})} CH_3CHO
$$

Acetylene

$$
HgSQ_4 \xrightarrow{\text{Acetaldehyde}}
$$

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

$$
2CH_3CHO + O_2 \xrightarrow{Manganousacetate} 2CH_3COOH
$$

 \Box 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.

 ${}^{13}_{2}$ C*HO* ${}^{18}_{2}$ ${}^{26}_{2}$ ^O_{*O*} ${}^{12}_{2}$ C*H*₃ COOH (c) *By the action of CO c* (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.

$$
CH_3OH + CO \xrightarrow{Co_2(CO)_8} CH_3COOH
$$

Method 30 $atm200^{\circ}C$ Accticacid

*Q*corrosive liquid with a sharp pungent odour of vinegar. It has a sour $-C-OH$ as tested as C $CH_2 - C - OH$ asive. taste.

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

(a) $CH_3COOC_2H_5 + H_2O \xrightarrow{H_2SO_4 \text{(conc.)}}$ molecular masses is due to more stronger hydrogen bonding between $CH_3COOC_2H_5 + H_2O \longrightarrow$
Ester acid molecules. This also explains dimer formation of acetic acid in (iii) It boils at 118°*C.* The high boiling point of acetic acid in comparison to alkanes, alkyl halides or alcohols of nearly same vapour state.

 $CH_3COOH + C_2H_5OH$ 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

(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:

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

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

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(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.

Property	Formic acid	Acetic acid
1. Acidic nature,		
(i) With electro-positive	Forms salts, Hydrogen is evolved.	Forms salts. Hydrogen is evolved.
metals	$HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$	$CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$
(ii) With bases	Forms salts.	Forms salts.
	$HCOOH + NaOH \rightarrow HCOONa + H2O$	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii) With carbonates and	Forms salts. Carbon dioxide is evolved.	Forms salts. Carbon dioxide is evolved.
bicarbonates	$HCOOH + NAHCO3 \rightarrow HCOONa + H2O + CO2$	$CH_3COOH + NaHCO_3 \rightarrow$
		$CH3COONa+ H2O+ CO2$
2. Ester formation	Forms esters when treated with alcohols.	Forms esters when treated with alcohols.
	$HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4(cone)}$
		$CH3COOC2H5 + H2O$
3. Reaction with PCl_5	Forms formyl chloride which decomposes into CO and	Forms acetyl chloride which is a stable compound.
	HCl.	$CH_3COOH + PCk_5 \rightarrow$
	$HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	$CH_3COCl + POCI_3 + HCl$
4. Heating of ammonium	Forms formamide.	Forms acetamide.
salt	$HCOONH_4 \rightarrow HCONH_2 + H_2O$	$CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5. Heating alone	it decomposes into $CO2$ and $H2$	Unaffected
	$HCOOH \rightarrow CO_2 + H_2$	
6. Heating with conc.	Decomposed into CO and H_2O	Unaffected
H_2SO_4	$HCOOH \xrightarrow[{}_{{}_{}^{}^{}}O_4]{} CO + H_2O$	
7. Reaction with Cl_2 in	Unaffected	Forms mono, di or trichloro acetic acids.
presence of red P		
8. Action of heat on salts,		
(i) Calcium salt	Forms formaldehyde.	Forms acetone.
	$(HCOO)_{2}Ca \rightarrow HCHO + CaCO_{3}$	$(CH_3COO_2Ca \rightarrow CH_3COCH_3 + CaCO_3)$
(ii) Sodium salt	Forms sodium oxalate.	Unaffected.
	$2HCOONa \xrightarrow{\text{heat}} COONa + H_2$	
	COONa	
(iii) Sodium salt with soda-	Forms sodium carbonate and H_2 .	Forms sodium carbonate and methane.
lime	$HCOONa+NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	$CH_3COONa+NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9. Electrolysis of sodium or	It evolves hydrogen.	It forms ethane.
potassium salt		
10. On heating with P_2O_5	Unaffected	Forms acetic anhydride.
		$2CH_3COOH \rightarrow P_2O_5 \rightarrow (CH_3CO_2O + H_2O)$
11. Reducing nature,		
(i) Tollen's reagent	Gives silver mirror or black precipitate.	Unaffected.
	$HCOOH + Ag2O \rightarrow 2Ag + CO2 + H2O$	
(ii) Fehling's solution	Gives red precipitate	Unaffected.
	$HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	
(iii) Mercuric chloride	Forms a white ppt. which changes to greyish black.	Unaffected.

Table : 28.1 Comparison of Formic Acid and Acetic Acid

Interconversions

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

(i) HCOOH-
Formicacid Formaldehyde heat *urun* $\begin{array}{rcl} HCOOH & \xrightarrow{CAOH_2} (HCOO)_2\ Ca & \xrightarrow{heat} & \xrightarrow{HCHO} \ \xrightarrow{Comaldehyde} & \xrightarrow{Formic acid} \end{array}$ Formic acid Calcium formate $\frac{1}{2} \frac{1}{2} CH_3 CH_2OH \leftarrow \frac{H_2O}{H^+} CH_3 \text{CH}_2OMgBr$ Ethyl alcohol H^+ Addition product $CH_3CHO \leftarrow \frac{10}{2}$ $CH_3CH_2OH \leftarrow \frac{H_2O}{H^+}$ CH_3CH_2OMgBr
Acetaldehyde Ethyl alcohol H^+ Addition product Aceticacid \downarrow ^[0] \rightarrow *CH*₃*COOH* (ii) Methyl and a methyle methyle and a methyle methyle and a method of \mathcal{M} $3¹$ $\begin{array}{c} HCHO \longrightarrow H_2/M \longrightarrow CH_3OH \longrightarrow CH_3I \longrightarrow CH_3I \end{array}$ Formaldehyde Methyl alcohol Methyl and Methyl $CH_3COOH \leftarrow \frac{H_2O}{H^+} \quad CH_3CN \text{ with } \atop \text{Methyl}}$
Acitic acid H^+ Methyl *CH*3*MgBr*

Arndt-Eistert homologation : This is a convenient method of converting an acid, *RCOOH* to *RCH*2*COOH*.

> $RCOOH \longrightarrow RCOCl \longrightarrow RCO$ ^{CH_2N_2} $\rightarrow RCOCHN_2$ ² ² ⁵ Hydrolysis *RCH*2*COOH RCH COOC ^H EtOH* $|Ag_2O$

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

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.

OH or *CH C O HO ^C ⁿ* || ² || () *HOOC*(*CH* ²

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

Oxalic Acid or Ethanedioic Acid *COOH* **or** $(COOH)_2$ **or** $(C_2H_2O_4)$ *l* or $($ *COOH* $)$ ₂ or $($ **C**₂ H ₂ O ₄ $)$
COOH

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*

CH₂OH
\n
$$
+4[Q - \frac{K_2C_2O_7}{H_2SO_4} - \frac{COOH}{COOH} + 2H_2O
$$
\n(ii) *Acidic nature*
\nGlycol
\n
$$
C
$$

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

$$
CN \qquad | +4H_2O \xrightarrow{2(HCl)} | +2NH_4Cl
$$
\n
$$
CN \qquad COOH \qquad \qquad COOH
$$
\n
$$
CN \qquad COOH
$$
\n
$$
COOH \qquad \qquad COOH
$$

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

$$
2Na + 2CO_2 \xrightarrow{\text{heat}} \begin{array}{c} COONa \\ COONa \\ COONa \\ \text{Sodium oxalate} \end{array} \qquad \qquad COOH \\ + Na_2CO_3 \rightarrow
$$

(iv) *Laboratory preparation*

$$
C_{12}H_{22}O_{11} + 18[O] \xrightarrow{HNO_3} 6[COOH] + 5H_2O
$$
\n
$$
C_{12}H_{22}O_{11} + 18[O] \xrightarrow{LNO_3} COOH
$$
\n
$$
C_{12}H_{5}OH
$$

(v) *Industrial method*

$$
2\text{HCOONa} \xrightarrow{\text{360}^{\circ}C} \begin{array}{c}\n\text{COONa} \\
\mid \\
\text{Sod-formate} \\
\text{Sod. tosmalle} \\
\text{Sod.} \text{oxalate}\n\end{array} \qquad \qquad \text{(iv) Reaction with PCI}_{S}:\n\qquad\n\begin{array}{c}\n\text{OONa} \\
\mid \\
\text{Sod.} \text{CONa} \\
\mid \\
\text{SOMa} \\
\mid \\
\text{S
$$

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

$$
CO + NaOH \xrightarrow{200^{\circ}C \atop 8-10 \text{ atm}} HCOONa
$$

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.

(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.

$$
\underbrace{(COOH)}_{\substack{2\\ \text{Hydrated oxalic} \\ \text{acid}}}\n 2H_2O \underbrace{-100-105^{\circ}C}_{\substack{2\\ \text{Anhydrous} \\ \text{oxalic acid}}}\n 2H_2O
$$

(a) At 200°C,
$$
(COOH)_2 \longrightarrow HCOOH + CO_2
$$

Formic acid

On further heating, formic acid also decomposes. $HCOOH \rightarrow CO_2 + H_2$

(b) *Heating with conc. H2SO⁴*

$$
\begin{array}{ll}\n\text{COOH} & \xrightarrow{H_2SO_4} \text{CO} + CO_2 + H_2O \\
\downarrow \text{COOH} & \xrightarrow{\text{(conc)}} \end{array}
$$

\n
$$
\text{open with conc. hydrochloric acid:} \quad\n \begin{array}{ccc}\n \text{COOH} & \text{COOK} & \text{KOH} & \text{COOK} \\
 \mid & + \text{KOH} \rightarrow & \mid & \text{COOK} \\
 \text{OOH} & \text{OCOK} & \text{COOK} \\
 \text{Oxaliceaid} & \text{Acid pot. oxalate} & \text{Pot. oxalate} \\
 \text{potassium in a current of carbon} & \mid & + 2\text{NaHCO}_3 \rightarrow & \mid & + 2\text{CO}_2 + 2\text{H}_2\text{O} \\
 \mid & + 2\text{NaHCO}_3 \rightarrow & \mid & \text{COONa} \\
 \text{COOH} & \mid & \text{COONa} & \text{COONa} \\
 \mid & \mid & + 2\text{NaHCO}_3 \rightarrow & \mid & \text{COONa} \\
 \end{array}
$$
\n

COONa Sod.oxalate

$$
\begin{array}{ccc}\nCOOH & COONa \\
| & + Na_2CO_3 \rightarrow | & + H_2O + CO_2 \\
COOH & COONa\n\end{array}
$$

COOH (iii) *Esterification*

$$
\begin{array}{ccc}\n| & +5H_2O & COOH & COOC_2H_5 \\
COOH & & | & COOC_2H_5 \\
\hline\n\text{Oxalicacid} & & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$
\n
$$
\begin{array}{ccc}\n| & +5H_2O & COOC_2H_5 \\
\hline\n\text{COOH} & COOC_2H_5 \\
\end{array}
$$

$$
COOH \n\begin{array}{c}\nCOCH \n\begin{array}{c}\nCOCl \\
\downarrow \\
COOH\n\end{array} + 2PCl_5 \rightarrow \begin{array}{c}\nCOCl \\
COCl \\
\downarrow \\
Ox|N\n\end{array} + 2POCl_3 + 2HCl\n\end{array}
$$

(v) *Reaction with ammonia*

(vi) *Oxidation* **:** When oxalic acid is warmed with acidified . *KMnO*⁴

2 3 2 3 5[] *KMnO*⁴ *^H* ²*SO*⁴ *^K* ²*SO*⁴ *MnSO*⁴ *^H* ²*^O ^O COOH COOH KMnO H SO O CO H O COOH COOH* 2 4 4 2 2 Oxalic acid [|] ² ⁴ (Purple) Pot.permanganate 4 2 2 | 2 3 5 2 10 8 [] 2 5 (1) **Methods of Preparation :** From acetic acid

*Oxalic acid decolourises the acidic solution. KMnO*⁴ Colourless

(vii) *Reaction with ethylene glycol*

Glycolicacid Glyoxalic acid

(ix) *Reaction with Glycerol* : At $100^{\circ} - 110^{\circ}C$, 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 $NaHCO₃$.

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

4 4 Calciumoxalate ² ⁴ Amm.oxalate ⁴ ² ² ⁴ Oxalicacid 2 2 4 ⁴ ² *^H ^C ^O* (*NH*) *^C ^O CaC ^O NH^O^H CaC^l*

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

(v) With hot conc. H_2SO_4 , it evolves carbon monoxide which

Malonic Acid or Propane-1,3-Dioic Acid

$$
CH_2
$$
 COOH
COOH or CH₂(COOH) ₂ or (C₃H₄O₄)

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.

$$
\begin{array}{ccccc}\n\text{C1} & C & C & C & C & C & C \\
\hline\n\text{C2} & & \text{C3} & C & C & C & C \\
\hline\n\text{C5} & & \text{C4} & C & C & C & C \\
\hline\n\text{C6} & & \text{C4} & C & C & C & C \\
\hline\n\text{C7} & & \text{C8} & C & C & C & C \\
\hline\n\text{C8} & & \text{C9} & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & C & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & C & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & C & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C2} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C1} & & \text{C2} & & \text{C3} & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C2} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C3} & & \text{C2} & & \text{C1} & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C2} & & \text{C1} & & \text{C2} & C & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C & C \\
\hline\n\text{C2} & & \text{C1} & & \text{C2} & C & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C2} & & \text{C1} & & \text{C2} & C & C & C & C \\
\hline\n\text{C1} & & \text{C1} & & \text{C1} & C & C & C & C \\
\hline\n\text{C1} & & \text
$$

$$
CH_2CNCOOH \xrightarrow{H_2O/H^+} CH_2 \xrightarrow{COOH} COOH
$$

Cyano aceticacid
Malonic acid

(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^{\bullet} ^{*CH*₂</sub>(*COOH*₎ $\rightarrow CH_3$ *COOH* + *CO*₂}

OH **FA**⁻OH

$$
COOH
$$
\n
$$
O = C - C - C
$$
\n
$$
= O - \frac{P_2 Q_5}{\text{heat}} \rightarrow O = C = C = Q - \frac{P_2 H_2 O}{\text{heat}}
$$
\n
$$
CHO
$$
\n
$$
CHO
$$
\n
$$
= O - \frac{1}{P_1}
$$
\n
$$
= O - \frac{P_2 Q_5}{\text{heat}} \rightarrow O = C = C = Q + 2H_2 O
$$

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

$$
RCH = O + H_2C\n\nAldehyde\n\nCOOH - \n
$$
RCH = CHCOOH + H_2O + CO_2
$$
\n
$$
RCH = CHCOOH + H_2O + CO_2
$$
\n
$$
\alpha \cdot \beta
$$
 unsaturated acid
$$

(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:

\n
$$
CH_{\alpha} = COOH
$$

 or or *CH CO ^H CH CO H 2 2* | *² ² ² (CH) (CO H) (C H O) ⁴ ⁶ 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*

 \Box This is an industrial method.

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

Succinicacid Malic acid CH₂COOH _{HII} CHOHCOOH | <u>"</u> 20001 20001 20001 20001 $|\longrightarrow|$ \leftarrow \longrightarrow $|\longrightarrow|$ *CHOHCOOH CHOHCOOH ^P*

(2) **Physical properties**

(i) It is a white crystalline solid. It melts at 188° *C* CH_2 - CH_2

(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 O* (*i)* it is a write crystalline $\frac{300^{\circ}C}{(H_2O)}$
 $\left(\frac{H_2O}{H_2CO}\right)^2$
 $\left(\frac{H_2O}{H_1CO}\right)^2$

(ii) It is fairly soluble in alcohol and ether but less soluble in *CH*₂*COOH* 2000 *CH*₂*CO* CH_2COOH \leftarrow H_2O CH_2CO $\frac{300^{\circ}C}{c}$ H_2CO \rightarrow O *C* \cdot 1 \cdot \cdot \cdot 0 **Succinicanhydride** $2\mathsf{C}\mathsf{C}$ Succinicacid $\frac{300^{\circ}C}{\circ}$ \rightarrow \rightarrow \circ (ii) *With ammonia* CH_2COONH_A $-H_2O$ (i) *Action of heat NH*₂ **4 heat** *CH*₂*COONH*₄
_{heat} If shows all the get CH₂COOH CH₂COONH₄ -H₂O $\frac{1}{3}$ $\sqrt{2}$ 4 heat Ammonium succinate $\begin{array}{ccc}\n| & \longrightarrow & | & \longrightarrow & | & \longrightarrow & \text{first} \\
\downarrow & \downarrow & \downarrow & \downarrow & \text{first} \\
\downarrow & \downarrow & \downarrow & \downarrow & \text{first} \\
\downarrow$ *CH CO* CH_2CONH_2 -NH₃ CH_2CO $H_{\text{Adipic acid}}$ Succinamide Succinimide **Succinimide Succinimide Succinimide Support** heat

(iii) *Reaction* with **Br**₂

(iv) *Reaction with ethylene glycol*
\n
$$
HOOC - (CH_2)_2 - CO\overline{QH} + H\overline{H}QCH_2 - H
$$
\n
$$
CH_2O\overline{H} + \overline{H}QCC - (CH_2)_2 - CO\overline{H} + ...
$$
\n
$$
H \downarrow H
$$

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

$$
CH_2-CH_2-COOH
$$
 or $(CH_2)_4(COOH)_2$ or $(C_6H_{10}O_4)$ (1) Methods of Preparation
\n CH_2-CH_2-COOH (2)

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

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

$$
CH_2-CH_2
$$

\n|
\nCH_2 CH_2
\nCH_2 CH_2
\n $CH_2 CH_2$
\n $CH_2 CH_2$
\n $Alipic acid$
\n $CH_2 CH_2$
\n $CH_2 CH_2$

(2) **Physical Properties**

 CH_2CO (i) It is a white crystalline solid. Its melting point is 150°C.

 $H₂$

water.

(3) **Chemical Properties**

It shows all the general reaction of dicarboxylic acids.

NH CH CO CH CONH 2 2 2 2 [|] [|] ³ *HOOC*(*CH*2)⁴ *COOH* Adipic acid *C = O + CO*² *+ H*2*O* heat *300°C H*2C | *H*2*C C C*

 $N - Br + HBr$. \therefore $(B_5 \rightarrow B_7)$ \rightarrow $(B_7 \rightarrow B_7)$ \rightarrow $B_7 + BB_7$ \rightarrow (B_7) (B_8) (B_9) $(B_9$ *diamine] H*2

nH₂N(CH₂)₆ NH₂ + nHO– C– (CH₂)₄ – C– OH
\nhexamethylenediamine\n
$$
\begin{bmatrix}\nO & 1 \\
O & 0 \\
O & 0\n\end{bmatrix}
$$
\n
$$
- (H - H2O)
$$
\n
$$
- (-\mathbf{N} - (CH2)6 - \mathbf{N} - C– (CH2)4 - C–)n –\nnylon-66
$$

 $-(CH_2)_2 - CO_1$ _n – $OH + H_2O$ **Unsaturated Acids :** When the double bond presents in the carbon
Polyester chain of an acid is called unsaturated acid.

Example:
$$
CH_2 = CH - COOH + H - C - COOH
$$

Acrylicacid $H-C-COOH$
Maleicacid

Acrylic Acid or Prop-2-Enoic Acid *CH*₂ = *CH* – *COOH* or $(C_3H_4O_2)$

(i) *From allyl alcohol*

$$
CH_2
$$
\n CH_2 \n

(ii) *By oxidation of acrolein*

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

(iii) *From propionic acid* **:** $CH_3CH_2COOH \xrightarrow{Bf_2/P}$ $CH_2 = CHCOOH + PCI_5 \rightarrow CH_2 = CH - COCl$
Propionic acid HVZ reaction $CH_2 = CHCOOH + PCI_5 \rightarrow CH_2 = CH - COCl$ *HVZ* reaction

 $CH_3CHBrCOOH \longrightarrow \frac{Alc. KOH}{CH_2} = CHCOOH$ (4) Uses : Its ester are used for making plastics such as Lucite $\xrightarrow{Alc.KOH} CH_2 = CHCOOH$ α -Bromopropionic acid α CH₃CHBrCOOH -

(iv) By heating β -hydroxy propionic acid

 $CH_2 - CH_2 - COOH \xrightarrow{ZnCl_2} CH_2 = CH - COOH$ The molecular formula of the simple
 H_2 . *OH* β -hydroxy propionic acid 2

(v) *From vinyl cyanide*

$$
HC \equiv CH + HCN \xrightarrow{Cu_2Cl_2/HCl} CH_2 = CH - CN
$$

Acetylene

$$
H-C-COOH
$$

W

$$
H-C-COOH
$$

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

(vi) *From ethylene cyanohydrin*

$$
CH_2-CH_2 \xrightarrow{\qquad \qquad HCN \qquad} CH_2-CH_2-CH_2-CM \xrightarrow{\text{Conc.} H_2SO_4} \qquad \qquad CH-CH_3 \xrightarrow{\qquad \qquad CH-CH_3} \qquad \q
$$

 $1 + 1 + 1$

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

\n $U_6H_6 + U_2 \xrightarrow{G_6H_6 + U_2O} C_2 \xrightarrow{U_2O_3} H_1$
\n $U_8H_2 \xrightarrow{G_0H_2O} C_2 \xrightarrow{G_0H_2O} CH_2$
\n U_9
\n U_9 <

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

$$
CH \equiv CH + CO + H_2O \xrightarrow{N(CO_A} CH_2 = CHCOOH
$$
 |
2U, 222U
U, 212U

(2) **Physical Properties**

 \Box It is colourless pungent smelling liquid. Its boiling point is 141°*C*.

 \Box It is miscible with water, alcohol and ether.

 \Box It shows properties of an alkene as well as of an acid.

(3) **Chemical Properties**

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

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

 $H-C-COOH$

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

$$
CH_2 = CHCOOH + Br_2 \xrightarrow{COCl_4} CH_2Br - CHBrCOOH
$$

\n(ii) By oxidation of further with sodium chlorate
\n $HC \xrightarrow{CH} CH_2$

$$
CH_2 = CHCOOH + HBr \rightarrow BrCH_2 - CH_2COOH
$$

\n $^\text{II} \quad ^\text{II} \quad ^\text{II} \quad ^+ \text{4}[\text{U}]$

(iii) *Oxidation*: In presence of dilute alkaline *KMnO*₄.
\n
$$
CH_2 = CHCOOH + [O] + H_2O \rightarrow CH_2OHCHOHCOOH
$$

\n $Clycericacid$
\n $CH_2CHCOOH$

□ On vigorous oxidation, oxalic acid is formed. (iv) *Salt formation*

$$
CH_2 = CHCOOH + KOH \rightarrow CH_2 = CHCO\overrightarrow{OK} + H_2O
$$

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

 $2\textit{CH}_{2} = \textit{CHCOO} \textit{Na}^{+} + \textit{H}_{2}\textit{O} + \textit{CO}_{2} \ \text{Sodium acrylate}$

(v) *Ester formation*

COOH

\n
$$
CH_2 = CHCOOH + HOC_2H_5 \xrightarrow[-H_2O]{\text{Conc.}H_2SO_4} \rightarrow
$$
\n
$$
CH_2 = CH - COOC_2H_5
$$
\nExpmyl acrylate

(vi) With PCI₅

$$
CH_2 = CHCOOH + PCl_5 \rightarrow CH_2 = CH - COCl
$$

Acrylchloride

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.

$$
H-C-COOH
$$

\n
$$
H-C-COOH
$$

\n
$$
Cis-form (Maleicacid)
$$

\n
$$
Transform (Fumaricacid)
$$

 $H^{\dagger}/H_2O \rightarrow CH_2 = CH - COOH$ (1) Methods of Preparation of Maleic Acid

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

$$
CH_2 \xrightarrow{+HCN} CH_2-CH_2-CN \xrightarrow{Conc.H_2SO_4} CH_2-CN \xrightarrow{Conc.H_2SO_4} CH_2-H_2O
$$
\n
$$
CH_2 \xrightarrow{CH_2-H_2O} CH_2-CN \xrightarrow{Conc.H_2SO_4} CH_2-H_2O
$$
\n
$$
CH_2 \xrightarrow{CH_2H_2O} CH_2 \xrightarrow{CH_2O} CH_2 = CHCOOH
$$
\n
$$
CH_2 = CH-CN \xrightarrow{H^+/H_2O} CH_2 = CHCOOH
$$
\n
$$
CH_2 = CH-CN \xrightarrow{H^+/H_2O} CH_2 = CHCOOH
$$
\n
$$
CH_2 = CH-CN \xrightarrow{H^+/H_2O} CH_2 = CHCOOH
$$
\n
$$
CH_2 = CH-CN \xrightarrow{H^+/H_2O} CH_2 = CHCOOH
$$
\n
$$
Haleicantly divide
$$
\n
$$
(acrylonitile)
$$
\n
$$
(acrvlonitile)
$$

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

$$
\underbrace{NaOH}_{\text{boil}} \rightarrow ||\underbrace{CH-COONa}_{\text{Codium salt}} \underbrace{H^+/H_2O}_{\text{Eodium salt}} \rightarrow ||\underbrace{CH-COOH}_{\text{Maleicacid}}
$$

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

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

$$
\begin{array}{ccc}\nH-C-COOH & HCO & HOOC-C-H \\
|| & || & || \\
H-C-COOH & \text{boil} & H-C-COOH \\
\end{array}
$$

$$
HC \longrightarrow CH
$$

\n
$$
HC \longrightarrow CH
$$

\n
$$
HC \longrightarrow CHO
$$

\n
$$
H^2Q \longrightarrow H^2Q^2
$$

\n
$$
H^2Q^2
$$

(iii) By heating malic acid at about 150°C for long time
\nCH(OH)COOH
\n
$$
HOOC-C-H
$$
\n
$$
HOOC-C-H
$$
\n
$$
H-C-COOH
$$
\n
$$
H-C-COOH
$$
\n
$$
Malicacid
$$

$$
CH_{2}COOH
$$

\n $|$
\n $CH_{3}(CH_{2})_{7} CH = CH(CH_{2})_{7} COOH$
\n $CH_{3}(CH_{2})_{7} CH = CH(CH_{2})_{7} COOH$
\n $CH_{3}(CH_{2})_{7} CH_{2} CH_{2}COOH$
\n $CH_{3}(CH_{2})_{7} CH_{2} CH_{2}CH_{2}COOH$

(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.

CHCOOH CHCOOH Maleicanhydride heat Maleicacid

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.

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.

Palmitic and stearic acids are waxy colourless solids

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.

$$
CH_3(CH_2)_7 CH = CH(CH_2)_7 COOH \xrightarrow(iii) Zn+H_2O
$$

\n
$$
CH_3(CH_2)_7 CH_2CHOH \rightarrow HOOGCH_2)_7 CHO
$$

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.

 \parallel $\frac{\text{mean}}{\text{mean}}$ \parallel $\frac{1}{2}$ *O*+ H_2O nature of monocarboxylic acid present in the glyceride. Oils contain *CHCO CHCO* 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).

> $H - C - Br$ fatty acids produced on hydrolysis is approximately 32% palmitic *COOH* palmitic acid and 3% stearic acid. $\begin{array}{c}\n\hline\n\text{Drywater} \\
> \hline\n\text{Drywater} \\
> \text{(anti-addition)} \\
> \hline\n\end{array}$ $\begin{array}{c}\n\text{Bf} - C - H \\
> \text{on the other hand, contains 84%} \\
> \hline\n\end{array}$ on the other hand, contains 84% oleic acid, 4% linoleic acid, 9% $\frac{a}{c}$ -*C*-*Br* and $\frac{18\%}{26}$ stearic acid, 45% oleic acid and 5% linolenic acid. Olive oil Lard (fat of hogs) is a solid fat and its composition in terms of

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

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

 $H - C - COOH$ \downarrow *H C Br H C Br (ii)* They are insoluble in water but soluble in ether, chloroform
 $H - C - H$ (anti-addition) $H - C - Br$ and benzene. $\frac{D_2 \text{ water}}{(anti-addition)}$ $H - C - Br$ and benzene. and benzene.

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

> > (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-

Fat or oil

(a) *By superheated steam*

2)7 COOH
\n
$$
CH_{2}O_{1}^{1}COC_{17}H_{35} \t CH_{2}OH
$$
\n
$$
CH_{2}O_{1}^{1}COC_{17}H_{35} \t CH_{2}OH
$$
\n
$$
CH_{2}O_{1}^{1}CO_{17}H_{35} \t CH_{2}OH + 3C_{17}H_{35}COOH
$$
\nisolids with
\ninsoluble in
\n $CH_{2}O_{1}^{1}COC_{17}H_{35} \t CH_{2}OH$ \n $CH_{2}O_{17}H_{35} \t CH_{2}OH$ \n $CH_{2}O_{17}H_{36} \t CH_{2}OH$ \n $Cl_{2}COH$ \n $Cl_{2}OCOR \t CH_{2}OH$ \n $CH_{2}OH$ \n $CH_{2}OCOH + 3NaOH \rightarrow CH_{2}OH + 3RCOONa$ \nis of acids, it

\n $CH_{2}OCOR \t CH_{2}OH$ \n $CH_{2}OH$ \n $CH_{2}OH$ \n $CH_{2}OH$ \n $CH_{2}OH$ \n $CH_{2}OH$ \n $Cl_{2}OH$ \n $CH_{2}OH$ \n $Cl_{2}OH$

Glycerol

2 *CH OCOR*

 2^{OII}

(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.

(iii) *Hydrogenolysis [Reduction to alcohol]*

$$
CH_{2}-O-C-C_{17}H_{35}
$$
 20 20

(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

 $=\frac{168,000}{M}$, Where M = 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.

 $CHOCC₁₇H₃₅$ sulphuric acid and steam distilled. The distillate is cooled, filtered $\frac{1}{2}$ determined by in
 $\frac{1}{2}$ the fat with alka *O* and titrated against 0.1 *N KOH*. *O* the fat with alkali solution and the mixture is acidified with dilute $CH₂ OCC₁₇H₃₅$ determined by hydrolysing a known weighed amount (5 grams) of *O to neutralize the distillate of 5 grams of hydrolysed fat.* It is (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*

(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.

*CH*₂*OH*

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

 $\frac{6H_2}{200 \text{ cm}}$ *CHOH* + 3*C*₁₇*H*₃₅*CH*₂*OH* (iv) Castor oil is used as purgative and codliver oil as a *CH OH* 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.

Property	Vegetable oils	Minerals oils
1. Composition	These are triesters of glycerol with higher fatty acids.	are hydrocarbons (saturated). These
		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	Decolourisation of pink colour occurs.	No effect.
phenolphthalein		
5. Burning	Burns slowly	Burn very readily.
6. Hydrogenation	Hydrogenation occurs in presence of nickel catalyst. Solid	No hydrogenation occurs.
	glycerides (fats) are formed.	

Table : 28.4 Difference between vegetable oils and Mineral oils

(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.

CH_2OCOR	CH_2OH	R_1COONa	...
$CHOCOR_2 + 3NaOH \rightarrow CHOH + R_2COONa$	(v) Partially esterified		
CH_2OCOR_3	CH_2OH	R_3COONa	detergents.
Triglyceride	Glycerol	Soop	

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.

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.

$$
CH_3(CH_2)_{10} CH_2 \overline{C}OH \mp H\overline{C} \cdot SO_3H \rightarrow
$$

Lauryl alcohol
$$
= \overline{SU(3)} \cdot \overline{SU(3)} \cdot \overline{O(1)}
$$

$$
CH_3(CH_2)_{10} CH_2 OSO_2OH \xrightarrow{\text{NaOH}} V1 \text{eIds high}
$$
\nLauryl hydrogen sulphate

\n
$$
C_{15} / C_{15}
$$

Sodium lauryl sulphate(Detergent)

The other examples are sodium cetyl sulphate, $C_{16}H_{33}$ *OSO₂ ONa* and sodium stearyl sulphate, $CH_3(CH_2)_{16} CH_2 OSO_3$ *Na*. Unlike ordinary soaps, they do not ¹¹ 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.

$$
CH_3
$$

\n CH_3
\n CH_3
\n CH_2 ₉ $CH = CH_2 + C_6H_6 \xrightarrow{A/C_3} CH_3(CH_2)_9$
\n CH_3
\n CH_3
\nWaxes obtained from plants and animals are different than
\n2-Dodecyl benzene

$$
\begin{array}{ccc}\n & CH_3 \\
\hline\n\frac{(i)H_2SO_4}{(i)NaOH} & CH_3 - (CH_2)_9 - CH_6 - C_6H_4 - SO_3Na \\
\hline\n&\text{(i)NaOH}\n\end{array}
$$

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.

$$
(CH_3)_3 N \diagup \frac{Br}{C_{18}H_{37}}
$$

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

$$
R-\bigodot -O-SO\bigg[\bigvee^{\oplus}H(-CH_2-CH_2OH)_3\bigg]
$$

 $R + 3NaOH \rightarrow \overrightarrow{C}HOH + R_2COONa$ (v) Partially esterified polyhydroxy compounds also acts as detergents. detergents.

$$
CH_2OH
$$

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

\n
$$
CH_2OH
$$

\n
$$
CH_2OH
$$

\n
$$
Pentaeryttritol monostearate
$$

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.

C₁₂ H_{25} *OSO*, *Na C*₁₅ *D*₃ *C*₁₅ *C*₁₃ *DCOONa* can be used for washing all t
 Part Hydrophobic Hydrophobic Hydrophobic Aydrophobic <i>Hydrophobic part

Sodium lauryl sulphate(Detergent) sodium palmitat (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.

 $CH_3(CH_2)_{10} CH_2\text{-}OH \mp HO_3O_3H \rightarrow$ Waxes are insoluble in water but are readily soluble in benzene, $CH_2(CH_2)_{10} CH_2 OSOOH \longrightarrow$ yields higher fatty acids and higher monohydric alcohols. petroleum, carbon disulphide etc. Waxes on hydrolysis with water

$$
\begin{array}{c}\n\overrightarrow{NaOH} \\
\longrightarrow \\
\overrightarrow{C_{15}H_{31}COOC_{16}H_{33}+H_2O}\n\end{array}
$$
\n
$$
\begin{array}{c}\nG_1H_{31}COOC_{16}H_{33} + H_2O \rightarrow G_1H_{31}COOH + G_1H_{33}OH \\
\hline\n\end{array}
$$
\n
$$
\begin{array}{c}\n\overrightarrow{C_{15}H_{31}COOH + G_{16}H_{33}OH \\
\hline\n\end{array}
$$
\n
$$
\begin{array}{c}\n\overrightarrow{C_{15}H_{31}COOH + G_{16}H_{33}OH \\
\hline\n\end{array}
$$

³ ² ¹⁰ ² ² *CH* (*CH*) *CH OSO ONa* When hydrolysis is carried with caustic alkalies, soap and higher monohydric alcohols are formed.

$$
C_{15}H_{31}COOC_{16}H_{33} + NaOH \rightarrow C_{16}H_{33}OH + C_{15}H_{31}COONa
$$

Sodium palmitate(Soop)

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, $C_{25}H_{51}COOC_{30}H_{61}$

CH₃ water proof coating and cosmetic preparations. Waxes are used in the manufacture of candles, polishes, inks,

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 $NH₂$, are referred to as substituted acids. For example,

> $CH_2CICOOH$; $CH_2OHCOOH$; Chloroacetc acid et Hydroxyacetic acid Aminoacetic acid quantum et al., $CH_2ClCOOH$; $CH_2OHCOOH$; CH_2NH_2COOH
Chloroacetc acid Hydroxyacetic acid Aminoacetic acid Aminoacetic acid

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

$$
\begin{array}{ccccc}\n6 & 5 & 4 & 3 & 2 & 1 \\
C & - & C & - & C & - & C \\
\hline\n\varepsilon & \delta & \gamma & \beta & \alpha\n\end{array}
$$
\n
$$
\begin{array}{ccccc}\nC \text{H(OH)CC} \\
2 & & & \\
C \text{H(OH)CC}\n\end{array}
$$

For example,

```
_3CHOHCOOH ; CH_3CHO.
\alpha-Hydroxypropionic acid<br>2-Hydroxypropanoic acid
```
-Hydroxypropionic acid β-Hydroxybutyric acid |
-Hydroxypropanoic acid 3-Hydroxybutanoic acid |

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 $CaCO₃$.

(1) **Method of Preparation**

From acetaldehyde :

$$
CH_3CHO + HCN \rightarrow CH_3CH(OH)CN \xrightarrow{H_2O/H^+} \rightarrow
$$
 $Red P$ $CHBFCC$
\n $Recaldehyde$ $Capophydrin$ $rac{P}{Br_2}$ $CHBFCC$

$$
\begin{array}{c}\nCH_3CHOHCOOH\\ \n \text{Lactic acid}\n \end{array}
$$

(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 in medicine as calcium and iron lactates, 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**

HO CH CO H HO C H CO H |

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

(1) **Methods of Preparation**

*CH*₂*OHCOOH*; *CH*₂*NH*₂*COOH*_s solution contains potassium tartrate which is also precipitated by (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 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.

\n
$$
\text{CHO} \xrightarrow{HCN} \xrightarrow{CH(OH)CN} \xrightarrow{H_2O/H^+} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{CH(OH)COOH} \xrightarrow{H_2O/H} \xrightarrow{H_2O/H
$$

(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 $CH₃CHOCOCH₃$ isomerism (four forms). Natural tartaric acid is the dextro variety. It contains two secondary alcoholic groups and two carboxylic groups. *COOH*

> **Optical Isomerism in tartaric acid** *COOH H C OH* $\begin{bmatrix}$ *cooн*) $\end{bmatrix}$ $\begin{bmatrix}$ *cooн*) *HO-C-H H-C-O H H-C-OH* $-C$ - OH HO - C - H H - C -| | | | | | | | | $COOH \setminus$ (cooh) *HO C H – C– O H H–C– OH COOH H C O* $- C - H$ $H - C - OH$ | | | | \uparrow | *COOH H C OH COOH H C OH* $-C$ -OH \sqrt{C} | \Box | *d*+ **Dextrorotatory** *l*-(Leavorotatory acid) Meso-Tartaric acid

> > Optical active

Tartaric acid

(i) d + Tartaric acid-Dextro-rotatory \Box (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 $Cd(OH)_2$ 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 $C_d(OH)_{2}$.

(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.

(4) **Uses :** It finds use in making lemonades, as acidulant in food and soft drinks and makes the lemon sour, as mordant in dyeing and 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.

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

Cinnamic acid

Phenyl acetic acid

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

□ Chromickthoxide *rin*₇ glacial acetic acid or Co-Mn acetate can also be taken in place of alkaline $KMnO₄$.

(viii) *From o-xylene* **[***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.

$$
C_6H_5COOH = C_6H_5COO + H^+ \qquad \qquad \text{as}
$$

Since the carboxylate anion (*ArCOO*) is resonance stabilised to a greater extent than the carboxylic acid (*ArCOOH*).

$$
\begin{array}{ccc}\nO & O & O \\
\parallel & | & \parallel \\
Ar - C - OH & \leftrightarrow Ar - C = OH & Ar - C - O & \leftrightarrow Ar - C = O\n\end{array}\n\qquad\n\begin{array}{ccc}\nCOOH & COOH & COOH \\
\parallel & | & \parallel \\
O & O & \leftrightarrow Ar - C = O & \downarrow\n\end{array}
$$

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

All Common Jane Barbara \mathbf{e}

 $A + H_2O \xrightarrow{H^+ or OH^-} C_6H_5COOH + CH_3OH$ decreases the acidity. Inductive effect affects all positions, *i.e.*, *o*–, *m*– (i) *Inductive effect* **:** If the substituent exerts–*I* effect, it increases the acidity of carboxylic acids, while if it exerts $+ I$ effect it 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.

Acidity is only ducto@ldctron 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.

 $C_6H_5COO + H^+$ acid is stronger acid than benzoic acid. Like other substituted benzoic $+$ M effects on and operate and hence only the *CQH*_dstrengthening –I effect takes part with the result *m*-hydroxybenzoic 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*

COOH COONa \bigcirc *+*2 *Na* \bigcap $+$ H_2 (b) *Reaction with Alkalies Or NaHCO*₃ Or $Na₂CO₃$:

(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 phenylacetie acid is deasily 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*

$$
COOH + PCI5 or $SOCl_2$ \longrightarrow $\bigodot + POCl_3 + HCl$
$$

(e) *Reaction with N3H* [*Schmidt reaction*] Benzoyl Chloride

(i) *Decarboxylation*

$$
\bigcirc \leftarrow \text{COOH} + \text{HCOOH} \xrightarrow{\text{MnO}} \bigcirc \text{CHO} + \text{CO}_2 + \text{H}_2\text{O}
$$

(j) *Hunsdiecker reaction* :

$$
C_6H_5COOAg + X_2 \xrightarrow{\text{in } CC/4} C_6H_5-X + CO_2 \uparrow + AgX
$$

 Silver berzoate $(B_2 \text{ or } C_2)$ heat $\xrightarrow{\text{heat}}$ Phenylhalide

(ii) *Reactions of Aromatic Ring*

(a) *Nitration*

(5) Uses : Benzoic acid Ys 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 [-Phenyl acrylic acid]

CH = CH – COOH

(1) **Methods of Preparation**

(i) *By Perkin's reaction*

$$
C_6H_5CHO + (CH_3CO_2O \xrightarrow{CH_3COONa} 180^\circ C
$$
\n
$$
C_6H_5CH = CHCOOH + CH_3COOH
$$
\nSodium\nphenoxide

(ii) *By Claisen condensation*

 C_2H_5 ONa

$$
C_6H_5CH = CHCOOC_2H_5 \xrightarrow{H_2O}
$$
It is a commercial method. The
Refer

$$
C_6H_5CH = CHCOOH + C_6H_5OH
$$
 isomers. Salicylic acid is more vo

(iii) *By knoevenagel reaction*

$$
C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{\mathit{N}H_3 \qquad \qquad}_{heat} \qquad (11) \text{ Reimer-Tiemann reaction}
$$
\n
$$
C_6H_5CH = CHCOOH + CO_2 + H_2O \qquad \qquad \bigodot \qquad \qquad_{f-CCl_4+ KOH} \xrightarrow{\text{Heat}} \bigodot \qquad \qquad O^H \xrightarrow{\text{Dil}}
$$

(iv) *Industrial method*

 $C_6H_5CHCl_2 + H_2CHCOONa \xrightarrow{200^\circ C} C_6H_5CH = CHCOOH + NaCl + HCl$ (111) From Denzene derivatives Sodium acetate **Exercía de Solidaria** e a constructiva e a constructi Benzalchloride Sodium acetate

(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.

$$
C_6H_5-C-H
$$
\n
$$
H-C-COOH
$$
\n
$$
H- C-COOH
$$
\n
$$
P = C-COOH
$$
\n
$$
C_6H_5-C-H
$$
\n
$$
C_7H
$$
\n
$$
C_8H_5-C-H
$$
\n
$$
C_8H_5-C-H
$$
\n
$$
C_9H_5-C-H
$$

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

(3) **Chemical properties**

Oxidation	C_6H_5CHO	$+ C_6H_5COOH$
CrO_3	Benzaldehyde	Benzoic acid
Reduction	$C_6H_5CH_2CH_2COOH$	β -Phenyl propionic acid
Reduction	$CC_6H_5CH_2CH_2CH_2OH$	
$LidIH_4$	3 -Phenyl propyl alcohol	
$-10^{\circ}C$	2 -Phenyl propyl alcohol	
Soda lime	$CC_6H_5CH = CHCH_2OH$	
Connamyl alcohol		
Soda lime	$CC_6H_5CH = CH_2$	
distilled	$CC_6H_5CH = CH_2$	
Conc. HNO ₃ /H ₂ SO ₄	2 - $CC_6H_4(CH)_2COOH$	
Conc. HNO ₃ /H ₂ SO ₄	$NO_2C_6H_4(CH)_2COOH$	
Conc. HNO ₃ /H ₂ SO ₄	$NO_2C_6H_4(CH)_2COOH$	
Conc. HNO ₃ /H ₂ SO ₄	$OC_6H_5CH = CHCOCl$	
Connamyl chloride	OH	
Chmanyl chloride	$CAH_5CH = CHCOCl$	
Chnamyl chloride	OH	
Salicylic acid [O-Hydrody' 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*

 $C_6H_5CH = CHCOOH + C_2H_5OH$ isomers. Salicylic acid is more volatile and separated by steam distillation.

(ii) *Reimer-Tiemann reaction*

(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**

ONa

Disodium salicylate

(ii) *Reaction with alcohols or phenols*

$$
\bigodot \left(\begin{array}{c}\nOH \\ + CH_3OH \xrightarrow{HCI(gas)} & \bigodot \n\end{array}\right) H_2O + H_2O
$$
\n
$$
\downarrow COOH + H_2O
$$

Methylic sail by late is an oily liquid (Methyl salicylate *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.

□ Aspirin is a white solid, melting point 135°C. Priquinsed as antipyretic and pain killer (analgesic action).

(v) *Reaction with ferric chloride solution*

(1) **Methods of preparation**

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

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.

COOH

 \bigcirc

(3) **Chemical properties**

Benzene-1,2-dicarboxylic acid (Phthalic acid)

Benzene-1,3-dicarboxylic acid (Isophthalic acid)

Benzene-1,4-dicarboxylic acid (Terphthalic acid)

(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^- , $-MH_2$, $-OR$

- and $O C R$ are known as acid derivatives.
	- $R C$ group is common to all the derivatives and is known *O*

O

as acyl group and these derivatives are termed as acyl compound.

The important derivatives are given below :

Group replacing $-OH$	Name	Structure	nitrogen in amide, hence ester is more
$(X = F, C\mid, Br, \Lambda)$	Acyl halide		Acyl Halides F
		$R-\overset{II}{C}-X$	where R may be alkyl or aryl gi
$-NH_2$	Amide	O $R-C-NH_2$	Methods of Preparation (1)
			From carboxylic acid: (i) $RCOOH + PCI_5 \rightarrow RCOCl + POC$
$-OR$	ester		$3RCOOH + PCl3 \rightarrow 3RCOCl$
		$R - C - OR$ $(R \text{ may be } R)$	(ii) Industrial method : By distill
$-OOCR$	anhydride		$3CH_3COONa + PCI_3 \xrightarrow{\text{heat}}$
		$R - \overline{C} - Q - \overline{C} - R$	$2CH3COONa+POCl3$ —heat

Reactivity

Acyl derivatives are characterised by nucleophilic substitution reactions.

R	Ne	Ne	(iii) With though chloride :
$C = D$: $NU = E$	$RCOOH + SOC/2 \rightarrow RCOC/4$	$SCOOH + SOC/2 \rightarrow RCOC/4$	
L	This is the best method because SO_2 easily escape leaving behind acyl chloride.		
$(L = X, NH_2, O - C - Ror OR)$	2. Physical properties : The lower answer is colourless liquid while the higher members are		

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

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 – $NH₂$ 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.

$$
\overline{C}
$$
 Acyl Halides $R - C$ C

 $R - C - X$ where *R* may be alkyl or aryl group.

O (1) **Methods of Preparation**

2 *NH R C* (i) *From carboxylic acid* **:**

 $RCOOH + PCI₅ \rightarrow RCOCl + POCI₃ + HCl$

 O 3*RCOOH* + *PCl*₃ \rightarrow 3*RCOCl* + *H*₃*PO*₃

 $R = \overline{C} - \overline{OR}$

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

 O O $3CH_3COONa + PCI_3 \xrightarrow{\text{heat}} 3CH_3COCl + Na_3PO_3$

 $R - C - O - C - R$
 $2CH_3COONa + POC_3 \xrightarrow{\text{heat}} 2CH_3COOL + \text{NaPO}_3 + \text{NaCl}$

Sodium acetate Acetylchloride

$$
(CH_3COO_2 Ca+ SO_2Cl_2 \xrightarrow{\text{heat}} 2CH_3COCl + CaSO_4
$$

Calciumacetate Sulphuryl
chloride Acetylchloride

Nu (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.

 Z_2 , $O - C - R$ or $O R$ (2) **Physical properties :** The lower acyl chloride are mobile,

> 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**

 Cl Cl R C O Nu Cl Nu R C O R C || | | | : ||

(i) *Hydrolysis*:
$$
CH_3COCl + HOH \rightarrow CH_3COOH + HCl
$$

\nAcetylchloride
\nAcetylchloride
\n $CH_3-C+2CH_2-N \equiv N \rightarrow C$
\n $CH_3-C-Cl+2CH_2-N \equiv N \rightarrow C$

$$
C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + H_2O
$$

Benzoylchloride
Benzoylchloride

(ii) *Reaction with alcohols (alcoholysis)*

$$
CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl
$$
 (ix) *Reaction with water*
Exply acetate

 $C_6H_5COCl + C_2H_5OH - \frac{aq NaOHor}{P}$ $C_6H_5COOC_2H_5 + HCl$ $C_73COCl + \frac{Cl_3COCl_2}{P}$ $C_713COCl$ C_8 $C_9H_5COCl + \frac{Cl_3COCl_2}{P}$ $C_113COCl$ Ethyl benzoate Benzoylchloride Ethyl alcohol Pyridine E $C_6H_5COCl + C_2H_5OH$ and NaOH or

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

(iii) *Reaction with salts of carboxylic acid*

$$
CH_3COCl + CH_3COO \t\t Na+ \xrightarrow{Pyridine} CH_3^1 C - O - C - CH_3^1
$$
\n
$$
CH_3COCl + CH_3COO \t\t Na+ \xrightarrow{Pyridine} CH_3^1 C - O - C - CH_3^1
$$
\n
$$
CH_3COCl + \frac{Pyridine}{A
$$
\n
$$
H_3COCl + \frac{Pyridine}{A}
$$
\n
$$
CH_3COCl + \frac{Pyridine}{A}
$$
\n
$$
CH_3COCl + \frac{Pyridine}{A}
$$

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

$$
CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl
$$
\n
$$
CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl
$$
\n
$$
C_6H_5COCl + 2NH_3 \rightarrow C_6H_5CONH_2 + NH_4Cl
$$
\n
$$
C_6H_5COCl + 2NH_3 \rightarrow C_6H_5CONH_2 + NH_4Cl
$$
\n
$$
Benzamide
$$

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

$$
CH_3COCl + H_2NC_2H_5 \rightarrow CH_3COMC_2H_5 \rightarrow CH_3COMC_2H_5
$$
\n
$$
CH_3COCl + (C_2H_5)_2NH \rightarrow CH_3COMC_2H_5)_{2} + HCl
$$
\n
$$
CH_3COCl + (C_2H_5)_2NH \rightarrow CH_3COMC_2H_5)_{2} + HCl
$$
\n
$$
(vi) Reduction : (vii) Reduction : (vi) Reduction : (viii) Reduction : (viv) Reduction
$$

$$
CH_3COCl \xrightarrow{LiAlH_4 \text{ or}} CH_3CH_2OH
$$

\n $NaBH_4 \xrightarrow{CH_3CH_2OH}$ (P
\n $Ch_3COCl \xrightarrow{LiAlH_4 \text{ or}} CH_3CH_2OH$ (d) I
\n (4) I

$$
CH_3COCl + H_2 \xrightarrow{Pd \mid BasO_4} CH_3CHO + HCl
$$

This reaction is called **Rosenmund reaction**.

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

$$
2CH_{3}COCl + (CH_{3})_{2} Cd \rightarrow 2CH_{3}COCH_{3} + CdCl_{2}
$$
\n
$$
\text{Dimethyl}\atop \text{Cadmium}\atop \text{Cadmium}
$$

$$
\begin{array}{ccc}\n\begin{array}{ccc}\n\downarrow & \nearrow & \downarrow \\
\downarrow & \nearrow & \downarrow\n\end{array} & \begin{array}{ccc}\n\downarrow & \downarrow & \downarrow \\
\downarrow & \downarrow & \downarrow \\
\downarrow & \downarrow & \downarrow\n\end{array}\n\end{array}
$$
\n
$$
2C_6H_5COCl + (CH_3)_2Cd \rightarrow 2C_6H_5COCH_3 + CdCl_2
$$
\n
$$
\begin{array}{ccc}\n\text{Actophenone} & \downarrow & \downarrow \\
\downarrow & \downarrow & \downarrow\n\end{array}
$$

Nu (viii) *Reaction with diazomethane*

$$
C\Gamma + H^{+} \rightarrow HCl
$$
\n
$$
C\Gamma + HOH \rightarrow CH_{3}COOH + HCl
$$
\n
$$
C\Gamma + HOH \rightarrow CH_{3}COOH + HCl
$$
\n
$$
C\Gamma + HOH \rightarrow CH_{3}COOH + HCl
$$
\n
$$
C\Gamma + HOH \rightarrow CH_{3}COOH + HCl
$$
\n
$$
C\Gamma + HCl \rightarrow CH_{3} - C - CI + 2\overline{C}H_{2} - N = N \rightarrow CH_{3} - C - CH - N = N
$$
\n
$$
Diazonethane
$$
\n
$$
C_{6}H_{5}COOH + H_{2}O
$$
\n
$$
C_{8}H_{5}COOH + H_{2}O
$$
\n
$$
C_{8}H_{5}COOH + H_{2}O
$$
\n
$$
C_{8}H_{6}COOH + H_{2}O
$$
\n
$$
C_{8}H_{7}COOH + H_{2}O
$$
\n
$$
C_{8}H_{8}COOH + H_{2}O
$$
\n
$$
C_{8}H_{9}COOH + H_{1}O
$$

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

(x) *Reaction with chlorine*

$$
CH_3COCl + CI_2 \xrightarrow{\text{Red }P} Cl-CH_2-CO-Cl+HCl
$$

Mono- α -chloroaceyl chloride

O O (xi) *Reaction with Grignard reagent*

$$
O-C-CH_3
$$

Canhydride
Methoded
Methoded
Accept
2. $CH_3COCH_3 + Mg$

(xii) *Reaction with KCN*

$$
CH_3COCl + KCN \rightarrow CH_3COCN \xrightarrow{H_2O} CH_3COCOOH
$$

Acetylcyanide Pyruvicacid

$$
\bigcirc COC_6H_5
$$
\n
$$
\bigcirc COC_6H_5
$$
\n
$$
+ HCl
$$
\n
$$
Salicylic
$$
\n
$$
2
$$
\n
$$
COOH + CIOCCH_3 \rightarrow \bigcirc COOH + HCl
$$
\n
$$
Acetytsalicylicacid
$$
\n
$$
(Aspirin)
$$
\n
$$
COOH + HCl
$$

(xiv) *Reaction with ether*

$$
CH_3COCl + C_2H_5OC_2H_5 \xrightarrow{ZnCl_2} \rightarrow
$$
Diethyl ether

Ethyl chloride $CH_3COOC_2H_5+ C_2H_5Cl$
Ethyl acetate Ethyl chloride

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

$$
\begin{array}{ccc}\nO & O & O \\
O & \parallel & \parallel & \parallel \\
C & \text{M} & \text{Acceylchloride} \\
C & \text{M} & \text{Acceylchloride} \\
\end{array}
$$

(xvi) *Reaction with hydroxylamine and hydrazine*

$$
CH_3COCI + H_2NOH \rightarrow CH_3CONHOH + HCl
$$

Hydroxyl
amine
(hydroxamic acid)

 CH_3COC /+ H_2 *NNH*₂ → $CH_3CONHNH_2$ + *HCl*
Hydrazine Acetylhydrazine 3 COCI+ H_2 IVIVII2 \rightarrow CH₃COIVIIIVII2+ HCI
Hydrazine Acetyl hydrazine

(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.

$$
\text{Acid Amides R} - \text{C} \stackrel{\text{O}}{\leftarrow} \text{NH}_2 \qquad \qquad \text{CH}_3 \text{CONH}_2 + \text{Na} \quad \text{C}
$$

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

(1) **Methods of preparation**

(i) *Ammonolysis of acid derivatives*

$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$	$C_6H_5CONH_2 + 4[H] \xrightarrow{Na/C_2H_5OH}$
$(CH_3CO)_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$	(iv) Dehydration
$C_6H_5COCl + NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$	(iv) Dehydration
$C_6H_5COCl + NH_3 \rightarrow C_6H_5CONH_2 + HCl$	$CH_3CONH_2 \xrightarrow{P_2C_5} CH_3C \equiv N + H_2O$
$C_6H_5COCl + NH_3 \rightarrow C_6H_5CONH_2 + HCl$	$CH_3CONH_2 \xrightarrow{P_2C_5} CH_3C \equiv N + H_2O$
$CH_3CONH_2 \xrightarrow{P_2C_5} CH_3C \equiv N + H_2O$	
$CH_3COCl + NH_3 \rightarrow C_6H_5CONH_2 + HCl$	$CH_3CONH_2 \xrightarrow{P_2C_5} CH_3C \equiv N + H_2O$
$CH_3COCl + NH_3 \rightarrow C_6H_5CONH_2 + HCl$	$CH_3CONH_2 \xrightarrow{P_2C_5} CH_3C \equiv N + H_2O$

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

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

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

 \Box Ammonium acetate is always heated in presence of glacial acetic acid to avoid the side product ($CH₃COOH$).

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

 $CH_3C \equiv N \frac{\text{Conc. } HCl}{H_2O} \cdot CH_3 \text{CONH}_2$
Acetamide $W = N \rightarrow \text{Cone.} HCl \rightarrow CH_3 \text{CONH}_2$ $C_6 H_5 \text{CONH}_2 + \text{HONO}$

(iv) *By heating carboxylic acid and urea*

$$
H_2N-C-NH_2+R-C-OH \xrightarrow{\text{heat}} R-C-NH_2+CO_2+NH_3
$$
 This is a
compoun

$$
O
$$

(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.

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

$$
H R H R H R
$$

\n
$$
H H R
$$
<

(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*

$$
CH_3CONH_2 + H_2O \xrightarrow{\text{Slowly}} CH_3COOH + NH_3
$$
\n
$$
CH_3CONH_2 + CH_3OH \xrightarrow{\text{TeV}} CH_3 + CH_2O + H_2O + H_2O + H_3COOH + NH_3
$$
\n
$$
CH_3CONH_2 + H_2O + H_2O + H_3COOH + NH_3
$$
\n
$$
CH_3CONH_2 + NaOH \xrightarrow{\text{Farnorrapidly}} CH_3COONa + NH_3
$$
\n
$$
CH_3 - Mg - Br + CH_3 - CONH_2 \rightarrow CH_4 + CH_3
$$
\n
$$
CH_3CONH_2 + NaOH \xrightarrow{\text{Farnorrapidly}} CH_3COONa + NH_3
$$
\n
$$
CH_3 - Mg - Br + CH_3 - CONH_2 \rightarrow CH_4 + CH_3
$$

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

It shows feebly acidic as well as basic nature.

$$
CH_3CONH_2 + HCl(\text{conc}) \rightarrow CH_3CONH_2.HCl
$$

Acetamidehydrochloride
(only stablein aqueoussolution)

$$
\underset{\text{Acetamide}}{2CH_3\text{CONH}_2} + \underset{\text{Mercuric}}{HgO} \rightarrow (\underset{\text{Mercuric}\\\text{Mercuric}\\\text{Mercuricacetamide}}{CH_3\text{CONH}_2} + H_2O
$$

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

_{Sodium accelerationide} 2

(iii) *Reduction*

$$
\mathit{CH_{3}COMH_{2}} + 4[H] \xrightarrow{\text{LiAlH}_{4}} \mathit{CH_{3}CH_{2}NH_{2}} + H_{2}O \\ \xrightarrow{\text{Extamide}} \\
$$

$$
\mathcal{C}_6H_5CONH_2 + 4[H] \xrightarrow{\text{NaI } C_2H_5OH} \mathcal{C}_6H_5CH_2NH_2 + H_2O
$$

Amm. acetate

\n
$$
CH_3COMH_2 \xrightarrow{\text{ } B_2O_5} CH_3C \equiv N + H_2O
$$
\nAcetamide

\nNetamide

$$
C_6H_5COMH_2 \xrightarrow{\text{ } B_2O_5 \text{ } } C_6H_5C \equiv N + H_2O
$$
\nBenzamide

$$
C_6H_5CONH_2 \xrightarrow{SOCl_2} C_6H_5C \equiv N
$$

Phenyicyanide

(v) *Reaction with nitrous acid*

$$
CH_3CONH_2 + HONO \xrightarrow{\text{NaNO}_2 \mid HCl} CH_3COOH + N_2
$$

Aceticacid

$$
C_6H_5CONH_2 + HONO \xrightarrow{\text{NaNO}_2 \mid HCl} C_6H_5COOH
$$

Benzolic acid
+ $N_2 + H_2O$

 $+H₂O$

 $H_2N - C - NH_2 + R - C - OH \xrightarrow{\text{Head}} R - C - NH_2 + CO_2 + NH_3$ This is an important reaction for reducing a carbon atom from a *O O* compound, *i.e.,* is changed to group. *CONH* ² *NH* ² (vi) *Hofmann bromamide reaction or Hofmann degradation* **:**

$$
CH_3CONH_2 \xrightarrow{Br_2} CH_3NH_2
$$

Acctamide *NaOH* or *KOH* Methyl anime(p-)

This reaction occurs is three steps:

$$
CH_3 - C - NH_2 + Br_2 + KOH \rightarrow CH_3CONHBr + KBr + H_2O
$$

\n
$$
CH_3 - C - NHBr + KOH \rightarrow CH_3 NCO + KBr + H_2O
$$

\n
$$
CH_3 - C - NHBr + KOH \rightarrow CH_3 NCO + KBr + H_2O
$$

\n
$$
CH_3NCO + 2KOH \rightarrow CH_3NH_2 + K_2CO_3
$$

\n
$$
Methylamine
$$

$$
H R \qquad \qquad \overline{CH_3CONH_2 + Br_2 + 4 KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O}
$$

 $H - N - C = O$ $H - N - C = O$ $H - N - C = O$ isolated; *N*-bromamides, *RCONHBr*; salts of these bromamides \Box In this reaction a number of intermediates have been

 $[$ *RCONBr*^{$^-$} $]$ *K*^{$+$}; Isocyanates, *RNCO*.

□ Nitrene rearranges to form isocyanate.

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

$$
CH_3CONH_2 + CH_3OH \xrightarrow[70^{\circ}C]{} CH_3COOCH_3 + NH_4Cl
$$

$$
\xrightarrow[70^{\circ}C]{} method
$$
 methyl acetate

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

CH₃MgBr

OH	$OMgBr$	Amyl acetate	Banana	Isobuty			
$CH_3 - C - NH_2$	CH_3	$CH_3 - C - NH_3$	CH_3	Amyl hurtate	Amyl hurtate	Asmine	Ethyl b
CH_3	(ii) Solubility : They are sparing!						
CM_3	(iii) Solubility : They are sparing!						
$CH_3 - C - CH_3$	(iii) Boiling points : Their boiling						
$CH_3 - C - CH_3$	Acetone	(3) Chemical properties					

(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.

$$
\begin{array}{c}\n\text{Esters, } R - C - OR \\
\parallel \\
O\n\end{array}
$$

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.

$$
P - C - \overline{O}H + H \overline{H}^1 O R \xrightarrow{H^+} R - C - OR + H_2 O
$$
\n
$$
CH_3 COOH + CH_2 N_2 \xrightarrow{\text{Ether}} CH_3 COOCH_3 + N_2
$$
\n
$$
C H_3 COOH + CH_2 N_2 \xrightarrow{\text{Ether}} CH_3 COOCH_3 + N_2
$$
\n
$$
H = \frac{L i A H_4}{R} + 4 H \xrightarrow{\text{L} i A H_4} \frac{L i A H_4}{R} \xrightarrow{\text{C} i A H_2 O} H_3 COOH + O H_2 N_2 \xrightarrow{\text{Ether}} CH_3 O H_
$$

 C_6H_5COOH+ CH_2N_2 $\xrightarrow{\text{Ether}} C_6H_5COOCH_3 + N_2$ Benzoicacid Diazomethane Methyl benzoate

With diazomethane is the best method.

(ii) *From acid chloride or acid anhydrides* CH_3CO CH_7 OC_2 $H_5 \rightarrow CH_3$ $COOC_2$ $H_5 + HCl$ mixture of oxides known as conner chro $L \rightarrow L$ U_1 U_2 H_3 U_3 U_4 H_5 H_6 H_7 H_8 H_9 H_9

 CH_3CO \rightarrow $OH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + CH_3COOH$ \rightarrow $R-\overset{C}{C}-OR+2H_2 \xrightarrow{CuO.CUC_2O_4} RCH_2$ *CH CO* $\frac{1}{3}$ CO \geq 0+ CH₃CH₂OH \rightarrow CH₃COOCH₂CH₃+ CH₃COOH $\frac{1}{R-C-OR+2H_2}$ <u>cuo.cuce</u> Ethyl acetate Ethyl alcohol Aceticanhydride $CH₃CO$

$$
C_6H_5CO\overline{Cl} + H_1OC_2H_5 \rightarrow C_6H_5COOC_2H_5 + HCl
$$
\n(iv) *Reaction with PCI₅ or SOCl₂*\n
$$
C_6H_5CO\overline{Cl} + HCl
$$
\n(iv) *Reaction with PCI₅ or SOCl₂*

(iii) *From alkyl halide :*

$$
C_2H_5Br + CH_3COOAg \rightarrow CH_3COOC_2H_5 + AgBr
$$

\n
$$
C_2H_5Br + CH_3COOAg \rightarrow CH_3COOC_2H_5 + AgBr
$$

\n
$$
C_2H_3COOC_2H_5 + SOCO_2 - CH_3CO_2
$$

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

$$
CH_3 - O - CH_3 + CO \xrightarrow{BF_3} CH_3 COOCH_3
$$

Method $350K$ **Method** $(v) Reaction with alcohols :$

(v)*From Tischenko reaction :*

$$
CH_3-C-H+O=C-CH_3 \xrightarrow{\mathcal{A}(OC_2H_5)_3} CH_3-C-OC_2H_5
$$
\n
$$
R-C \xrightarrow{\mathcal{O}} \mathcal{O} + \mathcal{R}OH \xrightarrow{H^+} R-C \xrightarrow{\mathcal{O}} \mathcal{O} + \mathcal{R}OH \xrightarrow{H^+} R-C \xrightarrow{\mathcal{O}} \mathcal{O} + \mathcal{R}H
$$

(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 :

CH 3 (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^o*C*.

(3) **Chemical properties**

(i) *Hydrolysis* **:**

$$
CH_3COOC_2H_5 + H_2O \underbrace{\overset{\text{dil. acid}}{\underset{\text{Letlyl acetate}}{\sum}} CH_3COOH + C_2H_5OH}_{\text{Acticacid}}CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH\\ \text{Etlyl acetate}}\overset{\text{Ethyl acetate}}{\underset{\text{Setlyl acetate}}{\sum}} CH_3COONa + C_2H_5OH
$$

 $\frac{1}{3}$ COO $\frac{1}{6}$ $\frac{1}{5}$ $\frac{1}{5}$ $\frac{1}{5}$ $\frac{1}{6}$ $\frac{1}{6}$ Hydrolysis of ester by alkalies (*NaOH*) is known as

saponification and leads to the formation of soaps \Box This reaction (saponification) is irreversible because a resonance stabilized carboxylate (acetate) ion is formed.

Esters, $R - C - OR$ \Box The acid hydrolysis of esters is reversible.

O (ii) *Reaction with ammonia* **(ammonolysis) :** *CH CO OC ^H ^H NH CH CONH ^C*2*^H* ⁵*OH* Acetamide 2 5 2 3 2 Ethyl acetate ³

(iii) *Reduction*

$$
CH_3COOC_2H_5 + 4[H] \xrightarrow{L iAlH_4} 2C_2H_5OH
$$

\n
$$
OR + H_2O
$$

\n
$$
CH_3COOC_2H_5 + 4[H] \xrightarrow{L iAlH_4} C_2H_5OH
$$

\n
$$
CH_2OH + 4H \xrightarrow{L iAlH_4} C_2H_5OH + C_2H_5OH + C_2H_5OH
$$

\n
$$
CH_3COOCH_3 + N_2
$$

\n
$$
CH_3COOCH_3 + N_2
$$

\n
$$
Ethyl acetate
$$

\n
$$
Ethyl heatate
$$

\n
$$
Benzylalcohol
$$

 \Box ⁶ *M*₃ *COUCM*₃+ *N*₂ \Box Reduction in presence of *Nal C*₂ *H*₅ *OH* is known as Bouveault Blanc reduction.

> \Box 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 $(CuO.CuCr₂O₄)$.

$$
\begin{array}{c}\nO \\
R-C- OR + 2H_2 \xrightarrow[525 K, 200-300atm]{} RCH_2OH + ROH \\
\end{array}
$$

 $CH_3COOC_2H_5+PCl_5\rightarrow CH_3COOC_1+ C_2H_5Cl+POCl_3$

2 Ethyl chloride 2 5 Acetylchloride *CH* ³*COOC*2*^H* ⁵ *SOCl*² *CH* ³*COCl ^C ^H Cl SO*

$$
\begin{array}{c}\nC_6H_5COOC_2H_5 + PCk_5 \rightarrow C_6H_5COCl + POCk_3 + C_2H_5Cl\\
\hline\n\text{Ethyl benzate} & \text{Benzoylchloride}\n\end{array}
$$

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

$$
\begin{array}{lll}\n\frac{2^{H_5/3}}{3} \rightarrow CH_3 - C - OC_2H_5 & & R - C & O + R'OH & \\
& & & C + R'COO_2H_5 + CH_3OH \rightarrow CH_3COOCH_3 + C_2H_5OH \\
& & & & \\
& & & & \\
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& & & & & \\
& & & & & \\
& & & & & \\
$$

 \Box This reaction is known as alcoholysis or trans esterification.

(vi) *Reaction with Grignard reagents*

$$
CH_3-C-OC_2H_5+CH_3MgBr \rightarrow \begin{bmatrix} O\\ H_3-C-OC_2H_5+CH_3MgBr \rightarrow \begin{bmatrix} O\\ H_3-C-OC_2H_5 \end{bmatrix} & \begin{bmatrix} O\\ H_3-C-DC_2H_5 \end{bmatrix} & O\\ CH_3-C+CO_2H_5+CH_3MgBr \rightarrow \begin{bmatrix} O\\ H_3-C+CO_2H_5 \end{bmatrix} & \begin{bmatrix} O\\ H_3-C-CO_2H_5 \end{bmatrix} & O\\ CH_3-C+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_5+CO_3H_3+CO_3H
$$

(vii) *Claisen condensation*

$$
CH_3 - C - \underbrace{[OC_2 H_5 + H}_{Etly|acetate(2 molecules)} + Na
$$
\n
$$
CH_3 - C - \underbrace{[OC_2 H_5 + H}_{Etly|acetate(2 molecules)} + CH_2 COOC_2 H_5 - \underbrace{C_2 H_5 O^- Na^+}_{}
$$
\n
$$
CH_3 - C + \underbrace{[C_2 H_5 + H}_{CUY|acetate(2 molecules)} + O
$$
\n
$$
CH_3 - C + \underbrace{[C_2 H_{CU} + H_{CU
$$

$$
CH_3 - C - CH_2 COOC_2 H_5 + C_2 H_5 OH
$$

\n
$$
CH_3 - C - CH_2 COOC_2 H_5 + C_2 H_5 OH
$$

\n
$$
CH - 2CH_3 COOC
$$

\n
$$
CH - 2CH_3 COOC
$$

(viii) *Reaction with hydroxyl amine*

$$
C H_3 - C - 0
$$

\n
$$
C H_3 - C - 0
$$

\n
$$
C H_3 - C - 0
$$

\n
$$
C H_4 - C
$$

\n
$$
C H_5 - C
$$

\n
$$
C H_5 - C
$$

\n
$$
C H_4 - C
$$

\n
$$
C H_5 - C
$$

\n

(ix) *Reaction with hydrazine*

Acid hydrazide

(x) *Halogenation*

 $CH_3COOC_2H_5 + Br_2 \xrightarrow{\text{RedP}} CH_2 BrCOOC_2H_5 + HBr$ (2) Physical properties

(xi) *Reaction with HI*

$$
CH_3COOC_2H_5 + HI \rightarrow CH_3COOH + C_2H_5OH
$$

Aceticacid Ethylalcohol

(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.

$$
CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH
$$
 (ii) Action with ammonia

Acid Anhydride
$$
\begin{array}{ccc}\nCH_3CO & O & \text{or} & (CH_3CO)_2O \\
CH_3CO & & & \\
\end{array}
$$
 (iii) Acetyl

(1) **Method of preparation**

(i) *From carboxylic acid*

OMgBr
\n $\begin{bmatrix}\n 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 &$

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

$$
CH_3COONa + CH_3COCl \xrightarrow{Py} CH_3COOCOCCH_3 + NaCl
$$

\n $C_6H_5COONa + C_6H_5COCl \xrightarrow{Py} C_6H_5COOCOC_6H_5$
\n Be
\n

NaCl

(iii) *From acetylene*

$$
CH_{2}COOC_{2}H_{5}+C_{2}H_{5}OH \n\begin{array}{ccc}\nCH & CH & CH_{3}COOH \xrightarrow{HgSO_{4}}\\
CH + 2CH_{3}COOH \xrightarrow{HgSO_{4}}\\
CH & CH & CH & CH \cdot\\
CH & CH_{3}CO \searrow^{HgCO} \searrow^{HgCO} \\
CH_{3}CHO + \n\begin{array}{ccc}\nCH_{3}CO & O & \n\end{array} \\
CH & CH & CH & \n\begin{array}{ccc}\nCH & \n\end{array} \\
CH & CH & \n\end{array} \\
CH & CH & \n\begin{array}{ccc}\nCH & \n\end{array} \\
CH & CH & \n\begin{array}{ccc}\nCH & \n\end{array} \\
CH & CH & \n\end{array} \\
CH & CH & \n\begin{array}{ccc}\nCH & \n\end{array} \\
CH & CH & \n\begin{array} \\
CH & \n\end{array} \\
CH & CH & \n\begin{array} \\
CH & \n\end{array} \\
CH & CH & \n\begin{array} \\
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CH & CH & \n\begin{array} \\
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CH & CH & \n\begin{array} \\
CH & \n\end{array} \\
CH & CH & \n\begin{array} \\
CH & \n\end{array} \\
CH & CH & \n\begin{array} \\
CH & \n\end{array} \\
CH & CH
$$

(iv) *From acetaldehyde* :

ix) **Reaction with hydrazine**
\n
$$
CH_3COOC_2H_5 + H_2NNH_2 \rightarrow CH_3CONHNH_2 + C_2H_5OH
$$

\n $CH_3COOC_2H_5 + H_2NNH_2 \rightarrow CH_3CONHNH_2 + C_2H_5OH$
\n $CH_3COOC_2H_5 + H_2NNH_2 \rightarrow CH_3CONHNH_2 + C_2H_5OH$
\n $CO_3CO_2H_5 + H_2NNH_2 \rightarrow CH_3CONHNH_2 + C_2H_5OH$

 \rightarrow (*CH*₃*CO*₂*O* + *H*₂*O*

(2) **Physical properties**

 $CH_3COOC_2H_5 + HI \rightarrow CH_3COOH + C_2H_5OH$ liquids with sharp irritating smell. The higher members of the family aceticacid *Ethyl alcohol* say well as the aromatic acid anhydrides are solids in nature (i) *Physical state* **:** Lower aliphatic anhydrides are colourless 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* **:**

$$
\begin{array}{c}\nO & O \\
\parallel \\
CH_3-C-O-C-CH_3+H_2O \rightarrow 2CH_3COOH \\
\hline\n\text{Aceticantlydride} & \text{Aceticacid}\n\end{array}
$$

$$
(CH_3CO_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4
$$

Acctamide
Amm. acetate

Acid Anhydride CH_3CO *O or* $(CH_3CO)_2O$ (iii) *Acetylation* : Acetic anhydride react with compound having active hydrogen.

$$
(CH_3CO_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH
$$

Ethylalcohol Ethylacetate

$$
(CH_3CO)_2O + H_2NC_2H_5 \rightarrow CH_3CONHC_2H_5 + CH_3COOH
$$

Etiv/amine\n
$$
O = C \left(\begin{array}{cc} OH & OH & NH_2 \\ \hline \end{array} \right)
$$

CH CO O HN C H CH CON C H CH COOH $(\mathcal{CH}_3CO)_2$ $O+$ $\mathcal{HN}(C_2H_5)_2 \rightarrow \mathcal{CH}_3$ $\mathcal{COM}(C_2H_5)_2 + \mathcal{CH}_3$ \mathcal{COOH} $\hspace{1.6cm} \text{Carbonicacid}$ $\hspace{1.6cm} \text{Caton}$

$$
(CH_3CO_2O + H_2NC_6H_5 \rightarrow CH_3CONHC_6H_5 + CH_3COOH
$$

Acctanilide\n
$$
\Box
$$
 First time isolated from urine in 1773 by Roulle and hence

$$
(CH_3CO_2O + \bigodot CH_3 CO/H \rightarrow \bigodot COCH_3 + CH_3COOH
$$

Salicylic acid Acetyl salicylic acid (Aspiriin)

(iv) *Action of dry HCl*

 $(CH_3CO_2O + HCl \rightarrow CH_3COCl + CH_3COOH$

(v) *Reaction with chlorine*

 $(CH_3CO)_2 O + Cl_2 \rightarrow CH_3 COCl + CH_2 CICOOH$
Acetylchloride Monochloroacetic (1) Method of preparation

(vi) *Reaction with PCl***⁵**

$$
(CH3CO2O+PCI5 \rightarrow 2CH3COCl+POCl3
$$

(vii) *Friedel craft's reaction*

$$
(CH_3CO_2O + C_6H_6 \xrightarrow{A/C_3} C_6H_5COCH_3 + CH_3COOH
$$
\n
$$
(ii) \t\t Laboratory preparation\nBerzene\n\n
$$
(iii) \t\t Laboratory preparation
$$
$$

(viii) *Reaction with acetaldehyde*

$$
(CH3CO2O + CH3CHO \rightarrow CH3CH(OOCCH3)2
$$

Acetaldehyde Ethylideneacetate

(ix) *Reduction*

$$
(CH_3CO)_2 O \xrightarrow{\text{LiAlH}_4} CH_3CH_2OH
$$

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

$$
CH_3CO\overline{OCOCH_3 + C_2H_5} - O - C_2H_5 \rightarrow 2CH_3COOC_2H_5
$$

Exchylether
Exchylacteric

 (x_i) *Action with* N_2O_5

$$
CH_3COOCOCH_3 + N_2O_5 \rightarrow CH_3 - C - O - N \bigotimes^O O
$$
\n
$$
O = C \bigotimes_{O \bigcup_{i=1}^{O C_2 H_5} + 2NH_3 \rightarrow O \bigotimes^O O
$$
\n
$$
C + \bigotimes_{O \bigcup_{i=1}^{O C_2 H_5} + 2NH_3 \rightarrow O \bigotimes^O O
$$

(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

\n
$$
O = \mathsf{C} \times \frac{\mathsf{NH}_2}{\mathsf{NH}_2} \quad \text{C}
$$

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.

the name urea was given.

 $COOH$ ³ + CH_3COOH \Box It was the first organic component laboratory from inorganic material (by heating a mixture of ammonium sulphate and potassium cyanate) by Wohler in 1828.

 \Box This preparation gave a death blow to Vital force theory.

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

 \Box 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 $CQ(NH_2)_2$. HNO₃ are obtained.

$$
2CQ(NH_2)_2.HNO_3+BaCO_3\rightarrow 2CQ(NH_2)_2+BaNO_3)_2+H_2O+CO_2
$$

\nUrea nitrate
\nUrea

(a)Wohler synthesis

 (ii)

$$
2KCNO + (NH_4)_2SO_4 \rightarrow 2NH_4CNO + K_2SO_4
$$

Potassiumeyanate Ammonium sulphate Ammonium cyanate

$$
NH_4CNO \xrightarrow{\text{Isomericchange}} NH_2CONH_2
$$

Ammonium cyanate On heating
^{On heating}

Urea

 $(CH_3CO_2O \frac{L|A|H_4}{F_1} \rightarrow CH_3CH_2OH$ evaporated when the crystals of urea are obtained. It can be \Box The solid residue is extracted with alcohol and the extract recrystalised from water.

(b) From phosgene or alkyl carbonate

$$
O = C \begin{cases} C_1 + 2NH_3 \rightarrow O = C \begin{cases} NH_2 + 2HCl \\ NH_2 \end{cases} \\ \begin{cases} NH_2 \end{cases} \end{cases}
$$
Carbonyl chloride
(Phosgene)

$$
C = C - N \left\{\n\begin{array}{c}\nO \\
O \\
O\n\end{array}\n\right.
$$
\n
$$
C = C \left\{\n\begin{array}{c}\nO C_2 H_5 \\
O C_2 H_5\n\end{array}\n+ 2NH_3 \rightarrow O = C \left\{\n\begin{array}{c}\nNH_2 \\
NH_2\n\end{array}\n+ 2C_2 H_5 OH\n\end{array}\n\right.
$$
\n
$$
C = O - N \left\{\n\begin{array}{c}\nO H_2 \\
O H_2\n\end{array}\n\right.
$$
\n
$$
C = O - N \left\{\n\begin{array}{c}\nO C_2 H_5 \\
O H_2\n\end{array}\n\right.
$$

(iii) *Industrial method*

(a) By partial hydrolysis of calcium cyanide

$$
\begin{array}{ccc}\n\text{CaC}_2 + N_2 & \xrightarrow{\text{heat}} & \text{CaC}\text{N}_2 + C \\
\text{Calcium} & \text{Calcium} \\
\text{Carbide} & \text{cyanamide}\n\end{array}
$$

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

$$
O = \bigotimes_{N=2}^{N=12} \bigotimes_{O \text{H}_2} \text{CacN}_2 \xrightarrow{-CaSO_4} H_2NCN \xrightarrow{-CaSO_4} \bigotimes_{O \text{yanamide}} H_2O_2 \bigotimes_{(U \text{rea})} H_2NCONH_2
$$

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

(b) From carbon dioxide and ammonia

$$
CO_{2} + 2NH_{3} \xrightarrow{\qquad 150-200^{\circ}C} NH_{2}COONH_{4} \xrightarrow{\qquad \qquad NH_{2}COONH_{2}-
$$
\n
$$
\xrightarrow{\text{heat}(140^{\circ}C)} NH_{2}CONH_{2}
$$
\n
$$
\xrightarrow{-H_{2}O} NH_{2}CONH_{2}
$$
\n
$$
\xrightarrow{\qquad \qquad \text{break}(140^{\circ}C)} NH_{2}CONH_{2}
$$
\n
$$
\xrightarrow{\qquad \qquad \text{break}(140^{\circ}C)} NH_{2}CONH_{2}
$$

(2) **Physical properties** : Urea is a colourless, odourless crystalline solid. It melts at $132^{\circ}C$. 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 $(K_b = 1.5 \times 10^{-14})$. It forms solt with strong acid.

$$
NH_2CONH_2 + HNO_3 \text{(conc)} \rightarrow NH_2CONH_2. HNO_3
$$
\n
$$
2NH_2CONH_2 + H_2C_2O_4 \rightarrow (NH_2CONH_2)_2H_2C_2O_4
$$
\n
$$
2NH_2CONH_2 + H_2C_2O_4 \rightarrow (NH_2CONH_2)_2H_2C_2O_4
$$
\n
$$
NAOH + Br_2 \rightarrow NaOBr + HBr
$$
\n
$$
NH_2CONH_2 + 3NaBrO \rightarrow N_2 + 2H_2O_4
$$
\n
$$
NHO_2
$$

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.

$$
H_2N \longrightarrow H_2 \longrightarrow H_2 \longrightarrow H_2N \longrightarrow H_2N \longrightarrow H_2N \longrightarrow H_2CONH_2 + (CH_3CO)_2O \rightarrow NH_2COMHCOCH_3
$$
\n
$$
H_2H_2 \longrightarrow H_2M \longrightarrow H_2CONH_2 + CH_3CO)_2O \rightarrow NH_2COMHCOCH_3 + CH_3COOH + CH_3
$$

An aqueous solution of urea is neutral.

(ii) *Hydrolysis*

$$
O = C \times \frac{|\overline{N}H_2 + H_1}{\overline{N}H_2 + H_1} \times \overline{H_1} \times \overline{H_2} + \overline{H_1} \times \overline{H_2} \times \overline{H_1} \times \overline{H_1} \times \overline{H_1} \times \overline{H_2} \times \overline{H_1} \times \over
$$

 NH_2 *CONH*₂ + 2*NaOH* \rightarrow 2*NH*₃ + *Na*₂*CO*₃

An enzyme, urease, present in soyabean and soil also brings hydrolysis .

$$
NH2CONH2 + 2H2O \rightarrow (NH4)2 CO3 \rightarrow 2NH3 + CO2 + H2O
$$

\n
$$
NH2CONH2 + SOCl2 \rightarrow H2N-C \equiv N + S
$$

(iii) *Action of heat*

$$
\mathit{NH}_2CO[\overline{NH}_2 + \overline{H}] \text{ HNCONH}_2 \xrightarrow{\text{heat}} \mathit{NH}_2CONHCOMH_2 + \mathit{NH}_3 \longrightarrow \text{NH}_2CONH_2 + \underbrace{\mathit{NH}_2SO_4 + SO_3 \rightarrow 2NH_2}_{\text{Biluret}}
$$

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° C, polymerisation takes place:

$$
NH2CONH2 + 3 NaBrO \rightarrow N2 + 2H2O + CO2 + 3 NaBr
$$

(vi) *Reaction with acetyl chloride or acetic anhydrides* NH_2 CONH $_2$ + CH_3 COCl \rightarrow NH $_2$ CONHCOCH $_3$ + HCl Acetyl chloride Acetyl urea (Ureide)

2 and \overline{z} and \overline{z} Acetyl urea

Aceticacid *CH* ³*COOH*

(vii) *Reaction with hydrazine*

$$
\begin{array}{ccc}\nNH_2CONH_2 + H_2N.NH_2 \xrightarrow{100^{\circ}C} NH_2CONH.NH_2 + NH_3 \\
^{Urea} &^\text{Hydrazine}\n\end{array}
$$

OH (viii) *Reaction with ethanol*

$$
H_2 NCQ\overline{NH_2} + H_1OC_2H_5 \xrightarrow{\text{heat}} H_2 NCQ\overline{NH_2} + H_1OC_2H_5 \xrightarrow{\text{heat}} H_2 NCOOC_2H_5 + NH_3
$$
\n
$$
Urethane
$$

(ix) *Reaction with chlorine water*

$$
O = C \left\langle \begin{array}{ccc} NH_2 & NHCl \\ + 2Cl_2 \rightarrow O = C \left\langle \begin{array}{ccc} & + 2HCl \\ \end{array} \right\rangle \right\langle HCl \\ \text{Urea} & \text{Dichlorourea} \end{array} \right.
$$

(x) *Dehydration*

$$
NH2CONH2 + SOCl2 \rightarrow H2N - C \equiv N + SO2 + 2HCl + H2O
$$

(xi) *Reaction with fuming sulphuric acid*

$$
NH_2CONH_2 + \underbrace{H_2SQ_4 + SQ_3}_{\text{Oleum}} \rightarrow 2NH_2SQ_3H + CQ_2
$$

(xii) *Formation of cyclic ureides* Oleum

$$
\left\langle \begin{array}{ccc}\n\frac{1}{\sqrt{11}} & \frac{1}{\sqrt{11}} & \frac{1
$$

2 5 2 5 Urea *PCl ^C ^H ^O CO NH H NH H O C*

(xiii) *Reaction with formaldehyde*

 $CH_2 = O + NH_2CONH_2 \xrightarrow{HCl} CH_2(OH)NHCOMH_2 \xrightarrow{CH_2=O}$ Monomethylol urea Formaldehyde Dimethylol urea (Urea-Formaldehyde) $CH_2(OH)$ *NHCONH*(*OH*)*CH*₂ \xrightarrow{heat} Resin Waal's forces

(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.,* HNO₂) to urea solution, nitrogen gas is evolved and gives effervescence due to carbon dioxide.

 $\mathcal{O} = \mathcal{O}$ + $CH_2 \xrightarrow{CH_2}$ with alkaline $K_2Cr_2O_7$ since under these condition $K_2Cr_2O_4$ is $V + C_2H_5O_6$
Urea *CH*₂ **CH**₂ NHH C_2H_5O *C NHH* $C_2H_5O^C$ **EX** Oxidation of 1° alcohols and aldehyde cannot be carried out

O During oxidation of alkyl benzenes with alkaline *KMnO*⁴ or *O*chain oxidised to –*COOH* group irrespective of its length. The ease $NH - C$ of oxidation of alkyl benzenes follows the order. acidified $K_2Cr_2O_7$, the aromatic nucleus remain intact but each side

O benzoic acid since it does not have any benzylic *H*-atom. $NH - C$ Tert butyl benzene however does not undergo oxidation to give

> Carboxylic acids are stronger acids than phenols since carboxylate ion is better stabilized by resonance than phenoxide ion.

 $= C \left\{ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \end{array} \right. \end{array} \right.$ alternation effect, *i.e.* melting point of an acid containing even C_2H_5O *CO* 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.

> $O = C \left(\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array} \right)$ + 2C₂ H₅ OH **E** Carboxylic acid do not give the characteristic reaction of the $NH - C = O$ carbonyl group. The reason being that $-c = 0$ 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 chloride and ester are lower than those of their parent acid due to absence of *H*-bonding in their molecule.

 $(OH)NH(ONH)CH_2 \longrightarrow$ Resin
Waal's forces of attraction owing to the larger size of their The boiling points of acid anhydrides are higher than those of the acids from which they are derived because of stronger Vander molecules.

> $\mathbb Z$ 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.

> \mathcal{L} 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.

 $\mathscr{\mathscr{L}}$ 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.

 \mathcal{L} 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.