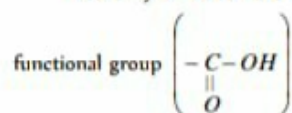


# Carboxylic acids and Their derivatives

## Carboxylic Acids

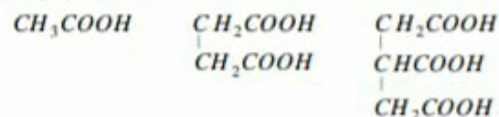
Carboxylic acids are the compounds containing the carboxyl



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

### Classification

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



Monocarboxylic acid      Dicarboxylic acid      Tricarboxylic acid

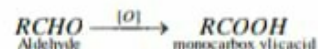
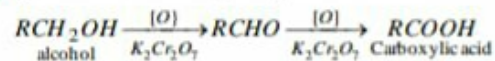
(2) Monocarboxylic acids of aliphatic series are commonly known as fatty acids such as palmitic acid ( $C_{15}H_{31}COOH$ ) and stearic acid ( $C_{17}H_{35}COOH$ ).

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

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

### Methods of preparation of monocarboxylic acid

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

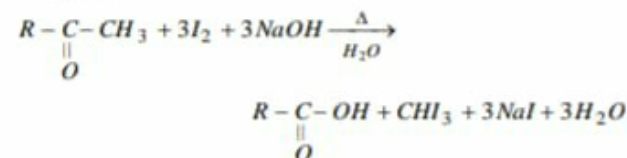


Aldehyde can be oxidized to carboxylic acid with mild oxidising agents such as ammoniacal silver nitrate solution [ $Ag_2O$  or  $Ag(NH_3)_2^+OH^-$ ]

Methanoic acid can not be prepared by oxidation method.

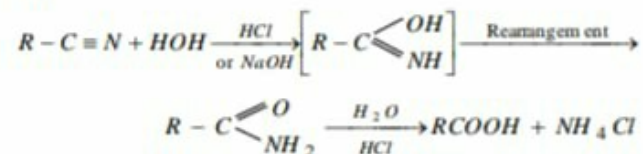
Ketones can be oxidized under drastic conditions using strong oxidising agent like  $K_2Cr_2O_7$ .

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

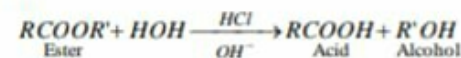


(2) **By Hydrolysis of nitriles, ester, anhydrides and acid chloride**

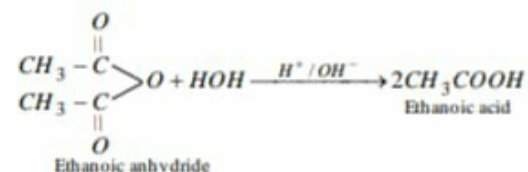
(i) **Hydrolysis of nitriles**



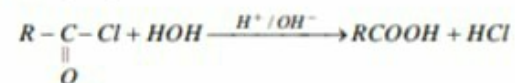
(ii) **Hydrolysis of Esters**

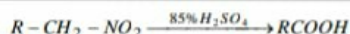


(iii) **Hydrolysis of Anhydrides**

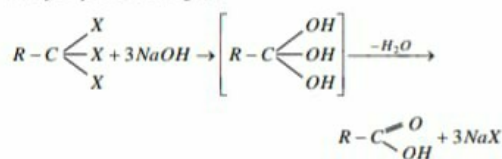


(iv) **Hydrolysis of acid chloride and nitro alkane**

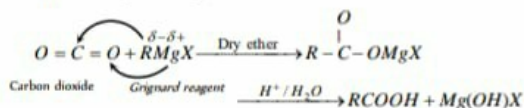




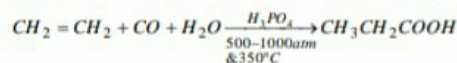
(v) **Hydrolysis of Trihalogen :**



(3) **From Grignard Reagent**



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

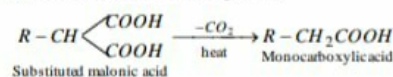


(5) **Special methods**

(i) **Carboxylation of sodium alkoxide**



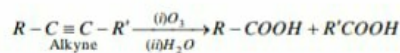
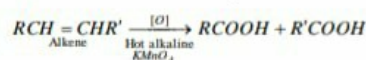
(ii) **Action of heat on dicarboxylic acid**



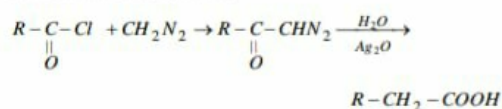
(iii) **From acetoacetic ester**



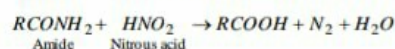
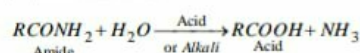
(iv) **Oxidation of alkene and alkyne**



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



(vi) **From acid amides**



## Physical properties of monocarboxylic acids

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

(2) **Solubility :** The lower members of the aliphatic carboxylic acid family (upto C) are highly soluble in water. The solubility decreases with

the increase in the size of the alkyl group. All carboxylic acids are soluble in alcohol, ether and benzene etc.

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

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

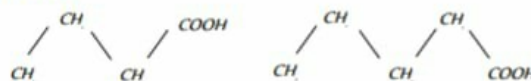
(3) **Melting point**

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

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

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

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

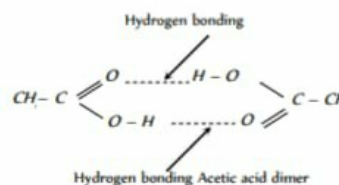


the two terminal groups lie on the opposite sides of the chain

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

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

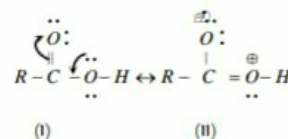
(4) **Boiling point :** Boiling point of carboxylic acids increase regularly with increase of molecular mass. Boiling points of carboxylic acids are higher than those of alcohols of same molecular mass. This is due to intermolecular hydrogen bonding between two acid molecules.



## Acidic nature of monocarboxylic acids

(i) **Cause of acidic nature**

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



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









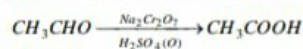
- (iv) In leather tanning.
- (v) As coagulating agent for rubber latex.
- (vi) As an antiseptic and in the treatment of gout.
- (vii) In the manufacture of plastics, water proofing compounds.
- (viii) In electroplating to give proper deposit of metals.
- (ix) In the preparation of nickel formate which is used as a catalyst in the hydrogenation of oils.
- (x) As a reducing agent.
- (xi) In the manufacture of oxalic acid.

#### Acetic Acid (Ethanoic Acid) ( $CH_3COOH$ )

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

##### (i) Preparation

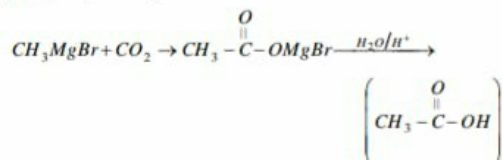
##### (i) By oxidation of acetaldehyde (Laboratory-preparation)



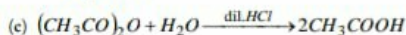
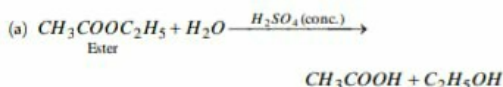
##### (ii) By hydrolysis of methyl cyanide with acid



##### (iii) By Grignard reagent

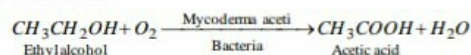


(iv) By hydrolysis of acetyl chloride, acetic anhydride or acetamide and ester



##### (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**.



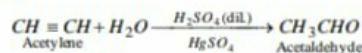
It is a slow process and takes about 8 to 10 days for completion. In this process, the following precautions are necessary:

- The concentration of the ethyl alcohol should not be more than 15%, otherwise the bacteria becomes inactive.
- The supply of air should be regulated. With less air the oxidation takes place only upto acetaldehyde stage while with excess of air, the acid is oxidised to  $CO$  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.

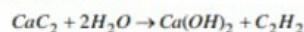
(b) From acetylene : Acetylene is first converted into acetaldehyde by passing through 40% sulphuric acid at 60°C in presence of 1%  $HgSO_4$  (catalyst).



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

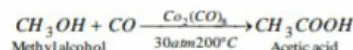


□ Acetylene required for this purpose is obtained by action of water on calcium carbide.



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

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



##### (2) Physical properties

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

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

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

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

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

(3) Uses : It is used,

- (i) As a solvent and a laboratory reagent.
- (ii) As vinegar for table purpose and for manufacturing pickles.
- (iii) In coagulation of rubber latex.
- (iv) For making various organic compounds such as acetone, acetic anhydride, acetyl chloride, acetamide and esters.
- (v) For making various useful metallic acetates, such as:
  - (a) Basic copper acetate which is used for making green paints.
  - (b)  $Al$ ,  $Fe$  and  $Cr$  acetates which are used as mordants in dyeing.
  - (c) Lead tetra-acetate which is a good oxidising agent.
  - (d) Basic lead acetate which is used in the manufacture of white lead.
  - (e) Aluminium acetate which is used in the manufacture of water-proof fabrics.
  - (f) Alkali acetates which are used as diuretics.

Table : 28.1 Comparison of Formic Acid and Acetic Acid

Property	Formic acid	Acetic acid
1. Acidic nature,		

(i) With electro-positive metals	Forms salts. Hydrogen is evolved. $HCOOH + Na \rightarrow HCOONa + \frac{1}{2}H_2$	Forms salts. Hydrogen is evolved. $CH_3COOH + Na \rightarrow CH_3COONa + \frac{1}{2}H_2$
(ii) With bases	Forms salts. $HCOOH + NaOH \rightarrow HCOONa + H_2O$	Forms salts. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
(iii) With carbonates and bicarbonates	Forms salts. Carbon dioxide is evolved. $HCOOH + NaHCO_3 \rightarrow HCOONa + H_2O + CO_2$	Forms salts. Carbon dioxide is evolved. $CH_3COOH + NaHCO_3 \rightarrow$ $CH_3COONa + H_2O + CO_2$
2. Ester formation	Forms esters when treated with alcohols. $HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 + H_2O$	Forms esters when treated with alcohols. $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4(conc.)}$ $CH_3COOC_2H_5 + H_2O$
3. Reaction with $PCl_5$	Forms formyl chloride which decomposes into $CO$ and $HCl$ . $HCOOH + PCl_5 \rightarrow HCOCl(HCl + CO) + POCl_3 + HCl$	Forms acetyl chloride which is a stable compound. $CH_3COOH + PCl_5 \rightarrow$ $CH_3COCl + POCl_3 + HCl$
4. Heating of ammonium salt	Forms formamide. $HCOONH_4 \rightarrow HCONH_2 + H_2O$	Forms acetamide. $CH_3COONH_4 \rightarrow CH_3CONH_2 + H_2O$
5. Heating alone	It decomposes into $CO$ and $H_2$ . $HCOOH \rightarrow CO_2 + H_2$	Unaffected
6. Heating with conc. $H_2SO_4$	Decomposed into $CO$ and $H_2O$ . $HCOOH \xrightarrow[H_2SO_4]{Conc.} CO + H_2O$	Unaffected
7. Reaction with $Cl_2$ in presence of red $P$	Unaffected	Forms mono, di or trichloro acetic acids.
8. Action of heat on salts, (i) Calcium salt	Forms formaldehyde. $(HCOO)_2Ca \rightarrow HCHO + CaCO_3$	Forms acetone. $(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$
(ii) Sodium salt	Forms sodium oxalate. $2HCOONa \xrightarrow{heat} \begin{matrix} COONa \\ COONa \end{matrix} + H_2$	Unaffected.
(iii) Sodium salt with soda-lime	Forms sodium carbonate and $H_2$ . $HCOONa + NaOH \xrightarrow{CaO} Na_2CO_3 + H_2$	Forms sodium carbonate and methane. $CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
9. Electrolysis of sodium or potassium salt	It evolves hydrogen.	It forms ethane.
10. On heating with $PO_5$	Unaffected	Forms acetic anhydride. $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
11. Reducing nature, (i) Tollen's reagent	Gives silver mirror or black precipitate. $HCOOH + Ag_2O \rightarrow 2Ag + CO_2 + H_2O$	Unaffected.
(ii) Fehling's solution	Gives red precipitate $HCOOH + 2CuO \rightarrow Cu_2O + CO_2 + H_2O$	Unaffected.
(iii) Mercuric chloride	Forms a white ppt. which changes to greyish black. $HgCl_2 \rightarrow Hg_2Cl_2 \rightarrow 2Hg$	Unaffected.
(iv) Acidified $KMnO_4$	Decolourises	Unaffected.
12. Acid (neutral solution) + $NaHSO_4$ + Sodium nitroprusside.	Greenish blue colour.	Unaffected.