4.	With 2,4-dinitro phenyl hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones
5.	With sodium hydroxide	Give brown resinous mass (formaldehyde does not give this test)	No reaction
6.	With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (formaldehyde does not respond to this test)	Red colour which changes to orange

Uses

- Formeldehyde is freely soluble in water. Its 40% solution in water is sold in market under the name **formalin**. Formaldehyde in the form of formalin (40% formaldehyde, 8% methanol and 52% water) is used for preserving biological specimens.
- It is also used in the manufacture of synthetic polymers like bakelite and synthetic dye stuffs like indigo.
- Acetaldehyde is used in the commercial preparation of a number of organic compounds such as acetic acid, ethyl acetate, *n*-butyl alcohol, etc.
- Paraldehyde is used in medicines as a hypnotic.
- Benzaldehyde is an important flavouring agent in perfume industry.
- It is used in manufacture of dyes like malachite green.
- Acetone is very important solvent and is extensively used as a solvent in industries and laboratories.
- It is used in the manufacture of thermosoftening plastic **(Perspex)**.
- It is used as one of the constitutents of liquid nail polish.

CARBOXYLIC ACIDS

- Carboxylic acids are organic compounds which have one or more carboxyl functional group ($-\overset{O}{\overset{||}{C}}-OH$) in their molecules.

$$-\underset{\underset{O}{||}}{C}- + -O-H \equiv -\overset{O}{\overset{||}{C}}-OH$$

Carbonyl   Hydroxyl   Carboxyl

Nomenclature

- The common or trivial names of carboxylic acids are based on their sources of origin. For example, formic acid (HCOOH) is so named because it was first obtained from red ants.

  In common system, the position of the substituents is indicated by the Greek letters (α, β, γ, δ, etc).

  The carbon atom adjacent to the carboxyl carbon is assigned the letter α, the next carbon on chain as β and so on. For example,

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-COOH$$

While writing IUPAC name of carboxylic acid '*e*' of alkane is replaced by '*oic acid*'. The carboxyl carbon is always given number 1 *i.e.*, it is always at terminal position.

$$R-\overset{O}{\overset{||}{C}}-OH \longrightarrow \text{Alkanoic acid}$$

- The position of the substituents is indicated by the following rules :
  - ➢ The longest chain containing the carboxylic group (–COOH) is selected.
  - ➢ The carbon chain is numbered from the carboxylic acid group. The carbon of carboxyl group is always given number 1.
  - ➢ The position of the substituents is indicated by the number. For example,

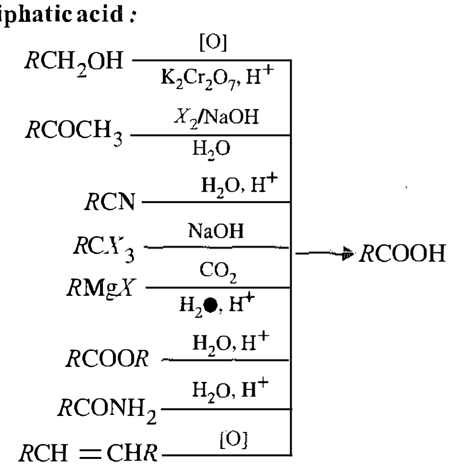
$$\overset{4}{C}H_3\overset{3}{C}H_2\underset{\underset{Br}{|}}{\overset{2}{C}}H\overset{1}{C}OOH \qquad C_6H_5\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$$

2-Bromobutanoic acid   3-Phenylpropanoic acid

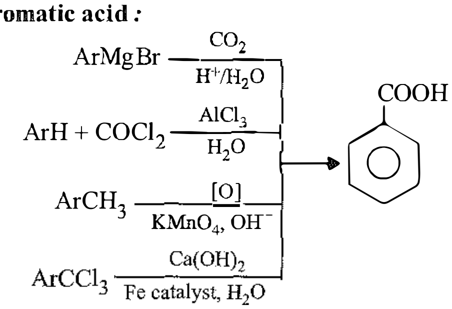
Monocarboxylic acid	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-COOH$	*Iso*-valeric acid	3-Methylbutanoic acid

Methods of Preparation

- **Aliphatic acid :**

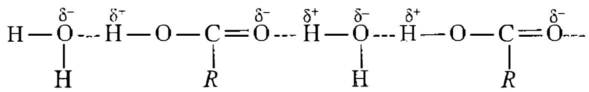


- **Aromatic acid :**



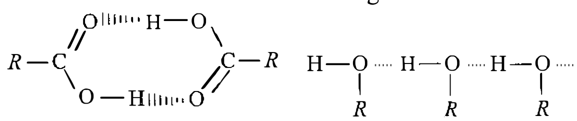
Physical Properties

- First three members are colourless, pungent smelling liquids. Next member butyric acid has odour of rancid butter, whereas next five members (C5 to C9) have goat like odour. But higher members (above C10) are colourless and odourless waxy solid due to low volatility Aromatic acids are colourless, odourless solids.
- Lower members are highly soluble in water because of H-bonding. This solubility decreases with increase in molecular mass. All are soluble in alcohol or ether.



Benzoic acid is sparingly soluble in cold water but is soluble in hot water, alcohol, ether.

- Carboxylic acids have higher boiling points and also they exist as dimer because of H-bonding.



Carboxylic acids have higher boiling points than the corresponding alcohols having same molecular mass.

Melting point of carboxylic acids do not show a regular pattern.

Fit closely and has higher melting points — Fit poorly and has lower melting points

Chemical Properties

- **Aliphatic acid :**

$R-\overset{O}{\overset{||}{C}}-OH$ —
- $\xrightarrow{Na/K/Ca/Zn} R-COONa + \frac{1}{2}H_2$
- $\xrightarrow{NaOH} RCOONa + H_2O$
- $\xrightarrow{NH_3} RCOO^-\overset{+}{N}H_4 \xrightarrow{Heat} RCONH_2 + H_2O$
- $\xrightarrow[SOCl_2/Pyridine]{PCl_5/PCl_3} RCOCl$
- $\xrightarrow{R'OH/conc.H_2SO_4} RCOOR'$ (Esterification reaction)
- $\xrightarrow[(ether)]{CH_2N_2} RCOOCH_3 + N_2$
- $\xrightarrow{\Delta/P_2O_5} (RCO)_2O + H_2O$ (Acid anhydride)
- $\xrightarrow[Ether]{R'CH_2MgBr} R'CH_3 + RCOOMgBr$
- $\xrightarrow[(dry)]{NaOH, CaO} R-H + Na_2CO_3$ (Decarboxylation)
- $\xrightarrow{LiAlH_4} RCH_2OH$ (Alcohol)
- $\xrightarrow[Electrolysis]{NaOH} R-R + 2CO_2 + 2e^-$ (Kolbe Electrolytic reaction)
- $\xrightarrow[(iii)\ Br_2\ in\ CCl_4]{(i)\ NH_3\ (ii)\ AgNO_3} R-Br + AgBr + CO_2$ (Hunsdiecker reaction)
- $\xrightarrow{red\ P/HI} R-CH_3$
- $\xrightarrow{HNO_3/conc.H_2SO_4} RNH_2 + CO_2 + N_2$ (Schmidt reaction)

- **Hell—Volhard Zelinsky reaction :**

$$RCH_2COOH + Cl_2 \xrightarrow[\Delta]{red\ P} RCHClCOOH \xrightarrow[red\ P,\ \Delta]{Cl_2} RCCl_2COOH$$

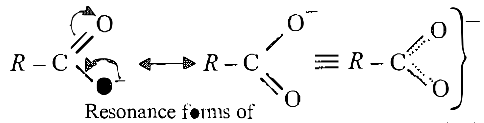
Acidity of Carboxylic Group

- The acidic character of carboxylic acids is due to release of H^+ ion in aqueous solution.

$RCOOH \rightleftharpoons RCOO^- + H^+$

This is explained with the help of resonance.

The resonating structures are as follows :

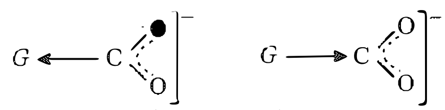


Resonance forms of carboxylate ion — Resonance hybrid

Due to electronegativity of oxygen atom, it attracts the electrons of the O – H bond towards itself. This helps in release of hydrogen as proton.

Thus, the acidity of carboxylic acid is due to powerful resonance stabilization of the anion.

- **Effect of substituents on acidity :** An electron withdrawing substituent having $-I$ effect stabilizes the anion by dispersing the negative charge and therefore, increases the acidity. On the other hand, electron releasing substituents having $+I$ effect intensify the negative charge on the anion resulting in the decrease of stability and thus decrease the acidity of the acid.



G-electron withdrawing group, acidity increases. — *G*-electron donating group, acidity decreases.

Hence the following sequence is observed :

$HCOOH > CH_3COOH > C_2H_5COOH$ and

$\begin{array}{c}COOH\\|\\COOH\end{array} > CH_2\begin{array}{l}COOH\\COOH\end{array} > \begin{array}{c}CH_2COOH\\|\\CH_2COOH\end{array}$

Uses

- Methanoic acid is used
  - In leather tanning.
  - As coagulating agent for rubber latex in rubber industry.
  - In textile dyeing and finishing.
  - In the manufacture of rayon and in plastic, rubber and silk industries.
  - As vinegar in cooking and in food industry.
- **Benzoic acid**
  - Sodium salts of benzoic acid is used as a food preservative.
  - Its esters are used in perfumery.