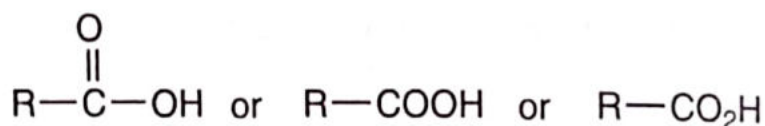


Organic compounds which contain the carboxyl functional group ( $-\text{COOH}$ ) are called the **Carboxylic Acids**. Their general formula is :



where R is an alkyl group.

The name *carboxyl* is derived from CARBonyl ( $\text{C}=\text{O}$ ) and hydroXYL ( $-\text{OH}$ ) because in the carboxyl group these two groups are directly bonded to each other. The properties of the carboxyl group are not simply those of carbonyl and hydroxyl groups combined; the two groups interact to give carboxylic acids their own distinctive properties.

Carboxylic acids are further classified as monocarboxylic acids, dicarboxylic acids, tricarboxylic acids etc., according as the number of  $-\text{COOH}$  groups present in the molecule is 1, 2, 3 or more. The long-chain monocarboxylic acids are commonly called **Fatty Acids** because many of them are obtained by the hydrolysis of animal fats or vegetable oils.

## MONOCARBOXYLIC ACIDS

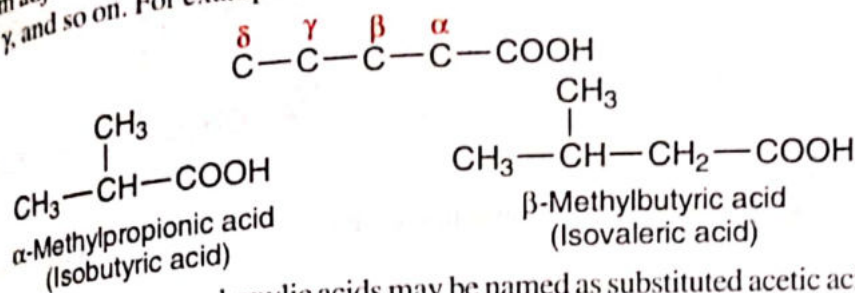
### NOMENCLATURE

There are three ways of naming carboxylic acids :

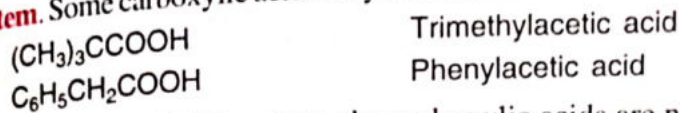
(1) **Common System.** The simple carboxylic acids are better known by their common names. The common names are usually derived from the Latin or Greek word that indicates the original source of the acid. They do not follow any rule except that all common names of acids end in *-ic acid*. For example,

HCOOH	Formic acid
CH <sub>3</sub> COOH	Acetic acid
CH <sub>3</sub> CH <sub>2</sub> COOH	Propionic acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Butyric acid
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	Valeric acid

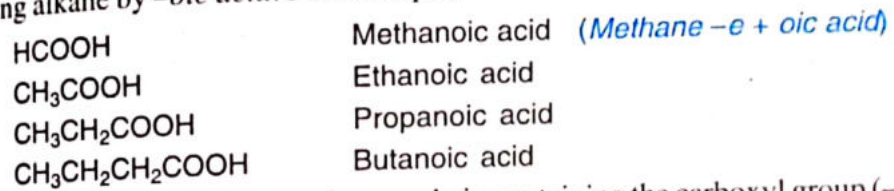
In the common system, Greek letters ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc.) are used to indicate the position of substituents. The carbon atom adjacent to the carboxyl carbon is assigned the letter  $\alpha$ , the next carbon on the chain is the next one  $\gamma$ , and so on. For example,



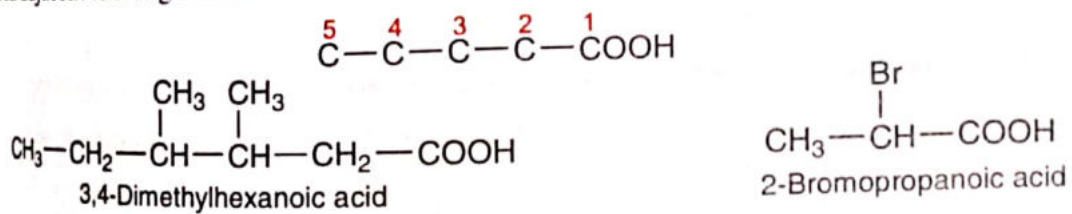
(2) **Derived System.** Some carboxylic acids may be named as substituted acetic acids. For example,



(3) **IUPAC System.** In the IUPAC system, the carboxylic acids are named as **Alkanoic acids** (alkane - e + oic acid). The systematic name of the individual acid is obtained by replacing the ending of the corresponding alkane by *-oic acid*. For example,



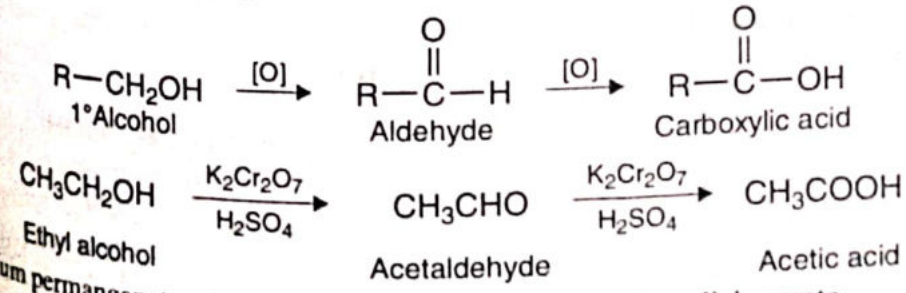
For naming higher members, the longest continuous chain containing the carboxyl group (-COOH) is selected. The number of carbon atoms in this chain gives the name of the parent alkane. The position of substituents is indicated by numbers. The carboxyl carbon is always given number 1, the carbon adjacent to it is given the number 2, and so on. For example,



**METHODS OF PREPARATION**

Carboxylic acids are prepared by the following methods :

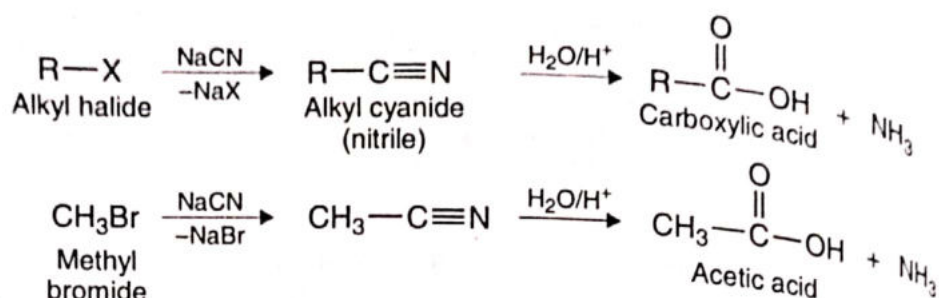
(1) **Oxidation of Primary Alcohols or Aldehydes.** Primary alcohols or aldehydes undergo oxidation with a mixture of potassium dichromate and sulfuric acid to form carboxylic acids. The alcohol is first oxidized to an aldehyde, and then to a carboxylic acid.



Potassium permanganate can also be used in place of potassium dichromate.

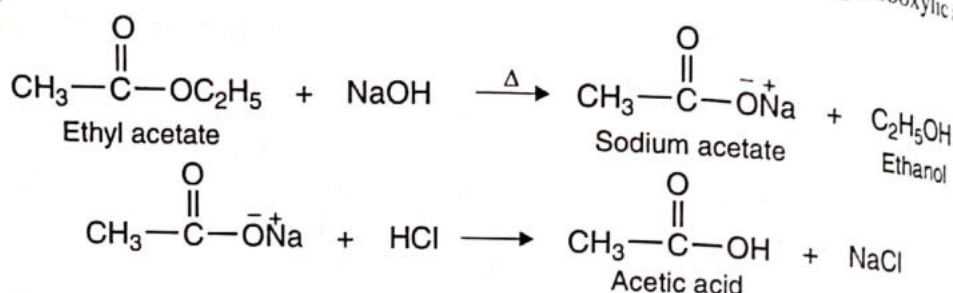
(2) **Hydrolysis of Nitriles (Alkyl Cyanides).** Nitriles or alkyl cyanides are compounds with the general formula  $\text{R}-\text{C}\equiv\text{N}$ . They are prepared by treating alkyl halides with sodium cyanide. The nitriles on acid-hydrolysis form carboxylic acids.



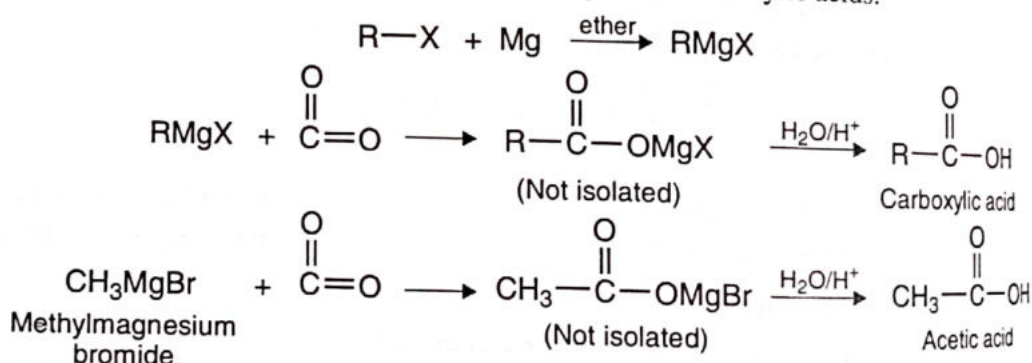


Notice that the acid produced by this method contains one more carbon atom than the original alkyl halide.

(3) **Hydrolysis of Esters.** When an ester is boiled with concentrated aqueous NaOH, sodium salt of the acid is formed. This on treatment with dilute HCl gives the corresponding carboxylic acid. For example,

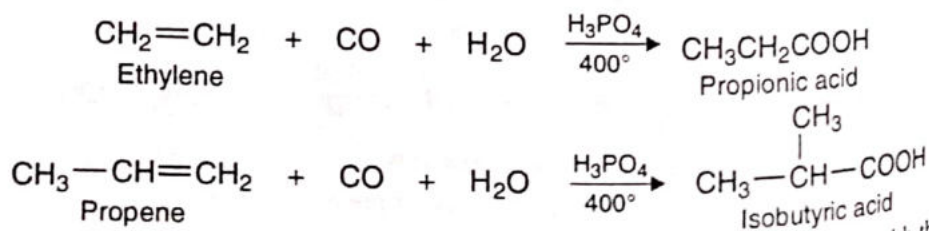


(4) **Reaction of Grignard Reagents with CO<sub>2</sub>.** Grignard reagents (RMgX) react with carbon dioxide to form addition products that can be hydrolysed to carboxylic acids.

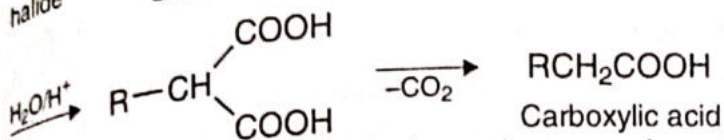
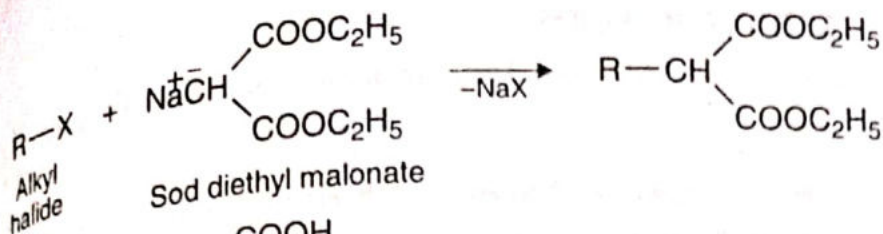


Notice that the acid formed by this method contains one more carbon than the original Grignard reagent. Organolithium compounds can also be used in place of Grignard reagents.

(5) **Carboxylation of Alkenes.** When an alkene is heated with carbon monoxide and steam under pressure with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) at 400°C, carboxylic acids are formed. This is a recent industrial method of making carboxylic acids and is called **Koch Reaction**.



(6) **Malonic Ester Synthesis.** This involves the reaction of an alkyl halide with the sodium derivative of diethyl malonate to give a substituted malonic ester. This can be hydrolysed and decarboxylated to yield an acid.



Notice that the acid produced by this method contains two carbon atoms more than the starting alkyl halide.

**PHYSICAL PROPERTIES**

- 1. Lower carboxylic acids (up to C<sub>10</sub>) are liquids with sharp or disagreeable odors. Higher members are waxlike solids and almost odorless.
- 2. Boiling points of carboxylic acids increase regularly with increase in molecular weight.
- 3. Melting points of carboxylic acids increase irregularly with increase of molecular weight. The odd members have markedly higher melting points than 'odd' members (Table 20.1).

**Table 20.1 MELTING AND BOILING POINTS OF SOME CARBOXYLIC ACIDS**

Name	Formula	mp °C	bp °C
Formic acid	HCOOH	8	101
Acetic acid	CH <sub>3</sub> COOH	16	118
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	-21	141
Butyric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	-7	164
Valeric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	-35	186

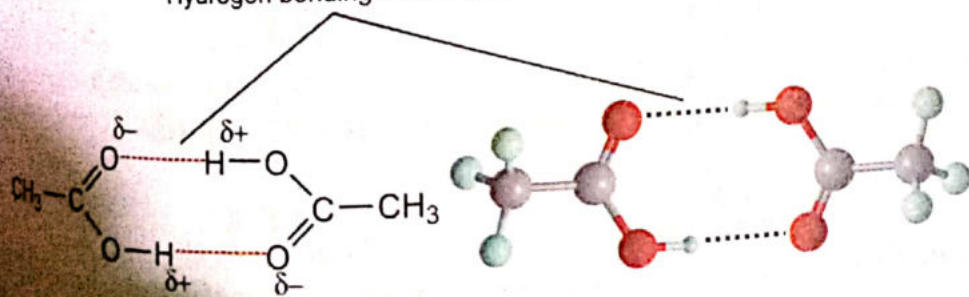
Boiling points of carboxylic acids are higher than those of alcohols of same molecular weight.

Example.

	Formula	MW	bp °C
Acetic acid	CH <sub>3</sub> COOH	60	118
1-Propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	60	97

This is attributed to hydrogen-bonding between acid molecules.

Hydrogen bonding in the dimer



Acetic acid dimer

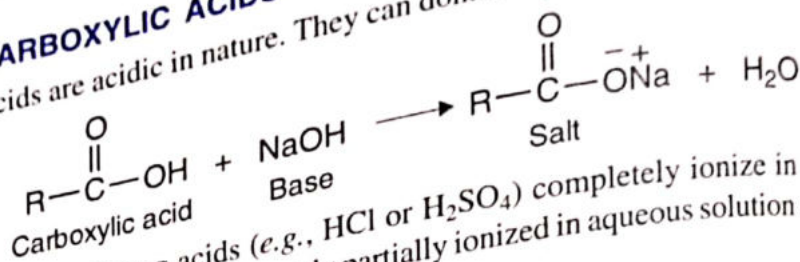
First four members are completely soluble in water. This is due to the ability of the carboxyl group to form hydrogen bonds with water molecules. As the hydrocarbon chain in the acid lengthens, the solubility of the acid in water falls off rapidly. Carboxylic acids are readily soluble in ethanol, ether, and benzene.

**IR spectrum.** Carboxylic acids show a broad O-H stretching vibrations at 2500-3300 cm<sup>-1</sup>, and a normally sharp C-H stretching band. They also show carbonyl (C=O) stretching vibrations at 1710-1720 cm<sup>-1</sup>.

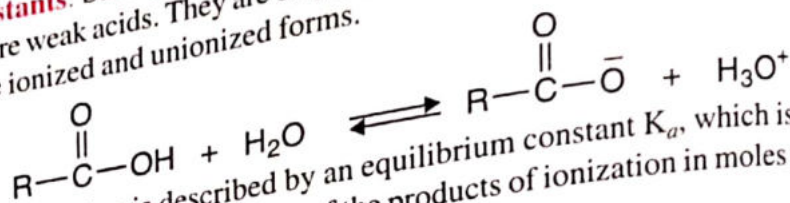


## ACIDITY OF CARBOXYLIC ACIDS

Carboxylic acids are acidic in nature. They can donate a proton and form salts with bases.



**Acidity Constants.** Strong acids (e.g., HCl or H<sub>2</sub>SO<sub>4</sub>) completely ionize in aqueous solution. Carboxylic acids are weak acids. They are only partially ionized in aqueous solution and an equilibrium exists between the ionized and unionized forms.

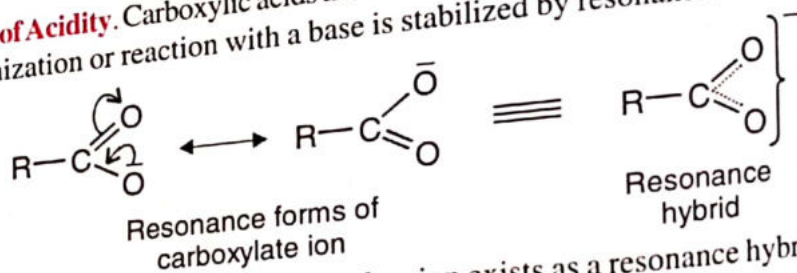


The extent of ionization is described by an equilibrium constant  $K_a$ , which is known as Acid Ionization Constant. It is defined as the concentration of the products of ionization in moles per litre divided by the concentration of the unionized acid.

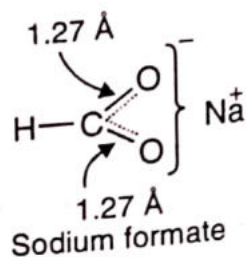
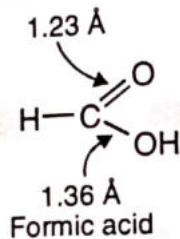
$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

The acidity constant describes the relative strength of a weak acid. Stronger acids will have higher numerical value of acidity constants.

**Explanation of Acidity.** Carboxylic acids are acidic and lose a proton readily because the carboxyl ion formed by ionization or reaction with a base is stabilized by resonance.



X-Ray studies support the fact that carboxylate ion exists as a resonance hybrid. For example, in formic acid the carbon-oxygen bonds have different lengths, whereas in sodium formate the carbon-oxygen bond lengths are identical and intermediate in length between those of normal double and single carbon-oxygen bonds.



The stability of carboxylate ion can also be explained on the basis of its molecular orbital structure. The carbon atom of carboxylate ion is  $sp^2$ -hybridized. It is bound to each oxygen atom by a  $\sigma$  bond. The unused carbon  $p$  orbital overlaps with  $p$  orbitals of both oxygen atoms to form stable delocalized molecular orbital (Fig. 20.1).

Notice that the four electrons are bound to three atoms (1 carbon + 2 oxygens). This delocalization of  $\pi$  electrons is responsible for the extra-stability of the carboxylate ion.

**Effect of Substituents on Acidity.** The most important factor affecting the acidity is the inductive effect of substituents on the  $\alpha$ -carbon atom.

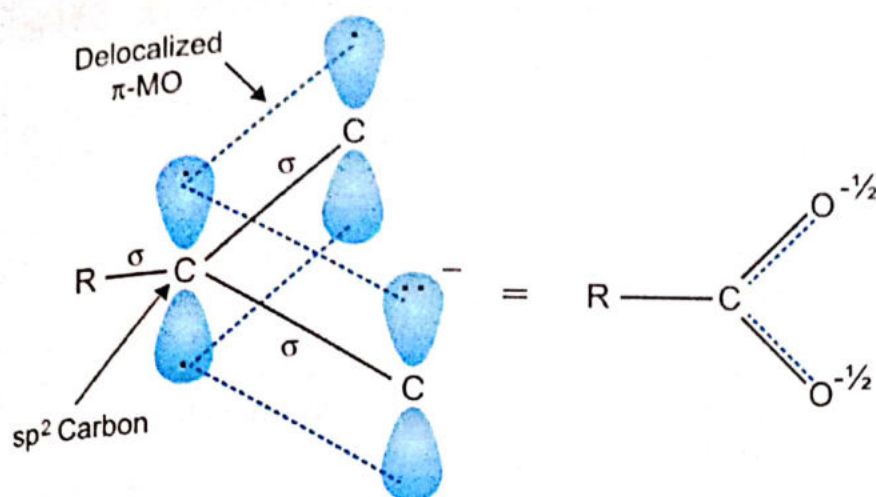
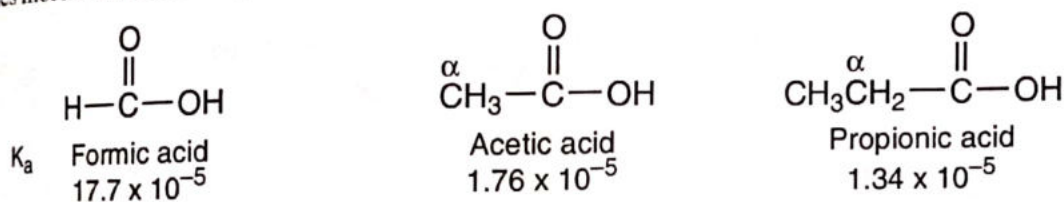
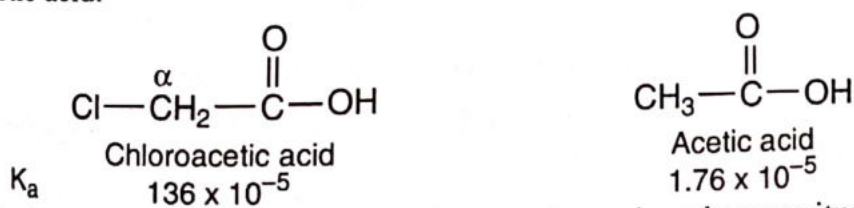


Fig. 20.1. Orbital structure of carboxylate ion.

(1) **Electron-releasing alkyl groups decrease the acidity.** This is because the electron-releasing groups increase the negative charge on the carboxylate ion and destabilize it. The loss of proton becomes more difficult. Also, as the size of the alkyl group increases, acidity decreases. For example,



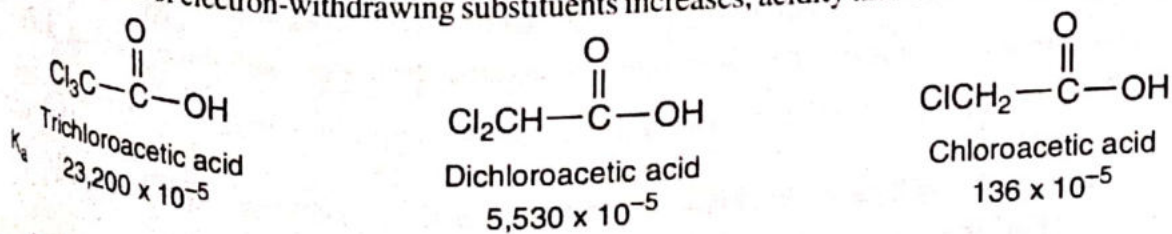
(2) **Electron-withdrawing substituents (Cl, Br, F, OH, CN) increase the acidity.** This is because the electron-withdrawing substituents decrease the negative charge on the carboxylate ion and stabilize it. The loss of proton becomes relatively easy. For example, chloroacetic acid is about 100 times stronger than acetic acid.



The strength of the electron-withdrawing substituents determines the magnitude of the effect on acidity. For example, fluoroacetic acid is stronger than chloroacetic acid since F is more electronegative than Cl.



As the number of electron-withdrawing substituents increases, acidity also increases. For example,



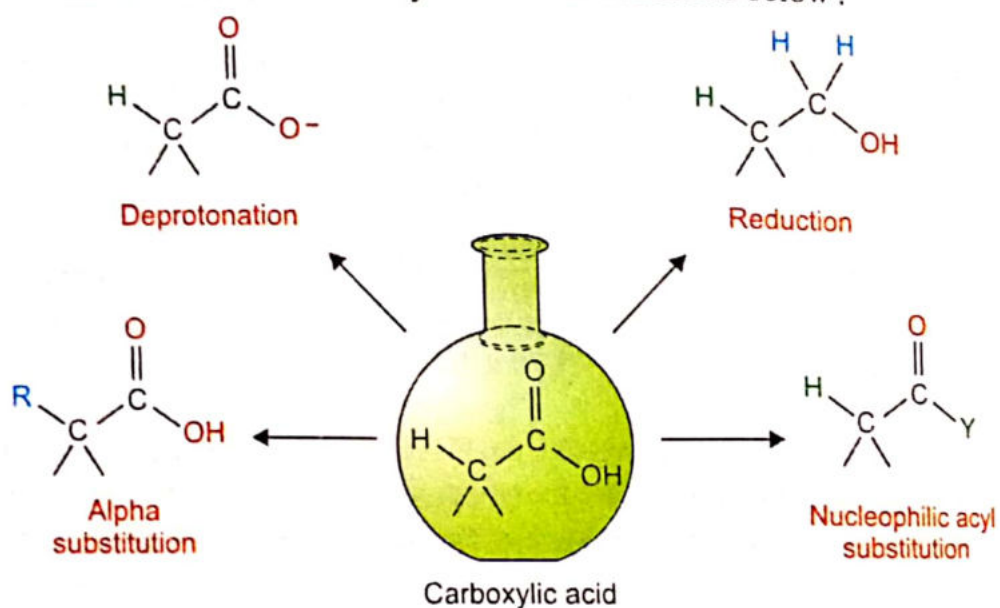


## Acidity of Carboxylic Acids

1. Strength of an acid is determined by the readiness with which they will donate a proton.
2. Acid strength will be increased by any factor which increases stability of the anion or which promotes proton loss.
3. Electron-releasing alkyl groups decrease the acidity.
4. Electron-withdrawing substituents (Cl, Br, F, OH, CN) increase the acidity. The strength of electron-withdrawing substituents determines the magnitude of its effect on acidity. As the number of electron-withdrawing substituents increases, acidity also increases.
5. *Remember* : The more halogen atoms attached to the acid molecule, the stronger the acid.
6. *Remember* : The closer the halogen atoms are attached to the carboxylic acid functional group, the stronger the acid.

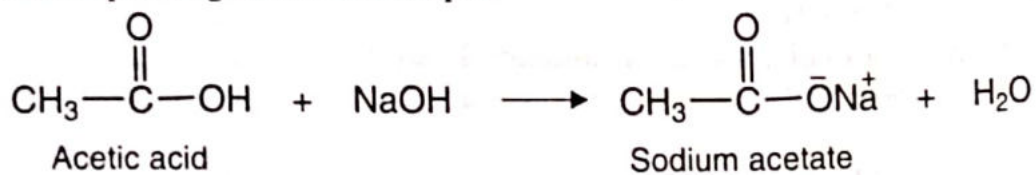
## CHEMICAL PROPERTIES

The main chemical reactions of carboxylic acids are described below :

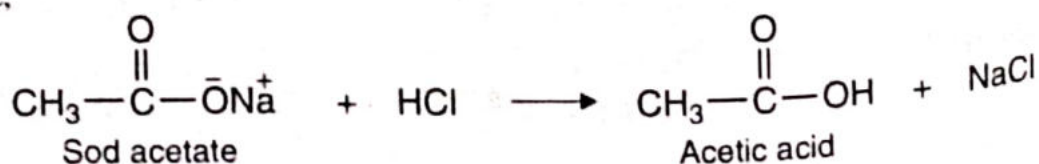


### Important reactions of Carboxylic acids.

(1) **Salt Formation.** Carboxylic acids react with hydroxides, carbonates, and bicarbonates form the corresponding salts. For example,



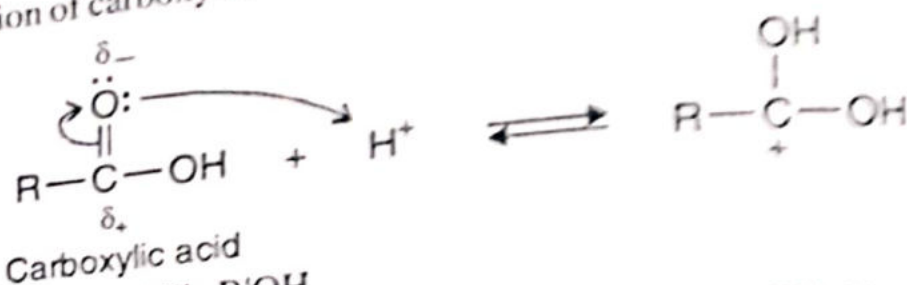
The carboxylic acids can be regenerated by treating these salts with dilute mineral acids  
example,



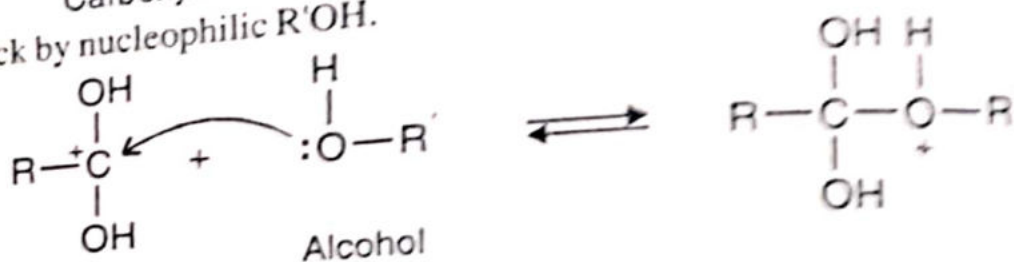




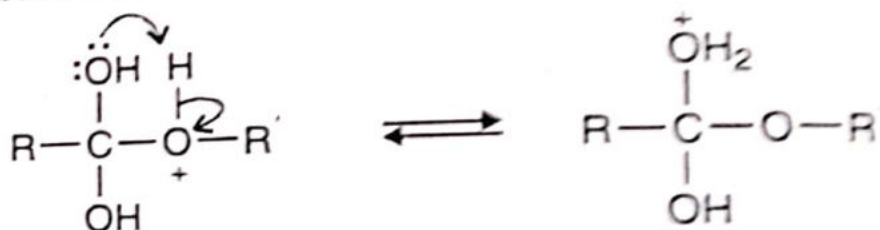
**Step 1.** Protonation of carboxylic acid.



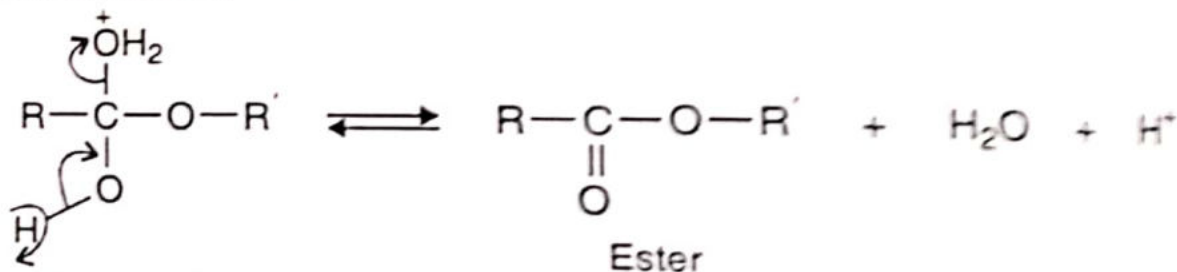
**Step 2.** Attack by nucleophilic R'OH.



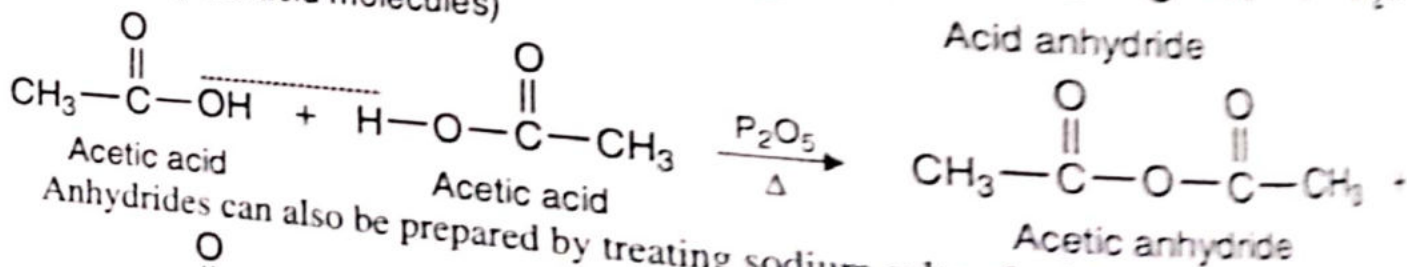
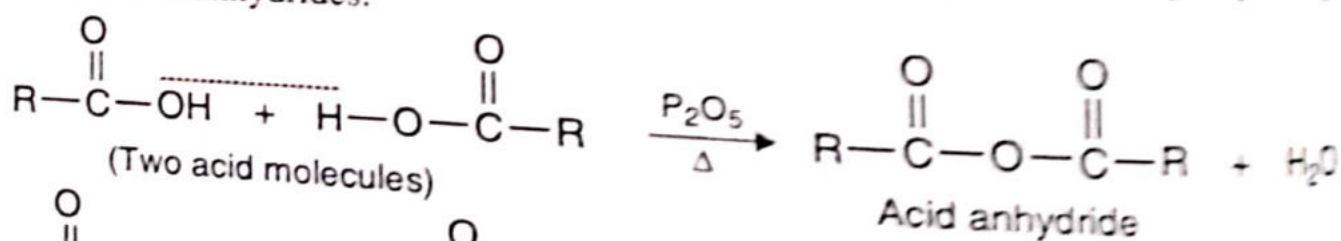
**Step 3.** Hydrogen ion transfer.



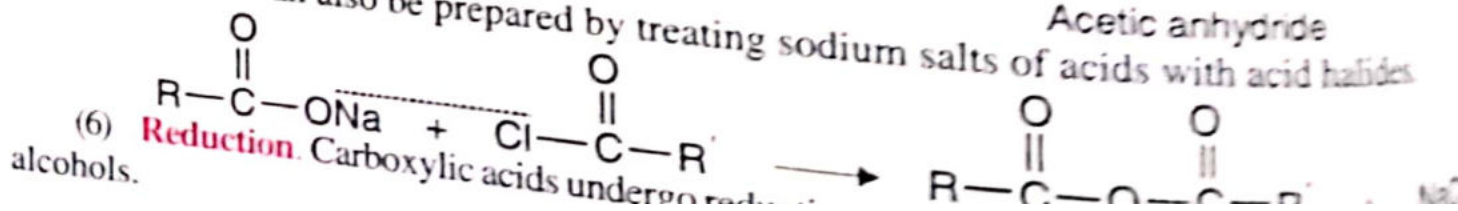
**Step 4.** Elimination of proton and water.



(5) **Formation of Anhydrides.** Carboxylic acids undergo dehydration with phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) to form acid anhydrides.

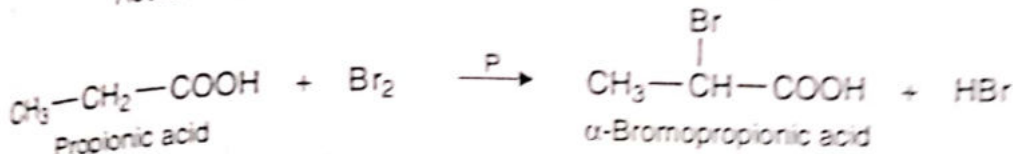
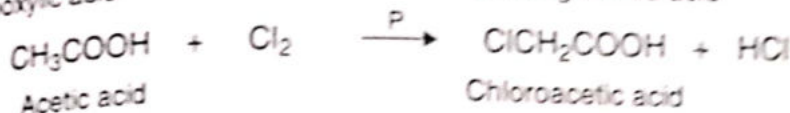
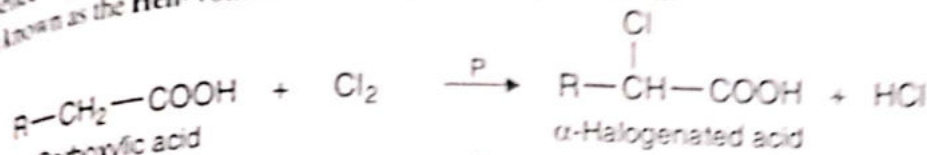


Anhydrides can also be prepared by treating sodium salts of acids with acid halides.

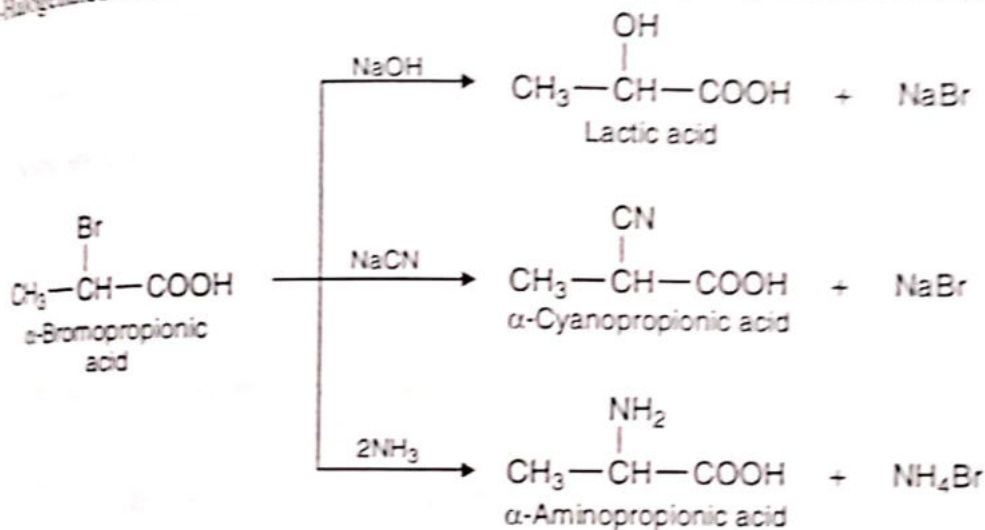


Carboxylic acids cannot be reduced with  $H_2/Ni$  or  $Na + C_2H_5OH$ .

**$\alpha$ -Halogenation.** When a carboxylic acid that contains  $\alpha$ -hydrogens is treated with  $Cl_2$  or  $Br_2$  in the presence of phosphorus, the  $\alpha$ -hydrogen atoms are replaced by chlorine or bromine atoms. This reaction is known as the **Hell-Volhard-Zelinsky (or HVZ) Reaction**.

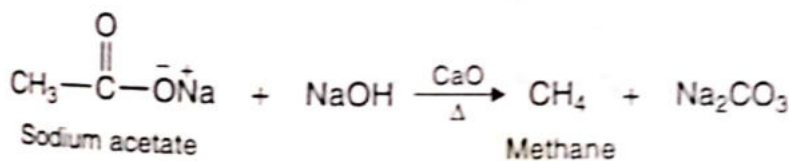


$\alpha$ -Halogenated acids are convenient starting materials for preparing other  $\alpha$ -substituted acids.

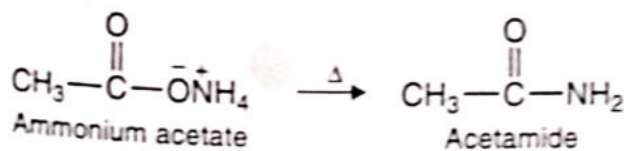


**REACTIONS OF SALTS OF CARBOXYLIC ACIDS**

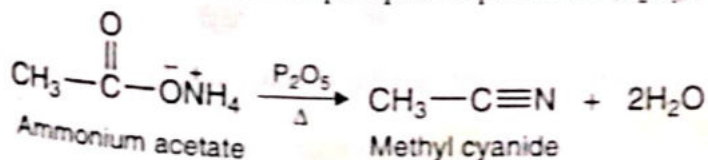
**(i) Action of Heat on Sodium Salts.** When sodium salts of carboxylic acids are heated with lime ( $NaOH + CaO$ ), alkanes are formed.



**(ii) Action of Heat on Ammonium Salts.** When ammonium salts are heated alone, amides are formed.

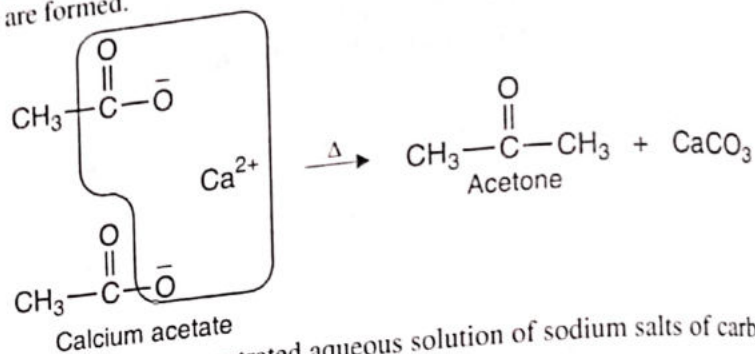


When the ammonium salts are heated with phosphorus pentoxide ( $P_2O_5$ ), cyanides are formed.

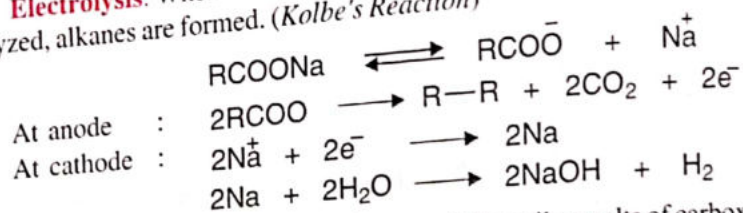




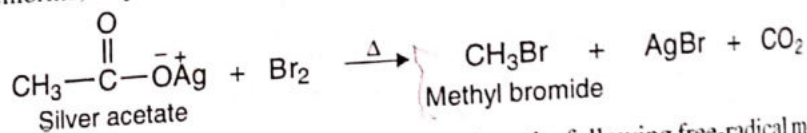
(3) **Action of Heat on Calcium Salts.** When calcium or barium salts of carboxylic acids are heated, ketones are formed.



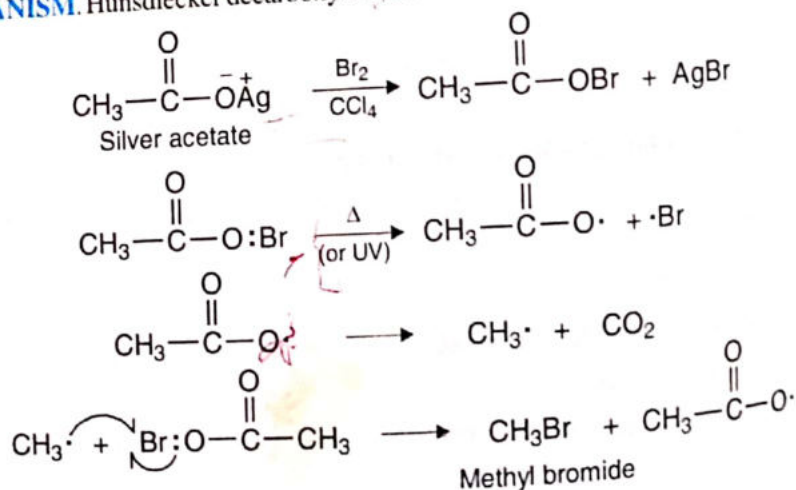
(4) **Electrolysis.** When concentrated aqueous solution of sodium salts of carboxylic acids electrolyzed, alkanes are formed. (Kolbe's Reaction)



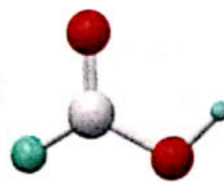
(5) **Reaction of Silver Salts with Halogens.** When silver salts of carboxylic acids are heated with bromine or chlorine, alkyl halides are formed. (Hunsdiecker Reaction)



**MECHANISM.** Hunsdiecker decarboxylation involves the following free-radical mechanism



**FORMIC ACID, Methanoic Acid, HCOOH**



Formic acid derives its name from the fact that it was first obtained by distillation of ants (*formica* = ant).

**Preparation.** Formic acid may be obtained as follows :