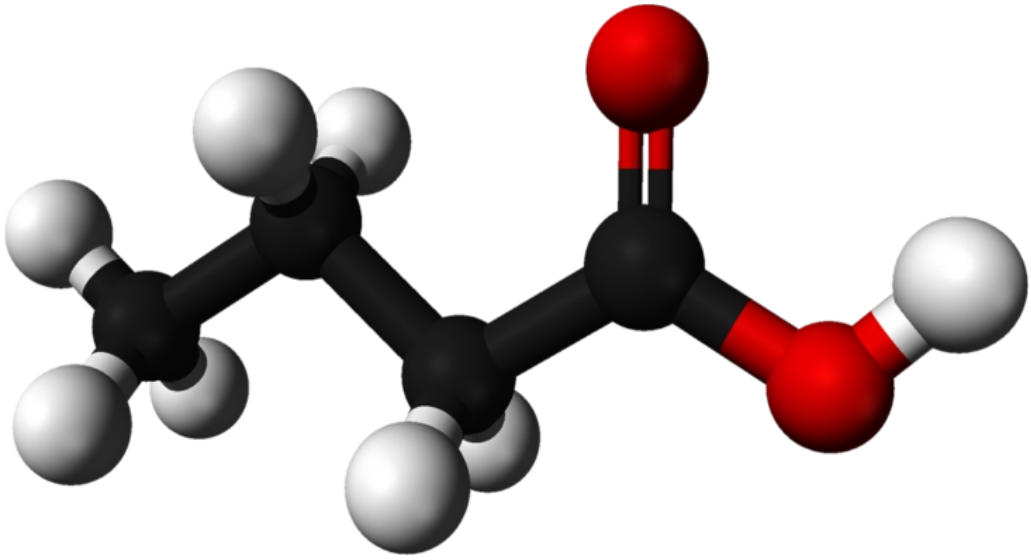
CHAPTER 9

CARBONYL COMPOUNDS II: CARBOXYLIC ACID AND FUNCTIONAL DERIVATIVES

Teaching Periods	07	Assessment	01	Weightage %	06



Students will be able to:

- ✓ Discuss the physical properties and acidity of carboxylic acid. (Understanding)
- ✓ Describe preparation of carboxylic acids by carbonation of Grignard's Reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzenes. (Applying)
- ✓ Conversion of carboxylic acids into their derivatives (acyl halides, acid anhydrides, esters, amides) without mechanism. (Applying)
- ✓ Enlist the important compounds of carboxylic acids and their derivatives with their application. (Applying)

INTRODUCTION

"Organic compounds which contain carbonyl group (C = O) attached to hydroxyl group (−OH) are referred as carboxylic acid". In these compounds one or two carboxyl groups (−COOH) are directly attached with the alkyl or aryl carbon chain.

Carboxylic acids are versatile compounds. They have many important applications in various fields. In food industry they are used as preservatives, flavouring and acidity regulators. They are used in the manufacturing of many pharmaceuticals such as asprin, ibuprofen and penicillin. Carboxylic acids are essential for many biological processes, including the breakdown of fat and carbohydrates. Carboxylic acids are used as starting materials in the manufacturing of polymers such nylon, polyester etc.

9.1 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

i) Colour and odour

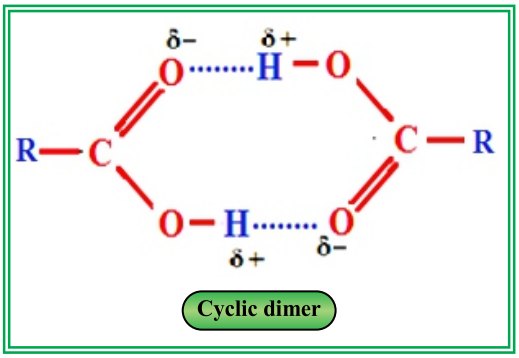
Aliphatic monocarboxylic acids are generally colourless. They have a pungent odour. However, the intensity of odour decreases with the length of chain.

ii) Solubility

Carboxylic acids are soluble in polar solvents such as water and alcohols, due to their ability to form hydrogen bonds with these solvents. However, as the length of carbon chain increases, their solubility in water decreases.

iii) Boiling points

Compared to alcohols, carboxylic acids are more polar and have a high tendency to form hydrogen bonds among themselves. As a result, carboxylic acids generally have higher boiling points than their corresponding alcohols. The hydrogen bonding in carboxylic acids mostly exists in cyclic dimer form.



Cyclic dimer

9.2 STRUCTURE OF CARBOXYLIC ACID

Structure of carboxylic acid is explained by the hybrid orbital theory (Fig.9.1). The carbonyl carbon is sp^2 hybridized, possessing three sp^2 hybrid orbitals and one p_z unhybridized orbital. These three sp^2 hybrid orbitals are oriented almost at an angle of 120° to give trigonal geometry whereas p_z unhybridized orbital of carbonyl carbon form pi bond with p_z orbital of oxygen atom.

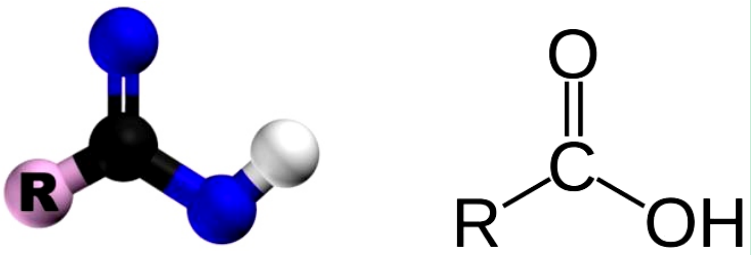


Fig 9.1: Structure of carboxylic acid

9.3 ACIDITY OF CARBOXYLIC ACID

"Carboxylic acids are considerably stronger acids than alcohols, phenols and water. However, they are weaker acids compared to mineral acids".

Table 9.1 **Comparative acid strength of carboxylic acid with alcohol, phenol and water**

Name of Compound	Molecular Formula	pKa Value
Acetic acid	CH_3COOH	5
Phenol	C_6H_5OH	10
Ethyl alcohol	C_2H_5OH	16
Water	H_2O	15.7

When carboxylic acids are dissolved in water, they undergo dissociation to produce carboxylate ions. This dissociation occurs because the carbon atom in the carboxyl group is electron withdrawing group, which leads to a weakening of hydrogen oxygen bond. Consequently, the carboxyl group is able to lose a proton in aqueous medium which makes it an acid.

Self Assessment

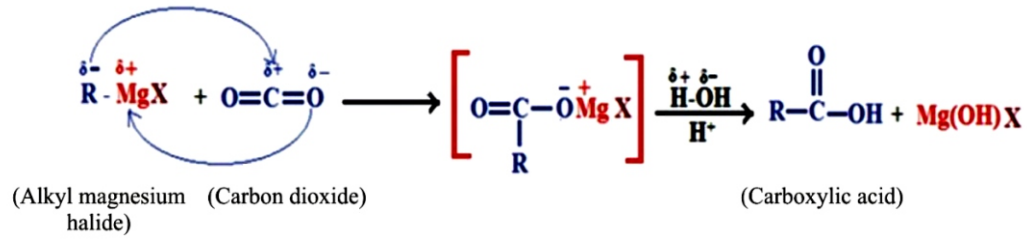
Carboxylic acids are more acidic than alcohol and explain on the basis of their pKa values.

9.4 PREPARATION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Carboxylic acids are prepared by the following different methods.

9.4.1 By the Carbonation of Grignard Reagent

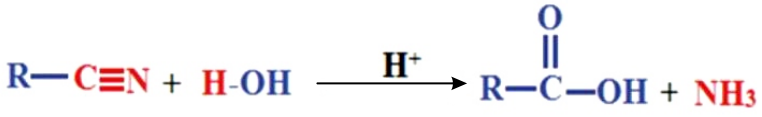
When Grignard reagent reacts with carbon dioxide, it changes into an addition product which on hydrolysis in acidic medium produce carboxylic acid.



(Alkyl magnesium halide) (Carbon dioxide) (Carboxylic acid)

9.4.2 By the Hydrolysis of Nitriles

Alkyl cyanide (nitrile) when reacts with water in the presence of acid, it changes into carboxylic acid with the liberation of ammonia gas.



(Alkyl cyanide) (Carboxylic acid)

9.4.3 By the Oxidation of Primary Alcohols

By using acidified oxidizing agents such as $K_2Cr_2O_7$ or $KMnO_4$ primary alcohols can be oxidized to form carboxylic acids. This process occurs through an intermediate stage where the alcohol is converted into an aldehyde.

$$\underset{\text{(Primary alcohol)}}{R\text{-}CH_2\text{-}OH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Aldehyde)}}{R\text{-}CHO} + H_2O$$

$$\underset{\text{(Acetaldehyde)}}{CH_3\text{-}CHO} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Acetic acid)}}{CH_3\text{-}COOH}$$

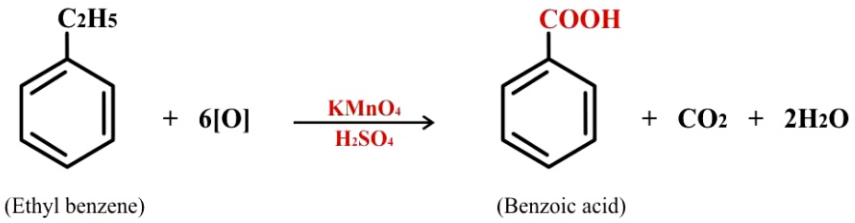
9.4.4 By the Oxidation of Aldehyde

Aldehydes oxidized when mixed with Potassium dichromate and sulphuric acid to produce carboxylic acid.

$$\underset{\text{(Aldehyde)}}{R\text{-}CHO} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{(Carboxylic acid)}}{R\text{-}COOH}$$

9.4.5 By the Oxidation of Alkyl Benzene

When an alkyl benzene reacts with potassium permanganate ($KMnO_4$) under acidic conditions, the alkyl group is oxidized to –COOH group.



9.5 REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Certain compounds are structurally derived from carboxylic acids by replacing a part of functional group of the carboxylic acid. Some common derivatives of carboxylic acids are given as.

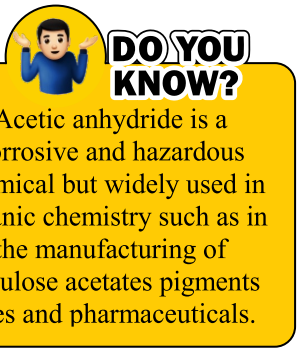
(i) **Esters:** They are formed by replacing the hydroxyl group of carboxylic acid with an alkyl or aryl group. Their general formula is R-COOR e.g. Ethyl acetate ($CH_3COOCH_2CH_3$), Methyl propionate ($CH_3CH_2COOCH_3$).

DO YOU KNOW?

Esters are mostly found in fruits. An ester named as ethyl butanoate ($C_3H_7COOC_2H_5$) is specifically found in pineapple which contributes its specific aroma and as flavour.

(ii) **Acid halides:** They are formed by replacing the hydroxyl group of carboxylic acid with a halogen (X) atom. Their general formula is RCOX e.g. Acetyl chloride (CH_3COCl), Propionyl chloride (CH_3CH_2COCl).

(iii) **Amides:** They are formed by replacing the hydroxyl group of carboxylic acid with an amino group. Their general formula is $RCONH_2$ e.g. Acetamide (CH_3CONH_2), Benzamide ($C_6H_5CONH_2$).



(iv) **Anhydrides:** They are formed by removing a water molecule from two carboxylic acid molecules. Their general formula is $(RCO)_2O$ e.g. Acetic anhydride $(CH_3CO)_2O$, Maleic anhydride ($C_4H_2O_3$).

9.5.1 Conversion of carboxylic acids into acyl halides

Like alcohols, the hydroxyl groups of carboxylic acids are easily replaced by halogen atom on heating with PCl_5, PCl_3 or $SOCl_2$. However, the thionyl chloride ($SOCl_2$) is generally preferred because the by-products obtained are in the gaseous state which are escaped out from reaction mixture to get pure acyl halides.

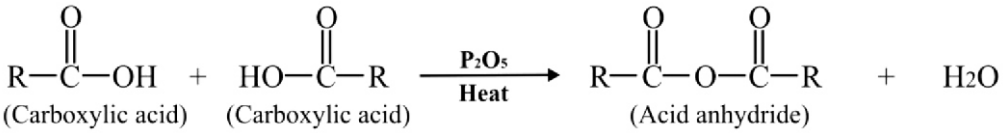
$$\underset{\text{(carboxylic acid)}}{R-COOH} + PCl_5 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + POCl_3 + HCl$$

$$\underset{\text{(carboxylic acid)}}{3R-COOH} + PCl_3 \longrightarrow \underset{\text{(Acyl halide)}}{3R-CO-Cl} + H_3PO_3$$

$$\underset{\text{(carboxylic acid)}}{R-COOH} + SOCl_2 \longrightarrow \underset{\text{(Acyl halide)}}{R-CO-Cl} + SO_2 + HCl$$

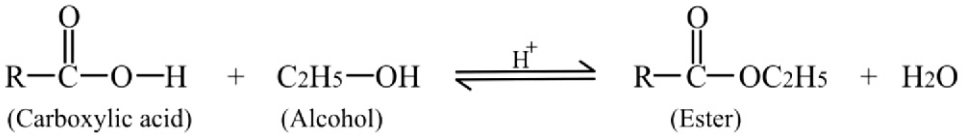
9.5.2 Conversion of Carboxylic Acids into Acid Anhydirdes

The formation of an acid anhydride involves a condensation reaction between two carboxylic acid molecules. This reaction is typically conducted in the presence of a dehydrating agent like phosphorus pentaoxide (P_2O_5).



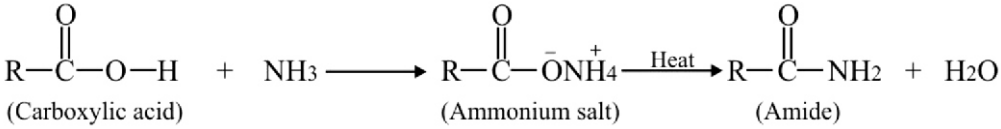
9.5.3 Conversion of Carboxylic Acids into Ester

Esters are produced from carboxylic acids through a reaction called esterification. In this reaction carboxylic acid reacts with an alcohol in the presence of a catalyst usually concentrated sulphuric acid to produce an ester and water.



9.5.4 Conversion of Carboxylic Acids into Amides

Amides can be produced by the reaction between carboxylic acid and ammonia, where an ammonium salt is formed, which upon heating yields the corresponding acid amide.

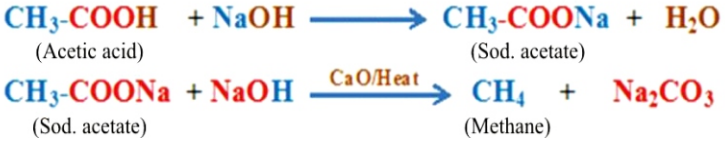


9.5.5 Conversion of Carboxylic Acids into Alcohols

Carboxylic acids upon catalytic reduction with lithium aluminum hydrides produce primary alcohols.

9.5.6 Conversion of Carboxylic Acids into Alkane

Carboxylic acids when reacted with caustic soda (base) they form salt of carboxylic acid which on further heating with soda-lime yield alkanes.



Self Assessment

Show the following conversions by means of chemical reactions:

- Methyl cyanide into acetic acid
- Acetic acid into an amide
- Ethanoic acid into ethanol

Uses of some common carboxylic acids and their derivatives

Citric Acid ($C_6H_8O_7$)

It is used as a preservative, flavor enhancer and acidity regulator.

Malic Acid ($C_4H_6O_5$)

It is used as a food additive and pH control agent.

Tartaric Acid ($C_4H_6O_6$)

It is commonly used in food and beverage industry.

DO YOU KNOW?

Butyric acid is a short chain fatty acid with the formula C_3H_7COOH. It is found in dairy products like butter, cheese and milk. It is responsible for distinct aroma and flavor of these products.

Acetic Acid (CH_3COOH)

It is used as a preservative and as a raw material of various chemicals.

Salicylic Acid (HOC_6H_4COOH)

It is used in the preparation of skin care products and in the production of aspirin.

Benzoic Acid (C_6H_5COOH)

It is used in the production of dyes, perfumes and plastics.

Acetamide (CH_3CONH_2)

It is used as a raw material in pharmaceuticals and drug synthesis.

Acetic anhydride ($C_4H_6O_3$)

It is used in making cellulose acetate and in the manufacturing of dyes.

The important compounds of carboxylic acids and their derivatives with their applications:

Common name	Structure	Occurrence and derivation of name	Applications
Formic acid	$HCOOH$	Ants (Latin; Formica)	Preservative and antibacterial agent in livestock feed
Acetic acid	CH_3COOH	Vinegar (Latin; Acetum)	Vinegar production, food preservative and flavoring agent
Propionic acid	CH_3CH_3COOH	Milk, butter and cheese (Greek Protos, First; pion, fat)	Animal feed additive for preventing mold growth
Butyric acid	$CH_3(CH_2)_2COOH$	Butter (Latin; Butyrum)	Flavoring agent in food products
Valeric acid	$CH_3(CH_2)_3COOH$	Valerian root (Latin; Valere, to be strong)	Manufacture of valerate esters used in perfumes
Caproic acid	$CH_3(CH_3)_4COOH$	Goat (Latin; Caper)	Pharmaceuticals and plasticizers

SOCIETY, TECHNOLOGY AND SCIENCE

Carboxylic Acids as food preservative

Carboxylic acids, such as benzoic acid, sorbic acid and propanoic acid, are commonly used as food preservatives due to their antimicrobial properties. These acids can prevent the growth of bacteria, yeast and molds that can cause the spoilage and food born illness. When added to food, carboxylic acids dissociate into their corresponding anions, which penetrate microbial cell membranes and inhibit the growth and metabolism of microorganisms. They also disrupt enzymes and cellular functions essential for microbial survival, leading to their death.

SUMMARY

- Organic compounds which contain carbonyl group ($>C=O$) attached to a hydroxyl group ($-OH$) are called carboxylic acid.
- Carboxylic acids are water soluble since they have ability to form hydrogen bonds with water.
- Boiling point of carboxylic acids are higher than their corresponding alcohols because they form hydrogen bonds themselves in a cyclic dimer form.
- The shape of carboxylic acid molecule is planar triangular in which carbonyl carbon is sp^2 hybridized.
- Carboxylic acids are stronger acids than alcohols, phenols and water. However, weaker than mineral acids.
- Carboxylic acids can be prepared by the oxidation of alcohols. The suitable oxidizing agents in this conversion are potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).
- There are four derivatives of carboxylic acid named as Ester, Acyl halide, Acetic anhydride and Acid amide.

- Carboxylic acids can be converted into acyl chloride, if they are treated with PCl_3, PCl_5 or $SOCl_2$.
- Carboxylic acids can be converted into esters, if they are heated with an alcohol in the presence of concentrated sulphuric acid.
- Carboxylic acids can be converted into amide, if they are treated with ammonia.

Multiple Choice Questions

(i) The most common compound found in pineapple is:
(a) Acetic acid (b) Ethanol
(c) Acetone (d) Ethyl butanoate

(ii) Two molecules of acetic acid on condensation gives:
(a) Ethyl acetate (b) Aceticamide
(c) Acylhalide (d) Acetic anhydride

(iii) Carboxylic acid is stronger acid than:
(a) HCl (b) HNO_3
(c) C_2H_5OH (d) H_2SO_4

(iv) The reagent that cannot produce an acyl halide in reaction with a carboxylic acid is:
(a) PCl_3 (b) PCl_5
(c) HCl (d) $SOCl_2$

(v) Benzoic acid is the product of oxidation of:
(a) Benzene (b) Ethyl Benzene
(c) Aniline (d) Phenol

(vi) Formation of acyl halide and amide by carboxylic acid involved
(a) Replacement of hydrogen (b) Replacement of carbonyl group
(c) Replacement of hydroxyl group (d) Replacement of oxygen

(vii) Formic acid is naturally found in:

(a) Venom of ants (b) Bees string

(c) Vinegar (d) Butter

(viii) Among the following compounds, the one with the highest boiling point is:

(a) Ethanol (b) Acetaldehyde

(c) Acetic acid (d) Ethyl chloride

(ix) The formula of caproic acid is:

(a) C_4H_9COOH (b) $C_5H_{11}COOH$

(c) $C_6H_{13}COOH$ (d) $C_7H_{15}COOH$

(x) The reaction of acetic acid with ethanol in the presence of conc. sulphuric acid gives:

(a) Ethyl acetate (b) Acetamide

(c) Ethane (d) Acetic anhydride

Short Questions

1. Explain why?
   i) The boiling points of carboxylic acids are high than alcohol?
   ii) The structure of carboxylic acid is trigonal planar?
2. What happens when:
   i) Formaldehyde reacts with a mixture of Potassium dichromate & sulphuric acid.
   ii) Carboxylic acid reacts with thionyl chloride
   iii) Carboxylic acid reacts with ammonia
   iv) Ethyl magnesium bromide reacts with carbon dioxide
3. Write down the commercial applications of carboxylic acids.
4. Write the natural sources of following carboxylic acids.
   (a) Formic acid (b) Acetic acid (c) Valeric acid (d) Caproic acid

Descriptive Questions

1. How is carboxylic acid prepared by:
   i) Carbonation of Grignard reagent
   ii) Hydrolysis of alkyl nitriles
   iii) Oxidation of primary alcohols
2. Explain the structure of carboxylic acid.
3. Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?
4. Convert the followings:
   i) Carboxylic acid into acid anhydride
   ii) Ester into carboxylic acid
   iii) Toluene into benzoic acid
5. Explain the following physical properties of carboxylic acids:
   (a) Solubility (b) Boiling point
6. Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.