

# CARBONYL COMPOUNDS II: CARBOXYLIC ACID AND FUNCTIONAL DERIVATIVES



"Organic compounds which contain carbonyl group (C=O) attached to hydroxyl group (-OH) are referred as carboxylic acid."

#### PHYSICAL PROPERTIES OF CARBOXYLIC ACID:

- > They are liquids with a sharp odor.
- > They are soluble in polar solvents such as water.
- > They have high boiling point as compared to alcohols due to stronger hydrogen bond.

#### **ACIDITY OF CARBOXYLIC ACID:**

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

Name of Compound	Molecular Formula	pKa Value
Acetic acid	CH <sub>3</sub> COOH	5
Phenol	C <sub>6</sub> H <sub>5</sub> OH	10
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH	16
Water	H <sub>2</sub> O	15.7

# PREPARATION OF CARBOXYLIC ACID:

1 By the Carbonation of Grignard Reagent

$$\begin{array}{c} \stackrel{\delta^{-} \stackrel{\delta^{+}}{\to} \stackrel{\delta^{-}}{\to} \stackrel{\delta$$

2 By the Hydrolysis of Nitriles



## 3 By the Oxidation of Primary Alcohols

R-CH<sub>2</sub>-OH + 
$$O$$
  $\xrightarrow{K_1Cr_1O_1/H_1SO_4}$  R-CHO +  $O$  (Aldehyde)

CH<sub>3</sub>-CHO +  $O$   $\xrightarrow{K_2Cr_2O_1/H_2SO_4}$  CH<sub>3</sub>-COOH (Acetaldehyde)

(Acetic acid )

#### 4 By the Oxidation of Aldehyde

R-CHO + [O] 
$$\xrightarrow{K_2Cr_2O_2/H_2SO_4}$$
 R-COOH

(Aldehyde) (Carboxylic acid)

## 5 By the Oxidation of Alkyl Benzene

#### **DERIVATIVES OF CARBOXYLIC ACIDS**



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 hydrogen atom of carboxylic group with an alkyl or aryl group. Their general formula is R-COOR.

## Conversion of Carboxylic Acids into Ester

The process in which carboxylic acid reacts with alcohol to form ester is called esterification.

$$\begin{array}{c} O \\ R-C-O-H \\ \end{array} + \begin{array}{c} C_2H_5-OH \\ \end{array} = \begin{array}{c} H^+ \\ \end{array} = \begin{array}{c} O \\ R-C-OC_2H_5 \\ \end{array} + \begin{array}{c} H_2O \\ \end{array}$$
(Carboxylic acid) (Alcohol) (Ester)

e.g: Ethyl acetate (CH₃COOC₂H₅), Methyl propionate (C₂H₅COOCH₃)

- (ii) Acid Halides: They are formed by replacing the hydroxyl group of carboxylic acid with a halogen atom (X). Their general formula is RCOX.
- e.g. Acetyl chloride (CH₃COCI), Propionyl chloride (C2H₅COCI) etc.

#### Conversion of carboxylic acids into acyl halides

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

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

$$R - COOH + SOCl_2 \longrightarrow R - CO - Cl + SO_2 + HCl$$
 \*\* pakcity.org \*\* (carboxylic acid) (Acyl halide)

(iii) Amides: They are formed by replacing the hydroxyl group of carboxylic acid with an amino group. Their general formula is RCONH<sub>2</sub>.

e.g. Acetamide (CH₃CONH₂), Benzamide (C6H5CONH₂) etc.

#### Conversion of Carboxylic Acids into Amides

$$R-C-O-H$$
 +  $NH_3$   $\longrightarrow$   $R-C-ONH_4$   $\xrightarrow{\text{Heat}}$   $R-C-NH_2$  +  $H_2O$  (Carboxylic acid) (Ammonium salt) (Amide)

(iv) Acid Anhydrides: They are formed by removing a water molecule from two carboxylic molecules. Their general formula is (RCO)<sub>2</sub>O.

e.g. Acetic Anhydride (CH₃CO)2O

## Conversion of Carboxylic Acids into Acid Anhydirdes

## Conversion of Carboxylic Acids into Alcohols

$$R - COOH + 4[H] \xrightarrow{LiAlH_4} R - CH_2 - OH + H_2O$$
 (Carboxylic acid) (Alcohol)

## 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.

CH<sub>3</sub>-COOH + NaOH 
$$\longrightarrow$$
 CH<sub>3</sub>-COONa + H<sub>2</sub>O

(Acetic acid) (Sod. acetate)

CH<sub>3</sub>-COONa + NaOH  $\xrightarrow{\text{CaO/Heat}}$  CH<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub>

(Sod. acetate) (Methane)



Show the following conversions by means of chemical reactions:

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



- $\rightarrow$  CH<sub>3</sub>CN + 2H<sub>2</sub>O  $\rightarrow$  CH<sub>3</sub>COOH + NH<sub>3</sub>
- CH₃COOH + NH₃ → CH₃COONH₄ -----heat----->CH₃COONH₂ + H₂O
- CH₃COOH + 4[H] ------LiAlH₄-----> C₂H₅OH + H₂O

# Uses of some common carboxylic acids and their derivatives

- Citric acid is used as flavor enhancer.
- Maleic acid is used as food additive.
- **❖** Tartaric Acid is used in food industry.
- Acetic acid is used as vinegar.
- Salicylic acid is used in the production of aspirin.
- Acet amide is used in drug synthesis.
- Acetic anhydride is used in making cellulose acetate.

Common	Structure	Occurrence and derivation of name	Applications
Formic acid	HCOOH Area of triangle A=bh	Ants (Latin; Formica)	Preservative and antibacterial agent in livestock feed
Acetic acid	CH <sub>3</sub> COOH	Vinegar (Latin; Acetum)	Vinegar production, food preservative and flavoring agent
Propionic acid	СН₃СН₃СООН	Milk, butter and cheese (Greek Protos, First; pion, fat)	Animal feed additive for preventing mold growth
Butyric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	Butter (Latin; Butyrum)	Flavoring agent in food products
Valeric acid	СН <sub>3</sub> (СН <sub>2</sub> ) <sub>3</sub> СООН	Valerian root (Latin; Valere, to be strong)	Manufacture of valerate esters used in perfumes
Caproic acid	CH <sub>3</sub> (CH <sub>3</sub> ) <sub>4</sub> COOH	Goat (Latin; Caper)	Pharmaceuticals and plasticizers

(x)

(c) Ethane

	Multiple Choice Questions		
(i)	The most common compound found  (a) Acetic acid  (c) Acetone	in pineapple is: (b) Ethanol (d) Ethyl butanoate	
(ii)	Two molecules of acetic acid on con (a) Ethyl acetate (c) Acylhalide	densation gives:  (b) Aceticamide  (d) Acetic anhydride	
(iii)	Carboxylic acid is stronger acid than (a) HCl (c) C <sub>2</sub> H <sub>5</sub> OH	t: (b) HNO <sub>3</sub> (d) H <sub>2</sub> SO <sub>4</sub> pakcity.org	
(iv)	The reagent that cannot produce carboxylic acid is:  (a) PCl <sub>3</sub> (c) HCl	an acyl halide in reaction with a  (b) PCl <sub>5</sub> (d) SOCl <sub>2</sub>	
(v)	Benzoic acid is the product of oxidat (a) Benzene (c) Aniline	tion of: (b) Ethyl Benzene (d) Phenol	
(vi)	Formation of acyl halide and amide l (a) Replacement of hydrogen (c) Replacement of hydroxyl group	by carboxylic acid involved (b) Replacement of carbonyl group (d) Replacement of oxygen	
(vii	Formic acid is naturally found in:  (a) Venom of ants (c) Vinegar	(b) Bees string (d) Butter	
(vii	<ul> <li>i) Among the following compounds, the is:</li> <li>(a) Ethanol</li> <li>(c) Acetic acid</li> </ul>	(b) Acetaldehyde (d) Ethyl chloride	
(ix)	The formula of caproic acid is: (a) C <sub>4</sub> H <sub>9</sub> COOH (c) C <sub>6</sub> H <sub>13</sub> COOH	(b) C <sub>5</sub> H <sub>11</sub> COOH (d) C <sub>7</sub> H <sub>15</sub> COOH	
ulphuri	action of acetic acid with ethanol ic acid gives:	in the presence of conc.	

(d) Acetic anhydride

#### **Short Questions**

- 1. Explain why?
  - i) The boiling points of carboxylic acids are high than alcohol?

Ans. The hydrogen bonding is stronger in carboxylic acid than alcohol that's why they have higher boiling point.

ii) The structure of carboxylic acid is trigonal planar? - pakcity.org



Ans. The carbon atom in carboxylic acid is sp<sup>2</sup> hybridized and sp<sup>2</sup> hybrid orbitals have a trigonal planar shape with 120° bond angle due to maximum repulsion of electron. Due to this fact, carboxylic acids have a trigonal planar structure.

- What happens when:
  - i) Formaldehyde reacts with a mixture of Potassium dichromate & sulphuric acid.

ii) Carboxylic acid reacts with thionyl chloride

$$R - COOH + SOCl_2 \rightarrow R - CO - Cl + SO_2 + HCl$$
 (carboxylic acid) (Acyl halide)

iii) Carboxylic acid reacts with ammonia

$$R-C-O-H$$
 +  $NH_3$   $\longrightarrow$   $R-C-ONH_4$   $\xrightarrow{Ileat}$   $R-C-NH_2$  +  $H_2O$  (Carboxylic acid) (Ammonium salt) (Amide)

iv) Ethyl magnesium bromide reacts with carbon dioxide

$$H_3C-CH_2-Mg-Br + O=C=O-C_2H_5-C-OMgBr - H_2O - C_2H_5-C-OH + Mg$$
OH

Write down the commercial applications of carboxylic acids.

# **Already Discussed Above**

- Write the natural sources of following carboxylic acids.
  - (a) Formic acid
- (b) Acetic acid (c) Valeric acid (d) Caproic acid

**Already Discussed Above** 

#### **Descriptive Questions**

- 1. How is carboxylic acid prepared by:
  - Carbonation of Grignard reagent
  - Hydrolysis of alkyl nitriles ii)
  - iii) Oxidation of primary alcohols

#### **Already Discussed Above**

2. Explain the structure of carboxylic acid. Repakcity.org



Ans. Structure of carboxylic acid is explained by hybrid orbital theory. The carbonyl carbon is sp<sup>2</sup> hybridized, possessing three sp<sup>2</sup> hybrid orbitals and one p<sub>z</sub> unhybridized orbital. These three sp<sup>2</sup> hybrid orbitals are oriented almost at an angle of 120° to give trigonal geometry whereas p₂ unhybridized orbital of carbonyl carbon form pi bond with p₂ orbital of oxygen atom.

3. Discuss the acidic nature of carboxylic acid. How is it stronger than other organic compounds and weaker than mineral acids?

#### **Already Discussed Above**

- Convert the followings:
  - Carboxylic acid into acid anhydride
  - Ester into carboxylic acid
  - Toluene into benzoic acid

ii) RCOOR + H<sub>2</sub>O ⇌ RCOOH + ROH

- iii) C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> + 3[O] ----KMnO<sub>4</sub>----> C<sub>6</sub>H<sub>5</sub>COOH + H<sub>2</sub>O
- 5. Explain the following physical properties of carboxylic acids: (b) Boiling point (a) Solubility

## **Already Discussed Above**

6. Write the names of four derivatives of carboxylic acids and give the equation for their preparation from acetic acid.

## **Already Discussed Above**