# **Fundamentals of Organic Chemistry CHEM 109**

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

**CHAPTER 7: Carboxylic Acids** 

### **Structure of Carboxylic Acids**

o The functional group common to all carboxylic acids is the carboxyl group.

The name is a contraction of the parts: the carbonyl and hydroxyl groups.

o The general formula for a carboxylic acid can be written in expanded or abbreviated forms.

- o Depending on whether an R or an Ar. residue is attached to the carboxyl group; Carboxylic acids are classified as;
  - Aliphatic Carboxylic Acids.

R-COOH (R = H or alkyl)  $CH_3$ -COOH Aliphatic acid Acetic acid

Aromatic Carboxylic Acids.

 $\label{eq:R} \begin{array}{ll} \text{Ar} & \text{—COOH} & (R = \mathrm{C_6H_{5}\text{--}}) \\ \text{Aromatic acid} & \end{array}$ 



### **Nomenclature of Carboxylic Acids**

#### **Common Names**

- o The common names of carboxylic acids all end in -ic acid.
- o These names usually come from some Latin or Greek word that indicates the original source of the acid.
- o Common name, substituents are located with Greek letters, beginning with the  $\alpha$ -carbon atom.

#### **IUPAC System**

o We replace the final **e** in the name of the corresponding alkane with the suffix **-oic** and add the word **acid**.

• IUPAC system, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way.

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### **Nomenclature of Carboxylic Acids**

Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, formica)	formic acid	methanoic acid
2	CH₃COOH	vinegar (Latin, acetum)	acetic acid	ethanoic acid
3	CH <sub>3</sub> CH <sub>2</sub> COOH	milk (Greek, protos pion, first fat)	propionic acid	propanoic acid
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	butter (Latin, butyrum)	butyric acid	butanoic acid
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	valerian root (Latin, <i>valere</i> , to be strong)	valeric acid	pentanoic acid
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH	goats (Latin, caper)	caproic acid	hexanoic acid
7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> COOH	vine blossom (Greek, oenanthe)	enanthic acid	heptanoic acid
8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH	goats (Latin, caper)	caprylic acid	octanoic acid
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> COOH	pelargonium (an herb with stork-shaped seed capsules; Greek, <i>pelargos</i> , stork)	pelargonic acid	nonanoic acid
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> COOH	goats (Latin, caper)	capric acid	decanoic acid

### **Nomenclature of Carboxylic Acids**

- o The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming.
- o The prefix oxo- is used to locate the carbonyl group of the aldehyde or ketone.

$$\begin{array}{c|ccccc} O & O & O \\ \parallel & 2 & 1 & 5 & \parallel 3 & 2 & 1 \\ HC - CH_2CO_2H & CH_3CCH_2CHCO_2H & H_3C-C=C-COO \\ \parallel & \parallel & \parallel & \parallel & \\ Br & But-2-enoic acid \\ 3-oxopropanoic acid & 2-bromo-4-oxopentanoic acid & (2-Butenoic acid) \end{array}$$

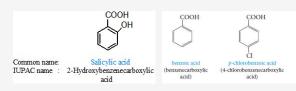
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### **Nomenclature of Carboxylic Acids**

Cycloalkane carboxylic acid

When the carboxyl group is attached to a ring, the ending -carboxylic acid is added to the name of the parent cycloalkane. (i.e. Cycloalkanecarboxylic acid)

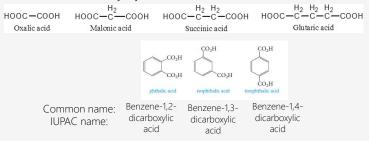
• Aromatic acids are named by attaching the suffix -oic acid or -ic acid to an appropriate prefix derived from the aromatic hydrocarbon.



#### **Nomenclature of Carboxylic Acids**

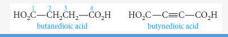
- o Dicarboxylic acids (acids that contain two carboxyl groups)
  - Common names.

They are known almost exclusively by their common names.



IUPAC system

They are given the suffix -dioic acid in the IUPAC system.



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## **Physical Properties of Acids**

- o Carboxylic acids are polar and they form hydrogen bonds with themselves or with other molecules.
- Carboxylic acids form dimer, with the individual units held together by two hydrogen bonds between the electron-rich oxygens and the electron-poor hydrogens.

#### **Boiling Points**

Therefore, they have high boiling points for their molecular weights-higher even those of comparable alcohols.

#### **Solubility in water**

Hydrogen bonding also explains the water solubility of the lower molecular weight carboxylic acids.

- The first four aliphatic acids (formic through butyric) are completely miscible in water.
- Aromatic acids are insoluble in water.

### **Physical Properties of Acids**

Structure	Name	Mol. Wt.	b.p. °C	Solubility in H₂O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH <sub>3</sub> CH <sub>2</sub> OH	Ethyl alcohol	46	78	Very soluble
CH <sub>3</sub> COOH	Acetic acid n-Propyl alcohol	60	118	Very soluble
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH		60	97	Very soluble
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	Valeric acid n-Hexyl alcohol	102	187	4.0 g/100 g H <sub>2</sub> O
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH2OH		102	156	0.6 g/100 g H <sub>2</sub> O
Ph-COOH	Benzoic acid	122	250	Insoluble
Ph-CH <sub>2</sub> CH <sub>2</sub> OH	3-Phenylethanol	122	250	Insoluble

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### **Acid Strength and Structure**

o Carboxylic acids (RCOOH) dissociate in water, yielding a carboxylate anion (RCOO-) and hydronium ion.

#### Why carboxylic acids are more acidic than alcohols?

- In ethoxide ion, the negative charge is localized on a single oxygen atom.
- In acetate ion, on the other hand, the negative charge can be delocalized through resonance.

$$\begin{array}{c} CH_3CH_2\overset{\cdots}{O}H & \stackrel{\longrightarrow}{\longleftarrow} CH_3CH_2\overset{\cdots}{O}:^- + H^+ \\ & \text{ethoxide ion} \\ \\ \vdots \overset{\circ}{O}: & \vdots \overset{\circ}{O}: \\ CH_3\overset{\cdots}{C}-\overset{\cdots}{O}H & \stackrel{\longrightarrow}{\longleftarrow} CH_3\overset{\cdots}{C}-\overset{\cdots}{O}:^- + H^+ \\ \\ \end{array}$$

$$\begin{bmatrix} \text{CH}_3 - \text{C} & \text{CH}_3 - \text{C} & \text{CH}_3 - \text{C} & \text{CH}_3 - \text{C} & \text{C} &$$

### **Acid Strength and Structure**

#### **Effect of Structure on Acidity; the Inductive Effect**

- o Acidities can vary depending on what other groups are attached to the molecule.
- o Recall that electron-withdrawing groups (-I) enhance acidity, and electron-releasing groups (+I) reduce acidity.

This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms.

$$_{O_2N}$$
  $\stackrel{\text{COOH}}{\longrightarrow}$   $>$   $\stackrel{\text{COOH}}{\longrightarrow}$   $>$   $\stackrel{\text{COOH}}{\longrightarrow}$   $>$   $\stackrel{\text{COOH}}{\longrightarrow}$ 

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#### **Acid Strength and Structure**

#### **Effect of Structure on Acidity; the Inductive Effect**

- o Formic acid is a substantially stronger acid than acetic acid.
  - This suggests that the methyl group is more electron-releasing (hence anion-destabilizing and acidity-reducing) than hydrogen.

$$\verb|HCOOH>CH_3COOH>CH_3CH_2COOH>CH_3CH_2COOH|\\$$

• Example: acetic acid with those of mono-, di-, and trichloroacetic acids. Comparison of acid strengths of acetic Acid and chlorinated acetic acids

### **Acid Strength and Structure**

#### **Effect of Structure on Acidity; the Inductive Effect**

The more chlorines, the greater the effect and the greater the strength of the acid.

o Comparison of acid strengths of butyric acid and the monochlorinated acids.

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### 1) Hydrolysis of Cyanides (Nitriles)

## **Preparation** of Acids

- o The reaction requires either acid or base.
  - In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.

• In base, the nitrogen atom is converted to ammonia and the organic product is the carboxylate salt, which must be neutralized in a separate step to give the acid.

$$R-C \equiv N+2 \text{ H}_2\text{O} \xrightarrow[a \text{ carboxylate salt}]{\text{NaOH}} R-C-O^-\text{Na}^+ + \text{NH}_3$$

o Alkyl cyanides are generally made from the corresponding alkyl halide.

$$\begin{array}{cccc} CH_3CH_2CH_2Br & \xrightarrow{NaCN} & CH_3CH_2CH_2CN & \xrightarrow{H_2O} & CH_3CH_2CH_2CO_2H + NH_4^+ \\ propyl bromide & butyronitrile & butyric acid \\ (1-bromopropane) & (butanenitrile) & (butanoic acid) \\ \end{array}$$

## 2) Reaction of Grignard Reagents with Carbon Dioxide (Carbonation of Grignard Reagent)

## **Preparation** of Acids

- Grignard reagents add to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCI.
- o The acid obtained has one more carbon atom (the reaction provides a way to increase the length of a carbon chain).

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### 1) Reactions with Bases: Salt Formation

## Reactions of Acids

o Carboxylic acids, when treated with a strong base, form carboxylate salts.

o Examples.

## 2) Nucleophilic Substitution Reactions

# Reactions of Acids

$$\begin{array}{c|c} & CH_3OH / H^{\textcircled{\tiny }} & R - C - OCH_3 \\ \hline & Ester & \\ & &$$

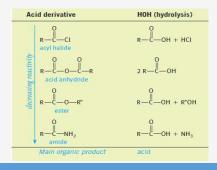
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### **Carboxylic Acid Derivatives**

o Carboxylic acid derivatives are compounds in which the hydroxyl part of the carboxyl group is replaced by various other groups.

$$\begin{array}{c|cccc} O & O & O & O & O & O \\ R-C-OR' & R-C-X & (Cl \ or \ Br) & R-C-O-C-R & R-C-NH; \\ ester & acyl halide & acid anhydride & primary amide \\ \end{array}$$

o All acid derivatives can be hydrolyzed to the corresponding carboxylic acid.



#### **Acid Chloride**

## Carboxylic Acid Derivatives

- o Acyl chlorides have the general formula RCOCI.
- o Acyl chlorides are more common and less expensive than bromides or iodides.
- Nomenclature:

Acyl chlorides, or acid chlorides, are named by replacing the <u>-ic acid</u> ending of the parent acid by <u>-yl chloride</u>.

Preparation:

They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.

$$\begin{array}{c} O \\ \parallel \\ R-C-OH+SOCl_2 \longrightarrow R-C-Cl+HCl+SO_2 \\ \\ O \\ R-C-OH+PCl_5 \longrightarrow R-C-Cl+HCl+POCl_3 \\ \end{array}$$

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#### **Acid Chloride**

## Carboxylic Acid Derivatives

• **Reactions:** They can react rapidly with most nucleophile.

$$\begin{array}{c} \text{NH}_{2}\text{O} \\ \text{R-C-Cl} \end{array} \xrightarrow{\text{H}_{2}\text{O}} \begin{array}{c} \text{RCO}_{2}\text{H} + \text{HCl} \\ \text{Acid} \\ \text{RCO}_{2}\text{R}' + \text{HCl} \\ \text{Ester} \end{array}$$

Examples:

$$\begin{array}{c|c} O & O \\ \parallel & \square \\ CH_3-C-Cl + HOH \xrightarrow{rapid} & CH_3-C-OH + HCl \\ acetyl chloride & acetic acid & (fumes) \\ \hline \\ O & \square \\ -C-Cl + CH_3OH \xrightarrow{room temp.} & \square \\ \hline \\ D & \square \\ -C-OCH_3 + HCl \\ \hline \\ D & \square \\ \\ D & \square \\ D & \square$$

#### **Esters**

## Carboxylic Acid Derivatives

- Esters are derived from acids by replacing the –OH group by an –OR group and have the general formula R/COOR.
- Nomenclature:
  - They are named in a manner analogous to carboxylic acid salts.
  - The R part of the —OR group is name first, followed by the name of the acid, with the —ic acid ending changed to —ate.

#### Preparation:

When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (HCl or  $H_2SO_4$ ), an equilibrium is established with the ester and water.

$$\begin{array}{c} O \\ \parallel \\ R-C-OH+HO-R' \xrightarrow{H^+} R-C-OR'+H_2O \\ acid & alcohol & ester \end{array}$$

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#### **Esters**

## **Carboxylic Acid Derivatives**

#### Reactions

• Cyclic esters (lactones) can be prepared from hydroxy acids if these groups can come in contact through bending of the chain.

• Saponification; esters are commonly hydrolyzed with base.

$$R - COP + Na^{+}HO^{-} \xrightarrow{heat} R - COP + R'OH$$
ester nucleophile salt of an acid alcohol

Ammonia converts esters to amides.

$$R - C \underset{\text{ester}}{ \bigcirc O} + \overset{\text{O}}{\text{NH}}_3 \longrightarrow R - C \underset{\text{amide}}{ \bigcirc O} + R'OH$$

#### **Amides**

## Carboxylic Acid Derivatives

- o Amides are the least reactive of the common carboxylic acid derivatives.
- o Primary amides have general formula RCONH<sub>2</sub>.
- Nomenclature:

Amides are named by replacing the  $\underline{-ic}$  or  $\underline{-oic}$  acid  $\underline{acid}$  ending of the acid name, either the common or the IUPAC name, with the  $\underline{-amide}$  ending.

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### **Amides**

## Carboxylic Acid Derivatives

#### Preparation:

- They can be prepared by the reaction of ammonia with esters, with acyl halides, or with acid anhydrides.
- Amides can also prepared by heating the ammonium salts of acids.

$$\begin{array}{c} O \\ \parallel \\ R-C-OH+NH_3 \longrightarrow \begin{array}{c} O \\ \parallel \\ R-C-O^-NH_4^+ \xrightarrow{heat} \begin{array}{c} O \\ \parallel \\ R-C-NH_2 + H_2O \end{array} \end{array}$$

#### Reactions

• Amides react with nucleophiles and they can be hydrolyzed by water.

$$\begin{array}{c} O \\ \parallel \\ R-C-NH_2+H-OH \xrightarrow{H^+or} R-C-OH+NH_3 \\ \text{amide} \end{array}$$

• Amides can be reduced by lithium aluminums hydride to give amines.

### **Acid Anhydrides**

## Carboxylic Acid Derivatives

- o Acid anhydrides have general formula RCOOCOR.
- Nomenclature:

The name of an anhydrides is obtained by naming the acid from which is derived and replacing the word acid with anhydride.

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### **Acid Anhydrides**

## Carboxylic Acid Derivatives

- Preparation
  - Acid anhydrides are derived from acids by removing water from two carboxyl groups and connecting the fragments.

$$\begin{array}{c|cccc} O & O & O & O \\ \parallel & \parallel & \parallel & \parallel & \parallel \\ R-C-OH & HO-C-R & R-C-O-C-R \\ two acid molecules & an acid anhydride \end{array}$$

Anhydrides can also be prepared from acid chlorides and carboxylate salts.
 This method is used for preparing anhydrides derived from two different carboxylic acids (mixed anhydrides).

$$CH_3CH_2CH_2 - C - Cl + Na^{+-}O - C - CH_3 \longrightarrow CH_3CH_2CH_2 - C - O - C - CH_3 + NaCl$$

## **Acid Anhydrides**

# Carboxylic Acid Derivatives

#### Reactions

• Anhydrides undergo nucleophilic acyl substitution reactions (*They are more reactive than esters, but less reactive than acyl halides*).

$$CH_{3}C - OH + CH_{3}C - OH$$

$$CH_{3}C - OR + CH_{3}C - OH$$

$$CH_{3}C - OH + CH_{3}C - OH$$

$$CH_{3}C - OH + CH_{3}C - OH$$

$$CH_{3}C - OH + CH_{3}C - OH$$

$$CH_{3}C - OH$$