Organic Chemistry
CHEM 145

2 Credit hrs

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Carboxylic Acids

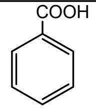
- **All carboxylic acids contain the carboxyl group, -COOH.**
- **Depending on whether an R or an Ar. residue is attached to the carboxyl group; Carboxylic acids are classified as aliphatic or aromatic.**
  - **Aliphatic Carboxylic Acids.**

R−COOH (R = H or alkyl)
Aliphatic acid

CH_3—COOH
Acetic acid

  - **Aromatic Carboxylic Acids.**

Ar—COOH ($R = C_6H_5$-)
Aromatic acid



Benzoic acid

Nomenclature of Carboxylic Acids

- The **common names** of carboxylic acids all end in *-ic acid*.

For example

- **Formic acid** is the acid that gives the characteristic sting to an ant bite (from the Latin *formica,* ant).
- **Acetic acid** is vinegar (from the Latin *acetum,* vinegar).
- **Butyric acid** is the compound that gives rancid butter its putrid smell (from the Latin *butyrum,* butter).
- **Fatty acids.**
  Long straight-chain carboxylic acids with even numbers of carbons, which were first isolated from fats and waxes.

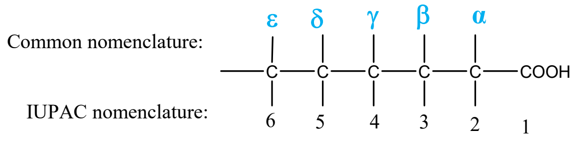
IUPAC System

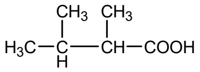
- The ending *-e* of the corresponding alkane is replaced by *-oic acid*.
- For example

  HCOOH is called *methanoic acid*.

  CH_3COOH is called *ethanoic acid*.

- If substituents are present on the acid chain.
  - Common nomenclature
    Their positions are located by Greek letters; α, β, γ, δ, ε,….etc
  - IUPAC system
    Numbers are used and the carboxylic carbon is numbered 1.





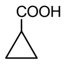
Common nome: a,B-Dimethylbutyric acid
IUPAC nomenclature: 2,3-Dimethylbutanoic acid

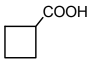
IUPAC and Common Names of Some Normal carboxylic Acids.

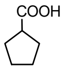
No. of carbon atoms	Formula	IUPAC name	Common name
1	HCOOH	Methanoic acid	Formic acid
2	CH_3COOH	Ethanoic acid	Acetic acid
3	CH_3CH_2COOH	Propanoic acid	Propionic acid
4	$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid
5	$CH_3(CH_2)_3COOH$	Pentanoic acid	Valeric acid

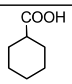
Cylcoalkane carboxylic acid

When the carboxyl group is attached to a saturated ring.

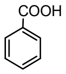
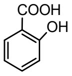

Cyclopropanecarboxylic acid


Cyclobutanecarboxylic acid


Cyclopentanecarboxylic acid


Cyclohexanecarboxylic acid

Aromatic carboxylic acids are generally called by their common names.

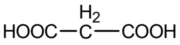



Common name:	Benzoic acid	Salicylic acid
IUPAC name:	Benzenecarboxylic acid (used as germicide and as food preservative)	2-Hydroxybenzenecarboxylic acid (raw material for aspirin)

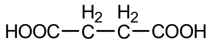
Dicarboxylic acids (acids that contain two carboxyl groups) are known almost exclusively by their common names.

HOOC—COOH

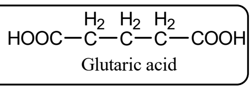
Oxalic acid


$HOOC-\overset{H_2}{C}-COOH$

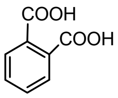
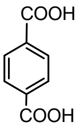
Malonic acid


$HOOC-\overset{H_2}{C}-\overset{H_2}{C}-COOH$

Succinic acid


$HOOC-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-COOH$

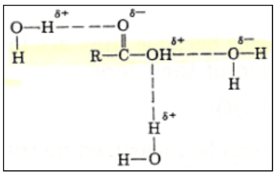
Glutaric acid

Common name:	Phthalic acid	Terephthalic acid
IUPAC name:	Benzene-1,2-dicarboxylic acid (medicinal uses; synthetic perfumes)	Benzene-1,4-dicarboxylic acid (constituent of Dacron)

Physical Properties of Carboxylic Acids

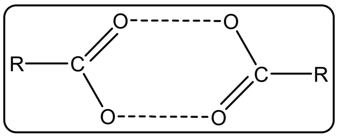
Carboxylic acids are capable of hydrogen bonding .



- Solubility in water.
  - The first four aliphatic acids (formic through butyric) are completely miscible in water.
  - Higher members of the series are less soluble because the long alkyl chain gives them alkane like characteristics.
  - Aromatic acids are insoluble in water.
- Boiling points.
  - The boiling points of carboxylic acids indicate a greater degree of association than for alcohols of comparable molecular weights.
  - For example,

    Acetic acid (mol wt = 60) boils at 118°C.

    n-Propyl alcohol (mol wt = 60) boils at only 97° C.
  - In fact, simple carboxylic acids exist as *hydrogen-bonded dimers* .



- The first nine aliphatic acids are colorless liquids that have sharp, acrid odors.
- Pure acetic acid is called *glacial acetic acid*

  because it solidifies into ice-1ike crystals at temperatures slightly below normal room temperature (about 17°C).
- Butyric acid smells like rancid butter and strong cheese.
- Acids of five to ten carbons have goat-like smells because they are present in the skin secretion of goats.
- Higher acids are wax-like solids and are practically odorless.
- Aromatic acids are also high-melting odorless solids.

Some Physical Properties of Acids and Alcohols of Corresponding Molecular Weights.

Structure	Name	Mol. Wt.	b.p. °C	Solubility in H_2O at 25°C
HCOOH	Formic acid	46	100	Very soluble
CH_3CH_2OH	Ethyl alcohol	46	78	Very soluble
CH_3COOH	Acetic acid	60	118	Very soluble
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	60	97	Very soluble
$CH_3(CH_2)_3COOH$	Valeric acid	102	187	4.0 g/100 g H_2O
$CH_3(CH_2)_4CH2OH$	*n*-Hexyl alcohol	102	156	0.6 g/100 g H_2O
Ph-COOH	Benzoic acid	122	250	Insoluble
Ph-CH_2CH_2OH	3-Phenylethanol	122	250	Insoluble

Acid Strength

- **The strength of an acid depends on the extent it ionizes.**
- **Common mineral acids, such as HCl or HNO_3, ionize completely and are considered therefore to be strong acids.**

$$\boxed{HCl \longrightarrow H^+ + Cl^-}$$

- **Carboxylic acids are weak acids.**

  Because they are incompletely ionized and exist in equilibrium with a solution of their ions.

$$\boxed{RCOOH \longrightarrow H^+ + RCOO^-}$$

Acid Strength and Acid Structure

- **Carboxylic acids are much more acidic than are alcohols even though both classes of compounds contain an OH group.**
  - **Why is this so?**

    The structures of their conjugate bases, the carboxylate anion and the alkoxide anion,

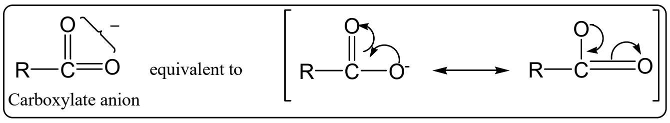
$\text{RCOOH} \longrightarrow \text{RCOO:}^{-} + \text{H}^{+}$

Carboxylic acid — Carboxylate anion

$\text{ROH} \longrightarrow \text{RO:}^{-} + \text{H}^{+}$

Carboxylic acid — Alkoxide anion

- **Carboxylic acids are stronger acid than alcohols because *Carboxylate anions are stabilized by resonance* and Alkoxide anions are not.**



- **Acid strength among carboxylic acids.**
  - **Generally, any factor that *stabilizes* the carboxylate anion of an acid will give it *greater* acid strength than an acid lacking that factor.**
  - **Conversely, any factor that *destabilizes* the carboxylate anion of an acid will make that acid *less* strong.**
- **The stronger acid is the one with the electron-withdrawing group compared to unsubstituted acid.**

  By dispersing the negative charge.

- **Examples of common electron-withdrawing, and acid-strengthening, groups are**

F, Cl, Br, NO_2, CN, SO_3H, COOH

Acid-strengthening substituents

- **Addition of any electron-donating substituent on the R (or Ar) portion of an acid decreases its acid strength relative to the parent unsubstituted acid.**
  - **The electron-donating group destabilizes the carboxylate anion.**

    By intensifying the negative charge.

- **The most common electron-donating, acid-weakening substituent is** *the alkyl group (methyl, ethyl, propyl, and so on.*
- **Formic acid (no alkyl group) is a stronger acid than acetic acid (one alkyl group).**

Comparison of Acid Strengths of Acetic Acid and Chlorinated Acetic Acids

Name	Structure	pK_a	Relative acid strength
Acetic acid	CH_3COOH	4.7	1
Chloroacetic acid	$ClCH_2COOH$	2.8	80
Dichloroacetic acid	$Cl_2CHCOOH$	1.3	2800
Trichloroacetic acid	Cl_3CCOOH	0.7	11000

Comparison of Acid Strengths of Butyric Acid and the Monochlorinated Acids

Name	Structure	pK_a	Relative acid strength
Butyric acid	$CH_3CH_2CH_2COOH$	4.82	1
α-Chlorobutyric acid	$CH_3CH_2CHClCOOH$	2.85	92
β-Chlorobutyric acid	$CH_3CHClCH_2COOH$	4.05	6
γ-Chlorobutyric acid	$ClCH_2CH_2CH_2COOH$	4.52	2

Preparation of Carboxylic Acids

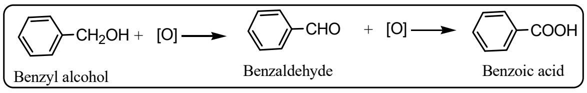
Preparation of Acids by Oxidation

A. Oxidation of Primary Alcohols or Aldehydes

- **Primary alcohols are oxidized to carboxylic acids by potassium permanganate, $KMnO_4$, or by a mixture of potassium dichromate, $K_2Cr_2O_7$, and sulfuric acid.**

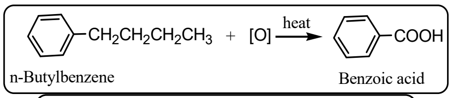
$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + [O] \longrightarrow CH_3COOH$$

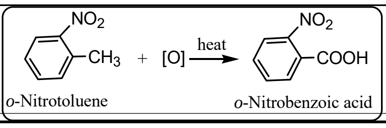
Ethyl alcohol — Acetaldehyde — Acetic acid



B. Oxidation of Alkylbenzenes

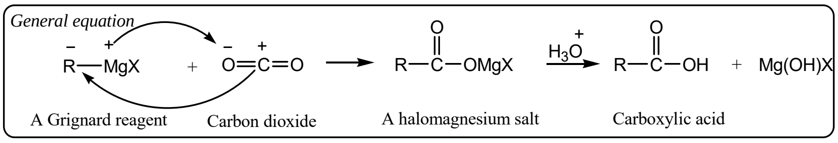
- **Vigorous oxidation of alkylbenzenes yields benzoic acid.**

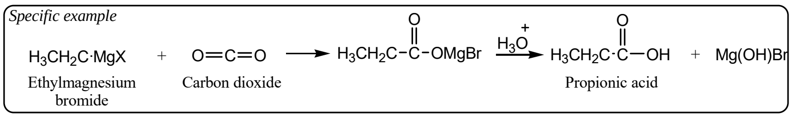




Carbonation of Grignard Reagents

- The addition of Grignard reagents to CO_2 in the form of dry ice proceeds in a similar fashion and yields the halomagnesium salt of a carboxylic acid.
- Hydrolysis of the salt gives an acid with one carbon more than the original Grignard reagent

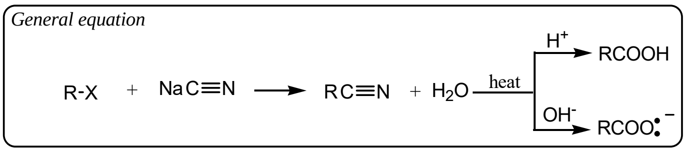


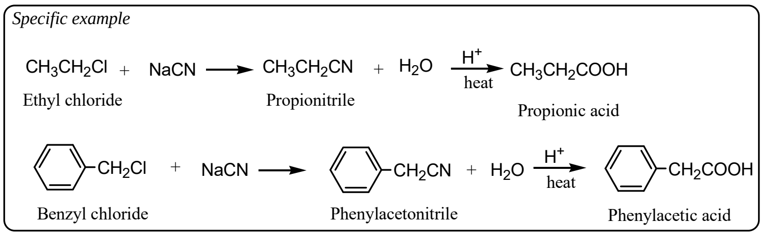


Hydrolysis of Nitriles

- Nitriles are compounds with the general formula RCN or ArCN.
- They are prepared by reacting a 1° or 2° alkyl halide with a cyanide salt.

- Acid hydrolysis of a nitrile yields a carboxylic acid. Alkaline hydrolysis yields a carboxylate salt.
- The carboxylate acid or salt contain one carbon more than the starting alkyl halide.





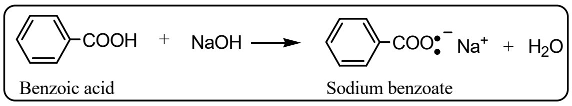
Reactions of Carboxylic Acids

Reactions with Bases: Salt Formation

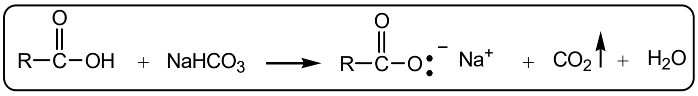
- Carboxylic acids react quantitatively with bases to form water-soluble salts.
- The metal cation is named first, followed by the name of the carboxylate anion.
- The latter is named by dropping the *-ic acid* ending from the name of the parent acid and replacing it with *–ate*.

$$\underset{\text{Formic acid}}{HCOOH} + KOH \longrightarrow \underset{\text{Potassium formate}}{HCOO^{-}\ K^{+}} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COO^{-}\ Na^{+}} + H_2O$$

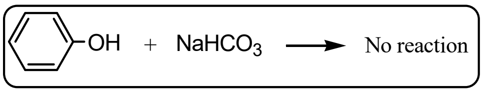


- Carboxylic acids will also react with a weak base like sodium bicarbonate, $NaHCO_3$, to form
  - Water-soluble salts.
  - Carbon dioxide is liberated as a by-product.



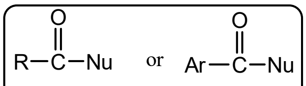
$$R-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{-}\ Na^{+} + CO_2\uparrow + H_2O$$

- Weaker acids like phenols react only with strong bases (NaOH or KOH) and will not react with $NaHCO_3$.



Carboxylic Acid Derivatives

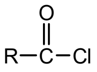
- When the OH of a carboxylic acid is replaced by a nucleophile, : Nu, a carboxylic acid derivative is produced.



$\mathrm{R-\overset{\overset{O}{\|}}{C}-Nu}$ or $\mathrm{Ar-\overset{\overset{O}{\|}}{C}-Nu}$

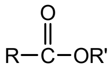
Carboxylic acid derivatives

- The RCO- portion of acid derivatives is called the acyl group. Aromatic acid derivatives contain the aryl group.
- The carboxylic acid derivatives are



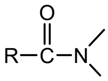
$\mathrm{R-\overset{\overset{O}{\|}}{C}-Cl}$

Acyl chloride
Acid chloride



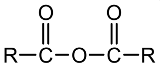
$\mathrm{R-\overset{\overset{O}{\|}}{C}-OR'}$

Ester



$\mathrm{R-\overset{\overset{O}{\|}}{C}-N<}$

Amide

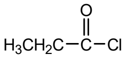
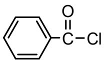


$\mathrm{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R}$

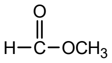
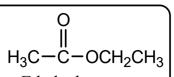
Acid anhydride

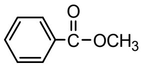
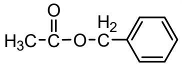
Nomenclature of Acid Derivatives

- Acyl chlorides, or acid chlorides, are named by replacing the *-ic acid* ending of the parent acid by *-yl chloride*.

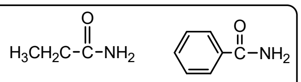
	 $\mathrm{H_3CH_2C-\overset{\overset{O}{\|}}{C}-Cl}$	
IUPAC name:	Propanoyl chloride	Benzoyl chloride
Common name:	Propionyl chloride	

- Esters are named as if they were formed from replacement of the carboxyl hydrogen by an alkyl group.
  - The alkyl group is named first followed by the name of the parent acid with the ending *-ate* in place of *-ic acid*.

	 $\mathrm{H-\overset{\overset{O}{\|}}{C}-OCH_3}$	 $\mathrm{H_3C-\overset{\overset{O}{\|}}{C}-OCH_2CH_3}$
IUPAC name:	Methyl methanoate	Ethyl ethanoate
Common name:	Methyl formate	Ethyl acetate

		
IUPAC name:	Methyl benzoate	Benzoyl ethanoate
Common name:		Benzyl acetate

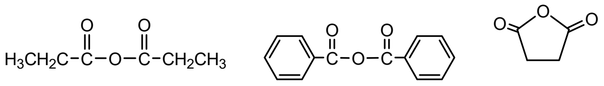
Amides are named by replacing the *-oic acid* or *-ic acid* of the parent acid's name by *–amide*.



IUPAC name:	Propanamide	Benzamide
Common name:	Propionamide	

IUPAC name:	*N*,*N*-Dimethylethanamide	*N*-Ethyl-*N*-methylmethanamide
Common name:	*N*,*N*-Dimethylacetamide	*N*-Ethyl-*N*-methylformamide

An **anhydride** is named by replacing the word *acid* with *anhydride* in the name of the acid from which it was formed.



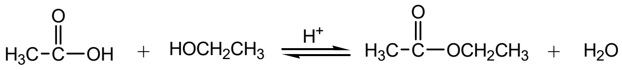
IUPAC name:	Propanoic anhydride	Benzoic anhydride	Succinic anhydride
Common name:	Propionic anhydride		

Esters from Carboxylic Acids: Esterfication

Esters are formed by treatment a carboxylic acid with a primary or secondary alcohol.

A small amount of mineral acid catalyst (H^+) is required to speed up esterification.

Specific example



$$H_3C-\overset{\overset{O}{\|}}{C}-OH + HOCH_2CH_3 \overset{H^+}{\rightleftharpoons} H_3C-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + H_2O$$

Acetic acid

Ethyl alcohol

Ethyl acetate