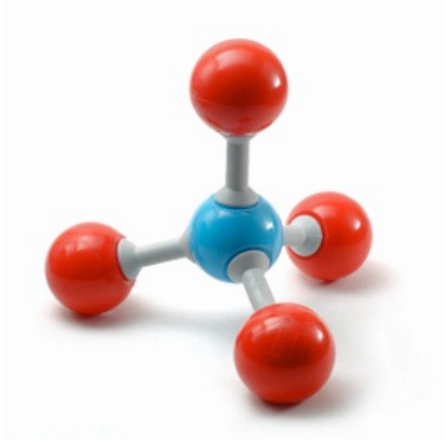
Ch14

Carboxylic Acids

Combining the hydroxyl and carbonyl functional groups.

To make more powerful functional groups.



version 1.0

Ch14

Carboxylic Acids & Esters

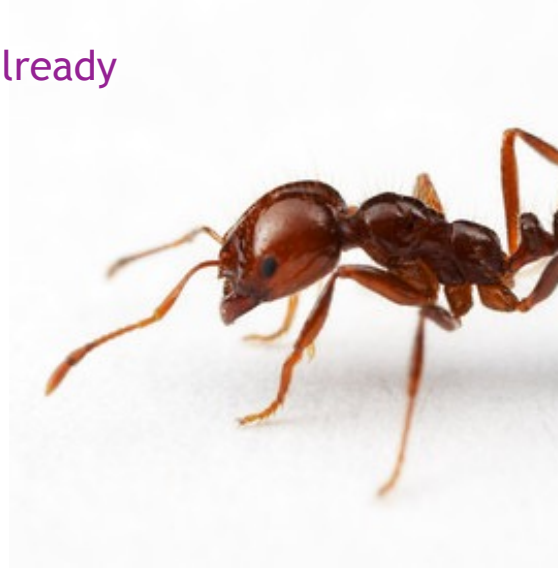
- Carboxylic Acids
  - Carboxyl Group
    - Compound Functional Groups
  - Properties & Structure
    - IM Forces
    - Acid-Base
  - Naming
    - Carboxylic Acids
    - Carboxylic Acid Salts
- Mixing Functional Groups
  - Adding/Changing Properties
  - Naming Substances w/ multiple functional groups
  - Willow Bark
- Esters
  - Structure & Properties
  - Naming
- Reactions
  - Esterification
  - Hydrolysis
  - Saponification

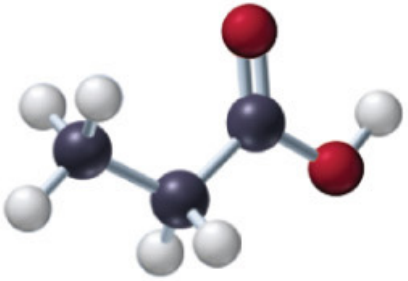
Carboxylic Acids

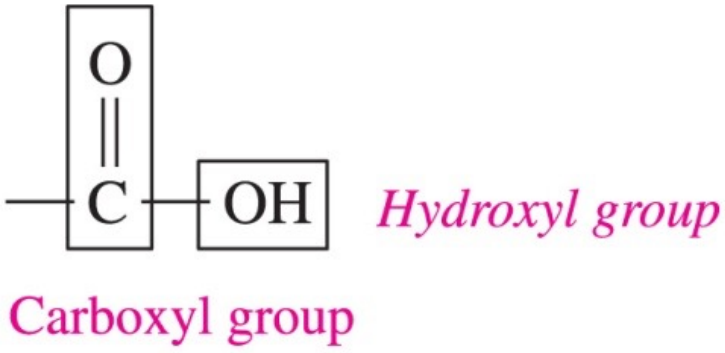
- Carboxylic Acids have many interesting properties.
  - Many of the sharp flavors we enjoy in food (vinegar, grapefruit, lemon…) are produced by simple substances of the carboxylic acid family of organic substances.
  - These organic molecules are acids. Like the simple binary acids you're already familiar with (HCl, HBr) they release free protons (H^+).
    - These substances have high acidity (low pH).
    - They neutralize bases like NaOH to form water.
  - Many toxins are simple carboxylic acids, like the formic acid in ant venom.
  - Salts formed from carboxylic acids cause food to be resistant to mold and microorganisms that cause spoilage.
  - They play important roles in how animals store and process energy.

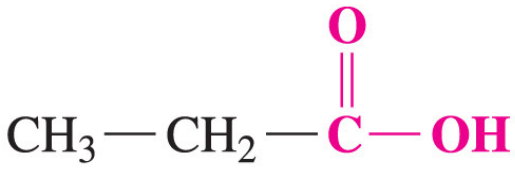
Carboxyl Functional Group

- Carboxylic Acids are defined by the carboxyl functional group.
  - The carboxyl group is a composite of two functional groups you're already familiar with.
    - The hydroxyl group.
    - The carbonyl group.









Carboxyl Functional Group

- Carboxylic Acids are defined by the carboxyl functional group.
  - The carboxyl group is a composite of two functional groups you're already familiar with.
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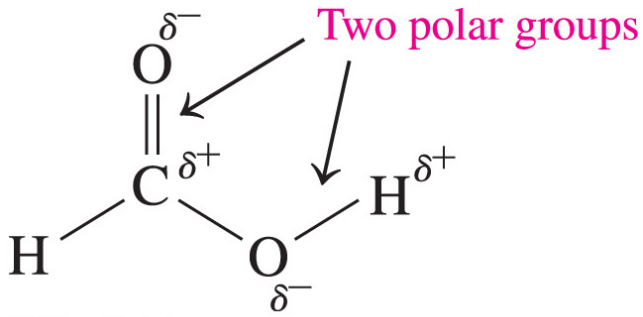
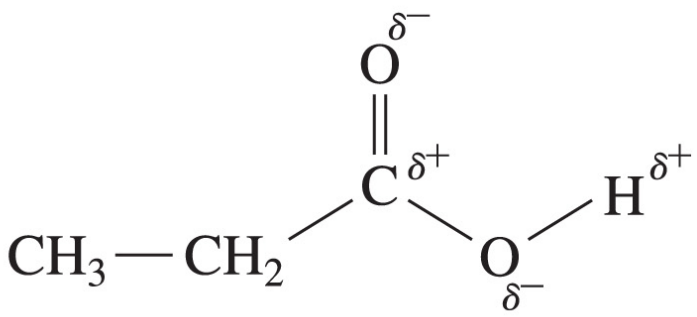
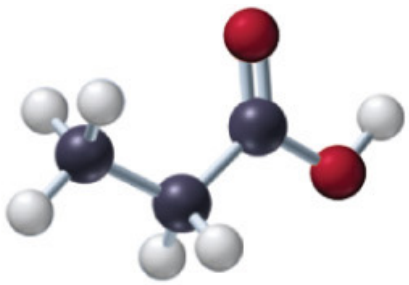
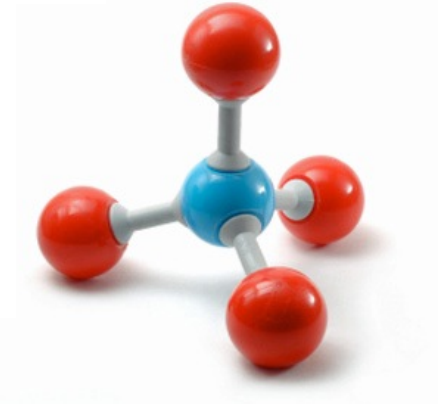
  - Carboxylic acids are strongly polar because they have two polar groups.









Ch14

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    - Compound Functional Groups
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Carboxyl Functional Group

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  - The carboxyl group is a composite of two functional groups you're already familiar with.
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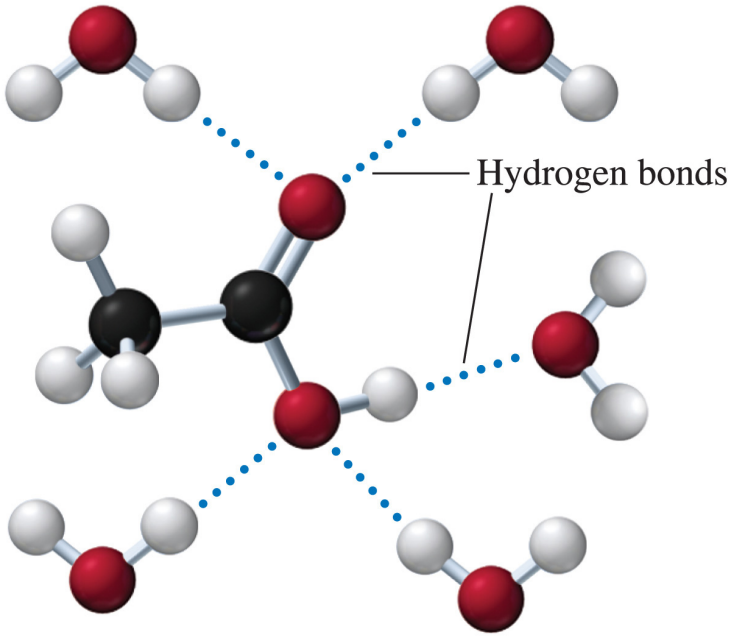
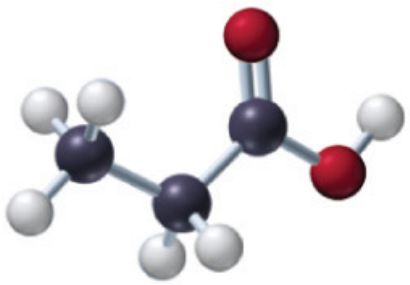
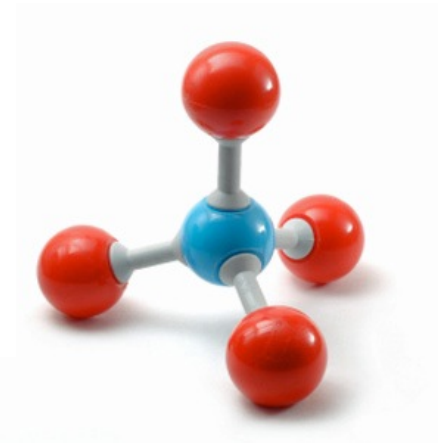
      - Both of those groups are polar.
  - Carboxylic acids are strongly polar because they have two polar groups.
  - Each carboxylic acids forms hydrogen bonds with many water molecules at once.
  - Carboxylic acids with up to four carbon atoms are very soluble in water
    - As the number of carbons increases, the solubility of the carboxylic acid in water is reduced.







Properties & Structure

- Carboxylic Acids are defined by the carboxyl functional group.
  - The carboxyl group is a composite of two functional groups you're already familiar with.
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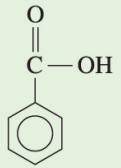
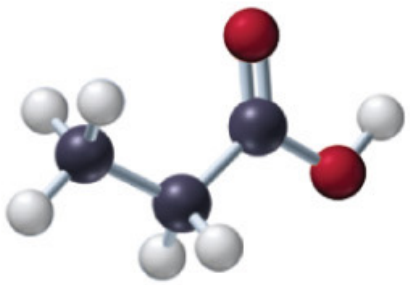
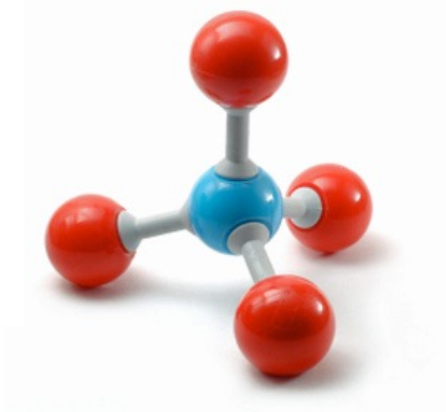
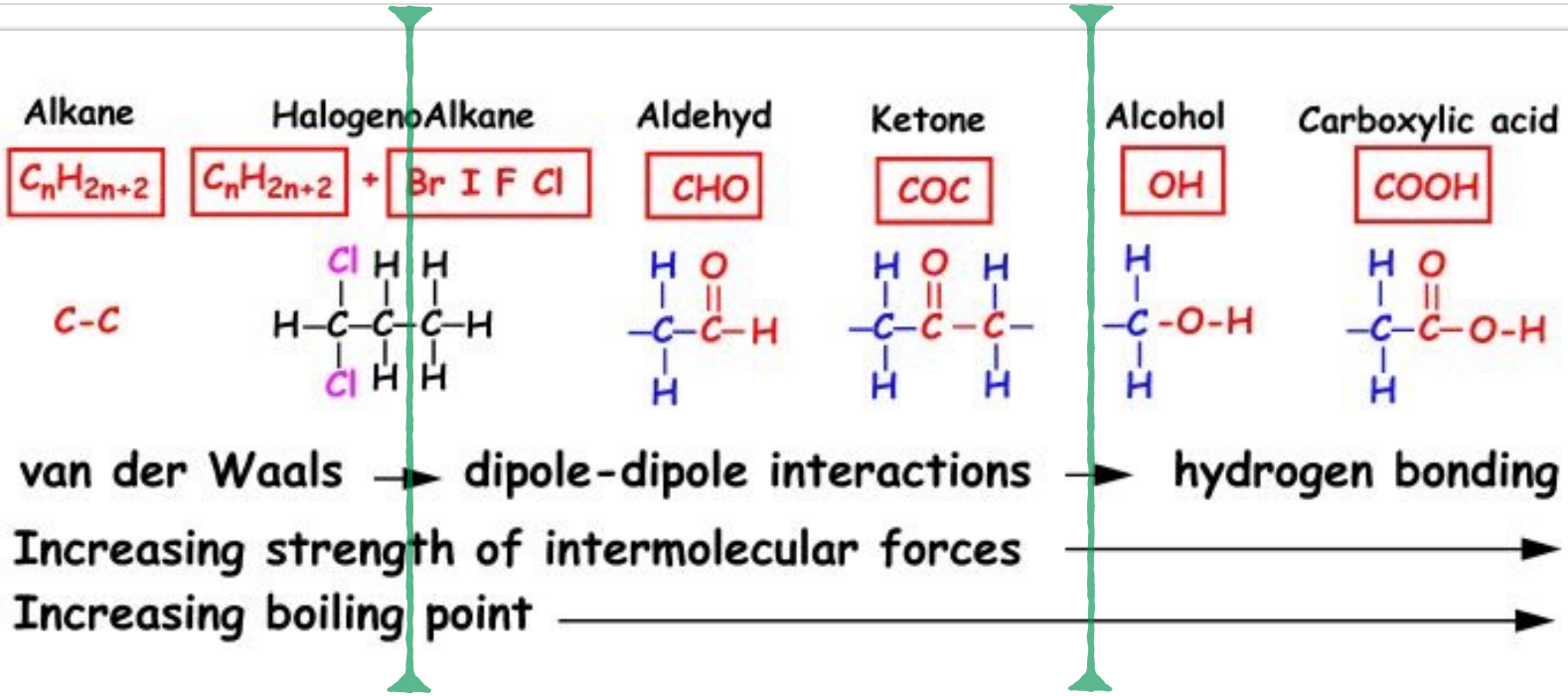
IUPAC Name	Condensed Structural Formula	Solubility in Water
Methanoic acid	$H-\overset{\overset{O}{\|\|}}{C}-OH$	Soluble
Ethanoic acid	$CH_3-\overset{\overset{O}{\|\|}}{C}-OH$	Soluble
Propanoic acid	$CH_3-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$	Soluble
Butanoic acid	$CH_3-CH_2-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$	Soluble
Pentanoic acid	$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$	Soluble
Hexanoic acid	$CH_3-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$	Slightly soluble
Benzoic acid		Slightly soluble

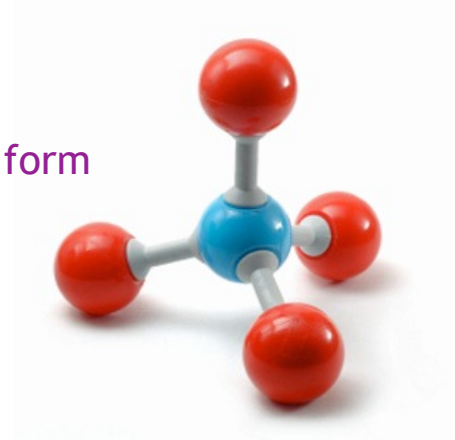




Properties & Structure



- Carboxylic Acids experience all three kinds of intermolecular forces:
  - Van der Waals Forces
  - Dipole-Dipole Forces
  - Hydrogen Bonding
- Because carboxylic acids have both a hydroxyl and carbonyl group they form more hydrogen bonds than alcohols.
- Carboxylic Acids have higher boiling points and melting points than even alcohols.



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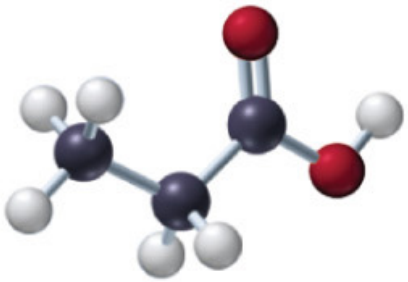
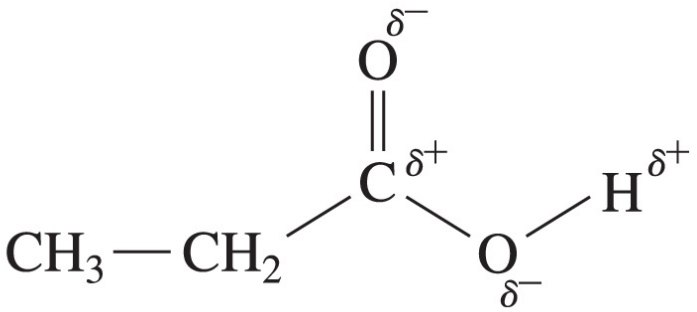
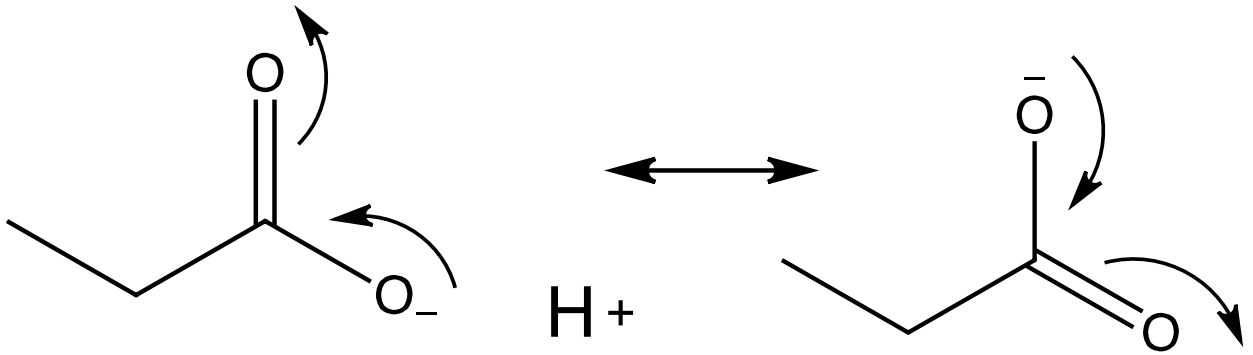
Properties & Structure

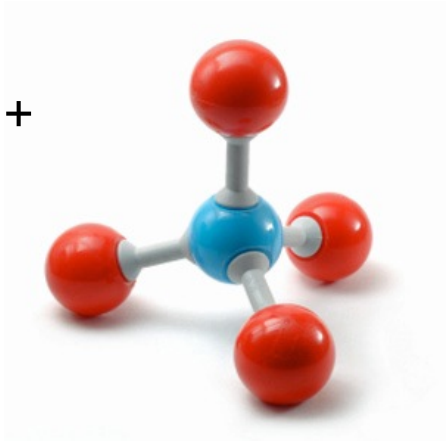
- Carboxylic Acids are defined by the carboxyl functional group.
  - Carboxylic acids are strongly polar because they have two polar groups.
  - The two polar groups cooperate to balance negative charge, stabilizing the molecule enough to allow it to release protons.
    - To act as an organic acid.







H+



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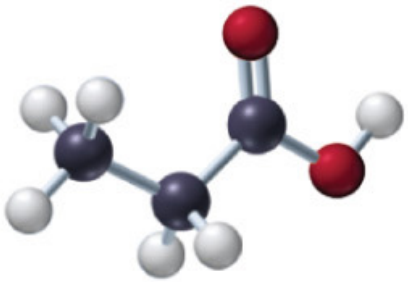
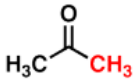
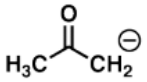
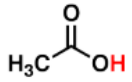
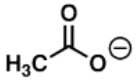
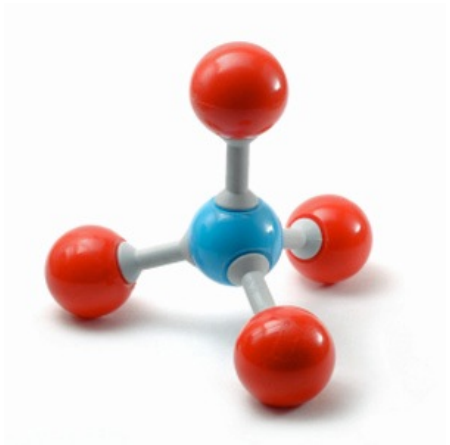


Functional group	Example	pKa	Conjugate Base
Alkane	H_3C–CH_3	~50	H_3C–$CH_2^{\ominus}$
Alkene		~43	
Ketone/ aldehyde		20-24	
Alcohol	H_3C–OH	17	H_3C–$O^{\ominus}$
Water	HO–H	16	$HO^{\ominus}$
Thiols	CH_3S–H	13	$CH_3S^{\ominus}$
Carboxylic acids		4	
Sulfuric acid	H_2SO_4	–3	$HSO_4^{\ominus}$
Hydrochloric acid	HCl	–6	$Cl^{\ominus}$



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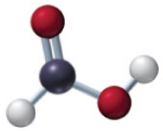
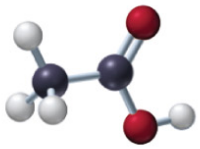
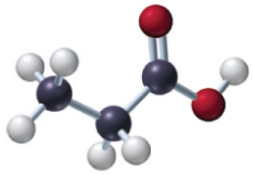
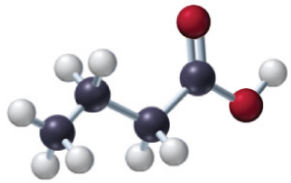
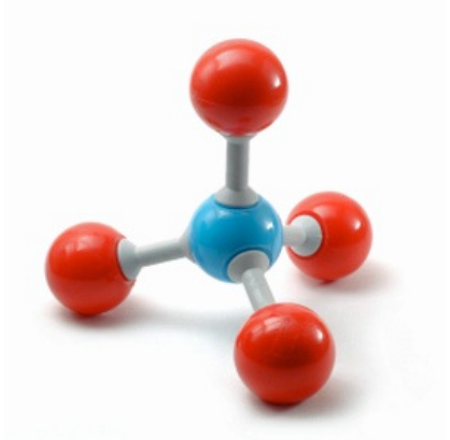
Naming Carboxylic Acids

- The simplest carboxylic acids are formic acid and acetic acid.
- Carboxylic acids are named with IUPAC using the family suffix -oic acid.

Condensed Structural Formula	IUPAC Name	Common Name	Ball-and-Stick Model
$H-\overset{\overset{O}{\|}}{C}-OH$	Methanoic acid	Formic acid	
$CH_3-\overset{\overset{O}{\|}}{C}-OH$	Ethanoic acid	Acetic acid	
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$	Propanoic acid	Propionic acid	
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$	Butanoic acid	Butyric acid	



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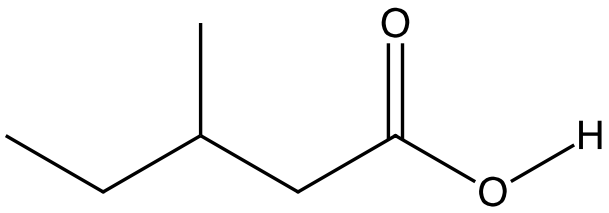
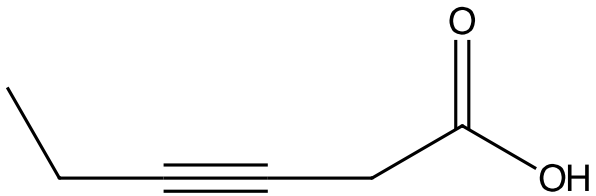
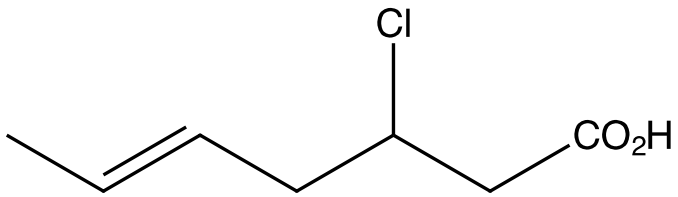


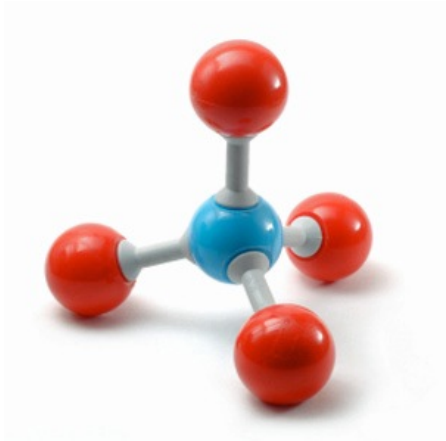
3-Methylpentanoic acid



3-Hexynoic acid



trans-3-Chloro-5-heptenoic acid



Carboxylate Ions

- Carboxylic Acids are defined by the carboxyl functional group.
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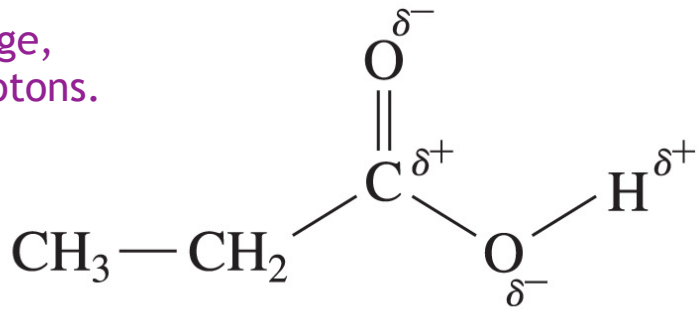
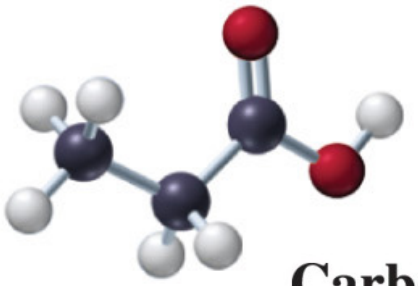
  - The two polar groups cooperate to balance negative charge, stabilizing the molecule enough to allow it to release protons.
    - To act as an organic acid.

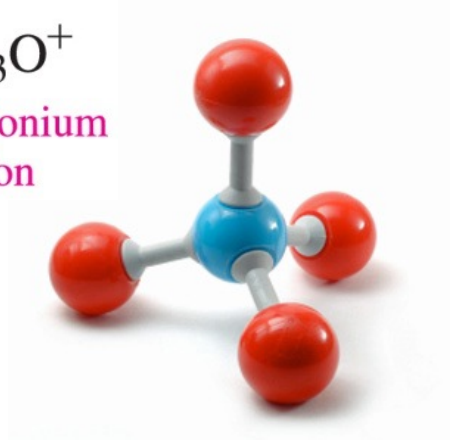




Carboxylic Acid → **Carboxylate Ion**

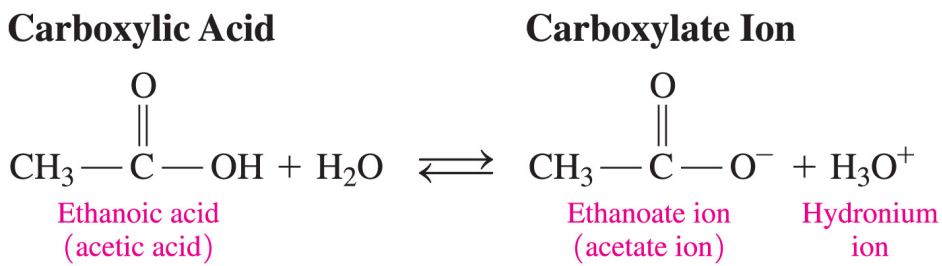
$$CH_3-\overset{\overset{O}{\|}}{C}-OH + H_2O \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-O^- + H_3O^+$$

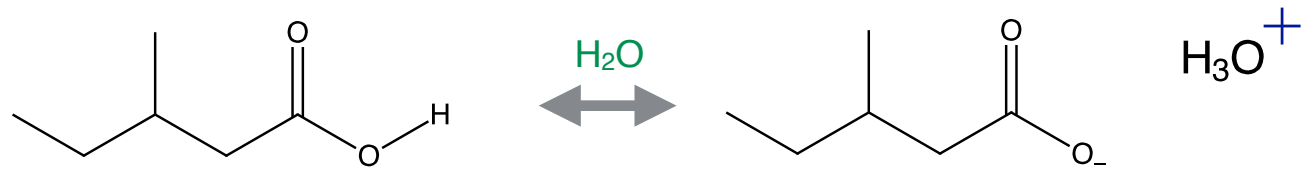
Ethanoic acid (acetic acid) | Ethanoate ion (acetate ion) | Hydronium ion



Carboxylate Ions

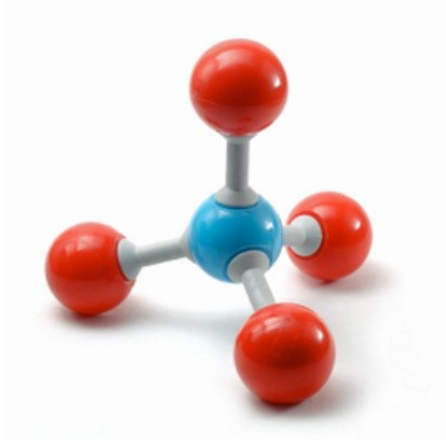
- The ions formed from carboxylic acids are named the same way.
- We use the family suffix -oate ion to name the carboxylate ion formed.





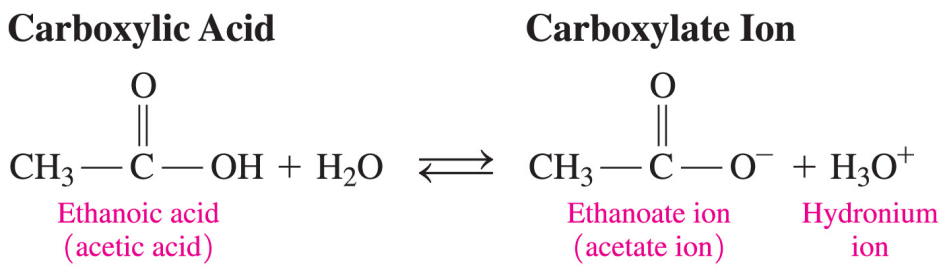
3-Methylpentanoic acid

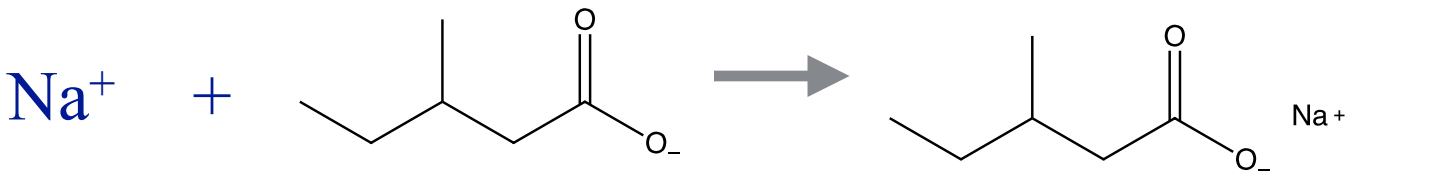
3-Methylpentanoate ion

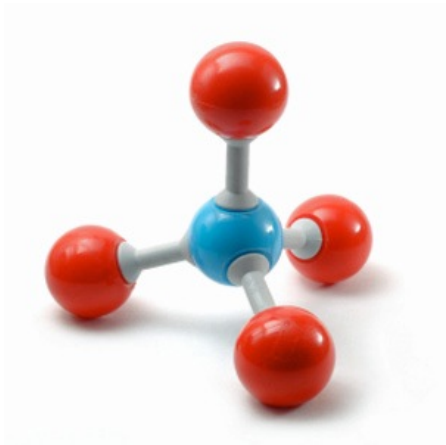


Carboxylate Ions

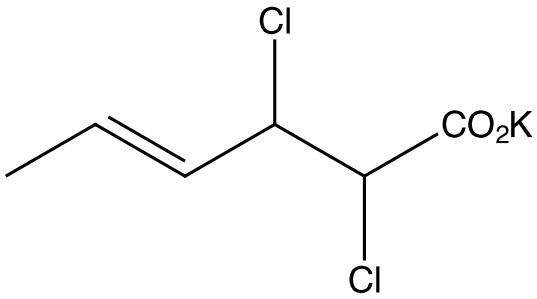
- The ions formed from carboxylic acids are named the same way.
- We use the family suffix -oate ion to name the carboxylate ion formed.
- You already know how to name the salts formed from ions (organic or otherwise).
- Just combine the name of the two ions.



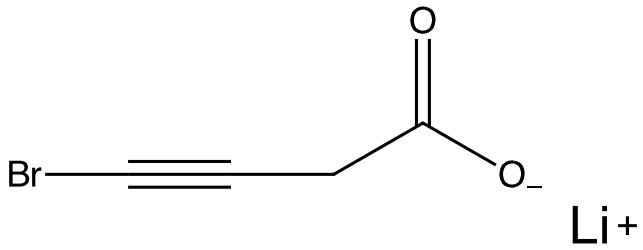




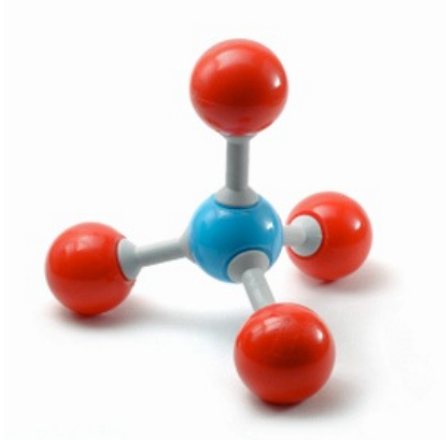
Examples



Potassium *trans*-2,3-Dichloro-4-hexenoate

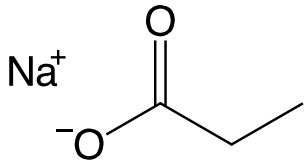


Lithium 4-Bromo-3-butynoate

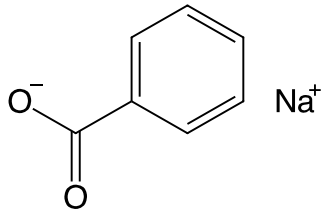


Examples

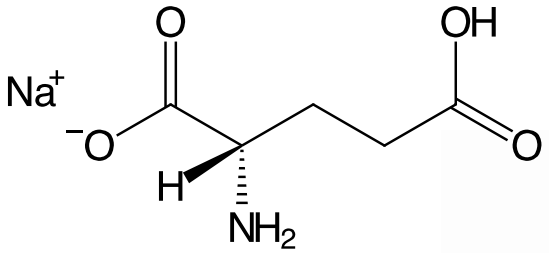
- Carboxylic acid salts are used as preservatives and flavor enhancers such as…
  - sodium propanoate, which is used in cheese and breads

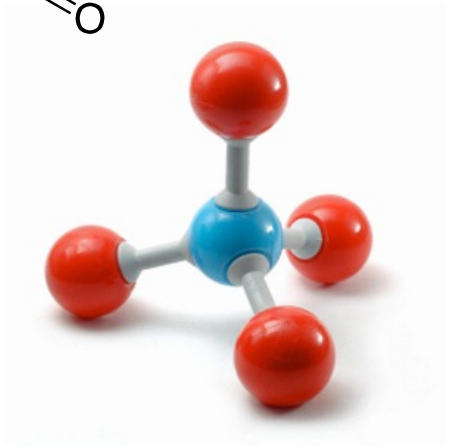


  - sodium benzoate, which inhibits growth of mold and bacteria and is added to fruit juices, margarine, relishes, salads, and jams



  - monosodium glutamate, MSG, which is added to meats, fish, vegetables, and baked goods to enhance flavor





Ch14

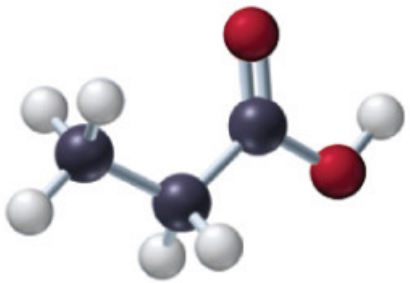
Carboxylic Acids & Esters

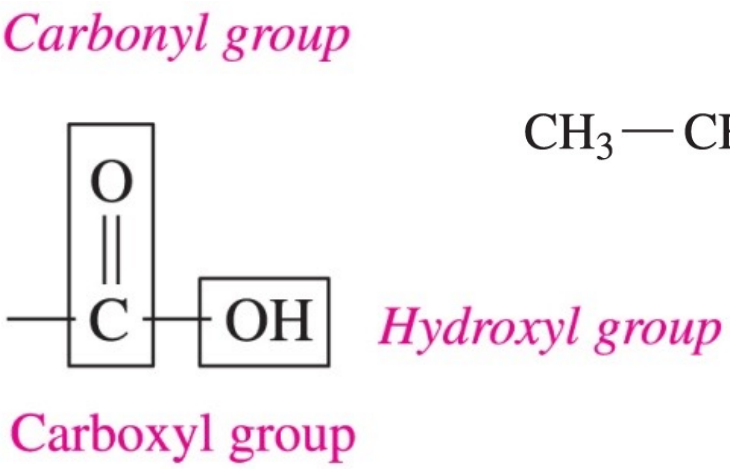
- Carboxylic Acids
  - Carboxyl Group
    - Compound Functional Groups
  - Properties & Structure
    - IM Forces
    - Acid-Base
  - Naming
    - Carboxylic Acids
    - Carboxylic Acid Salts

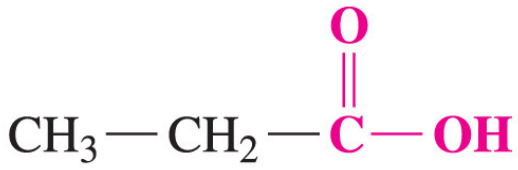
→ Mixing Functional Groups
  - Adding/Changing Properties
  - Naming Substances w/ multiple functional groups
  - Willow Bark
- Esters
  - Structure & Properties
  - Naming
- Reactions
  - Esterification
  - Hydrolysis
  - Saponification

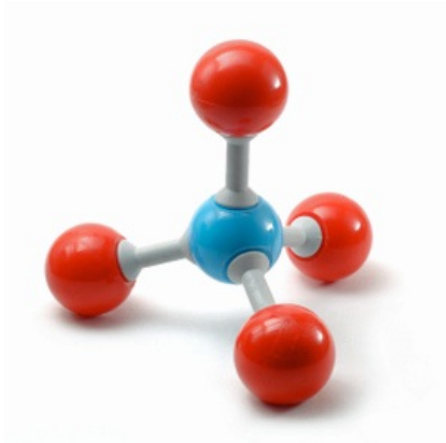
Mixing Functional Groups

- As structures get larger, they will start containing more than one functional group.
  - Carboxylic acids contain both carbonyl and hydroxyl groups.
  - When they're connected we often describe the combination as a new functional group, the carboxyl group in this case.
- The functional groups will interact, creating new dynamics within the molecule and therefore new properties.
  - The hydroxyl group behaves *differently* in the alcohol, phenol, and carboxylic families.









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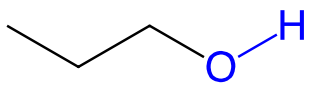
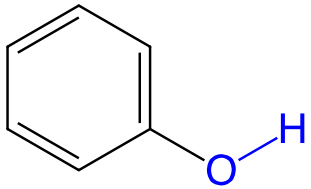
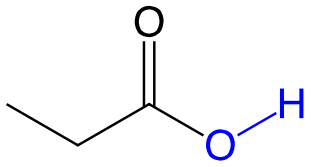
Alcohol Family

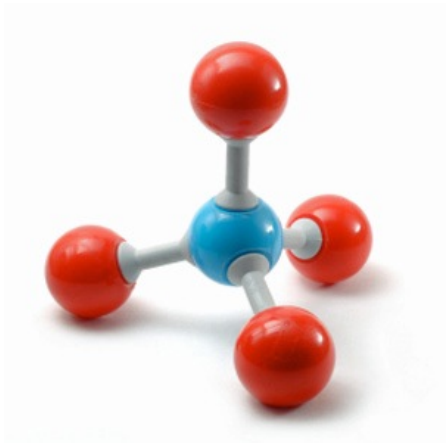


Phenol Family



Carboxylic Acid Family





Mixing Functional Groups

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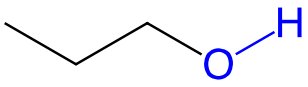
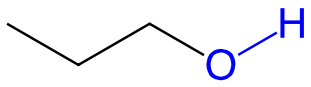
Alcohol Family



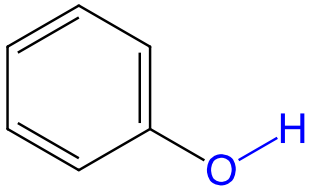
pKa = 14-16
(not acidic)

- Somewhat soluble in water.
- High pH (not acidic)

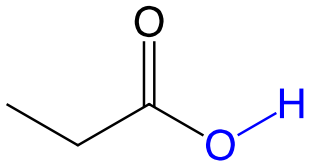
Alcohol Family

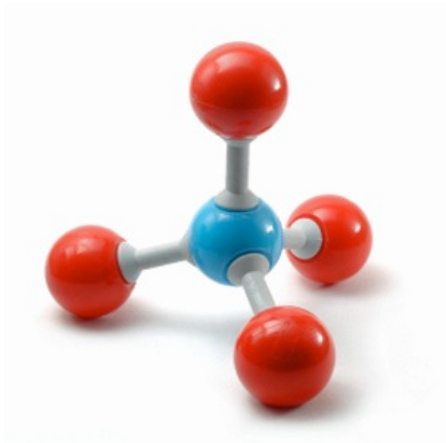


Phenol Family



Carboxylic Acid Family

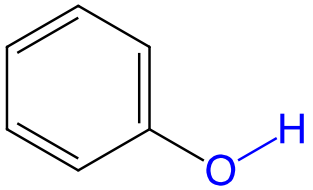




Mixing Functional Groups

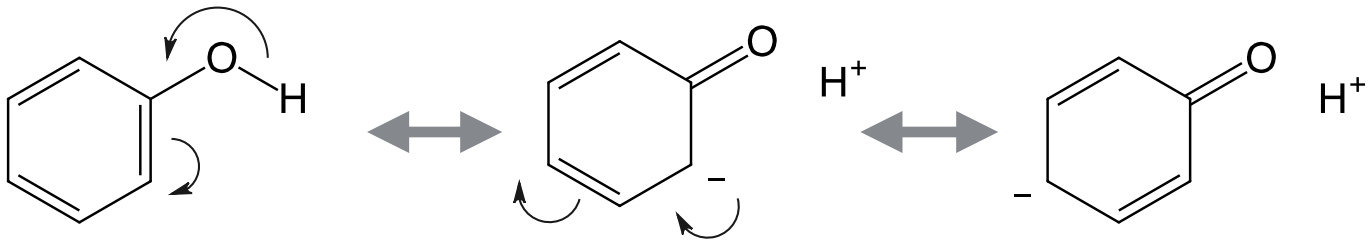
- The functional groups will interact, creating new dynamics within the molecule and therefore new properties.
  - The hydroxyl group behaves *differently* in the alcohol, phenol, and carboxylic families.
  - Structural features, like unsaturations, can change it's behavior and therefore the properties of the substance.

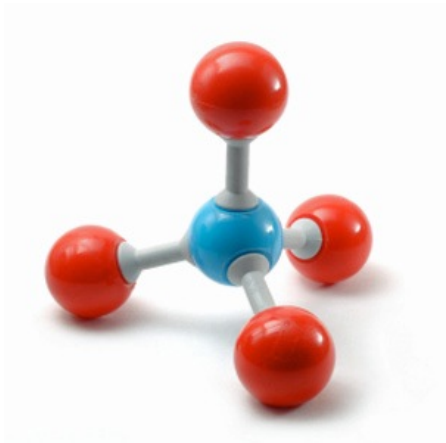
Phenol Family



pKa = 10
(slightly acidic)

- More soluble in water.
- Moderate pH.





Mixing Functional Groups

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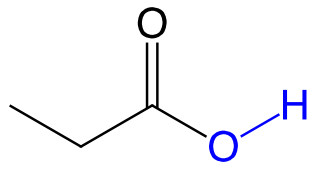
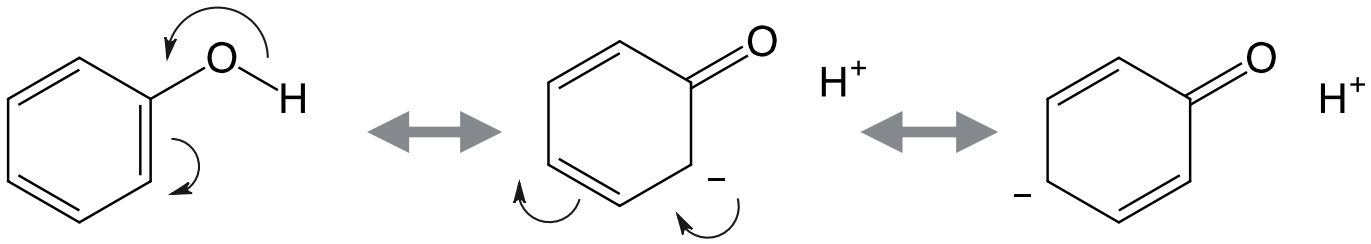
  - The hydroxyl group behaves *differently* in the alcohol, phenol, and carboxylic families.
  - Structural features, like unsaturations, can change it's behavior and therefore the properties of the substance.
  - Other functional groups, like carbonyls, can also interact and change behavior and properties.

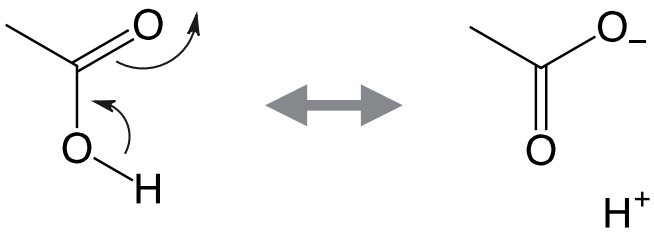
Carboxylic Acid Family

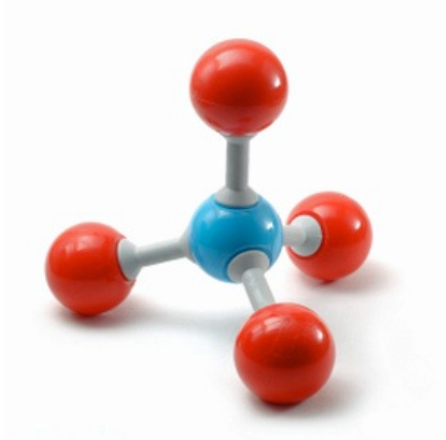


pKa = 4
(an acid)

- Very soluble in water.
- High pH.







Mixing Functional Groups

- The functional groups will interact, creating new dynamics within the molecule and therefore new properties.
  - The hydroxyl group behaves *differently* in the alcohol, phenol, and carboxylic families.
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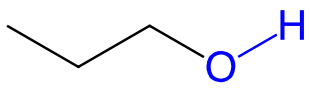
  - Other functional groups, like carbonyls, can also interact and change behavior and properties.

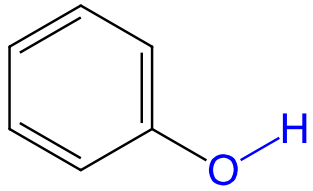
Alcohol Family



pKa = 14-16
(not acidic)

- Somewhat soluble in water.
- High pH (not acidic)

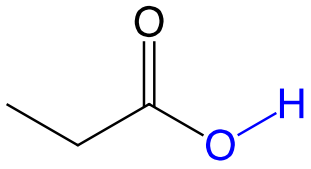
Phenol Family



pKa = 10
(slightly acidic)

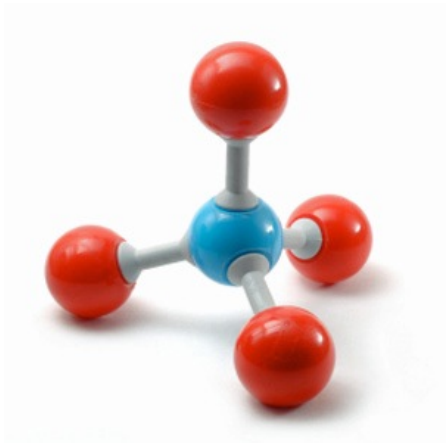
- More soluble in water.
- Moderate pH.

Carboxylic Acid Family



pKa = 4
(an acid)

- Very soluble in water.
- Low pH (acidic)



Ch14

Carboxylic Acids & Esters

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  - Carboxyl Group
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  - Properties & Structure
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  - Esterification
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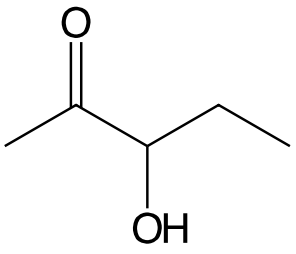
  - Saponification

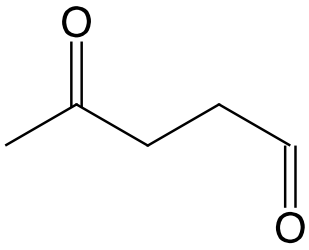
Mixing Functional Groups

- As structures get larger, they will start containing more than one functional group.
  - Carboxylic acids contain both carbonyl and hydroxyl groups.
  - When they're connected we often describe the combination as a new functional group, the carboxyl group in this case.
- When the functional groups are not connected, we need a way to assign a family and address the functional groups that don't define that family.
- For simple mixed functional group compounds, we assign them to the family of the most oxidized functional group in the mole
  - Aldehydes trump ketones (they can be further oxidized, ketones can't)

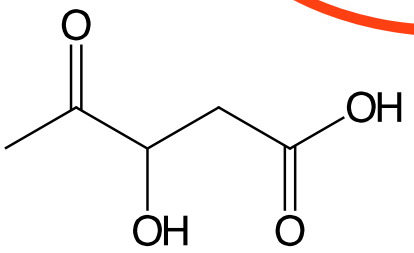
How do we assign addresses to the other functional groups?



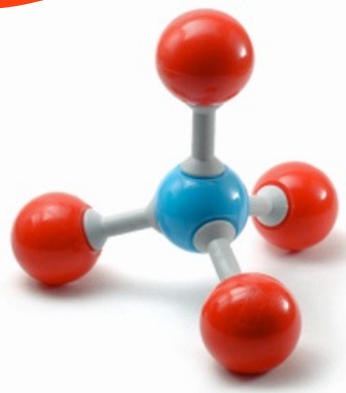
Name it as a ketone.



Name it as an aldehyde.



Name it as a carboxylic acid.

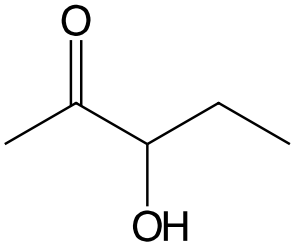


Mixing Functional Groups

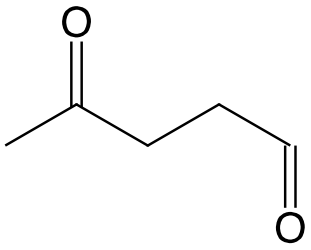
- For simple mixed functional group compounds, we assign them to the family of the most oxidized functional group in the molecule.
  - Aldehydes trump ketones (they can be further oxidized, ketones can't)
- The other functional groups get demoted to substituents and addressed with the same system we've been using all along.

Functional Group		Prefix (used as substituent)
—OH	Hydroxyl Group	hydroxy-
—SH	Thiol Group	sulfanyl-
—CO—	Carbonyl Group	oxo-

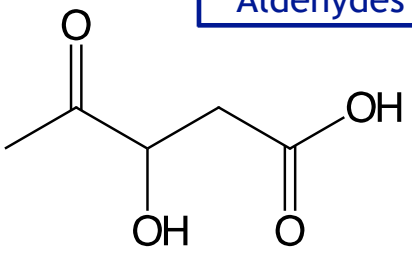
Family	Suffix (for family)	Functional Group
Alcohols	-ol	—OH
Phenols	-phenol	—OH
Thiols	-thiol	—SH
Ketones	-one	—CO—
Aldehydes	-al	—CO—



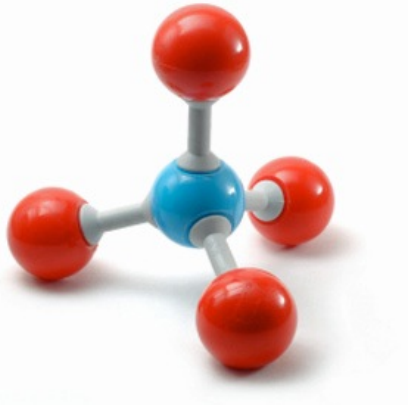
Name it as a ketone.



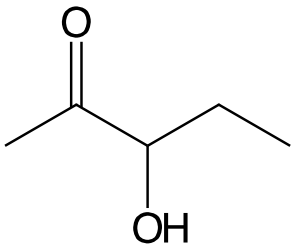
Name it as an aldehyde.



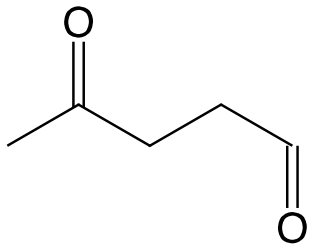
Name it as a carboxylic acid.



Examples

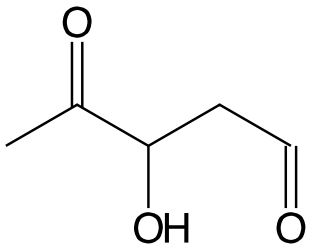


3-Hydroxy-2-pentanone

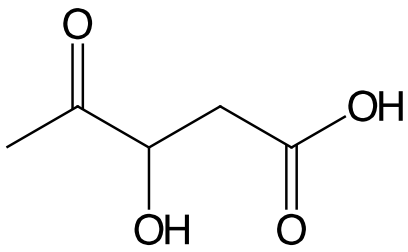


4-Oxopentanal

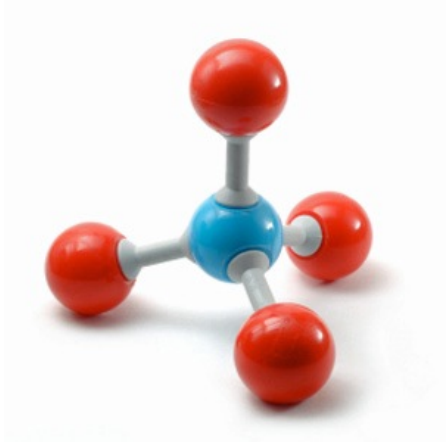
Functional Group		Prefix (used as substituent)
—OH	Hydroxyl Group	hydroxy-
—SH	Thiol Group	sulfanyl-
—CO—	Carbonyl Group	oxo-



3-Hydroxy-4-oxopentanal



3-Hydroxy-4-oxopentanoic acid



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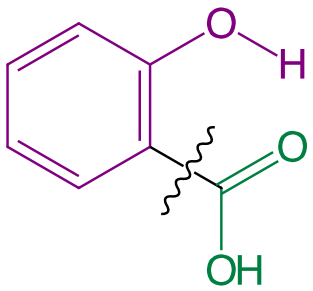
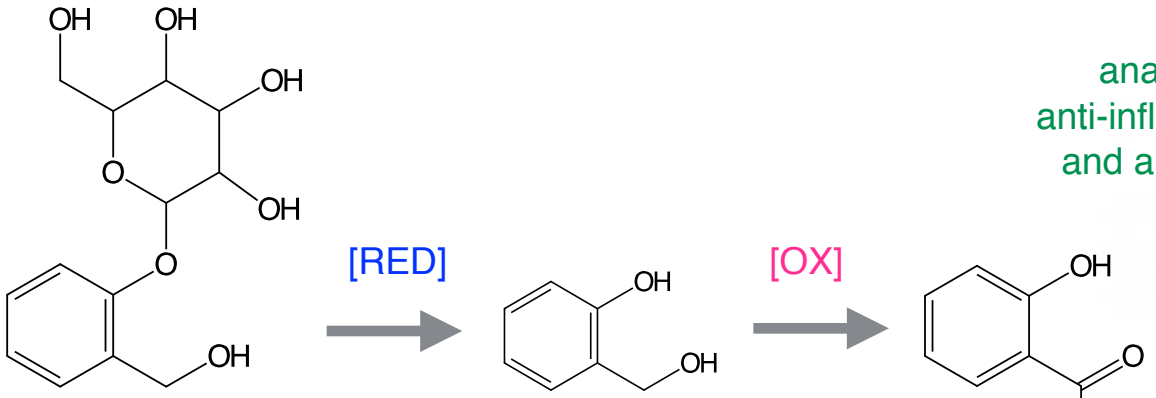
  - Hydrolysis
  - Saponification

Willow Bark

salicylic acid



- By the 1800s, chemists discovered that salicin from the willow tree bark and leaves was responsible for pain relief, fever reduction and reduced inflammation.
- The body converts salicin to salicylic acid by reducing the ether and then oxidizing the primary alcohol to a carboxylic acid.
- Salicylic acid is the substance that has analgesic, anti-inflammatory, and antipyretic properties.



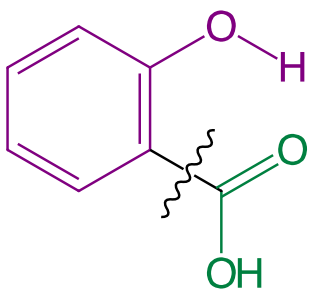
salicilin
(willow bark)

salicylic acid

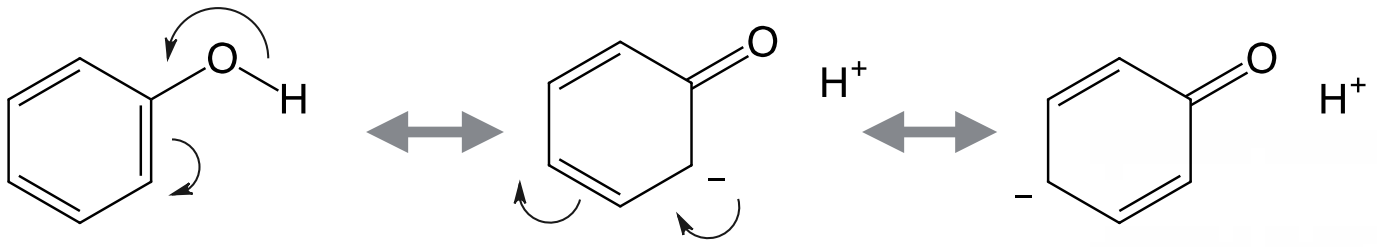
analgesic,
anti-inflammatory,
and antipyretic

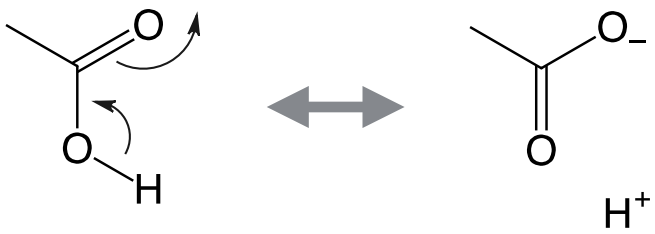
Willow Bark

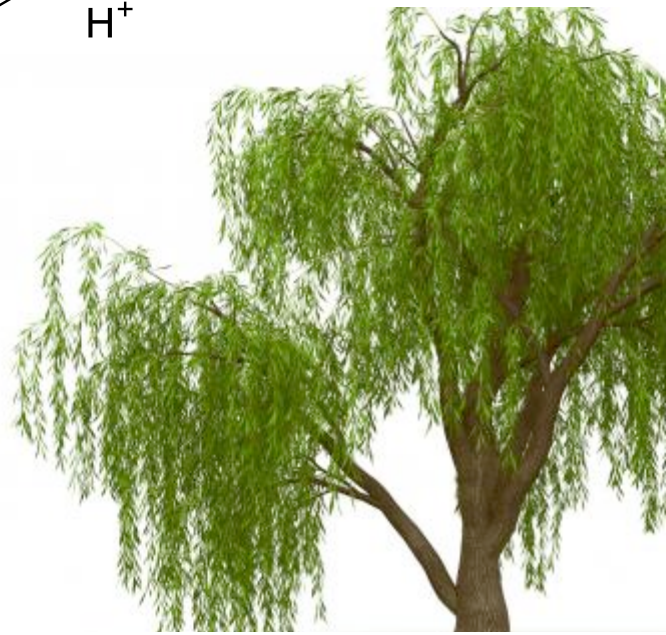
salicylic acid



- Salicylic acid is the substance that has analgesic, anti-inflammatory, and antipyretic properties.
- Salicylic acid is very acidic and can cause upset stomachs, that side effect makes it difficult to use in many cases.
- Phenols and carboxylic acids are acidic, but other substances with these functional groups don't have the same side effect.

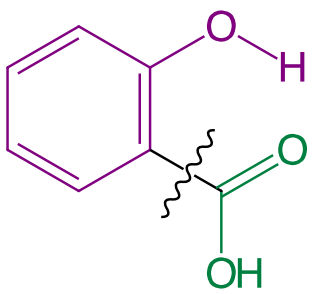




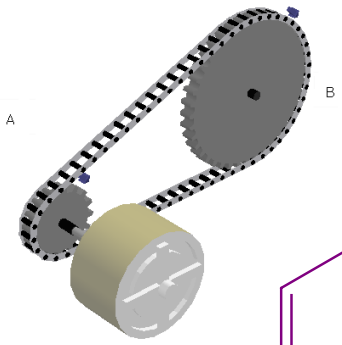


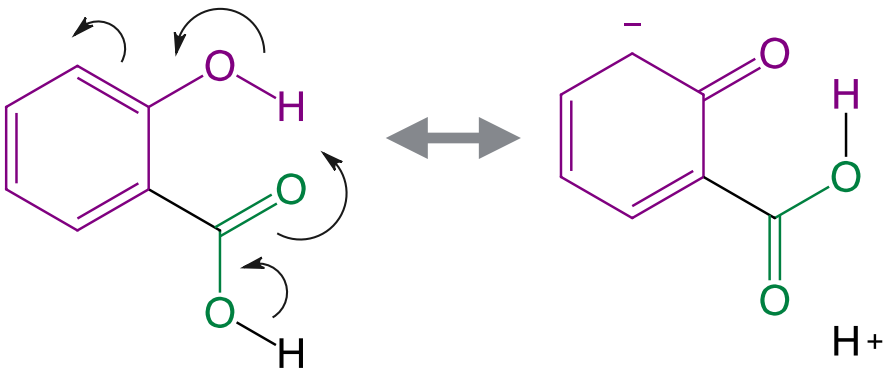
Willow Bark

salicylic acid

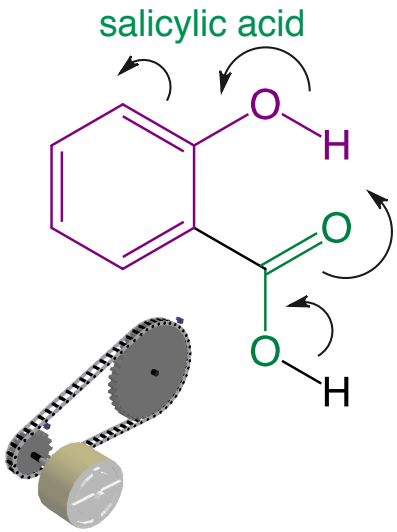


- Salicylic acid is the substance that has analgesic, anti-inflammatory, and antipyretic properties.
- Salicylic acid is very acidic and can cause upset stomachs, that side effect makes it difficult to use in many cases.
- Phenols and carboxylic acids are acidic, but other substances with these functional groups don't have the same side effect.
- In salicylic acid, the functional groups interact to create that greater acidity.

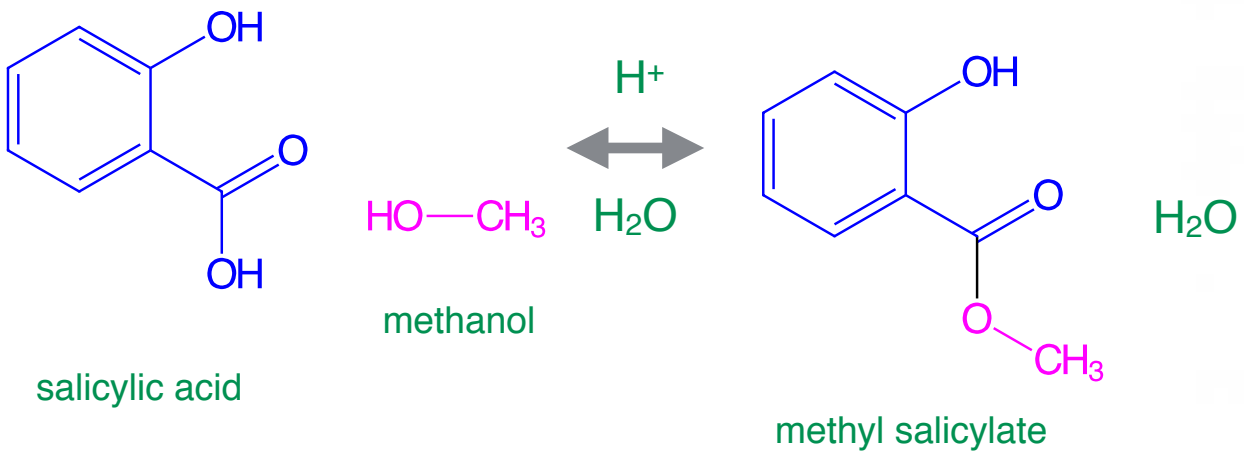




Willow Bark

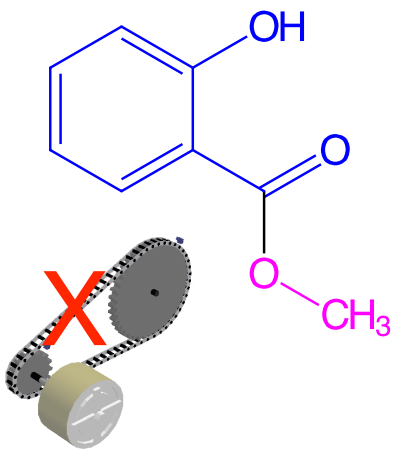


- Chemists tried to improve on salicylic acid to reduce that side effect while retaining it's other useful properties.
- The first thing they tried was replacing the hydrogen in the carboxylic acid with a methyl group.
- Carboxylic Acids and alcohols can react in acid and water to combine. This is a reversible reaction.
- This is a condensation or esterification reaction.



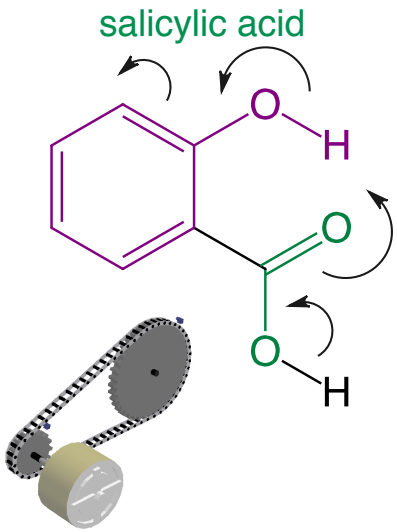
Oil of Wintergreen

methyl salicylate

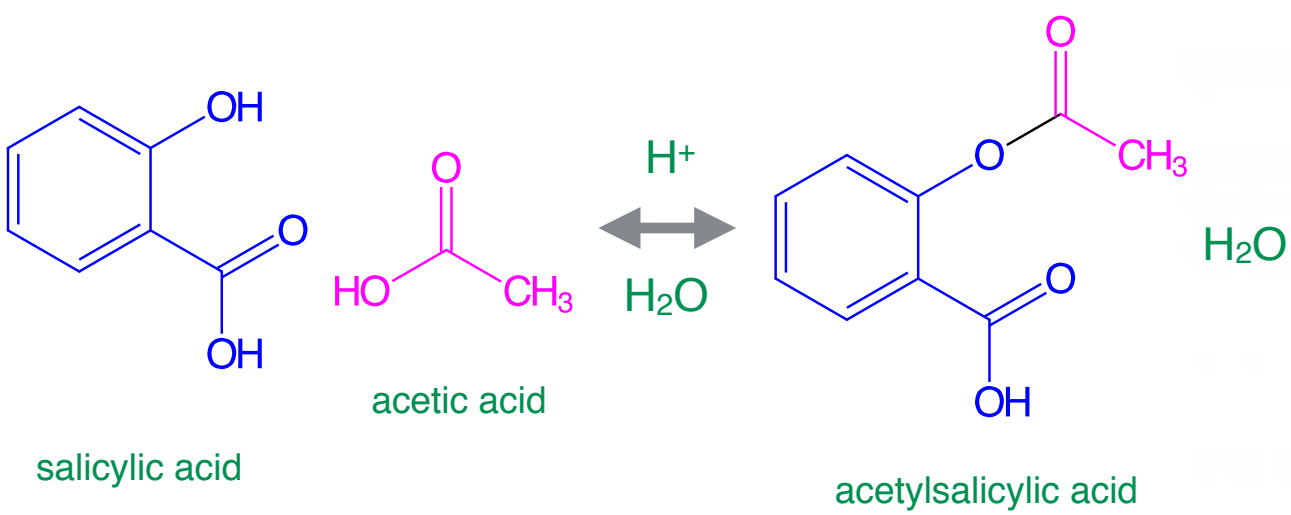


- Methyl salicylate (oil of wintergreen) retained many of the properties of salicylic acid.
  - It's still an analgesic (pain reliever).
- It lost other properties.
  - Without the carboxylic acid group it is less acidic.
    - It's also less water soluble, more greasy.
  - It's not easily consumed.
- It has other properties all it's own.
  - In small quantities it's used as food flavoring, it's responsible for the mint taste in spearmint gum.
  - It can be absorbed through the skin. It's the active ingredient in Tiger Balm, Icy Hot, and Bengay ointments.
  - It has a high toxicity. One spoonful is three times a lethal dose.
    - In 2007 a professional runner died from using too much Bengay.

Willow Bark



- Chemists tried to improve on salicylic acid to reduce that side effect while retaining it's other useful properties.
- The next thing they tried was replacing the hydrogen in the phenol with an acetal group.
- Carboxylic Acids and alcohols can react in acid and water to combine. This is a reversible reaction.
- They used the same esterification reaction to disrupt the phenols contribution to salicylic acids high acidity.

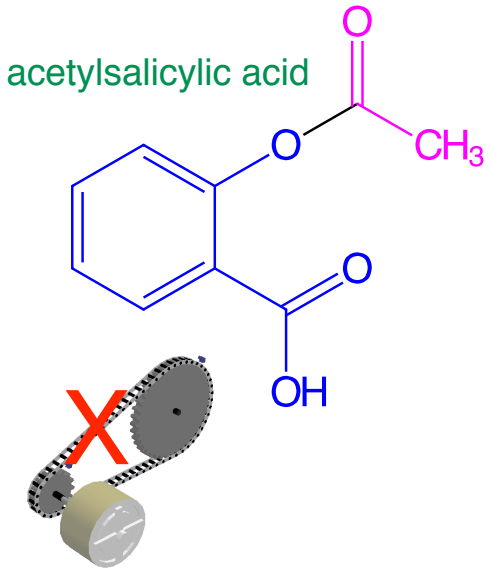


salicylic acid

acetic acid

acetylsalicylic acid

Aspirin



- Acetylsalicylic acid (aspirin) retained many of the properties of salicylic acid.
  - It's still an analgesic (pain reliever)
  - It's also an antipyretic (fever reducer)
  - It's an anti-inflammatory agent
- It lost other properties.
  - It doesn't have the same disruptive effect on the stomach.
- Bayer chemicals introduced aspirin as a product in 1897 and has been selling it ever since.

Ch14

Carboxylic Acids & Esters

- Carboxylic Acids
  - Carboxyl Group
    - Compound Functional Groups
  - Properties & Structure
    - IM Forces
    - Acid-Base
  - Naming
    - Carboxylic Acids
    - Carboxylic Acid Salts

- Mixing Functional Groups
  - Adding/Changing Properties
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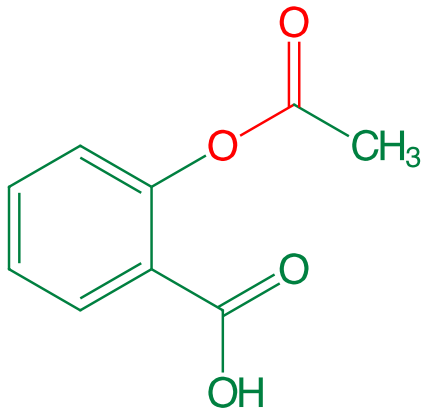
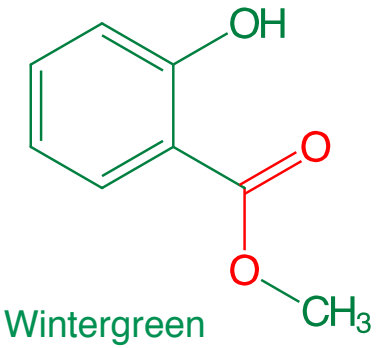
  - Willow Bark
- Esters
  - Structure & Properties
  - Naming
- Reactions
  - Esterification
  - Hydrolysis
  - Saponification

Esters

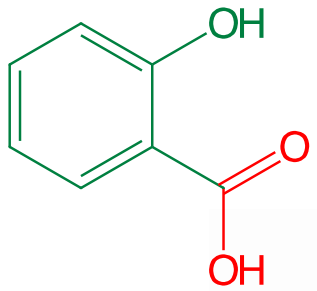
- Both oil of wintergreen and aspirin are examples of another family of organic compounds.
- Esters are substances derived from an acid (organic or inorganic) in which at least one -OH (hydroxyl) group is replaced by an -O-alkyl or -O-aryl group.
- Usually, esters are derived from a carboxylic acid and an alcohol.
- Esters comprise most naturally occurring fats and oils.



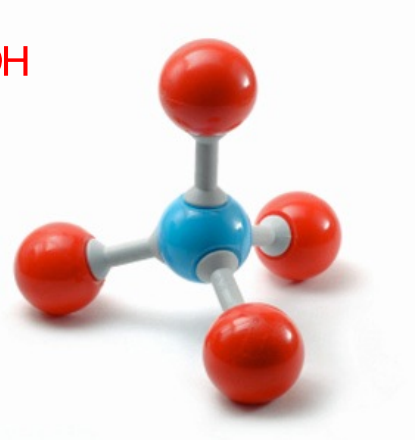
Aspirin
An Ester



Oil of Wintergreen
An Ester

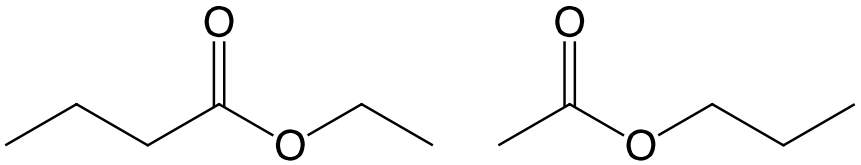


Salicylic acid
A Carboxylic Acid



Esters

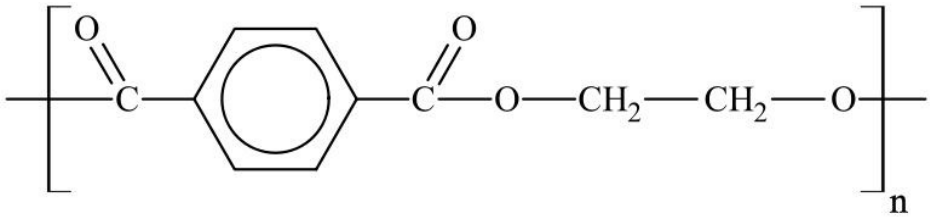
- Many of the fragrances of perfumes and flowers and the flavors of fruits are due to esters.
- Simple esters are volatile, so we can smell them, and they are soluble in water, so we can taste them.
  - Being a hydrogen bond accepter esters are reasonably water soluble.
  - Having no hydroxy group, they cannot be a hydrogen bond donator, so they have a lower boiling point (more volatile).

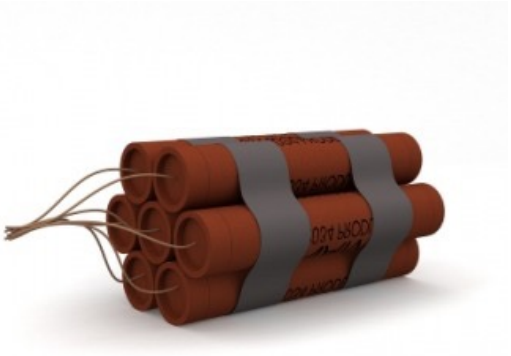


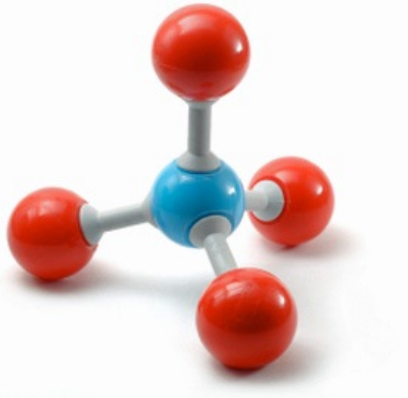
Condensed Structural Formula and Name	Flavor/Odor
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_3$ Propyl ethanoate (propyl acetate)	Pears
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3$ Pentyl ethanoate (pentyl acetate)	Bananas
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ Octyl ethanoate (octyl acetate)	Oranges
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$ Ethyl butanoate (ethyl butyrate)	Pineapples
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3$ Pentyl butanoate (pentyl butyrate)	Apricots

Esters

- Esters are used in many ways.
  - Fragrant esters are used in perfumes, essential oils, food flavorings, and cosmetics.
  - Natural esters are found in pheromones
  - Nitrated esters, such as nitroglycerin, are known for their explosive properties.
  - Polymers formed from esters are called polyesters are used to make plastics and synthetic cloth.
  - Esters are used to make surfactants (soaps, detergents, cleansers…)







Ch14

Carboxylic Acids & Esters

- Carboxylic Acids
  - Carboxyl Group
    - Compound Functional Groups
  - Properties & Structure
    - IM Forces
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  - Naming
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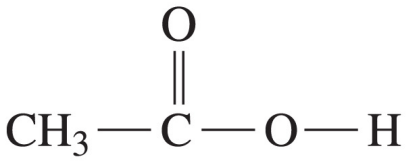
  - Esterification
  - Hydrolysis
  - Saponification

Esters

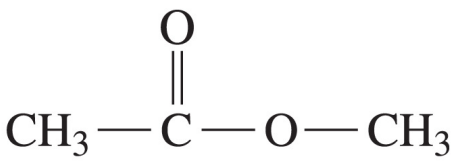
- Simple esters are named with the family suffix -oate.
- The name has two parts.
  - Start with the underlying carboxylic acid and replace the -oic acid with -oate. That's the second part.
  - In front of that put the substituent bonded to the oxygen, as if it were a chain branch.

Carboxylic Acid

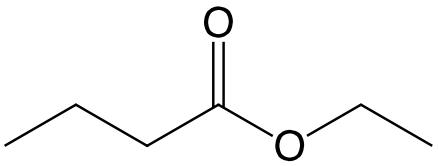


Ethanoic acid
(acetic acid)

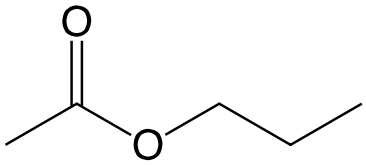
Ester



Methyl ethanoate
(methyl acetate)



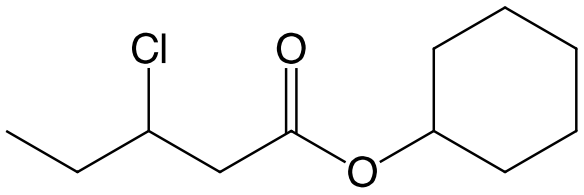
Ethyl butanoate



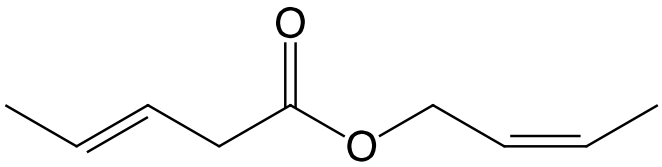
Propyl ethanoate

Esters

- Simple esters are named with the family suffix -oate.
- The name has two parts.
  - Start with the underlying carboxylic acid and replace the -oic acid with -oate. That's the second part.
  - In front of that put the substituent bonded to the oxygen, as if it were a chain branch.



Cyclohexyl 3-chloropentanoate



cis-2-Butenyl *trans*-3-pentenoate

Ch14

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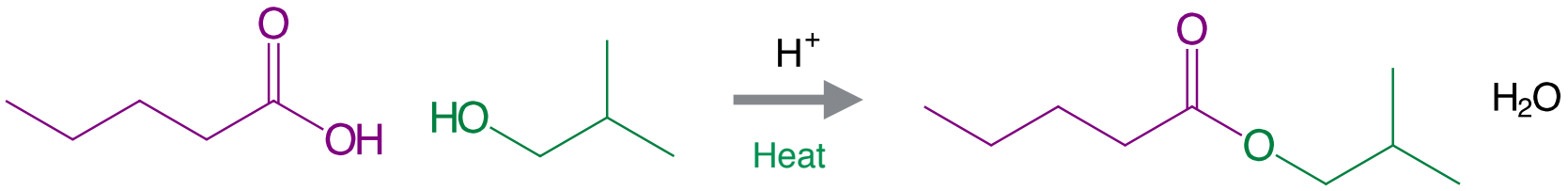
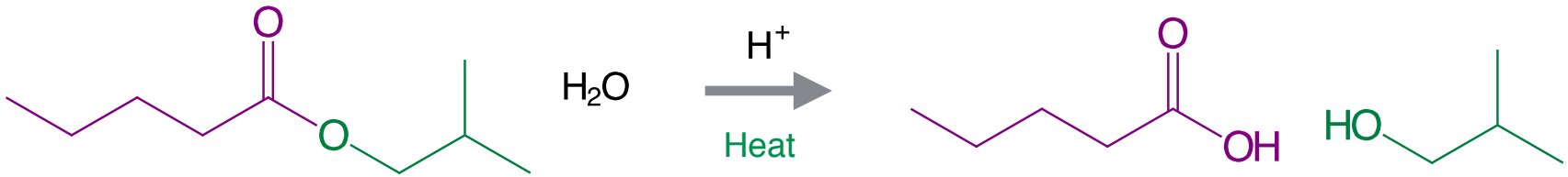
Reactions of Esters

- Esters are formed by condensing an alcohol and a carboyxlic acid.
- The reaction is also called an esterification of a carboxylic acid.
- It's an equilibrium reaction, but driven forward by using a large excess of the alcohol.



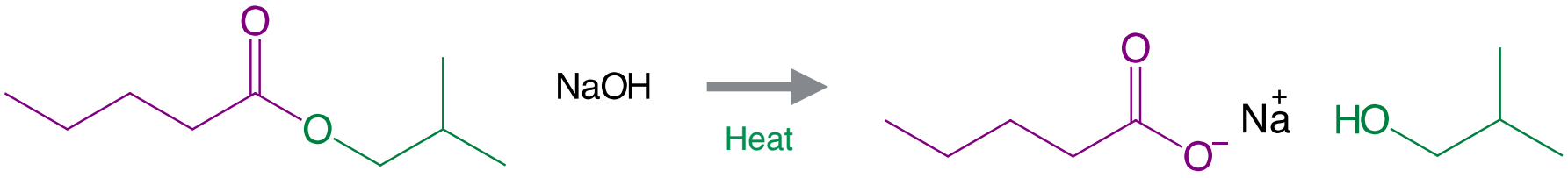
Reactions of Esters

- Hydrolysis of esters is breaking them into alcohols and carboxylic acids.
- It can be accomplished with acid and heat.
  - It's an equilibrium reaction, but driven forward by using a large excess water.
  - It's the reserve of esterification.



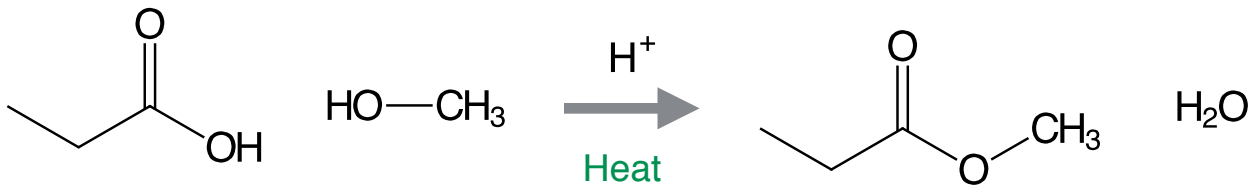
Reactions of Esters

- Hydrolysis of esters is breaking them into alcohols and carboxylic acids.
- Hydrolysis can also be accomplished with strong base.
- This type of hydrolysis is called saponification (soap making).
- It produces carboxylic acid salts instead of acids.

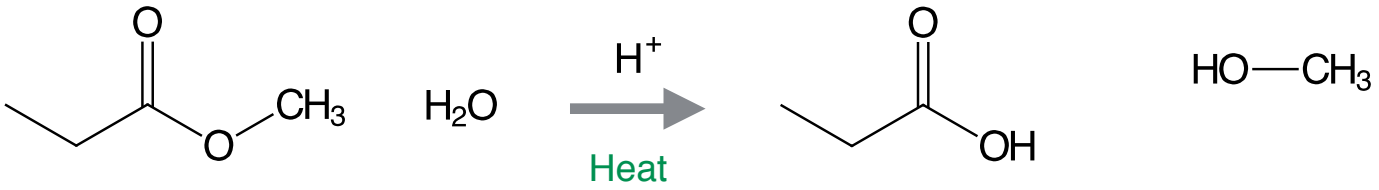


Reaction Summary

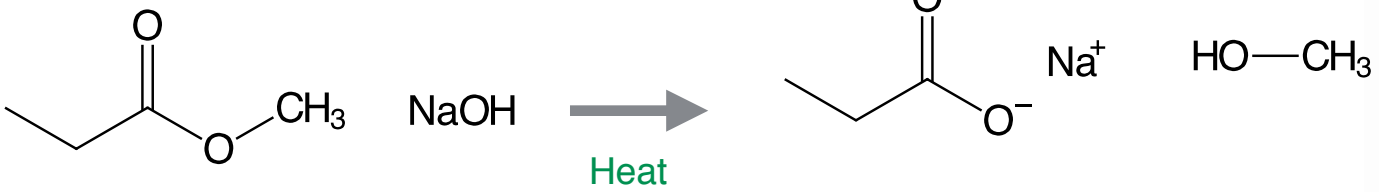
- Esterification:

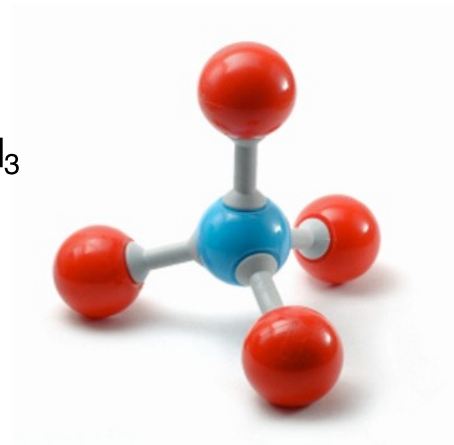


- Hydrolysis:



- Saponification:





Ch14

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Questions?