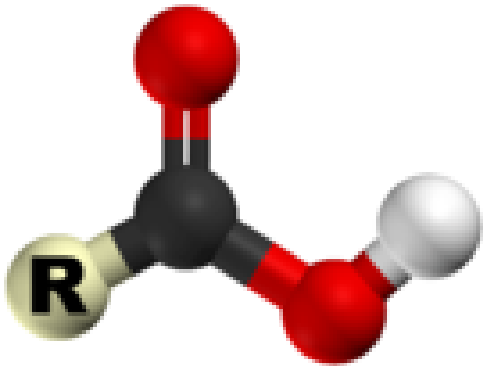
# 2302106 – Basic Organic Chemistry for ISE – Part II

## Lecture 5-1

# Carboxylic and Derivatives - Structure and Property

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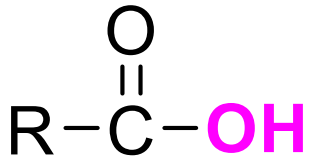
**Recommended Textbook:**

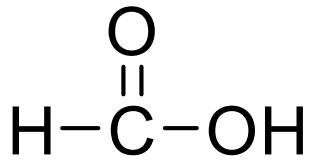
Chapter 20 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

# What is Carboxylic Acid?

***Carboxyl* = *carb*onyl group + hydr*oxyl* group**

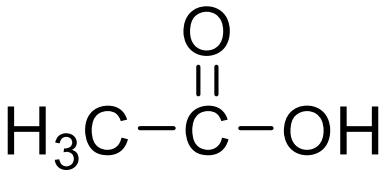



- Distinctly **acidic**




formic acid

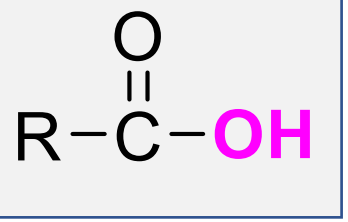
methanoic acid



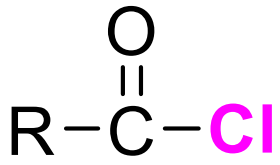

acetic acid

ethanoic acid

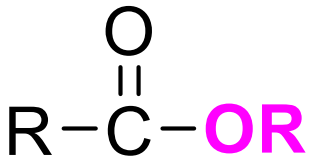
# Carboxylic Acid Derivatives



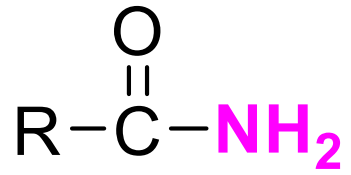

## Acid Chloride

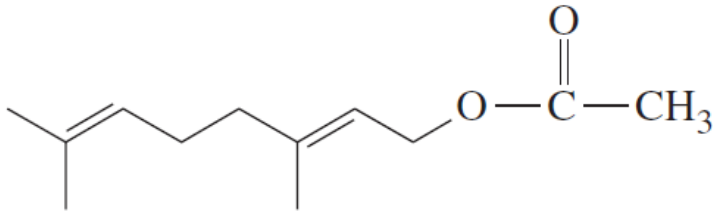



## Ester

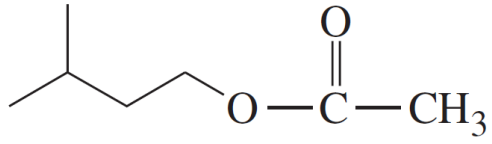



## Amide

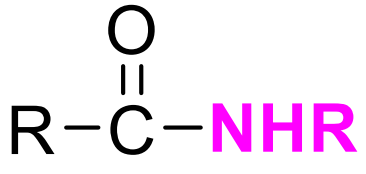


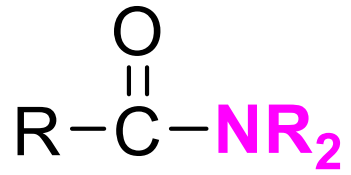




geranyl acetate
(geranium oil)

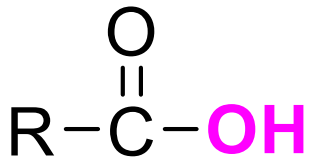
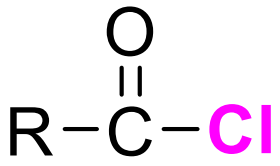
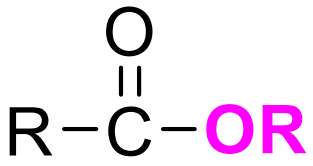
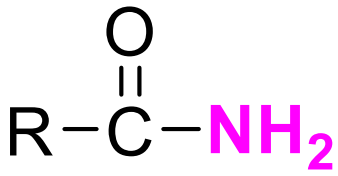



isoamyl acetate
(banana oil)

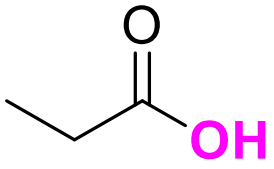


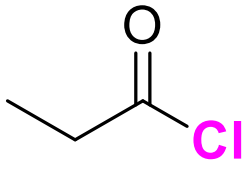



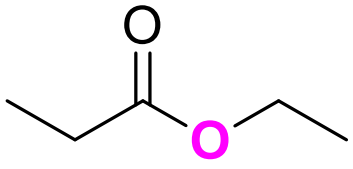

# Nomenclature - Suffix

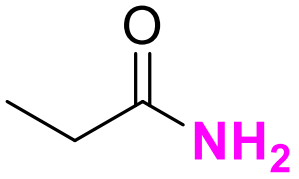
| Carboxylic acid | Acid Chloride | Ester | Amide |
|---|---|---|---|
|  |  |  |  |
| **-oic acid** | **-oyl chloride** | **-oate** | **-amide** |

**Examples:**



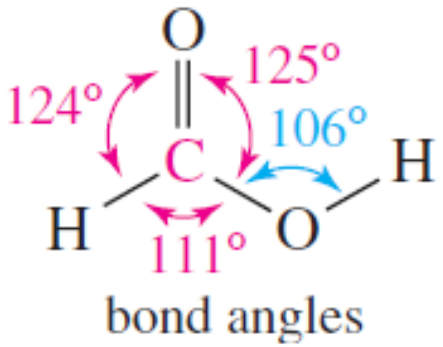




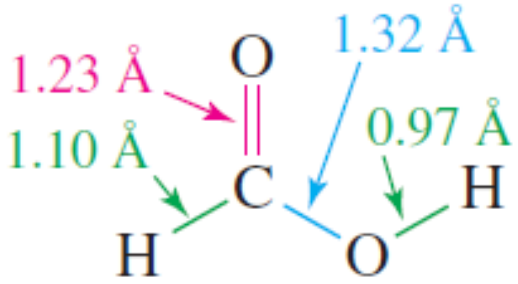


# Carboxylic acid and derivatives - Structure

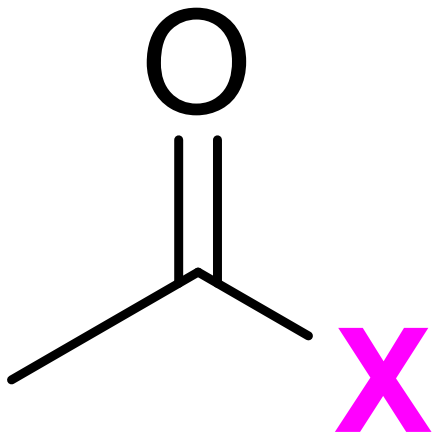
- The **sp²** hybrid carbonyl carbon atom is **planar**, with nearly **trigonal** bond angles



bond angles



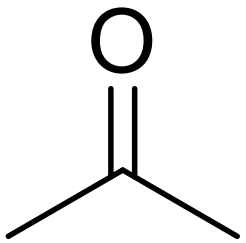
bond lengths



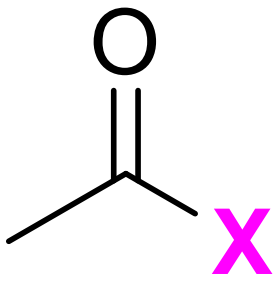
# Carboxylic acid and derivatives - Structure

- One of the unshared electron pairs on the hydroxyl oxygen atom is **delocalised** into the electrophilic pi system of the carbonyl group

Ketone

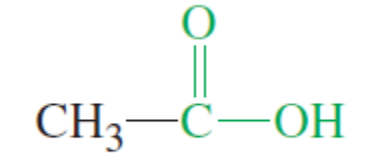



Carbox. Deriv.

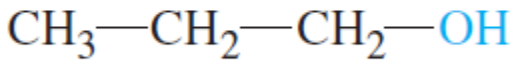


# Physical Properties – Boiling Point

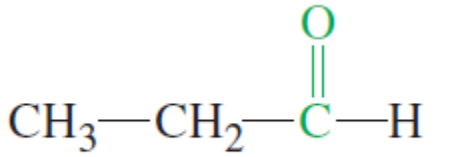
- Carboxylic acids boil at considerably **higher temperatures** than do alcohols, ketones, or aldehydes of similar molecular weights



acetic acid, bp 118 °C

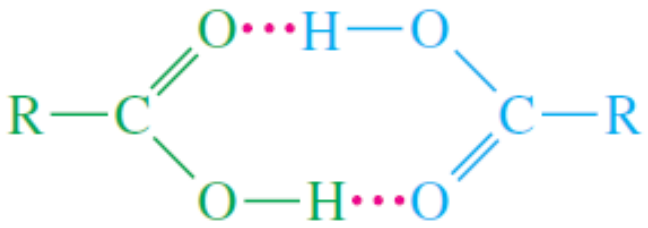


propan-1-ol, bp 97 °C



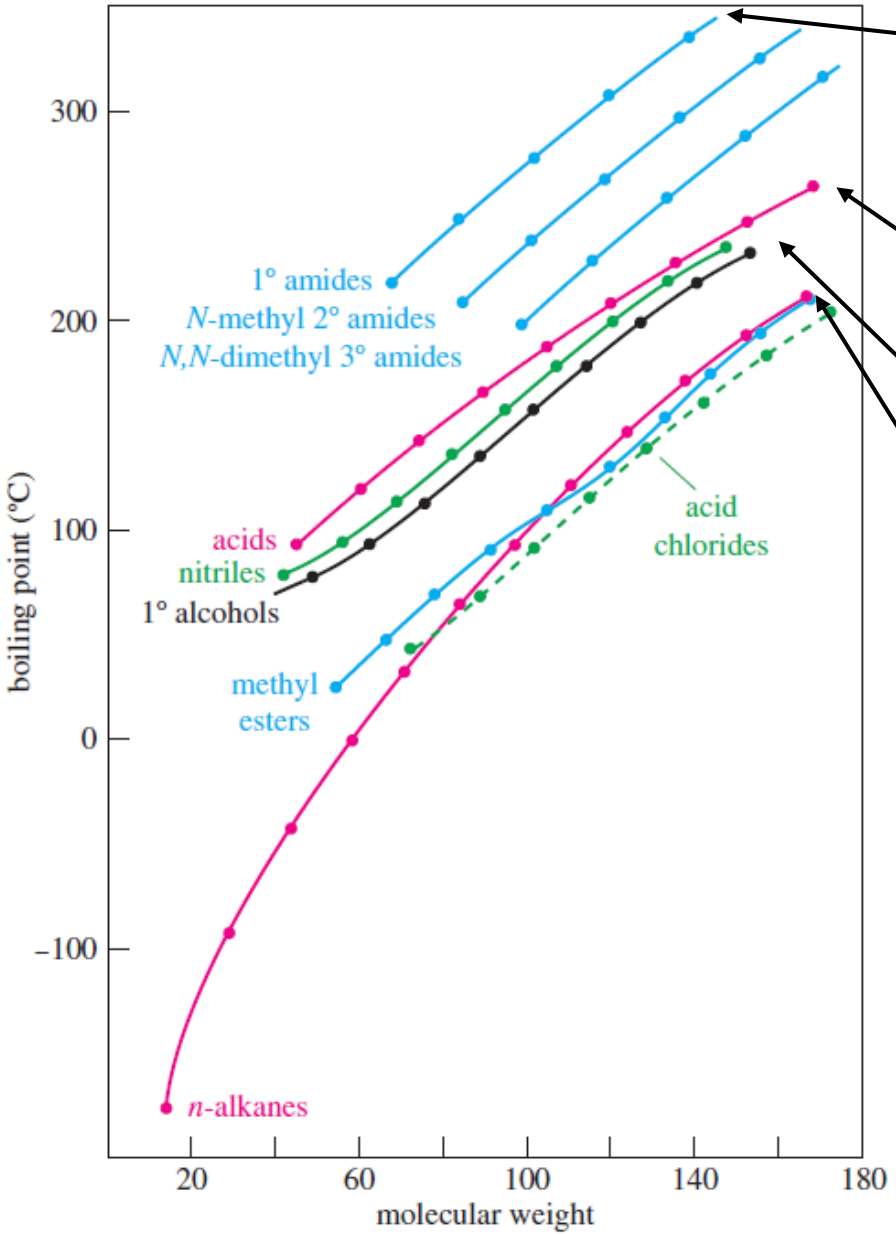
propionaldehyde, bp 49 °C

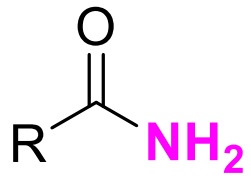
- The high boiling points of carboxylic acids result from formation of a stable, **hydrogen bonded dimer**; effectively doubling the molecular weight

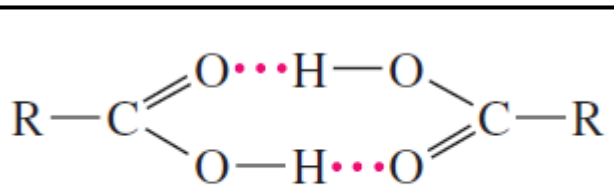


hydrogen-bonded acid dimer

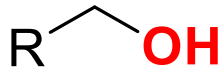
# Physical Properties – Boiling Point

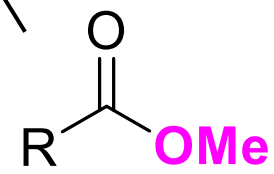



carboxylic acid dimer



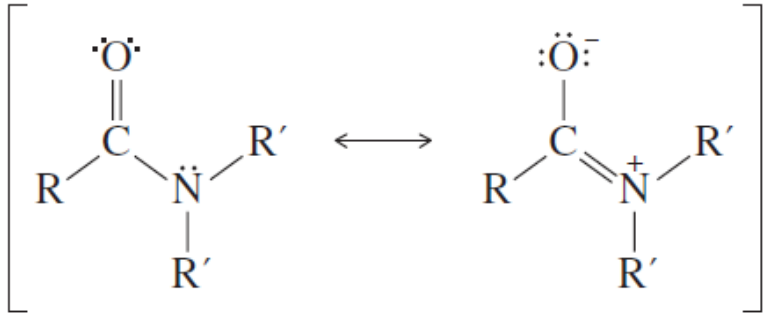



# Physical Properties – Boiling Point

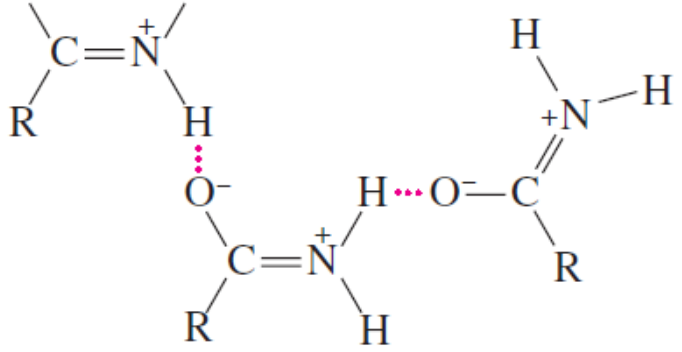
- **Amides** have surprisingly high boiling points

| Examples (MW 55–60) | bp (°C) |
|---|---|
| $CH_3CONH_2$ | 222 |
| $CH_3COOH$ | 118 |
| $CH_3CH_2CH_2OH$ | 97 |
| $CH_3CH_2CN$ | 97 |
| $HCOOCH_3$ | 32 |
| $CH_3CH_2CH_2CH_3$ | 0 |

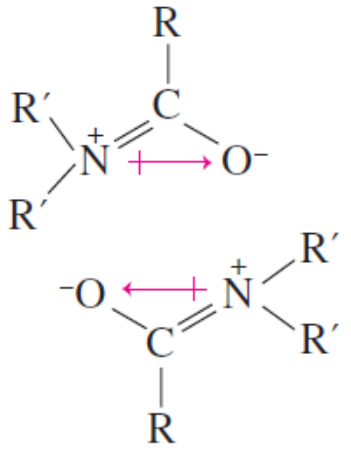
The resonance picture shows a **partial negative charge on oxygen** and **a partial positive charge on nitrogen**



dipolar resonance in amides



strong hydrogen bonding in amides



intermolecular attractions in amides

# Physical Properties – Water Solubilities

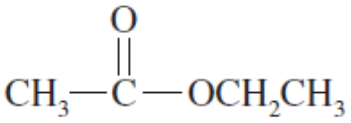
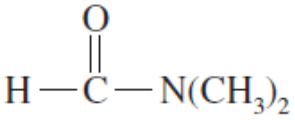
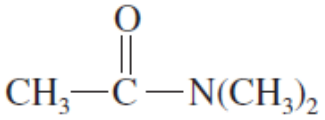
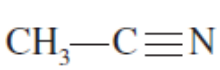
- Carboxylic acids form **hydrogen bonds** with water and alcohol
- The lower molecular-weight acids are **miscible** with water
- As the length of the hydrocarbon chain increases, water solubility decreases until acids with more than **10 carbon atoms are nearly insoluble** in water

| IUPAC Name | Common Name | Formula | mp (°C) | bp (°C) | Solubility (g/100 g $H_2O$) |
|---|---|---|---|---|---|
| methanoic | formic | HCOOH | 8 | 101 | ∞ (miscible) |
| ethanoic | acetic | $CH_3COOH$ | 17 | 118 | ∞ |
| propanoic | propionic | $CH_3CH_2COOH$ | −21 | 141 | ∞ |
| prop-2-enoic | acrylic | $H_2C{=}CH{-}COOH$ | 14 | 141 | ∞ |
| butanoic | butyric | $CH_3(CH_2)_2COOH$ | −6 | 163 | ∞ |
| 2-methylpropanoic | isobutyric | $(CH_3)_2CHCOOH$ | −46 | 155 | 23.0 |
| *trans*-but-2-enoic | crotonic | $CH_3{-}CH{=}CH{-}COOH$ | 71 | 185 | 8.6 |
| pentanoic | valeric | $CH_3(CH_2)_3COOH$ | −34 | 186 | 3.7 |
| 2,2-dimethylpropanoic | pivalic | $(CH_3)_3C{-}COOH$ | 35 | 164 | 2.5 |
| hexanoic | caproic | $CH_3(CH_2)_4COOH$ | −4 | 206 | 1.0 |
| octanoic | caprylic | $CH_3(CH_2)_6COOH$ | 16 | 240 | 0.7 |
| decanoic | capric | $CH_3(CH_2)_8COOH$ | 31 | 269 | 0.2 |

- Most carboxylic acids are also quite soluble in relatively **nonpolar solvents** such as chloroform because the acid continues to exist in its **dimeric form**

# Physical Properties – Solubilities

- Acid derivatives are **soluble in common organic solvents** such as alcohols, ethers, chlorinated alkanes, and aromatic hydrocarbons
- Acid chlorides cannot be used in **nucleophilic solvents** such as water and alcohols
- Many of the smaller esters, amides, and nitriles are **relatively soluble in water** because of their **high polarity** and their ability to form **hydrogen bonds**

| Compound | Name | mp (°C) | bp (°C) | Water Solubility |
|---|---|---|---|---|
|  | ethyl acetate | –83 | 77 | 10% |
|  | dimethylformamide (DMF) | –61 | 153 | miscible |
|  | dimethylacetamide (DMA) | –20 | 165 | miscible |
|  | acetonitrile | –45 | 82 | miscible |

# Physical Properties – Example

Rank the boiling point of these compounds