

# Chapter 17

## Carboxylic Acids and Their Derivatives

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Chapter 17 suggested problems: 36, 38, 40, 42, 44, 52, 54, 56, 62, 64, 66, 70

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### Class Notes

#### I. Carboxylic acids (organic acids) and their derivatives

##### A. General

1. Functional group of carboxylic acids
2. Carboxylic acid derivatives
  - a. Acid halides (acyl halides)
  - b. Acid anhydrides
  - c. Esters
  - d. Amides

##### B. Synthesis of carboxylic acids

1. Most commonly formed by the oxidation of alcohols and aldehydes, many are naturally occurring

##### C. Nomenclature

1. Longest continuous chain that contains the COOH group
2. Substitute "oic acid" for "e" for alkane name
3. Acids are always terminal groups
4. Substitute "alkane 'dioic acid' " if the molecule contains two acid functionalities
5. When an acid group is attached to a ring (-COOH) the compound is benzoic acid and the acid group is attached to C-1 on the ring
6. Acceptable common names of carboxylic acids (IUPAC - common name)
  - a. Methanoic acid - formic acid
  - b. Ethanoic acid - acetic acid

- c. Propanoic acid - propionic acid
- d. Butanoic acid - butyric acid
- e. Dodecanoic acid - lauric acid
- f. Tetradecanoic acid - myristic acid
- g. Hexadecanoic acid - palmitic acid
- h. Octadecanoic acid - stearic acid
- i. Ethanedioic acid - oxalic acid
- j. Propanedioic acid - malonic acid
- k. Butanedioic acid - succinic acid
- l. Pentanedioic acid - glutaric acid
- m. Hexanedioic acid - adipic acid

#### D. Physical properties

##### 1. General

- a. Capable of both dipole-dipole and hydrogen bonds
- b. Acids commonly exist as dimers by forming pairs of hydrogen bonds
- c. Highest MP/BP per molecular weight of any class yet discussed in this course (except for amides)
- d. Solubility trends

##### 2. Acidity of carboxylic acids

- a. Carboxylic acids are the most acidic class of compounds that contain only C, H, and O atoms
- b. Much stronger acids than water or alcohols
- c. Despite this, carboxylic acids are still weak acids
- d. Average percent dissociation is about 1-5% or less, as compared to the mineral acids
- e. Acid dissociation constants are used to calculate percent dissociation; these  $K_a$  values are always less than 1, often much less than 1
- f. The partial positive charge on the carbonyl carbon helps make the compound acidic - it results in a weakened O-H bond
- g. The resonance stabilization of carboxylate ion adds to the ease of ionization
- h. Electron withdrawing substituents make acids more acidic, e.g. trifluoroacetic acid
- i. Electron-donating substituents make acids less acidic, e.g. benzoic acid

## 3. Carboxylate salts

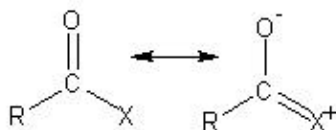
- a. The product of the reaction between a carboxylic acid and a strong base
  - i. Strong bases: Group I and II hydroxides, ammonium hydroxide
- b. The product of a neutralization reaction between the acid and base
- c. These are ionic compounds and not covalent
- d. Greater solubility in aqueous solution than carboxylic acids - sodium salts of lauric, myristic, and palmitic acids are readily soluble in aqueous solution
- e. Ion-dipole interactions are stronger than dipole-dipole interactions or hydrogen bonding
- f. The solubility of acids increases in basic solutions, because carboxylic acids are converted to carboxylates - think in terms of equilibrium

## 4. Soaps and their cleaning actions

- a. Most common soaps are sodium or potassium salts of fatty (long chain) carboxylic acids
- b. Micelle formation, hydrophobicity, hydrophilicity, and amphipathicity

## E. Reactions of carboxylic acids and acid derivatives

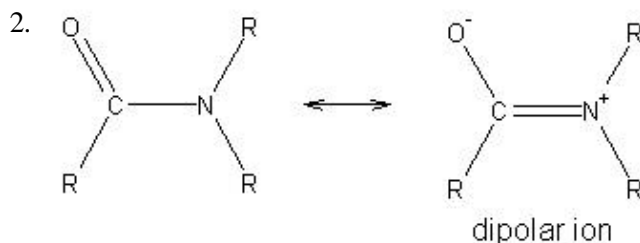
1. Nucleophilic acyl substitution: replacement of one group bonded to the carbonyl carbon with another
2. Reactivity and ease of leaving depend on how well the atom bonded to the carbonyl group donate electrons to it



3. Most reactive: halogens > anhydrides > alkoxides > amine (least reactive)
4. These derivatives can be hydrolyzed: the addition of water results in formation of the original acid and the other compound

## II. Amides

- A. Formed by the reactions of carboxylic acids with amines; the hydrolysis of amides
- B. Unsubstituted (primary), monosubstituted (secondary), and disubstituted (tertiary) amides
- C. Amides and intermolecular forces
  1. Amides have the highest MP and BP of any class of compound considered in Chem 1120



3. The ionic resonance form (i.e., the dipolar ion form) results in very strong dipole-dipole interactions between molecules, which are stronger than hydrogen bonds
4. This is because the bonds formed are even more polar than hydrogen bonds
5. Hydrogen bondings can also occur, in addition to the strong dipole-dipole interactions, in primary and secondary amides

#### D. Amides and resonance: imine form

#### E. Nomenclature

1. Unsubstituted: replace "oic acid" with amide - e.g., formic acid and formamide
2. Monosubstituted and disubstituted amides: identify alkyl groups as substituents with an "N" locant to designate their bonding to the amide nitrogen atom: formamide and N,N-dimethylformamide

### III. Esters

- A. Many esters are naturally occurring: "Esters often form a significant fraction of the fragrant oil of fruits and flowers. The aroma of oranges, for example, contains 30 different esters along with 10 carboxylic acids, 34 alcohols, 34 aldehydes and ketones, and 36 hydrocarbons." (Carey: 787)

- B. Formed by the reactions of carboxylic acids with alcohols

- C. Esterification reactions: acid-catalyzed, reversible



1. R groups can be either alkyl or aryl groups
2. The formation of thioesters can result from the acid-catalyzed reaction of carboxylic acids and thiols
3. Hydrolysis of esters: a molecule reacts with water, both molecules are split and recombine (remember LeChatlier's principle)
  - a. Both esterification and ester hydrolysis are biologically important processes in digestion, membrane formation, etc.
  - b. Ester hydrolysis in the presence of strong bases (saponification) produces the metal carboxylate salt instead of the carboxylic acid

- i. Picture the reverse of the above esterification with NaOH in the place of water on the product side (although water must also be present)
- ii. The base is not a catalyst but is consumed during the reaction
- iii. The formation of the salt drives the reaction strongly to the product, not very reversible
- iv. Used to make soaps from animal fats and vegetable oils

#### D. Nomenclature

1. Alkyl part of alkoxy group named first, named as alkyl group
2. Acyl part named second, change acid name from "oic acid" to oate"

#### E. Physical properties

1. Polarity is lower than in aldehydes and ketones, resulting in weaker intermolecular forces and concomitantly lower MP/BP

### IV. Acid anhydrides and acid halides

- A. Not found in biological systems because highly reactive with water
- B. The synthesis of esters with these compounds is more efficient than esterification with carboxylic acids
- C. Acid anhydrides: formed by the reactions of carboxylic acids with other carboxylic acids
  1. Symmetric and unsymmetric anhydrides
  2. Acetic acid vs. acetic anhydride
  3. Benzoic acid vs. benzoic anhydride
  4. Nomenclature: substitute "anhydride" for "acid" in name
- D. Acid halides: formed by the reactions of carboxylic acids with thionyl chloride:  $\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$ 
  1. Acetyl chloride (ethanoyl chloride)
  2. Benzoyl bromide
  3. Nomenclature: substitute "yl halide" for "oic acid" in name

### V. Phosphoric acid anhydride

- A. Phosphoric acid is a weak acid but stronger than most carboxylic acids
- B. Structure of phosphoric acid
- C. Dehydration of monophosphoric acid and the formation of diphosphoric acid and triphosphoric acid

D. Formation of phosphate esters

1. Same mechanism as acid-catalyzed esterification of carboxylic acids
2. Same nomenclature rules
3. Relevance: the role of phosphate esters in biological membranes, etc.

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