13. Carboxylic Acids (text 14.1 – 14.9)

A. Structure and Nomenclature

• The carboxylic acid functional group results from the connection of a carbonyl group to a hydroxyl group.



RCOOH or RCO₂H

- The functional group retains some properties of a carbonyl group, some of a hydroxyl group, plus some properties unique to COOH. The geometry, hybridization, and polarization of the atoms are the same as in C=O and OH.
- In IUPAC nomenclature, the COOH group is always given priority, with the C of COOH assigned as atom #1. The e in the word alkane is changed to oic acid.





propanoic acid

4-bromo-2-butenoic acid

• For complicated compounds, we can use the ending carboxylic acid. If we use this system, the carboxylic acid system does not count as part of the parent hydrocarbon.



• The simplest acids are known by their common names. (You don't need to know all names in text Table 14.1)



 If a molecule contains a C=O as well as the acyl group, the C=O is denoted by using the prefix oxo.



³⁻oxobutanoic acid

• Like carbonyl compounds, Greek letters are often used to denote substituent positions.



B. Properties

- As seen in Chapter 2, carboxylic acids are acidic. Acids generally taste sour. Vinegar is 5% acetic acid by volume.
- They are very polar compounds that can have extensive H-bonding and have bp higher than similarly sized alcohols.

CH ₃ CH ₂ CH ₂ CH ₂ OH	bp 118°
CH ₃ CH ₂ COOH	bp 141°

 In solution, the carboxlic acid groups of adjacent molecules H-bond with each other to form weakly bonded dimers.



- Carboxylic acids have polar bonds located at one end of the molecule, and it is this polar end, termed the hydrophillic end, that interacts with water.
- The other end of the molecule, represented by the R group, is non-polar (termed the hydrophobic end) and is insoluble.
- When the R group is small (< 6 carbons), the carboxylic acid is water-soluble. As the length of the C chain increases, solubility in water goes down.

C. Spectroscopy

IR spectrum has two characteristic, strong peaks: the OH at 2400 – 3400 cm⁻¹, and the C=O at 1700 – 1725 cm⁻¹.



 In proton NMR, the acidic H of the COOH appears far downfield, between 10 – 13 ppm. Often this is off of the scale for the plot, so it is "offset" by a certain amount.



D. Reactions

1. Preparation

 Preparation is by the oxidation of 1° alcohols and aldehydes. Recall that 2° alcohols and ketones cannot be oxidized to carboxylic acids.



• Remember that most oxidations of 1° alcohols continue through the aldehyde all the way to the acid, except for oxidation by PCC, which stops at the aldehyde.

2. Reduction to 1° alcohols

The COOH group is quite resistant to reduction. However, it can be reduced to a 1° OH using LiAlH₄ followed by treatment with H₂O. NaBH₄ is not strong enough.



• Other reagents that hydrogenate alkenes and carbonyl groups don't do anything to carboxylic acids. So, it is possible to carry out selective reduction by carefully choosing the reducing agent.



3. Decarboxylation of β -keto acids

 Carboxylic acids with a beta-keto group decarboxylate when heated, to eliminate CO₂. (*i.e.* break C–C bond)



- This proceeds through a cyclic intermediate to form an enol, which tautomerizes to ketone.
- The cyclic conformation is ideally arranged for the facile elimination of stable carbon dioxide. Thus, only acids with beta-keto groups undergo this reaction.



• What is the product of the following reaction?



4. Conversion to acid derivatives

• When the OH of a carboxylic acid is replaced by Nu, either directly or indirectly, the product is an acid derivative.



• We will look at 4 acid derivatives in the next chapter:



- All the compounds are acid derivatives, since they all have a carbon with an oxidation number of +3 (same as acid).
- In aldehydes and ketones, the oxidation number of the carbonyl group carbon is lower. So, the conversion of an aldehyde to an acid is an oxidation, while the conversion of an acid to its derivative is a substitution.
- Because the OH group is a poor leaving group, it is not easy to convert a carboxylic acid directly to each one of the four derivatives. However, acid chlorides and esters are can be prepared relatively simply.

a. Fischer esterification

 The acid-catalyzed formation of esters from an acid and an alcohol was studied by Emil Fischer in the 19th century.



- This reaction is reversible. Product formation can be increased by using an excess of starting alcohol or removing the water formed as a co-product. Treatment of an ester with H⁺ and water regenerates RCOOH and R'OH.
- The group that remains unchanged in carboxylic acid and derivative reactions is the acyl group.



- In these reactions, a group or atom bonded to the acyl group is replaced by another group or atom. The mechanism is of reaction is nucleophilic acyl substitution.
- The substitution proceeds by a slow nucleophilic addition to the acyl carbon. This is then followed by a fast elimination step. Nucleophilic acyl substitution is therefore also termed an *addition-elimination reaction*.
- The strong C=O bond is always retained. It is broken in the addition step but regenerated in the elimination step.

• Mechanism of acid-catalyzed Fischer esterification:



• If the OH of the alcohol is on the same carbon chain as the COOH, an intramolecular (*i.e.* reaction within molecule) reaction occurs to form a lactone (a cyclic ester).



- Lactones are usually identified by the position of the carbon atom that bears the O group.
- b. Formation of acid chlorides
- Treatment of a carboxylic acid with SOCl₂ replaces the OH group with a CI atom (as seen with alcohols).



- Acid chlorides are the most reactive of all acid derivatives, since the withdrawing CI atom increases the positive charge on the acyl C atom. So, acid chlorides are often used to make other acid derivatives.
- Pages covered: Chapter 14, 402 422
- Problems: 7, 11, 18, 21, 27, 29, 30, 32, 38, 40, 43
- 2005: 43, 44; 2006: 40, 41; 2007: 40, 41; 2008: 40, 41

Past test questions:

- This molecule is what type of compound?
 - o Aldehyde
 - o Hemiacetal
 - o Enone
 - o Lactone
 - o Acetal



• The molecule shown on the previous question is formed by the acid-catalyzed cyclization of which one of the following?



• Which one of the following liberates CO₂ upon moderate heating?



MCAT questions:

- Which one of the following has the most acidic proton?
 - o Pentanoic acid
 - o 2-hydroxypentanoic acid
 - o 2-methylpentanoic acid
 - o 2-nitropentanoic acid

- The ester shown is produced by the acid-catalyzed reaction of ethanol with acetic acid. What molecule is the source of the O atom indicated by the arrow?
 - Acetic acid
 - o Ethanol
 - o Water
 - o Oxygen



- The formation of the ester shown above is a reversible reaction. How can the yield of the ester be increased?
 - I. Increase the concentration of ethanol
 - II. Increase the concentration of acetic acid
 - III. Increase the concentration of the acid catalyst
 - $_{\rm O}$ I and II only
 - o II and III only
 - o I and III only
 - $\circ\,$ I, II, and III