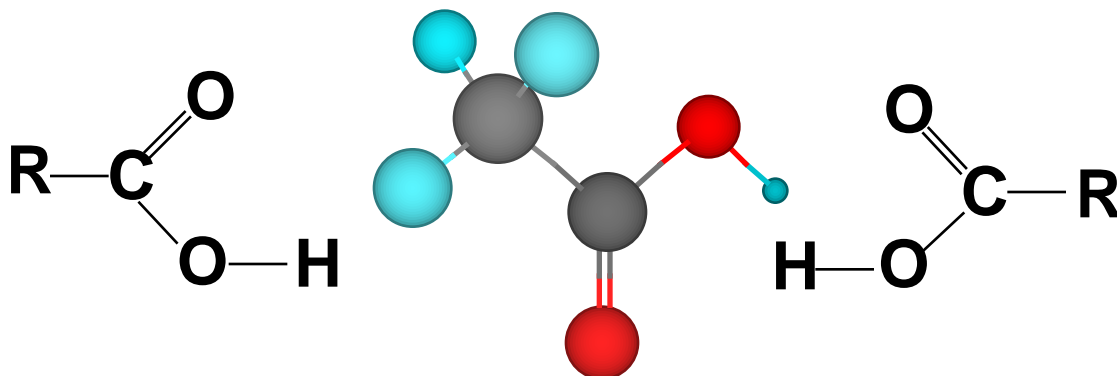


12



CARBOXYLIC ACIDS

CHAPTER SUMMARY

12.1 Structure of Carboxylic Acids

Carboxylic acids are structurally characterized by the **carboxyl group**, a carbon-oxygen double bond with a directly attached OH group. This is a very reactive functional group because (1) there are three polar bonds, the carbon-oxygen double and single bonds and the oxygen-hydrogen bond; (2) the double bond has electrons in a pi-bond; and (3) there are two unshared electron pairs on each oxygen. Carboxylic acids have an unpleasant odor and taste; they are found widely in nature.

12.2 Nomenclature of Carboxylic Acids

A. Simple Carboxylic Acids

Carboxylic acids are almost always named using a suffix. The suffix **oic acid** is attached to the name for the longest continuous carbon chain. If the acid group is attached to a ring the suffix **carboxylic acid** is used.

B. Polyfunctional Carboxylic Acids

Of the functional groups, carboxylic acids are the highest priority and named with a suffix; the other functional groups - aldehydes, ketones, alcohols and amines are named with prefixes if in a molecule where a carboxylic acid has received the suffix designation.

C. General Procedure for Naming Organic Compounds

A general procedure for naming organic compounds is given in this chapter since this is the last major functional group covered. **The procedure for naming organic compounds is:**

- (1) Name the longest continuous carbon chain.
- (2) Name carbon-carbon double and triple bonds with suffixes en and yn respectively; if all carbon-carbon bonds are single, use an.
- (3) Name the highest priority functional group with a suffix (acid > aldehyde > ketone > alcohol > amine) and the others with prefixes.
- (4) Number the carbon chain giving preference to the functional group named by a suffix, then multiple bonds (carbon-carbon double bonds take priority over triple bonds when making a choice is necessary), then groups named with prefixes.
- (5) Name all other groups with prefixes and number them.

D. Common Names of Carboxylic Acids

Carboxylic acids are also named with common names that often describe a familiar source or property of the compound.

12.3 Physical Properties of Carboxylic Acids

The boiling points of carboxylic acids are high relative to other classes of compounds due to **hydrogen bonding**; carboxylic acid molecules can hydrogen bond in two places and as a result often exist as dimers. Lower molecular weight carboxylic acids are water soluble.

12.4 Acidity of Carboxylic Acids

A. Reactions of Acids with Base: Salt Formation

Acidity is the characteristic property of carboxylic acids; they react with strong bases like sodium hydroxide and weaker bases such as sodium bicarbonate. The ability to be neutralized by sodium bicarbonate distinguishes carboxylic acids from phenols.

B. Explanation for the Acidity of Carboxylic Acids

The acidity of carboxylic acids is the result of **resonance stabilization** in the **carboxylate anion** formed upon ionization or neutralization of the acid.

C. Structure and Relative Acidities of Carboxylic Acids

The acidity of carboxylic acids is described by the **acidity constant**, K_a , and its negative logarithm, pK_a . Large K_a 's and small pK_a 's denote high acidities. Acid strength is influenced by substituents on the carboxylic acid molecule. **Electron-withdrawing groups** disperse the negative character of the carboxylate ion and increase acidity whereas **electron-releasing groups** intensify the negative charge and decrease acidity. The **strength, number, and proximity** of electron-withdrawing groups can have dramatic effects on relative acidities.

D. Nomenclature of the Salts of Carboxylic Acids

Salts of carboxylic acids are named by changing the **oic acid** suffix of the acid to **ate** and preceding it by the name of the **cation**.

CONNECTIONS 12.1 Food Preservatives**12.5 Preparations of Carboxylic Acids****A. Oxidation of Alkylbenzenes****B. Oxidation of Primary Alcohols****C. Hydrolysis of Nitriles****D. Carbonation of Grignard Reagents**

SOLUTIONS TO PROBLEMS**12.1 IUPAC Nomenclature**

- (a) heptanoic acid; (b) 4,4,4-tribromobutanoic acid; (c) 1,5-pentandioic acid; (d) cyclohexanecarboxylic acid (e) m-methylbenzoic acid; (f) 3-chlorocyclobutanecarboxylic acid

12.2 IUPAC Nomenclature

- (a) 2-hydroxypropanoic acid; (b) 1-cyclopentenecarboxylic acid; (c) 3-hexyn-1,6-dioic acid

12.3 IUPAC Nomenclature

- (a) 4-amino-2-pentenoic acid; (b) 4-hydroxy-2,5-cyclohexadien-1-carboxylic acid; (c) 3,5-dioxohexanoic acid

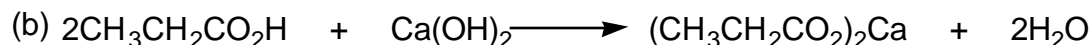
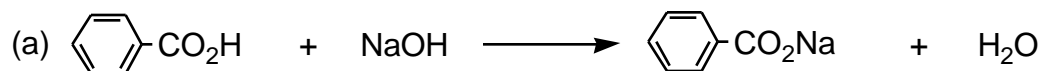
12.4 Boiling Points of Carboxylic Acids

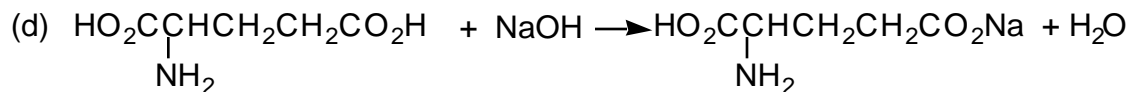
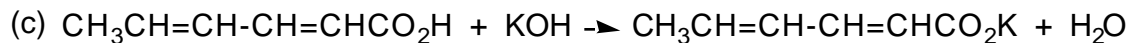
The compounds decrease in boiling point in the order given as capacity for hydrogen bonding decreases in this order. The first one has two carboxylic acid groups and thus two sites for hydrogen bonding. The second has only one carboxylic acid group and there are none, no O-H bonds at all, in the third.

12.5 Water Solubility of Carboxylic Acids

most soluble ethanoic acid > pentanoic acid > decanoic acid **least soluble**
(all proportions) (3.7g/100g) (0.2g/100g)

As the molecular weight of the acids increase the proportion of non-polar hydrocarbon to polar carboxyl group increases. As a result, the solubility in the polar solvent, water, decreases.

12.6 Neutralization of Carboxylic Acids



12.7 Relative Acidities of Carboxylic Acids and Phenols

Both phenols and carboxylic acids are neutralized by the strong base sodium hydroxide. Since both are water soluble, there would be no obvious visible difference with this reagent, even if there were a difference in extent of reaction. However, phenols are a lot less acidic than carboxylic acids and will not react with the weak base sodium bicarbonate. If one adds sodium bicarbonate to aqueous solutions of these compounds, bubbles of carbon dioxide will be visible as the bicarbonate and propanoic acid neutralize one another. Since the phenol does not react, no CO_2 evolution will be observed.

12.8 Relative Acidities

least
acidic

butane < butanol < phenol < butanoic acid < nitric acid

most
acidic

12.9 Relative Acidities

Numerically larger acidity constants mean greater acidity. However, smaller pK_a 's denote greater acidity.

(a) ii < iii < v < iv < i (b) iii < iv < ii < i

12.10 Relative Acidities

(a) iii < ii < iv < i

All of these compounds have three electron withdrawing groups on the carbon next to the carboxylic acid. Relative acidity depends on the strength of the groups. Electronegativity of halogens is $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

(b) iv < i < iii < ii

Relative acidities depend on the number and proximity of electron withdrawing groups. The most acidic, ii, has two chlorines on the carbon directly adjacent to the acid group. In iii, one of the two chlorines has been moved one carbon away. In i, both chlorines are two carbons away from the acid and in iv, there is only one chlorine and it is as far from the acid as it can be.

(c) i < ii < iii

The most acidic, iii, has two acid groups; each acts as an electron-withdrawing group on the other and increases acidity. ii has neither electron-withdrawing or electron-releasing groups, and i has one electron-releasing group which decreases acidity.

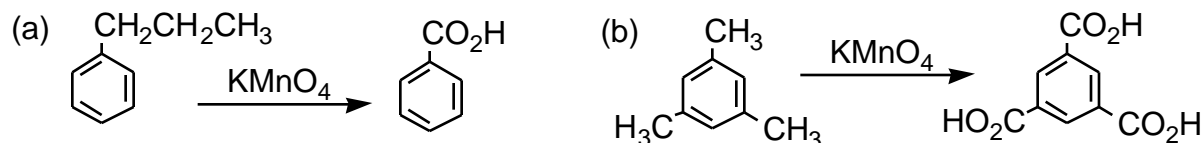
(d) meta < para < ortho

Each has one electron-withdrawing group. Because of resonance, the ortho and para chloro's increase acidity more than meta. In addition, the ortho is closer and thus this is the most acidic.

12.11 Nomenclature of Carboxylic Acid Salts

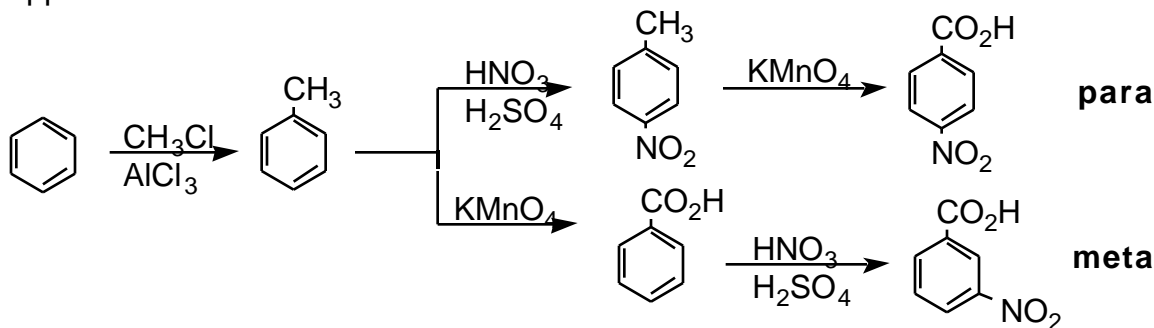
- (a) Sodium ethanoate; (b) calcium propanoate; (c) potassium 2-butenoate
(d) ammonium p-bromobenzoate

12.12 Preparations of Carboxylic Acids

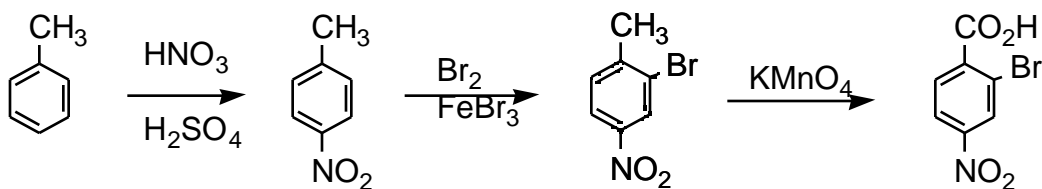
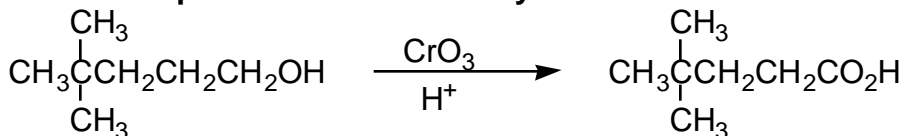
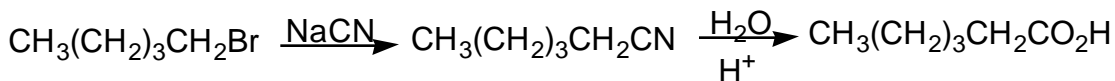
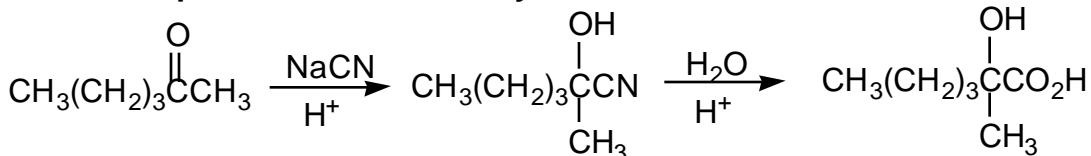
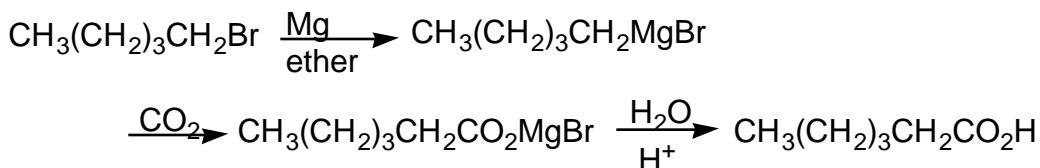


12.13 Preparations of Carboxylic Acids

(a) The important thing to remember here is that the methyl group is an ortho-para director whereas the carboxylic acid group directs meta. For the para isomer one would oxidize the methyl after introducing the nitro group; just the opposite would be done to obtain the meta isomer.



(b) Directive effects are important. The methyl directs the nitro para. The methyl and nitro both direct to the desired position for the bromine. Oxidation gives the requested compound.

**12.14 Preparations of Carboxylic Acids****12.15 Preparations of Carboxylic Acids****12.16 Preparations of Carboxylic Acids****12.17 Preparations of Carboxylic Acids****12.18 Nomenclature of Carboxylic Acids:** Section 12.2A

- (a) nonanoic acid; (b) pentanoic acid; (c) 4-methylpentanoic acid;
 (d) 3-ethyl-5-methylhexanoic acid; (e) 1,4-butandioic acid
 (f) 2,2,2-trichloroethanoic acid

12.19 Nomenclature of Carboxylic Acids: Section 12.2A

- (a) cycloheptanecarboxylic acid; (b) cyclobutane -1,3-dicarboxylic acid;
 (c) 3-ethylcyclopentanecarboxylic acid

12.20 Nomenclature of Carboxylic Acids: Section 12.2A

- (a) 2,4-dichlorobenzoic acid; (b) p-nitrobenzoic acid;
 (c) m-methylbenzoic acid

12.21 Nomenclature of Polyfunctional Carboxylic Acids: Section 12.2B

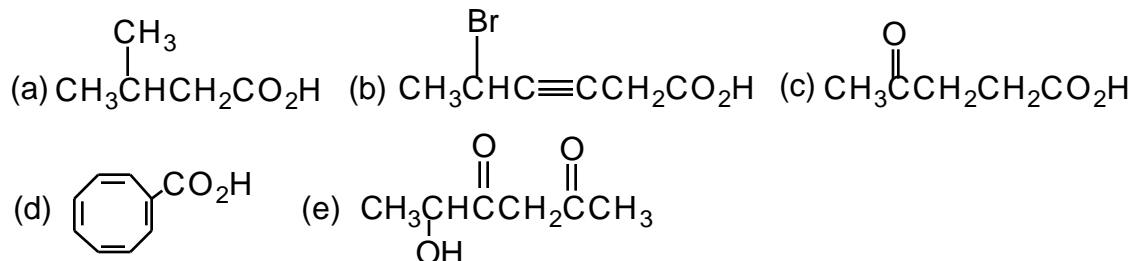
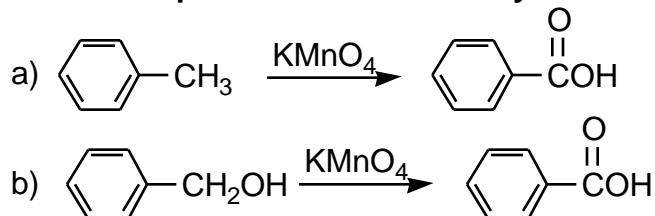
- (a) 2-hexenoic acid; (b) 5-hydroxyhexanoic acid;
 (c) 4-oxocyclohexanecarboxylic acid; (d) 1-cyclobutenecarboxylic acid;
 (e) 2-buten-1,4-dioic acid; (f) 3,5-dioxohexanoic acid;
 (g) 2,4-hexadienoic acid; (h) 4-oxo-2-pentynoic acid;
 (i) 4-amino-2-butenic acid

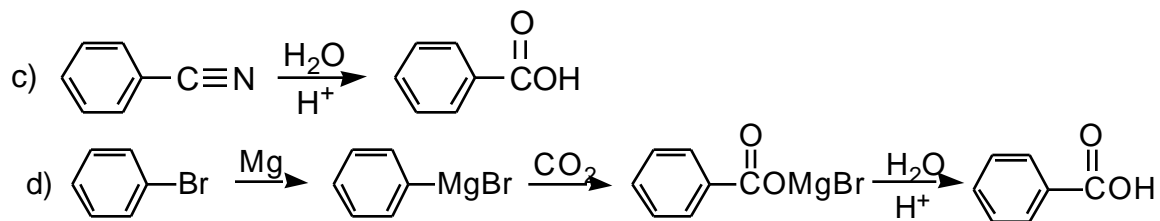
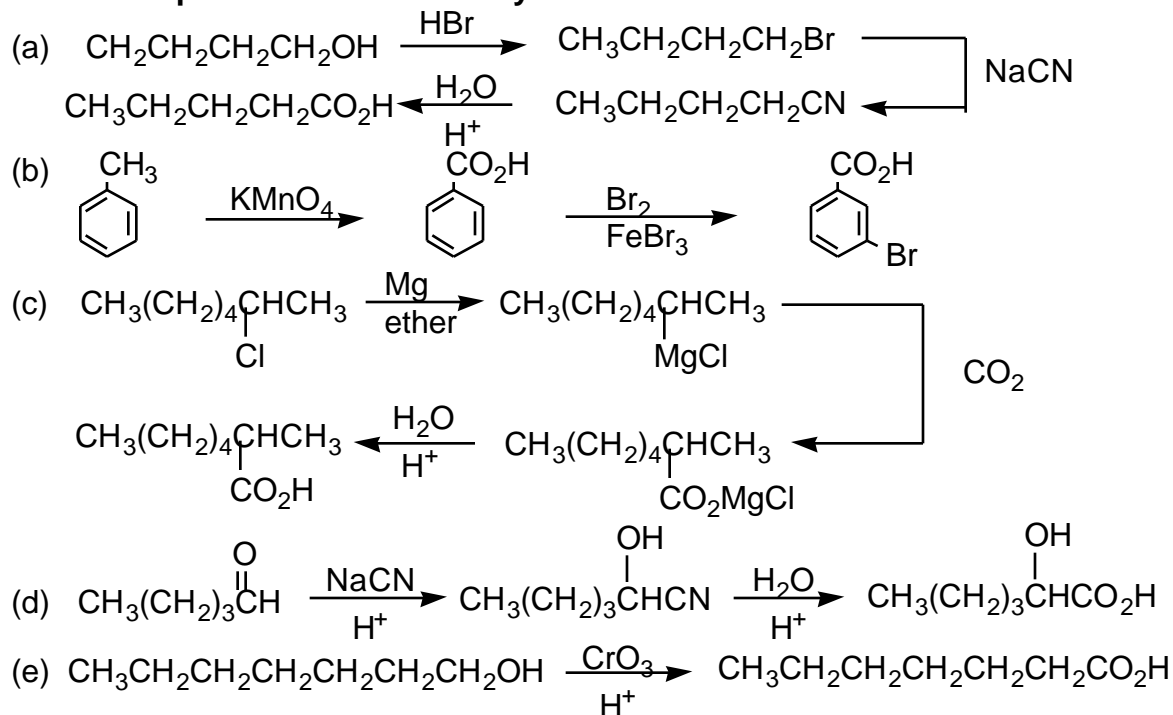
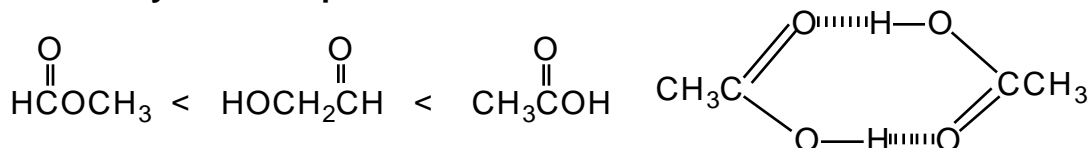
12.22 Nomenclature of Organic Compounds: Section 12.2C

- (a) 2-butenal; (b) 6-amino-2,4-hexandien-1-ol; (c) 3-hydroxy-2,4-pentandione;
 (d) 3-hexyn-2,5-dione; (e) 4-hydroxy-2-cyclohexen-1-one;
 (f) N,N-dimethyl-2-cyclopentenamine; (g) 4-hydroxy-2-heptenoic acid;
 (h) 8-bromo-7-hydroxy-2-octen-5-yn-4-one

12.23 Nomenclature of Carboxylic Acid Salts: Section 12.4D

- (a) sodium butanoate; (b) calcium ethanoate;
 (c) potassium 4,4,4-tribromobutanoate; (d) ammonium 2,4-dibromobenzoate;
 (e) sodium cyclopentanecarboxylate; (f) sodium 4-oxo-2-pentenoate

12.24 IUPAC Nomenclature: Section 12.2**12.25 Preparations of Carboxylic Acids:** Section 12.5

**12.26 Preparations of Carboxylic Acids:** Section 12.5**12.27 Physical Properties:** Section 12.3

The lowest boiling compound has no O-H bonds and cannot hydrogen bond. In the compound with the highest boiling point, the O-H bond is polarized by the C=O making the hydrogen bonding even stronger. Also in ethanoic acid, two molecules can orient so that hydrogen bonding can occur in two positions.

12.28 Physical Properties: Section 12.3

The dramatic difference in boiling points between chloroethane and ethanoic acid is a result of the ability of ethanoic acid to hydrogen bond. Bromoethane has a higher boiling point than chloroethane because bromoethane has a higher molecular weight. However, this increase in molecular weight doesn't

come close to offsetting the hydrogen bonding ability of ethanoic acid in influencing boiling points.

12.29 Acidity: Section 12.4B-C

Least Acidic \longrightarrow **Most Acidic**

- a) 4 < 2 < 3 < 1 b) 3 < 2 < 1 c) 2 < 4 < 1 < 3
 d) 4 < 1 < 3 < 2 e) 3 < 2 < 1 f) 3 < 1 < 4 < 2

(a) The electronegativity of the halogens is $F > Cl > Br$; the acidity is in the same direction because electron-withdrawing groups increase acidity. The #4 compound doesn't have an electron-withdrawing group and is least acidic.

(b) The carbon oxygen double bond is an electron-withdrawing group and will increase acidity. The closer to the acid group, the more effective and acidity is in this direction.

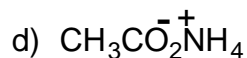
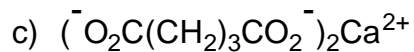
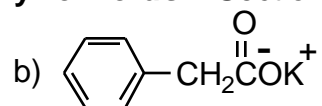
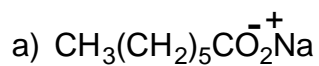
(c) Each compound has two bromines; these are electron-withdrawing groups and will increase acidity. The proximity of the bromines to the acid group is the determining factor. In the least acidic they are on carbons 3 and 4; in the next, carbons 2 and 4; in the next, carbons 2 and 3; and in the most acidic, both are on carbon 2.

(d) Chlorine is electron-withdrawing and will increase acidity. On a benzene ring the effect will be greatest with the chlorine is ortho or para to the acid group. In the least acidic, there is only one chlorine and it is meta; the compound with just one chlorine, but para, is next. The other two compounds have two chlorines. In each one is para and the other is either meta or ortho; the ortho is more effective and this is the most acidic.

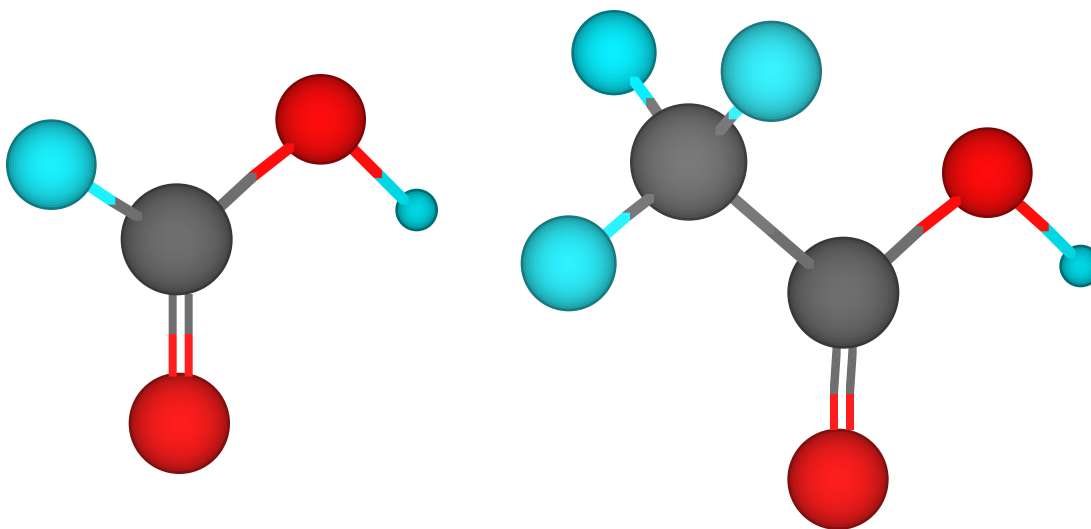
(e) These are dicarboxylic acids. Acid groups are electron-withdrawing so each can increase the acidity of the other. The determining factor here is how close they are to one another.

(f) These are four different classes of organic compounds. Alkanes are not acidic. Alcohols are very slightly acidic but no so much as phenols in which the anion formed from ionization is resonance stabilized. Carboxylic acids are the most acidic because of the electron-withdrawing carbon-oxygen double bond and the resonance stabilization of the anion.

12.32 Neutralization Reactions of Carboxylic Acids: Section 12.4A

**ACTIVITIES WITH MOLECULAR MODELS**

1. Make molecular models of formic acid, a component of the sting of ants, and acetic acid, which is 5% of most vinegars.



2. There are two carboxylic acids with the formula of $\text{C}_4\text{H}_8\text{O}_2$. Make molecular models of each.

