1.1 Functional Groups

Figure 1
The design and synthesis of new materials with specific properties, like the plastic in this artificial ski run, is a key focus of the chemical industry.

With the huge number of organic substances, we would have great difficulty memorizing the properties of each compound. Fortunately, the compounds fall into **organic families** according to particular combinations of atoms in each molecule. The physical properties and reactivity of the compounds are related to these recognizable combinations, called **functional groups**. These functional groups determine whether the molecules are readily soluble in polar or non-polar solvents, whether they have high or low melting and boiling points, and whether they readily react with other molecules.

So, if we can recognize and understand the influence of each functional group, we will be able to predict the properties of any organic compound. If we can predict their properties, we can then design molecules to serve particular purposes, and devise methods to make these desired molecules.

organic family a group of organic compounds with common structural features that impart characteristic physical properties and reactivity

functional group a structural arrangement of atoms that imparts particular characteristics to the molecule

In this chapter, we will discuss each organic family by relating its properties to the functional groups it contains. Moreover, we will focus on how one organic family can be synthesized from another; that is, we will learn about the reaction pathways that allow one functional group to be transformed into another. By the end of the chapter, we will have developed a summary flow chart of organic reactions, and we will be able to plan synthetic pathways to and from many different organic molecules. After all, designing the synthesis of new molecules, ranging from high-tech fabrics to "designer drugs," is one of the most important aspects of modern organic chemistry (**Figure 1**).

Before discussing each organic family, let's take a look at what makes up the functional groups. Although there are many different functional groups, they essentially consist of only three main components, one or more of which may be present in each functional group. Understanding the properties of these three components will make it easy to understand and predict the general properties of the organic families to which they belong (**Figure 2**):

- carbon−carbon multiple bonds, −C=C− or −C≡C−
- single bonds between a carbon atom and a more electronegative atom, e.g., −C−O−, −C−N−, or −C−Cl
- carbon atom double-bonded to an oxygen atom, −C=O

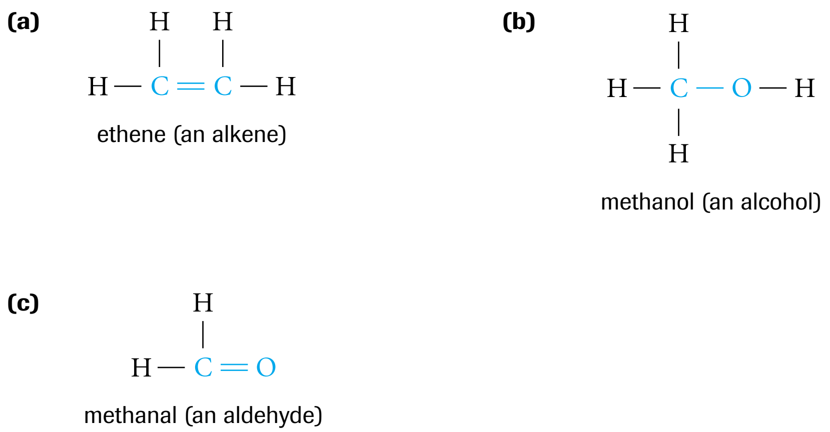

Figure 2
Examples of the three main components of functional groups:
(a) A double bond between two carbon atoms
(b) A single bond between carbon and a more electronegative atom (e.g., oxygen)
(c) A double bond between carbon and oxygen

Carbon–Carbon Multiple Bonds

When a C atom is single-bonded to another C atom, the bond is a strong covalent bond that is difficult to break. Thus, the sites in organic molecules that contain C—C bonds are not reactive. However, double or triple bonds between C atoms are more reactive. The second and third bonds formed in a multiple bond are not as strong as the first bond and are more readily broken. This allows carbon–carbon multiple bonds to be sites for reactions in which more atoms are added to the C atoms. The distinction between single and multiple bonds is not always clear-cut. For example, the reactivity of the six-carbon ring structure found in benzene indicates that there may be a type of bond intermediate between a single and a double bond. This theory is supported by measured bond lengths. You will learn more about the strengths of single and multiple bonds in Chapter 4.

Single Bonds Between Carbon and More Electronegative Atoms

Whenever a C atom is bonded to a more electronegative atom, the bond between the atoms is polar; that is, the electrons are held more closely to the more electronegative atom. This results in the C atom having a partial positive charge and the O, N, or halogen atom having a partial negative charge. Any increase in polarity of a molecule also increases intermolecular attractions, such as van der Waals forces. As more force is required to separate the molecules, the melting points and boiling points also increase (**Figure 3**).

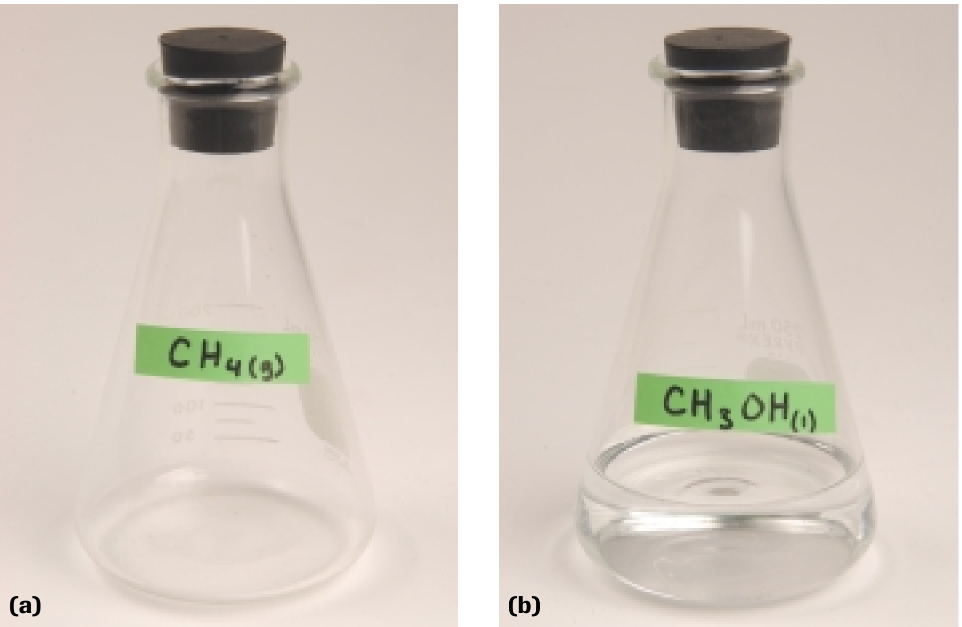

Figure 3
(a) Nonpolar substances, with weak forces of attraction among the molecules, evaporate easily. In fact, they are often gases at room temperature.
(b) Polar substances, with strong forces of attraction among the molecules, require considerable energy to evaporate.

If the O or N atoms are in turn bonded to an H atom, an —OH or —NH group is formed, with special properties. The presence of an —OH group enables an organic molecule to form hydrogen bonds with other —OH groups. The formation of these hydrogen bonds not only further increases intermolecular attractions, it also enables these molecules to mix readily with polar solutes and solvents. You may recall the saying "like dissolves like." The solubility of organic compounds is affected by nonpolar components and polar components within the molecule. Since N is only slightly less electronegative than O, the effect of an N—H bond is similar to that of an O—H bond: —NH groups also participate in hydrogen bonding.

LEARNING TIP

When atoms have different electronegativities (**Table 1**), the bonds that form between them tend to be polar, with the electrons displaced toward the more electronegative atom. Many properties of compounds of these elements are explained by the polarity of their bonds.

Table 1 Electronegativities of Common Elements

Element	Electronegativity
H	2.1
C	2.5
N	3.0
O	3.5

Double Bonded Carbon and Oxygen

The third main component of functional groups consists of a C atom double-bonded to an O atom. The double covalent bond between C and O requires that *four* electrons be shared between the atoms, all four being more strongly attracted to the O atom. This makes the C=O bond strongly polarized, with the accompanying effects of raising boiling and melting points, and increasing solubility in polar solvents.

SUMMARY Three Main Components of Functional Groups

Multiple bonds between C atoms

−C=C− −C≡C−	Unlike single C−C bonds, double and triple bonds allow atoms to be added to the chain.

C atom bonded to a more electronegative atom (O, N, halogen)

C−O C−N C−Cl, C−Br, C−F	Unequal sharing of electrons results in polar bonds, increasing intermolecular attraction, and raising boiling and melting points.
C−OH or C−NH−	These groups enable hydrogen bonding, increasing solubility in polar substances.

C atom double-bonded to an O atom

C=O	The resulting polar bond increases boiling point and melting point.

Practice

Understanding Concepts

1. Explain the meaning of the term "functional group."
2. Are double and triple bonds between C atoms more reactive or less reactive than single bonds? Explain.
3. Would a substance composed of more polar molecules have a higher or lower boiling point than a substance composed of less polar molecules? Explain.
4. Describe the three main components of functional groups in organic molecules.

Section 1.1 Questions

Understanding Concepts

1. What is the effect of the presence of an —OH group or an —NH group on
   (a) the melting and boiling points of the molecule? Explain.
   (b) the solubility of the molecule in polar solvents? Explain.
2. Identify all components of functional groups in the following structural diagrams. Predict the solubility of each substance in water.
   (a) $CH_3—O—H$
   (b) $CH_3CH=CHCH_3$
   (c) $CH_3CH=O$
   (d) $CH_3CH_2C(=O)OH$ (drawn as $CH_3CH_2C=O$ with OH bonded below the C)
3. The compounds water, ammonia, and methane are formed when an oxygen atom, a nitrogen atom, and a carbon atom each bonds with hydrogen atoms.
   (a) Write a formula for each of the three compounds.
   (b) Predict, with reference to electronegativities and intermolecular forces, the solubility of each of the compounds in the others.
   (c) Of the three compounds, identify which are found or produced by living organisms, and classify each compound as organic or inorganic. Justify your answer.