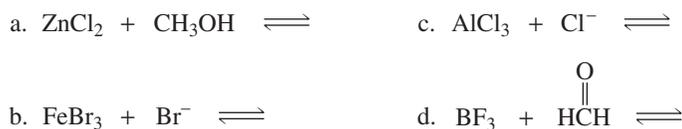
**PROBLEM 48**

What is the product of each of the following reactions?

**PROBLEM 49**

Show how each of the following compounds reacts with HO^- :

**Summary**

Organic compounds are compounds that contain carbon. The **atomic number** of an atom equals the number of protons in its nucleus. The **mass number** of an atom is the sum of its protons and neutrons. **Isotopes** have the same atomic number, but different mass numbers.

An **atomic orbital** indicates where there is a high probability of finding an electron. The closer the atomic orbital is to the nucleus, the lower is its energy. **Degenerate orbitals** have the same energy. Electrons are assigned to orbitals following the **aufbau principle**, the **Pauli exclusion principle**, and **Hund's rule**.

The **octet rule** states that an atom will give up, accept, or share electrons in order to fill its outer shell or attain an outer shell with eight electrons. **Electropositive** elements readily lose electrons; **electronegative** elements readily acquire electrons. The **electronic configuration** of an atom describes the orbitals occupied by the atom's electrons. Electrons in inner shells are called **core electrons**; electrons in the outermost shell are called **valence electrons**. **Lone-pair electrons** are valence electrons that are not used in

bonding. Attractive forces between opposite charges are called **electrostatic attractions**. An **ionic bond** is formed by a transfer of electrons; a **covalent bond** is formed by sharing electrons. A polar covalent bond has a **dipole**, measured by a **dipole moment**. The **dipole moment** of a molecule depends on the magnitudes and directions of the bond dipole moments.

Lewis structures indicate which atoms are bonded together and show **lone pairs** and **formal charges**. A **carbocation** has a positively charged carbon, a **carbanion** has a negatively charged carbon, and a **radical** has an unpaired electron.

According to **molecular orbital (MO) theory**, covalent bonds result when atomic orbitals combine to form **molecular orbitals**. Atomic orbitals combine to give a **bonding MO** and a higher energy **antibonding MO**. Cylindrically symmetrical bonds are called **sigma (σ) bonds**; **pi (π) bonds** form when *p* orbitals overlap side-to-side. Bond strength is measured by the **bond dissociation energy**. A σ bond is stronger than a π bond. All **single**

bonds in organic compounds are σ bonds, a **double bond** consists of one σ bond and one π bond, and a **triple bond** consists of one σ bond and two π bonds. Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds. To form four bonds, carbon promotes an electron from a $2s$ to a $2p$ orbital. C, N, and O form bonds using **hybrid orbitals**. The **hybridization** of C, N, or O depends on the number of π bonds the atom forms: No π bonds means that the atom is sp^3 **hybridized**, one π bond indicates that it is sp^2 **hybridized**, and two π bonds signifies that it is sp **hybridized**. Exceptions are carbocations and carbon radicals, which are sp^2 hybridized. The more s character in the orbital used to form a bond, the shorter and stronger the bond is and the larger the bond angle is. Bonding and lone-pair electrons around an atom are positioned as far apart as possible.

An **acid** is a species that donates a proton, and a **base** is a species that accepts a proton. A **Lewis acid** is a species that accepts a share in an electron pair; a **Lewis base** is a species that donates a share in an electron pair.

Acidity is a measure of the tendency of a compound to give up a proton. **Basicity** is a measure of a compound's affinity for a proton. The stronger the acid, the weaker is its conjugate base. The strength of an acid is given by the **acid dissociation constant** (K_a). Approximate pK_a values are as

follows: protonated alcohols, protonated carboxylic acids, protonated water < 0 ; carboxylic acids ~ 5 ; protonated amines ~ 10 ; alcohols and water ~ 15 . The **pH** of a solution indicates the concentration of positively charged hydrogen ions in the solution. In **acid–base reactions**, the equilibrium favors reaction of the strong and formation of the weak.

The strength of an acid is determined by the stability of its conjugate base: The more stable the base, the stronger is its conjugate acid. When atoms are similar in size, the more acidic compound has its hydrogen attached to the more electronegative atom. When atoms are very different in size, the more acidic compound has its hydrogen attached to the larger atom. **Inductive electron withdrawal** increases acidity; acidity decreases with increasing distance between the electron-withdrawing substituent and the ionizing group.

Delocalized electrons are electrons shared by more than two atoms. A compound with delocalized electrons has **resonance**. The **resonance hybrid** is a composite of the **resonance contributors**, which differ only in the location of their lone-pair and π electrons.

The **Henderson–Hasselbalch equation** gives the relationship between pK_a and pH: A compound exists primarily in its acidic form in solutions more acidic than its pK_a value and primarily in its basic form in solutions more basic than its pK_a value.

Key Terms

- | | | |
|--|---|---------------------------------------|
| acid (p. 39) | dipole (p. 12) | lone-pair electrons (p. 13) |
| acid–base reaction (p. 40) | dipole moment (μ) (p. 12) | mass number (p. 4) |
| acid dissociation constant (K_a) (p. 41) | double bond (p. 30) | molecular weight (p. 4) |
| acidity (p. 40) | electronegative (p. 8) | molecular orbital (p. 20) |
| antibonding molecular orbital (p. 21) | electronegativity (p. 10) | molecular orbital (MO) theory (p. 20) |
| atomic number (p. 4) | electropositive (p. 7) | node (p. 18) |
| atomic orbital (p. 5) | electrostatic attraction (p. 8) | nodal plane (p. 19) |
| atomic weight (p. 4) | electrostatic potential map (p. 11) | nonbonding electrons (p. 13) |
| aufbau principle (p. 6) | equilibrium constant (p. 41) | nonpolar covalent bond (p. 10) |
| base (p. 39) | excited-state electronic configuration (p. 6) | nonpolar molecule (p. 26) |
| basicity (p. 40) | formal charge (p. 13) | octet rule (p. 7) |
| bond (p. 8) | free radical (p. 14) | orbital (p. 4) |
| bond dissociation energy (p. 21) | ground-state electronic configuration (p. 6) | orbital hybridization (p. 26) |
| bond length (p. 21) | Heisenberg uncertainty principle (p. 18) | organic compound (p. 2) |
| bonding molecular orbital (p. 21) | Henderson–Hasselbalch equation (p. 51) | Pauli exclusion principle (p. 6) |
| bond strength (p. 21) | Hund's rule (p. 7) | pH (p. 41) |
| buffer solution (p. 53) | hybrid orbital (p. 26) | pi (π) bond (p. 23) |
| carbanion (p. 14) | hydride ion (p. 9) | pK_a (p. 41) |
| carbocation (p. 14) | hydrogen ion (p. 9) | polar covalent bond (p. 10) |
| condensed structure (p. 16) | inductive electron withdrawal (p. 47) | proton (p. 9) |
| conjugate acid (p. 40) | ionic bond (p. 8) | proton-transfer reaction (p. 40) |
| conjugate base (p. 40) | ionic compound (p. 9) | quantum mechanics (p. 4) |
| constitutional isomer (p. 18) | ionization energy (p. 7) | radial node (p. 18) |
| core electrons (p. 7) | isotopes (p. 4) | radical (p. 18) |
| covalent bond (p. 9) | Kekulé structure (p. 16) | resonance (p. 51) |
| degenerate orbitals (p. 5) | Lewis acid (p. 54) | resonance contributors (p. 50) |
| delocalized electrons (p. 50) | Lewis base (p. 54) | resonance hybrid (p. 50) |
| debye (D) (p. 12) | Lewis structure (p. 13) | sigma (σ) bond (p. 20) |

sigma (σ) bonding molecular orbital (p. 21)
 single bond (p. 29)
 tetrahedral bond angle (p. 28)

tetrahedral carbon (p. 28)
 trigonal planar carbon (p. 30)
 triple bond (p. 32)
 valence electrons (p. 7)

valence-shell electron-pair repulsion (VSEPR) model (p. 24)
 wave equation (p. 4)
 wave functions (p. 4)

Problems

50. Draw a Lewis structure for each of the following species:

- | | | |
|----------------------------|------------------------------|----------------------------|
| a. H_2CO_3 | d. N_2H_4 | g. CO_2 |
| b. CO_3^{2-} | e. CH_3NH_2 | h. NO^+ |
| c. H_2CO | f. CH_3N_2^+ | i. H_2NO^- |

51. Give the hybridization of the central atom of each of the following species, and tell whether the bond arrangement around it is linear, trigonal planar, or tetrahedral:

- | | | |
|--------------------|--------------------|------------------------------|
| a. NH_3 | d. CH_3 | g. HCN |
| b. BH_3 | e. $^+\text{NH}_4$ | h. $\text{C}(\text{CH}_3)_4$ |
| c. $^-\text{CH}_3$ | f. $^+\text{CH}_3$ | i. H_3O^+ |

52. Draw the condensed structure of a compound that contains only carbon and hydrogen atoms and that has

- three sp^3 hybridized carbons.
- one sp^3 hybridized carbon and two sp^2 hybridized carbons.
- two sp^3 hybridized carbons and two sp hybridized carbons.

53. Predict the indicated bond angles:

- | | |
|---|--|
| a. the C—N—H bond angle in $(\text{CH}_3)_2\text{NH}$ | f. the H—C—H bond angle in $\text{H}_2\text{C}=\text{O}$ |
| b. the C—N—C bond angle in $(\text{CH}_3)_2\text{NH}$ | g. the F—B—F bond angle in $^-\text{BF}_4$ |
| c. the C—N—C bond angle in $(\text{CH}_3)_2\text{NH}_2^+$ | h. the C—C—N bond angle in $\text{CH}_3\text{C}\equiv\text{N}$ |
| d. the C—O—C bond angle in CH_3OCH_3 | i. the C—C—N bond angle in $\text{CH}_3\text{CH}_2\text{NH}_2$ |
| e. the C—O—H bond angle in CH_3OH | |

54. Give each atom the appropriate formal charge:

- | | | | |
|------------------------------------|--|---|--|
| a. $\text{H}:\ddot{\text{O}}:$ | c. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ | e. $\text{H}-\ddot{\text{C}}-\text{H}$ | g. $\begin{array}{c} \text{H}-\ddot{\text{C}}-\text{H} \\ \\ \text{H} \end{array}$ |
| b. $\text{H}:\ddot{\text{O}}\cdot$ | d. $\text{H}-\ddot{\text{N}}-\text{H}$ | f. $\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{N} & -\text{B}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$ | h. $\begin{array}{c} \text{CH}_3-\ddot{\text{O}}-\text{CH}_3 \\ \\ \text{H} \end{array}$ |

55. Draw the ground-state electronic configuration for:

- | | | | |
|-------|---------------------|-------|---------------------|
| a. Ca | b. Ca^{2+} | c. Ar | d. Mg^{2+} |
|-------|---------------------|-------|---------------------|

56. Write the Kekulé structure for each of the following compounds:

- | | | |
|------------------------------|--------------------------------|--|
| a. CH_3CHO | c. CH_3COOH | e. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CN}$ |
| b. CH_3OCH_3 | d. $(\text{CH}_3)_3\text{COH}$ | f. $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$ |

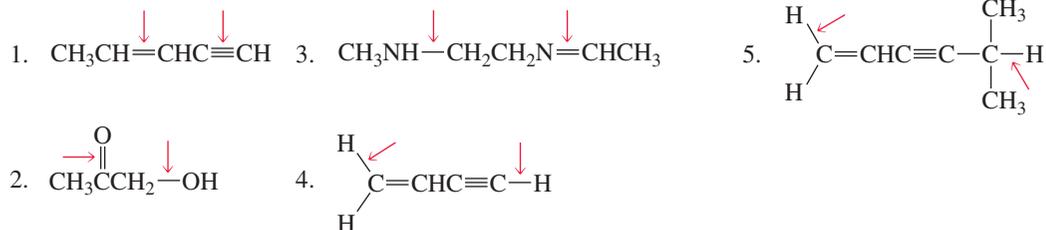
57. Show the direction of the dipole moment in each of the following bonds (use the electronegativities given in Table 1.3):

- | | | |
|----------------------------|----------------------------|---------------------------------------|
| a. CH_3-Br | c. $\text{HO}-\text{NH}_2$ | e. CH_3-OH |
| b. CH_3-Li | d. $\text{I}-\text{Br}$ | f. $(\text{CH}_3)_2\text{N}-\text{H}$ |

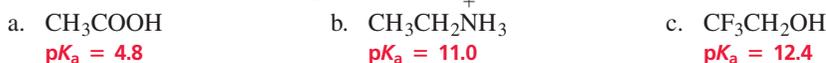
58. What is the hybridization of the indicated atom in each of the following molecules?

- | | | |
|---|---|--|
| a. $\text{CH}_3\overset{\downarrow}{\text{C}}=\text{CH}_2$ | c. $\text{CH}_3\overset{\downarrow}{\text{C}}\text{H}_2\text{OH}$ | e. $\text{CH}_3\overset{\downarrow}{\text{C}}=\text{NCH}_3$ |
| b. $\text{CH}_3\overset{\leftarrow}{\text{C}}\overset{\text{O}}{\parallel}{\text{C}}\text{H}_3$ | d. $\text{CH}_3\overset{\downarrow}{\text{C}}\equiv\text{N}$ | f. $\text{CH}_3\overset{\downarrow}{\text{O}}\text{CH}_2\text{CH}_3$ |

59. a. Which of the indicated bonds in each molecule is shorter?
 b. Indicate the hybridization of the C, O, and N atoms in each of the molecules.



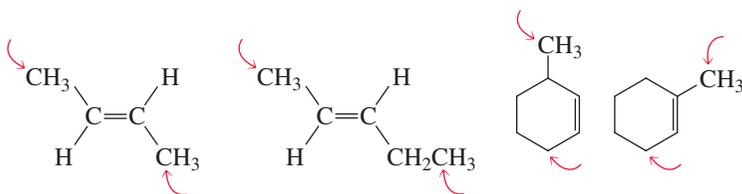
60. For each of the following compounds, draw the form in which it will predominate at pH = 3, pH = 6, pH = 10, and pH = 14:



61. Which of the following molecules have tetrahedral bond angles?



62. Do the sp^2 hybridized carbons and the indicated atoms lie in the same plane?



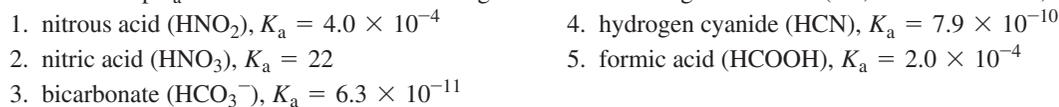
63. Give the products of the following acid-base reactions, and indicate whether reactants or products are favored at equilibrium (use the $\text{p}K_a$ values that are given in Section 1.17):



64. For each of the following molecules, indicate the hybridization of each carbon atom and give the approximate values of all the bond angles:

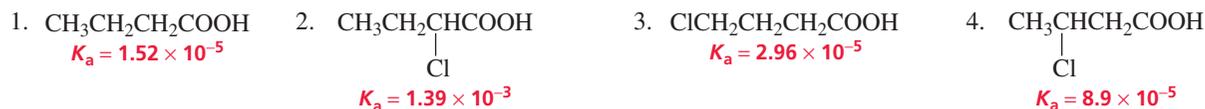


65. a. Estimate the $\text{p}K_a$ value of each of the following acids without using a calculator (i.e., between 3 and 4, between 9 and 10, etc.):



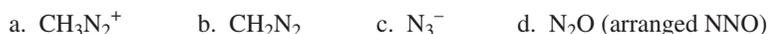
- b. Determine the $\text{p}K_a$ values, using a calculator.
 c. Which is the strongest acid?

66. a. List the following carboxylic acids in order of decreasing acidity:

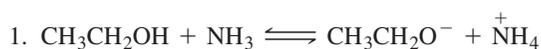


- b. How does the presence of an electronegative substituent such as Cl affect the acidity of a carboxylic acid?
 c. How does the location of the substituent affect the acidity of a carboxylic acid?

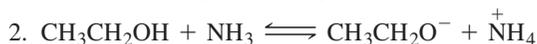
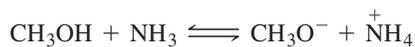
67. Draw a Lewis structure for each of the following species:



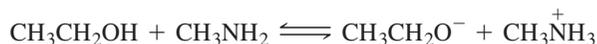
68. a. For each of the following pairs of reactions, indicate which one has the more favorable equilibrium constant (that is, which one most favors products):



or

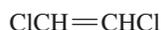


or



b. Which of the four reactions has the most favorable equilibrium constant?

69. The following compound has two isomers:



One isomer has a dipole moment of 0 D, and the other has a dipole moment of 2.95 D. Propose structures for the two isomers that are consistent with these data.

70. Knowing that $\text{pH} + \text{pOH} = 14$ and that the concentration of water in a solution of water is 55.5 M, show that the $\text{p}K_a$ of water is 15.7. (*Hint:* $\text{pOH} = -\log[\text{HO}^-]$.)

71. Water and diethyl ether are immiscible liquids. Charged compounds dissolve in water, and uncharged compounds dissolve in ether.

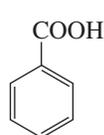
$\text{C}_6\text{H}_{11}\text{COOH}$ has a $\text{p}K_a$ of 4.8 and $\text{C}_6\text{H}_{11}\overset{+}{\text{N}}\text{H}_3$ has a $\text{p}K_a$ of 10.7.

a. What pH would you make the water layer in order to cause both compounds to dissolve in it?

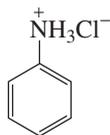
b. What pH would you make the water layer in order to cause the acid to dissolve in the water layer and the amine to dissolve in the ether layer?

c. What pH would you make the water layer in order to cause the acid to dissolve in the ether layer and the amine to dissolve in the water layer?

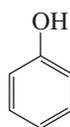
72. How could you separate a mixture of the following compounds? The reagents available to you are water, ether, 1.0 M HCl, and 1.0 M NaOH. (*Hint:* See problem 70.)



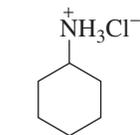
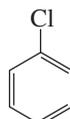
$\text{p}K_a = 4.17$



$\text{p}K_a = 4.60$



$\text{p}K_a = 9.95$



$\text{p}K_a = 10.66$

73. Using molecular orbital theory, explain why shining light on Br_2 causes it to break apart into atoms, but shining light on H_2 does not break the molecule apart.

74. Show that $K_{\text{eq}} = \frac{K_a \text{ reactant acid}}{K_a \text{ product acid}} = \frac{[\text{products}]}{[\text{reactants}]}$

75. Carbonic acid has a $\text{p}K_a$ of 6.1 at physiological temperature. Is the carbonic acid/bicarbonate buffer system that maintains the pH of the blood at 7.3 better at neutralizing excess acid or excess base?

76. a. If an acid with a $\text{p}K_a$ of 5.3 is in an aqueous solution of pH 5.7, what percentage of the acid is present in the acidic form?

b. At what pH will 80% of the acid exist in the acidic form?

77. Calculate the pH values of the following solutions:

a. a 1.0 M solution of acetic acid ($\text{p}K_a = 4.76$)

b. a 0.1 M solution of protonated methylamine ($\text{p}K_a = 10.7$)

c. a solution containing 0.3 M HCOOH and 0.1 M HCOO^- ($\text{p}K_a$ of $\text{HCOOH} = 3.76$)