Organic Chemistry 9th edition McMurry Solutions Manual

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Chapter 2 – Polar Covalent Bonds; Acids and Bases

Chapter Outline

I. Polar covalent bonds (Sections 2.1–2.3).

A. Electronegativity (Section 2.1).

1. Although some bonds are totally ionic and some are totally covalent, most chemical bonds are polar covalent bonds.
   a. In these bonds, electrons are attracted to one atom more than to the other atom.
2. Bond polarity is due to differences in electronegativity (EN).
   a. Elements on the right side of the periodic table are more electronegative than elements on the left side.
   b. Carbon has an EN of 2.5.
   c. Elements with EN > 2.5 are more electronegative than carbon.
   d. Elements with EN < 2.5 are less electronegative than carbon.
3. The difference in EN between two elements can be used to predict the polarity of a bond.
   a. If ΔEN < 0.4, a bond is nonpolar covalent.
   b. If ΔEN is between 0.4 and 2.0, a bond is polar covalent.
   c. If ΔEN > 2.0, a bond is ionic.
   d. The symbols Δ+ and Δ– are used to indicate partial charges.
   e. A crossed arrow is used to indicate bond polarity.
      i. The tail of the arrow is electron-poor, and the head of the arrow is electron-rich.
4. Electrostatic potential maps are also used to show electron-rich (red) and electron-poor (blue) regions of molecules.
5. An inductive effect is an atom's ability to polarize a bond.

B. Dipole moment (Section 2.2).

1. Dipole moment is the measure of a molecule's overall polarity.
2. Dipole moment (μ) = Q x r, where Q = charge and r = distance between charges.
   a. Dipole moment is measured in debyes (D).
3. Dipole moment can be used to measure charge separation.
4. Water and ammonia have large values of D; methane and ethane have D = 0.

C. Formal charge (Section 2.3).

1. Formal charge (FC) indicates electron "ownership" in a molecule.
2. $(\text{FC}) = \begin{bmatrix} \text{\# of valence} \\ \text{electrons} \end{bmatrix} - \begin{bmatrix} \dfrac{\text{\# of bonding electrons}}{2} \end{bmatrix} - \begin{bmatrix} \text{\# nonbonding} \\ \text{electrons} \end{bmatrix}$

II. Resonance (Sections 2.4–2.6).

A. Chemical structures and resonance (Section 2.4).

1. Some molecules (acetate ion, for example) can be drawn as two (or more) different electron-dot structures.
   a. These structures are called resonance structures.

SAMPLE

b. The true structure of the molecule is intermediate between the resonance structures.
c. The true structure is called a resonance hybrid.
2. Resonance structures differ only in the placement of π and nonbonding electrons.
a. All atoms occupy the same positions.
3. Resonance is an important concept in organic chemistry.
B. Rules for resonance forms (Section 2.5).
1. Individual resonance forms are imaginary, not real.
2. Resonance forms differ only in the placement of their π or nonbonding electrons.
a. A curved arrow is used to indicate the movement of electrons, not atoms.
3. Different resonance forms of a molecule don't have to be equivalent.
a. If resonance forms are nonequivalent, the structure of the actual molecule resembles the more stable resonance form(s).
4. Resonance forms must obey normal rules of valency.
5. The resonance hybrid is more stable than any individual resonance form.
C. A useful technique for drawing resonance forms (Section 2.6).
1. Any three-atom grouping with a multiple bond adjacent to a nonbonding *p* orbital has two resonance forms.
2. One atom in the grouping has a lone electron pair, a vacant orbital or a single electron.
3. By recognizing these three-atom pieces, resonance forms can be generated.
III. Acids and bases (Sections 2.7–2.11).
A. Brønsted–Lowry definition (Section 2.7).
1. A Brønsted–Lowry acid donates an H^+ ion; a Brønsted–Lowry base accepts H^+.
2. The product that results when a base gains H^+ is the conjugate acid of the base; the product that results when an acid loses H^+ is the conjugate base of the acid.
3. Water can act either as an acid or as a base.
B. Acid and base strength (Section 2.8–2.10).
1. A strong acid reacts almost completely with water (Section 2.8).
2. The strength of an acid in water is indicated by K_a, the acidity constant.
3. Strong acids have large acidity constants, and weaker acids have smaller acidity constants.
4. The pK_a is normally used to express acid strength.
a. $pK_a = -\log K_a$
b. A strong acid has a small pK_a, and a weak acid has a large pK_a.
c. The conjugate base of a strong acid is a weak base, and the conjugate base of a weak acid is a strong base.
5. Predicting acid–base reactions from pK_a (Section 2.9).
a. An acid with a low pK_a (stronger acid) reacts with the conjugate base of an acid with a high pK_a (stronger base).
b. In other words, the products of an acid–base reaction are more stable than the reactants.

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6. Organic acids and organic bases (Section 2.10).
   a. There are two main types of organic acids:
      i. Acids that contain hydrogen bonded to oxygen.
      ii. Acids that have hydrogen bonded to the carbon next to a C=O group.
   b. The main type of organic base contains a nitrogen atom with a lone electron pair.

C. Lewis acids and bases (Section 2.11).
   1. A Lewis acid accepts an electron pair.
      a. A Lewis acid may have either a vacant low-energy orbital or a polar bond to hydrogen.
      b. Examples include metal cations, halogen acids, group 3 compounds and transition-metal compounds.
   2. A Lewis base has a pair of nonbonding electrons.
      a. Most oxygen- and nitrogen-containing organic compounds are Lewis bases.
      b. Many organic Lewis bases have more than one basic site.
   3. A curved arrow shows the movement of electrons from a Lewis base to a Lewis acid.

IV. Noncovalent interactions in molecules (Section 2.12).

A. Dipole–dipole interactions occur between polar molecules as a result of electrostatic interactions among dipoles.
   1. These interactions may be either attractive or repulsive.
   2. The attractive geometry is lower in energy and predominates.

B. Dispersion forces result from the constantly changing electron distribution within molecules.
   1. These forces are transient and weak, but their cumulative effect may be important.

C. Hydrogen bonds.
   1. Hydrogen bonds form between a hydrogen bonded to an electronegative atom and an unshared electron pair on another electronegative atom.
   2. Hydrogen bonds are extremely important in living organisms.
   3. Hydrophilic substances dissolve in water because they are capable of forming hydrogen bonds.
   4. Hydrophobic substances don't form hydrogen bonds and usually don't dissolve in water.

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Solutions to Problems

2.1 After solving this problem, use Figure 2.2 to check your answers. The larger the number, the more electronegative the element.

More electronegative	*Less electronegative*
(a) H (2.1)	Li (1.0)
(b) Br (2.8)	B (2.0)
(c) Cl (3.0)	I (2.5)
(d) C (2.5)	H (2.1)

Carbon is slightly more electronegative than hydrogen.

2.2 As in Problem 2.1, use Figure 2.2. The partial negative charge is placed on the more electronegative atom, and the partial positive charge is placed on the less electronegative atom.

(a) $\overset{\delta+}{H_3C}—\overset{\delta-}{Cl}$

(b) $\overset{\delta+}{H_3C}—\overset{\delta-}{NH_2}$

(c) $\overset{\delta-}{H_2N}—\overset{\delta+}{H}$

(d) $H_3C—SH$
Carbon and sulfur have identical electronegativies.

(e) $\overset{\delta-}{H_3C}—\overset{\delta+}{MgBr}$

(f) $\overset{\delta+}{H_3C}—\overset{\delta-}{F}$

2.3 Use Figure 2.2 to find the electronegativities of each element. Calculate ΔEN and rank the answers in order of increasing ΔEN.

Carbon:	EN = 2.5	Carbon:	EN = 2.5	Fluorine:	EN = 4.0
Lithium:	EN = 1.0	Potassium:	EN = 0.8	Carbon:	EN = 2.5
	ΔEN = 1.5		ΔEN = 1.7		ΔEN = 1.5

Carbon:	EN = 2.5	Oxygen:	EN = 3.5
Magnesium:	EN = 1.2	Carbon:	EN = 2.5
	ΔEN = 1.3		ΔEN = 1.0

The most polar bond has the largest ΔEN. Thus, in order of increasing bond polarity:

$H_3C — OH < H_3C — M_gBr < H_3C — Li$, $H_3C — F < H_3C — K$

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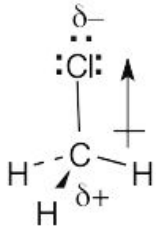
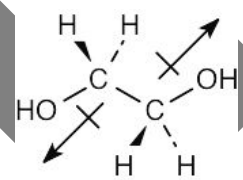
2.4 In an electrostatic potential map, the color red indicates regions of a molecule that are electron-rich. The map shows that chlorine is the most electronegative atom in chloromethane, and the direction of polarity of the C–Cl bond is:



Chloromethane

2.5

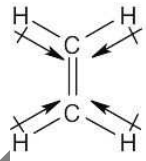
Ethylene glycol



The dipole moment of ethylene glycol is zero because the bond polarities of the two carbon–oxygen bonds cancel.

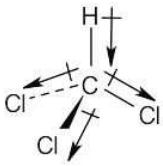
2.6 For each bond, identify the more electronegative element, and draw an arrow that points from the less electronegative element to the more electronegative element. Estimate the sum of the individual dipole moments to arrive at the dipole moment for the entire molecule.

(a)



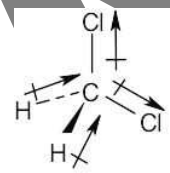
0 dipole moment

(b)



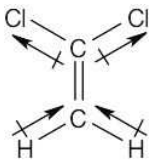
net dipole moment

(c)



net dipole moment

(d)



net dipole moment

2.7 To find the formal charge of an atom in a molecule, follow these two steps:

(1) Draw an electron-dot structure of the molecule.

(2) Use the formula in Section 2.3 (shown below) to determine formal charge for each atom. The periodic table shows the number of valence electrons of the element, and the electron-dot structure shows the number of bonding and nonbonding electrons.

$$\text{Formal charge (FC)} = \begin{bmatrix} \text{\# of valence} \\ \text{electrons} \end{bmatrix} - \begin{bmatrix} \dfrac{\text{\# of bonding electrons}}{2} \end{bmatrix} - \begin{bmatrix} \text{\# nonbonding} \\ \text{electrons} \end{bmatrix}$$

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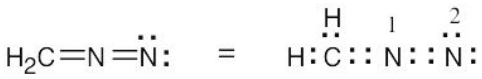
(a)



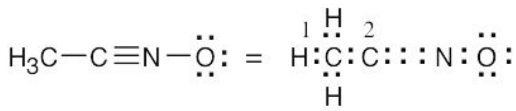
For carbon: $FC = 4 - \frac{8}{2} - 0 = 0$

For nitrogen 1: $FC = 5 - \frac{8}{2} - 0 = +1$

For nitrogen 2: $FC = 5 - \frac{4}{2} - 4 = -1$

Remember: *Valence electrons* are the electrons characteristic of a specific element. *Bonding electrons* are those electrons involved in bonding to other atoms. *Nonbonding electrons* are those electrons in lone pairs.

(b)



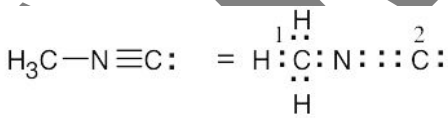
For carbon 1: $FC = 4 - \frac{8}{2} - 0 = 0$

For carbon 2: $FC = 4 - \frac{8}{2} - 0 = 0$

For nitrogen : $FC = 5 - \frac{8}{2} - 0 = +1$

For oxygen: $FC = 6 - \frac{2}{2} - 6 = -1$

(c)



For carbon 1: $FC = 4 - \frac{8}{2} - 0 = 0$

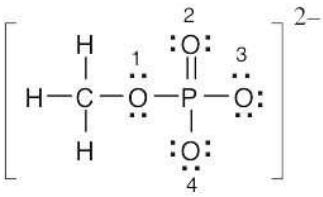
For carbon 2: $FC = 4 - \frac{6}{2} - 2 = -1$

For nitrogen : $FC = 5 - \frac{8}{2} - 0 = +1$

SAMPLE

2.8

$$\text{Formal charge (FC)} = \left[\begin{matrix}\text{\# of valence}\\ \text{electrons}\end{matrix}\right] - \left[\frac{\text{\# of bonding electrons}}{2}\right] - \left[\begin{matrix}\text{\# nonbonding}\\ \text{electrons}\end{matrix}\right]$$



Methyl phosphate

For oxygen 1: $FC = 6 - \frac{4}{2} - 4 = 0$

For oxygen 2: $FC = 6 - \frac{4}{2} - 4 = 0$

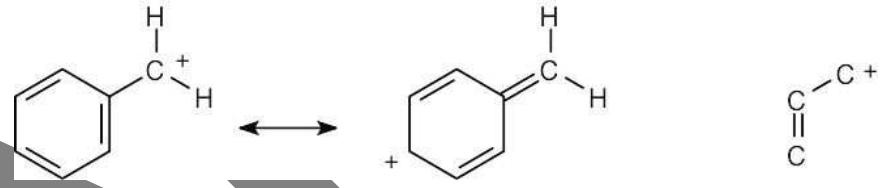
For oxygen 3 : $FC = 6 - \frac{2}{2} - 6 = -1$

For oxygen 4: $FC = 6 - \frac{2}{2} - 6 = -1$

Oxygen atoms 3 and 4 each have a formal charge of –1, and oxygen atoms 1 and 2 have a formal charge of 0.

2.9 Try to locate the three-atom groupings that are present in resonance forms.

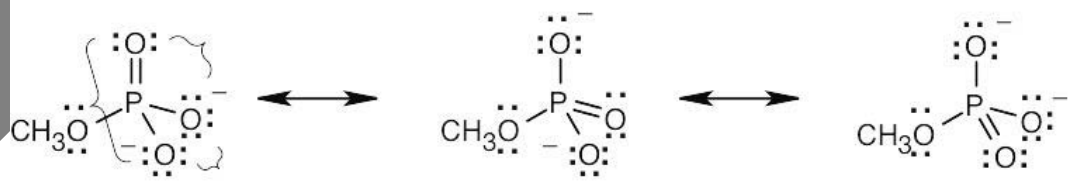
(a) These two structures represent resonance forms. The three-atom grouping (C–C double bond and an adjacent vacant *p* orbital) is pictured on the right.



(b) These two structures represent different compounds, not resonance structures.

2.10 Look for three-atom groupings that contain a multiple bond next to an atom with a *p* orbital. Exchange the positions of the bond and the electrons in the *p* orbital to draw the resonance form of each grouping.

(a) Methyl phosphate anion has 3 three-atom groupings and thus has 3 resonance forms.



Recall from Chapter 1 that phosphorus, a third-row element, can form more than four covalent bonds

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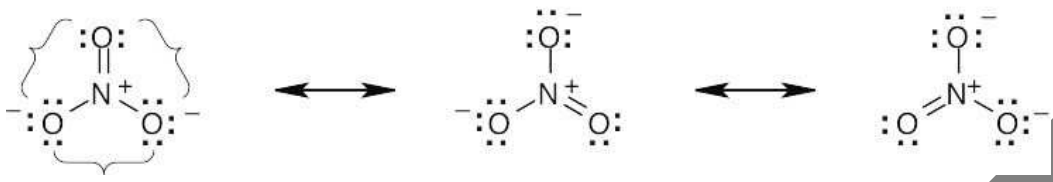
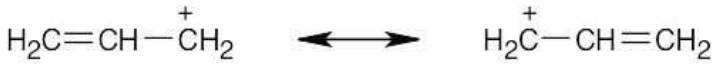
(b)



(c)



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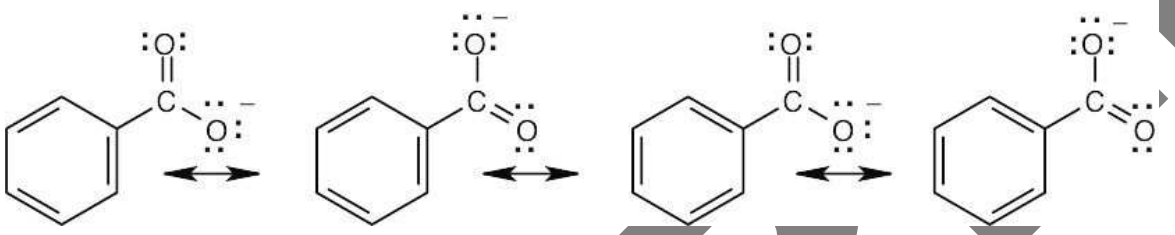
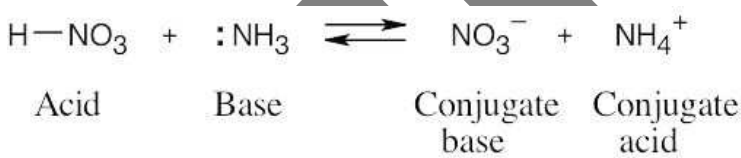


2.11 When an acid loses a proton, the product is the conjugate base of the acid. When a base gains a proton, the product is the conjugate acid of the base.

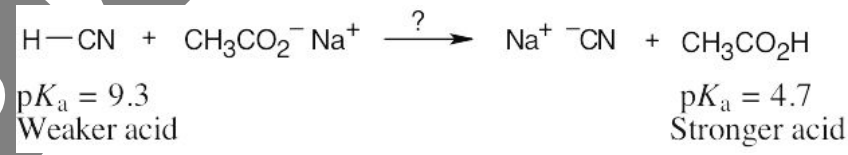


2.12 Recall from Section 2.8 that a stronger acid has a smaller pK_a and a weaker acid has a larger pK_a. Accordingly, phenylalanine (pK_a = 1.83) is a stronger acid than tryptophan (pK_a = 2.83).

2.13 HO–H is a stronger acid than H_2N–H. Since H_2N^- is a stronger base than HO^-, the conjugate acid of H_2N^- (H_2N–H) is a weaker acid than the conjugate acid of HO^- (HO–H).

2.14 Use Table 2.3 to find the strength of each acid. A reaction takes place as written if the stronger acid is the reactant.

(a)



Remember that the lower the pK_a, the stronger the acid. Thus CH_3CO_2H, not HCN, is the stronger acid, and the above reaction will not take place to a significant extent in them direction written.

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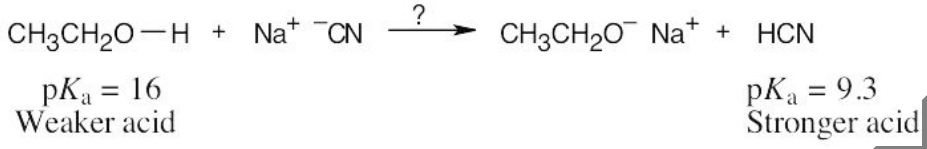
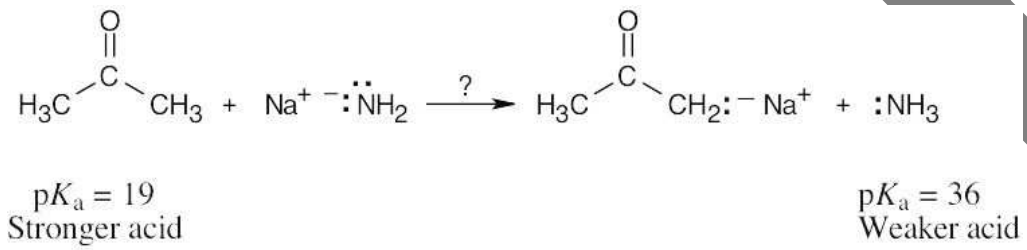
(b)



Using the same reasoning as in part (a), we can see that the above reaction will not occur to a significant extent.

2.15

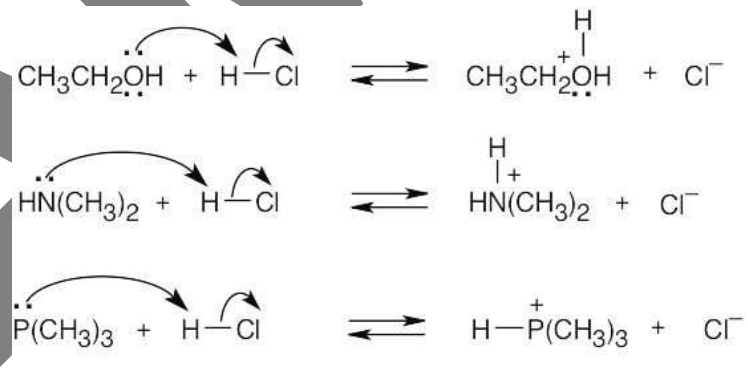


As written, the above reaction will take place to virtual completion due to the large difference in pK_a values.

2.16 Enter –9.31 into a calculator and use the INV LOG function to arrive at the answer $K_a = 4.9 \times 10^{-10}$.

2.17 Locate the electron pair(s) of the Lewis base and draw a curved arrow from the electron pair to the Lewis acid. The electron pair moves from the atom at the tail of the arrow (Lewis base) to the atom at the point of the arrow (Lewis acid).(Note: electron dots have been omitted from Cl^- to reduce clutter.)

(a)



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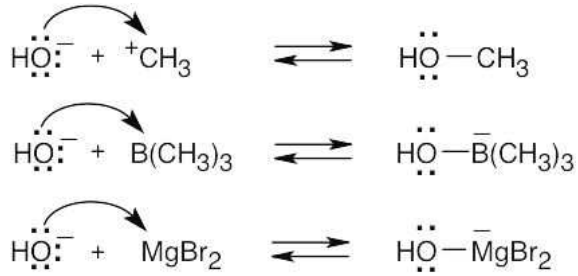

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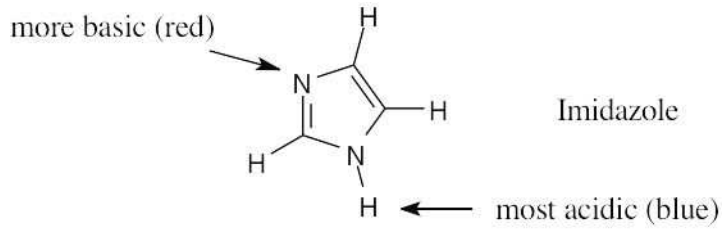
2.18 (a) The nitrogen on the left is more electron-rich and more basic. The indicated hydrogen is most electron-poor (bluest) and is most acidic.



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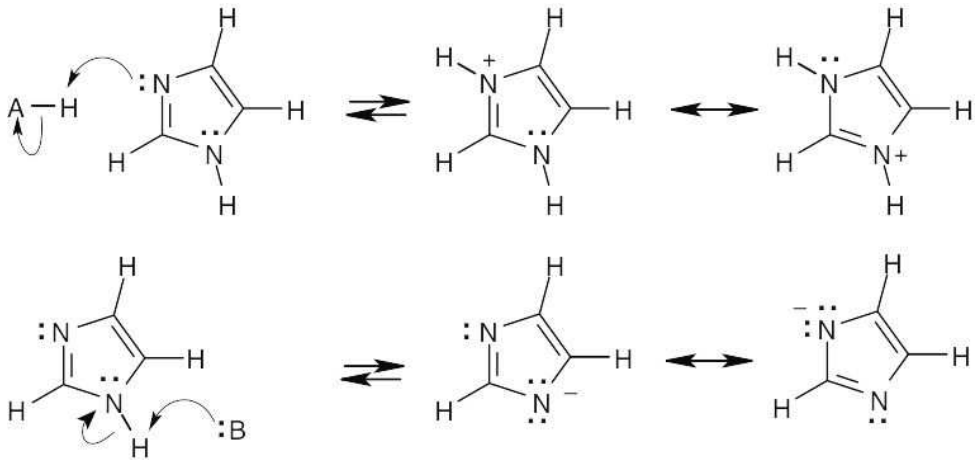
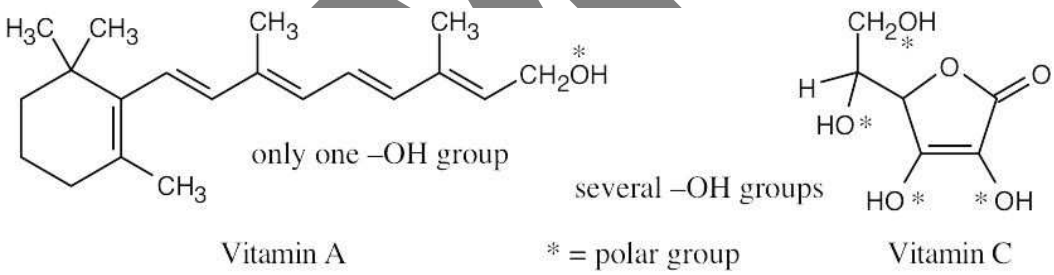


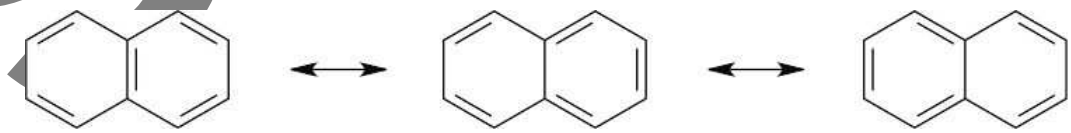
2.19



Vitamin C is water-soluble (hydrophilic) because it has several polar –OH groups that can form hydrogen bonds with water. Vitamin A is fat-soluble (hydrophobic) because most of its atoms can't form hydrogen bonds with water.

Visualizing Chemistry

2.20 Naphthalene has three resonance forms.



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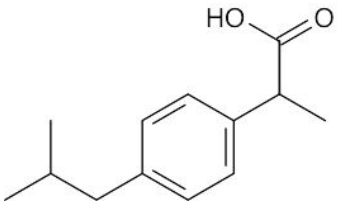
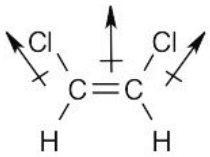
2.21



Ibuprofen

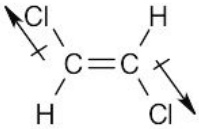
2.22 Electrostatic potential maps show that the electron-rich regions of the cis isomer lie on the same side of the double bond, leading to a net dipole moment. Because the electron-rich regions of the trans isomer are symmetrical about the double bond, the individual bond dipole moments cancel, and the isomer has no overall dipole moment.

net dipole moment



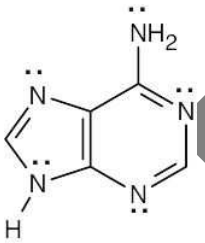
cis-1,2-Dichloroethylene

zero dipole moment



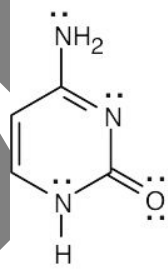
trans-1,2-Dichloroethylene

2.23 (a)



Adenine

(b)

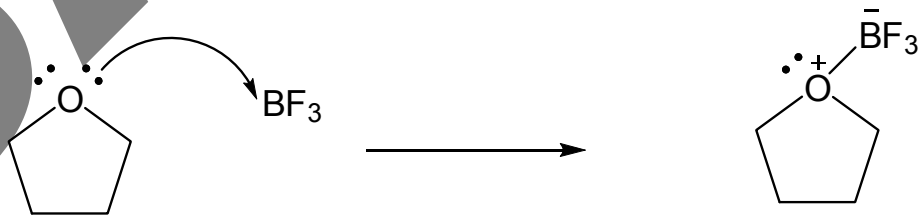


Cytosine

Mechanism Problems

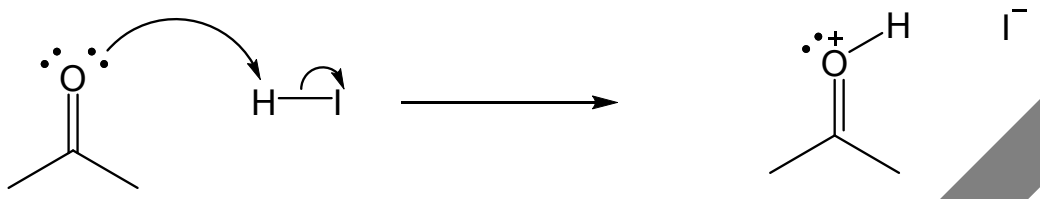
2.24

(a)

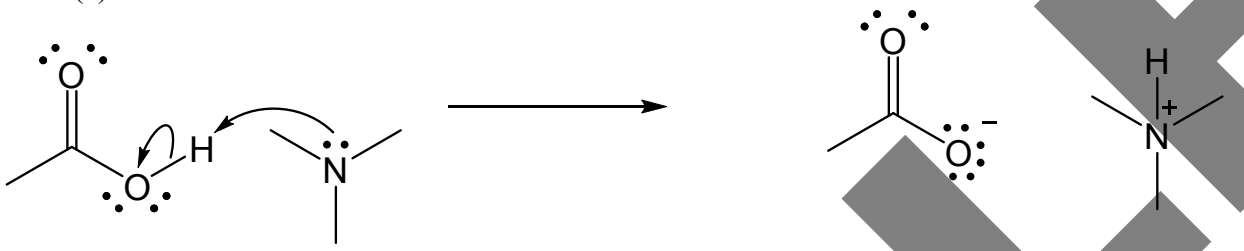


SAMPLE

(b)

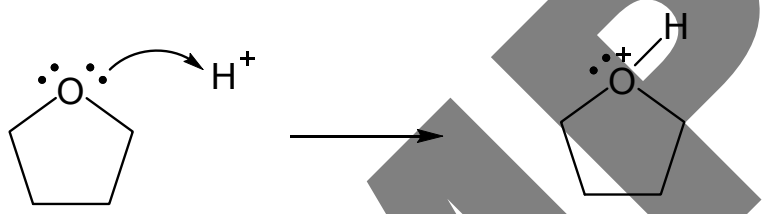


(c)



2.25

(a)



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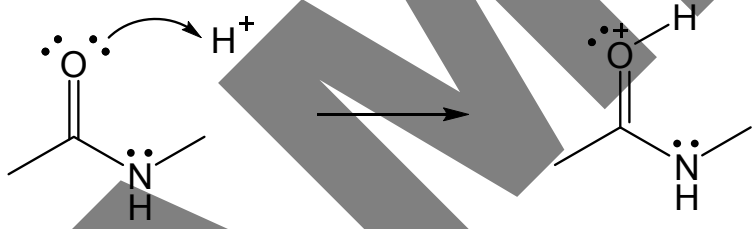

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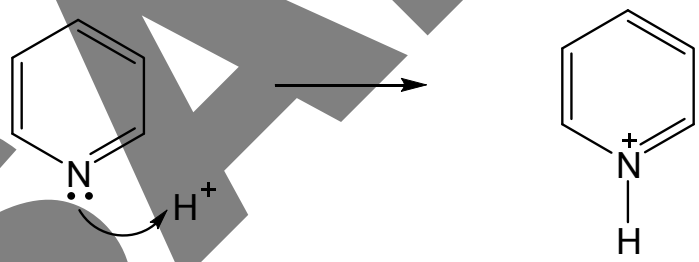
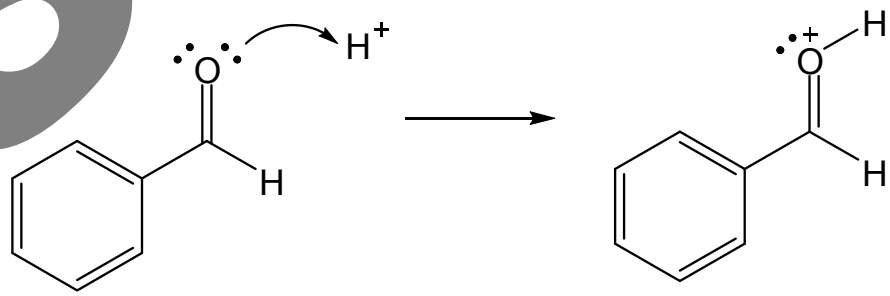


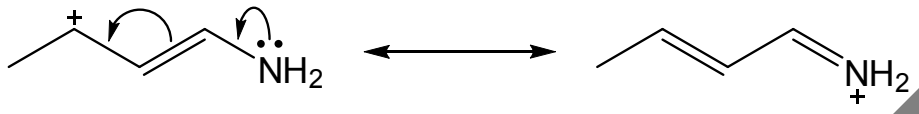
(d)



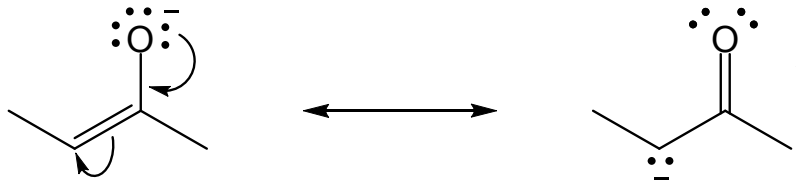
SAMPLE

2.26

(a)



(b)



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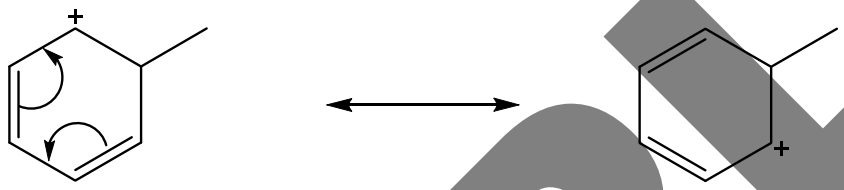
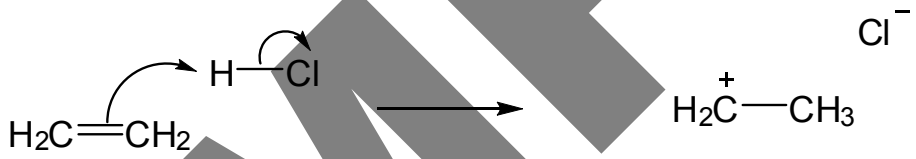
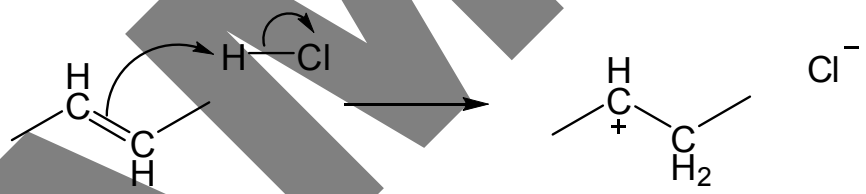


2.27

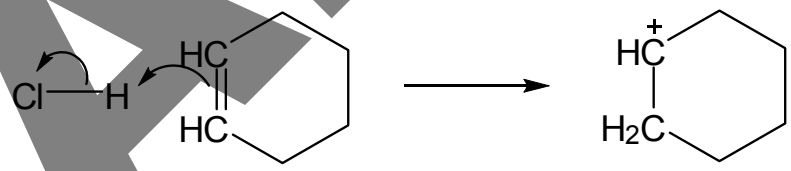
(a)



(b)



(c)



Additional Problems

Electronegativity and Dipole Moments

2.28 Use Figure 2.2 if you need help. The most electronegative element is starred.

(a) $CH_2\overset{*}{F}C1$ (b) $\overset{*}{F}CH_2CH_2CH_2Br$ (c) $H\overset{*}{O}CH_2CH_2NH_2$ (d) $CH_3\overset{*}{O}CH_2Li$

SAMPLE

2.29 *More polar* *Less polar*

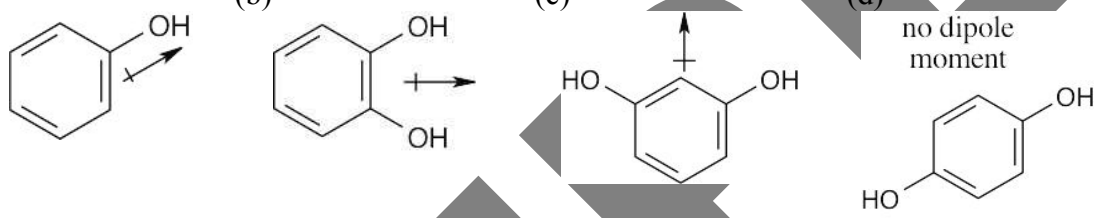
(a)

(b)

(c)

(d)

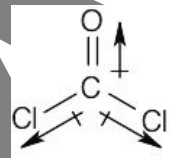
2.30 (a) (b) (c) (d)



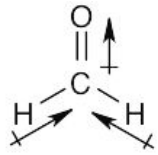
2.31 (a) In Section 2.2, we found that $\mu = Q \times r$. For a proton and an electron separated by 100 pm, μ = 4.80 D. If the two charges are separated by 136 pm, μ = 6.53 D.

(b) Since the observed dipole moment is 1.08 D, the H–Cl bond has (1.08 D / 6.53 D) x 100 % = 16.5 % ionic character.

2.32 In phosgene, the individual bond polarities tend to cancel, but in formaldehyde, the bond polarities add to each other. Thus, phosgene has a smaller dipole moment than form aldehyde.



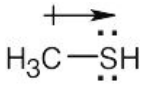
Phosgene



Formaldehyde

2.33 The magnitude of a dipole moment depends on both charge and distance between atoms. Fluorine is more electronegative than chlorine, but a C–F bond is shorter than a C–Cl bond. Thus, the dipole moment of CH_3F is smaller than that of CH_3Cl.

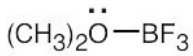
2.34 The observed dipole moment is due to the lone pair electrons on sulfur.



SAMPLE

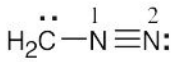
Formal Charges

2.35 To save space, molecules are shown as line-bond structures with lone pairs, rather than as electron-dot structures.

(a) 

Oxygen: $FC = 6 - \frac{6}{2} - 2 = +1$

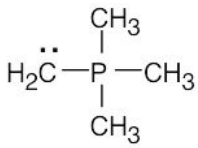
Boron: $FC = 3 - \frac{8}{2} - 0 = -1$

(b) 

Carbon: $FC = 4 - \frac{6}{2} - 2 = -1$

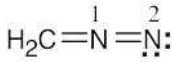
Nitrogen 1: $FC = 5 - \frac{8}{2} - 0 = +1$

Nitrogen 2: $FC = 5 - \frac{6}{2} - 2 = 0$

(c) 

Carbon: $FC = 4 - \frac{6}{2} - 2 = -1$

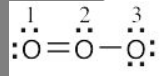
Phosphorus: $FC = 5 - \frac{8}{2} - 0 = +1$

(d) 

Carbon: $FC = 4 - \frac{8}{2} - 0 = 0$

Nitrogen 1: $FC = 5 - \frac{8}{2} - 0 = +1$

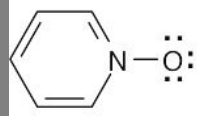
Nitrogen 2: $FC = 5 - \frac{4}{2} - 4 = -1$

(e) 

Oxygen 1: $FC = 6 - \frac{4}{2} - 4 = 0$

Oxygen 2: $FC = 6 - \frac{6}{2} - 2 = +1$

Oxygen 3: $FC = 6 - \frac{2}{2} - 6 = -1$

(f) 

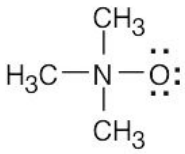
Nitrogen: $FC = 5 - \frac{8}{2} - 0 = +1$

Oxygen: $FC = 6 - \frac{2}{2} - 6 = -1$

SAMPLE

2.36 As in Problem 2.31, molecules are shown as line-bond structures with lone-pair electrons indicated. Only calculations for atoms with non-zero formal charge are shown.

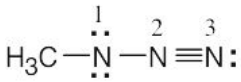
(a)



Oxygen: $FC = 6 - \frac{2}{2} - 6 = -1$

Nitrogen: $FC = 5 - \frac{8}{2} - 0 = +1$

(b)

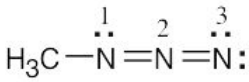


Nitrogen 1: $FC = 5 - \frac{4}{2} - 4 = -1$

Nitrogen 2: $FC = 5 - \frac{8}{2} - 0 = +1$

Nitrogen 3: $FC = 5 - \frac{6}{2} - 2 = 0$

(c)



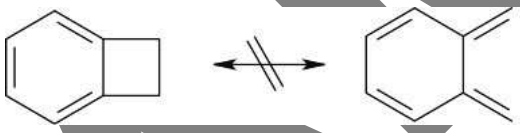
Nitrogen 1: $FC = 5 - \frac{6}{2} - 2 = 0$

Nitrogen 2: $FC = 5 - \frac{8}{2} - 0 = +1$

Nitrogen 3: $FC = 5 - \frac{4}{2} - 4 = -1$

Resonance

2.37 Resonance forms do not differ in the position of nuclei. The two structures in (a) are not resonance forms because the positions of the carbon and hydrogen atoms outside the ring are different in the two forms.

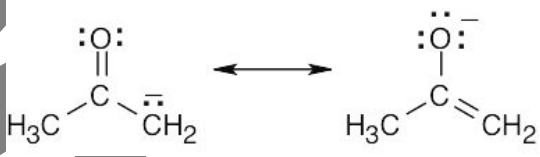


not resonance structures

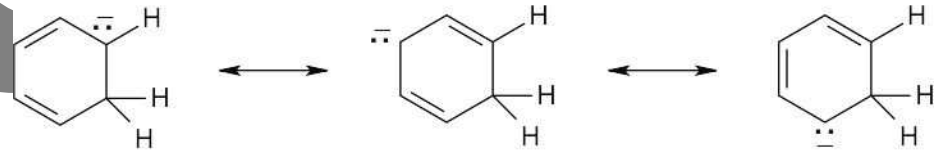
The pairs of structures in parts (b), (c), and (d) represent resonance forms.

2.38

(a)

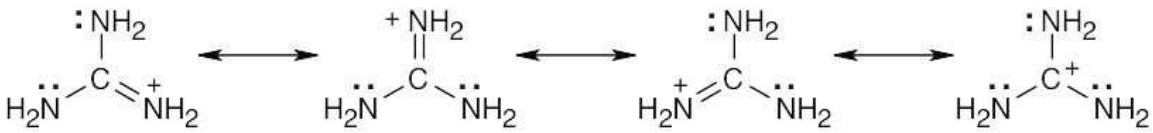


(b)



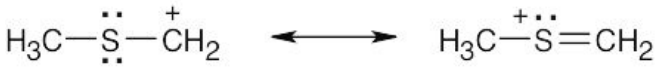
SAMPLE

(c)

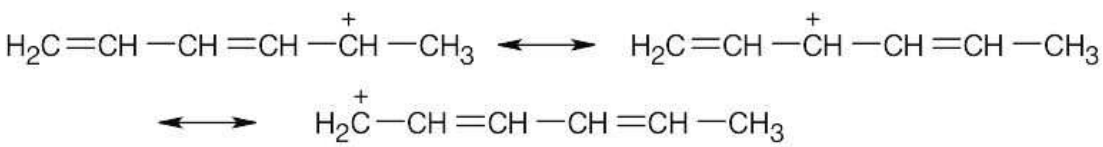


The last resonance structure is a minor contributor because its carbon lacks a complete electron octet.

(d)



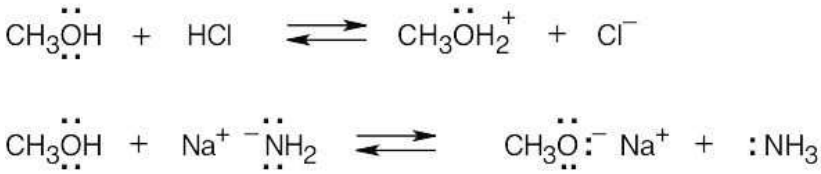
(e)



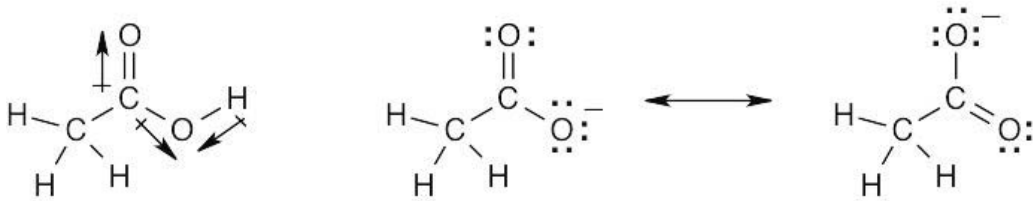
2.39 The two structures are not resonance forms because the positions of the carbon atoms are different in the two forms.

Acids and Bases

2.40



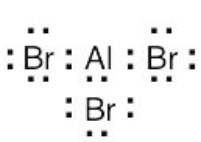
2.41



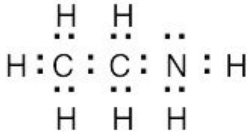
The O–H hydrogen of acetic acid is more acidic than the C–H hydrogens. The –OH oxygen is electronegative, and, consequently, the –O–H bond is more strongly polarized than the –C–H bonds. In addition, the acetate anion is stabilized by resonance.

2.42

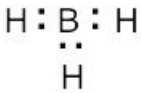
(a)



(b)

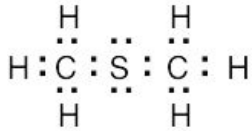


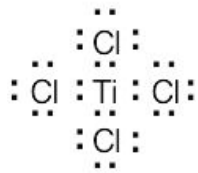
(c)



SAMPLE

(d)

(e) 

(f) 

The Lewis acids shown below can accept an electron pair either because they have a vacant orbital or because they can donate H^+. The Lewis bases have nonbonding electron pairs.

Lewis acids: $AlBr_3$, BH_3, HF, $TiCl_4$

Lewis bases: $CH_3CH_2\ddot{N}H_2$, $H_3C-\ddot{S}-CH_3$

2.43

(a) $CH_3OH + H_2SO_4 \rightleftharpoons CH_3OH_2^+ + HSO_4^-$

stronger base, stronger acid, weaker acid, weaker base

(b) $CH_3OH + NaNH_2 \rightleftharpoons CH_3O^-\,Na^+ + NH_3$

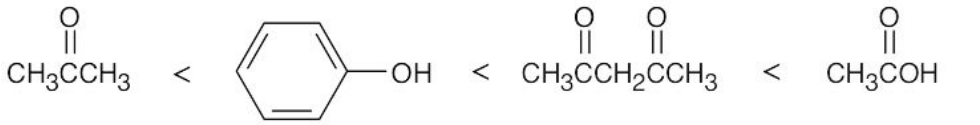
stronger acid, stronger base, weaker base, weaker acid

(c) $CH_3NH_3^+\,Cl^- + NaOH \rightleftharpoons CH_3NH_2 + H_2O + NaCl$

stronger acid, stronger base, weaker base, weaker acid

2.44 The substances with the largest values of pK_a are the least acidic.

Least acidic ⟶ *Most acidic*



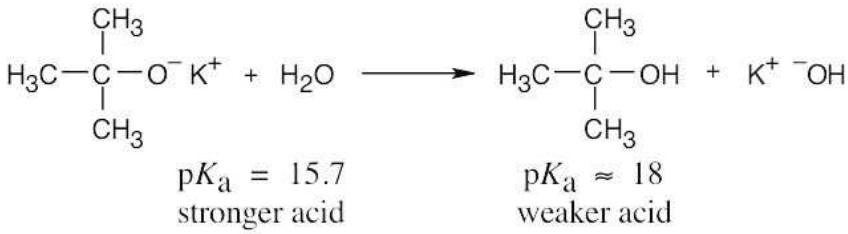
pK_a = 19.3 pK_a = 9.9 pK_a = 9 pK_a = 4.76

2.45 To react completely (> 99.9%) with NaOH, an acid must have a pK_a at least 3 units smaller than the pK_a of H_2O. Thus, all substances in the previous problem except acetone react completely with NaOH.

2.46 The stronger the acid (smaller pK_a), the weaker its conjugate base. Since NH_4^+ is a stronger acid than $CH_3NH_3^+$, CH_3NH_2 is a stronger base than NH_3.

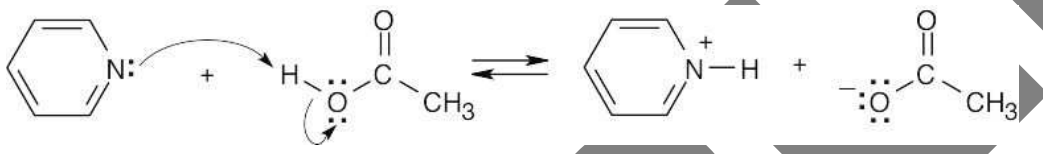
SAMPLE

2.47



The reaction takes place as written because water is a stronger acid than *tert*-butyl alcohol. Thus, a solution of potassium *tert*-butoxide in water can't be prepared.

2.48



2.49 (a) Acetone: $K_a = 5 \times 10^{-20}$ (b) Formic acid: $K_a = 1.8 \times 10^{-4}$

2.50 (a) Nitromethane: $pK_a = 10.30$ (b) Acrylic acid: $pK_a = 4.25$

2.51

$$\underset{[0.050\ M]}{\text{Formic acid}} + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} \underset{[x]}{\text{Formate}^-} + \underset{[x]}{H_3O^+}$$

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

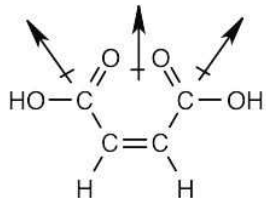
If you let 0.050 – x = 0.050, then x = 3.0×10^{-3} and pH = 2.52. If you calculate x exactly using the quadratic equation, then x = 2.9×10^{-3} and pH = 2.54.

2.52 Only acetic acid will react with sodium bicarbonate. Acetic acid is the only substance in Problem 2.40 that is a stronger acid than carbonic acid.

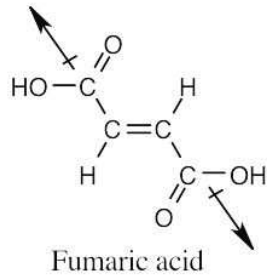
SAMPLE

General Problems

2.53 In maleic acid, the individual dipole moments add to produce a net dipole moment for the whole molecule. The individual dipole moments in fumaric acid cancel, resulting in a zero dipole moment.



Maleic acid

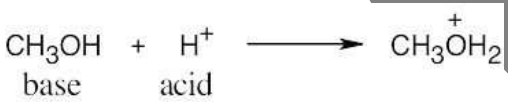


Fumaric acid

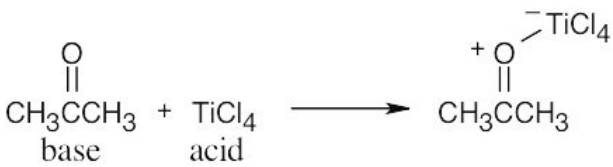
2.54 Sodium bicarbonate reacts with acetic acid to produce carbonic acid, which breaks down to form CO_2. Thus, bubbles of CO_2 indicate the presence of an acid stronger than carbonic acid, in this case acetic acid, as the pK_a values indicate. Phenol does not react with sodium bicarbonate.

2.55 Reactions (a) and (c) are reactions between Brønsted–Lowry acids and bases; the stronger acid and stronger base are identified. Reactions (b) and (d) occur between Lewis acids and bases.

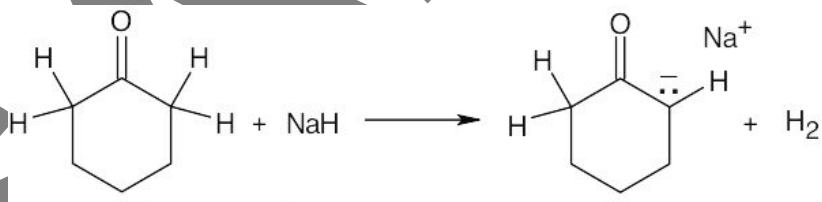
(a)



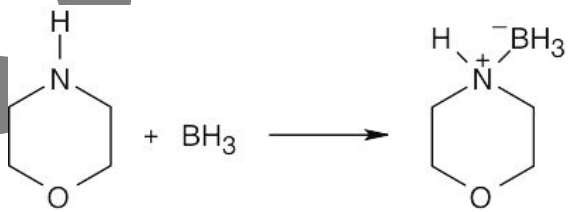
(b)



(c)



(d)

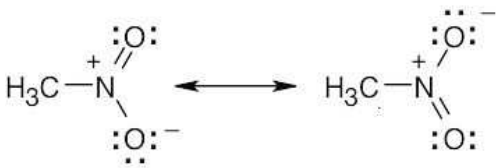


SAMPLE

2.56 Pairs (a) and (d) represent resonance structures; pairs (b) and (c) do not. For two structures to be resonance forms, all atoms must be in the same positions in all resonance forms.

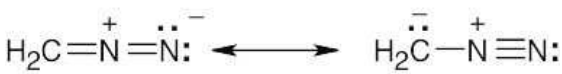
2.57

(a)

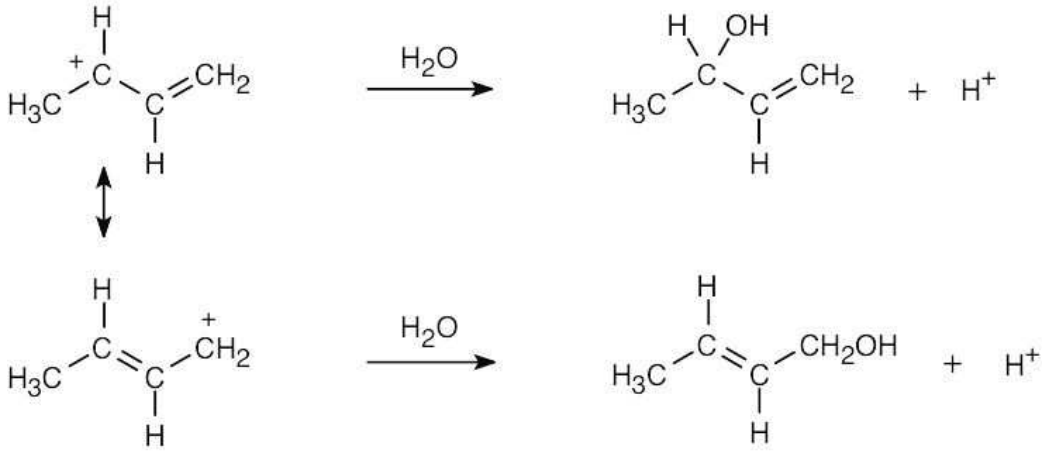


(b)

(c)

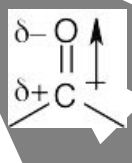


2.58 The cation pictured can be represented by two resonance forms. Reaction with water can occur at either positively charged carbon, resulting in two products.

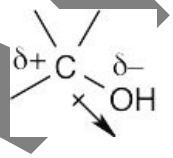


2.59

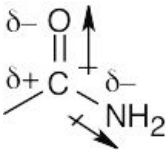
(a)



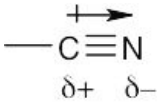
(b)



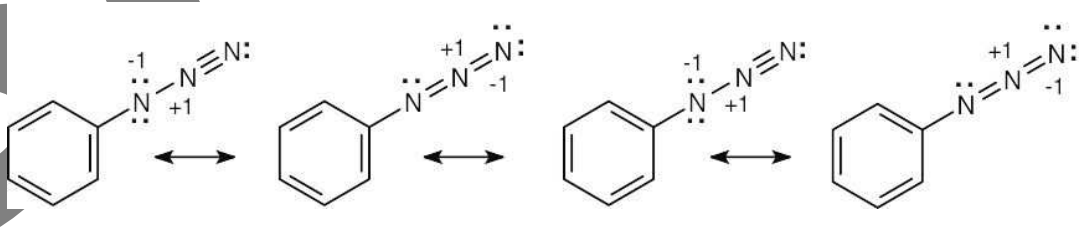
(c)



(d)

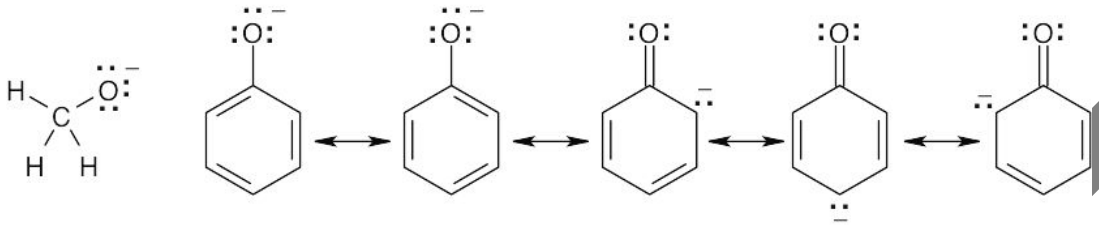


2.60



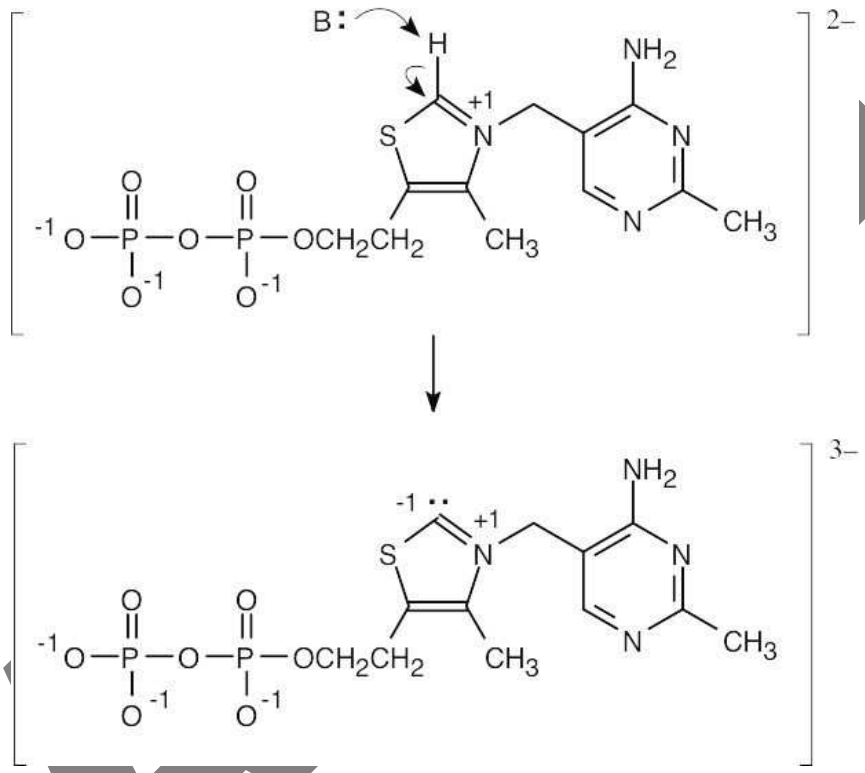
SAMPLE

2.61

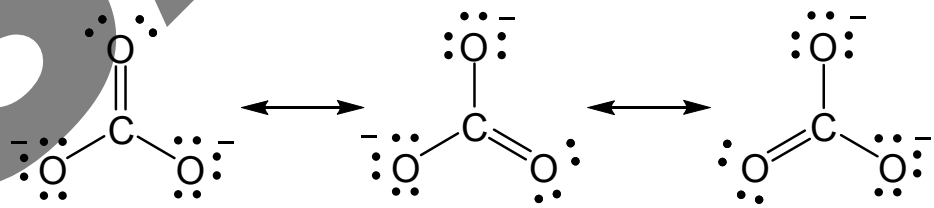


When phenol loses a proton, the resulting anion is stabilized by resonance. The methanol anion is not stabilized by resonance.

2.62

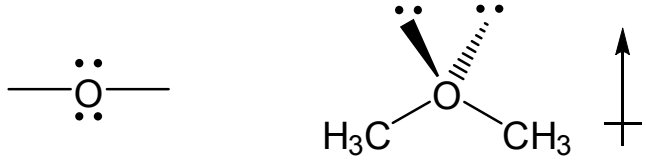


2.63 (a) The central carbon of carbonate ion is sp^2 and trigonal planar. The three resonance forms contribute equally to the overall resonance hybrid. Thus, the molecule has no dipole.

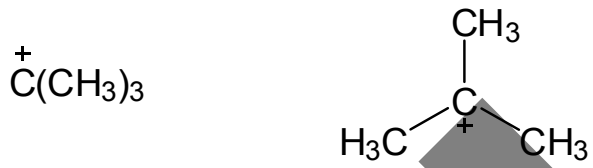


SAMPLE

(b) The oxygen is sp^3 hybridized and tetrahedral. Therefore, there is a dipole pointing towards the lone pairs.

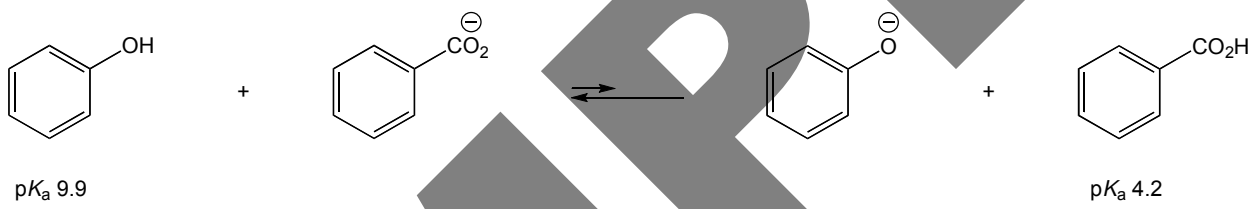


(c) The carbocation is sp^2 hybridized and trigonal planar. Thus, there is no dipole.



2.64 The equilibrium always favors the weaker acid/base pair (acid with the higher pK_a)

(a)



(b)

$CH_3CH_2CH_2OH + NH_2^- \rightleftharpoons CH_3CH_2CH_2O^- + NH_3$

pK_a 16.1 pK_a 36

The "a" in p*K*a here should be subscript.

(c)

$CH_3^- + CH_3NO_2 \rightleftharpoons CH_4 + CH_2NO_2^-$

pK_a 10.3 pK_a 60

The "a" in p*K*a here should be subscript.

2.65 (a) London dispersion forces

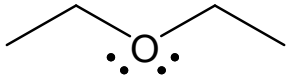
(b) Hydrogen bonding

(c) Hydrogen bonding causes the carboxylic acids interact with one another and that force is stronger than the dispersion forces between acetic acid and oil.

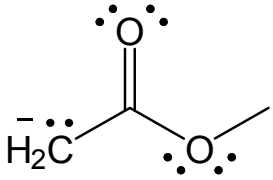
SAMPLE

2.66

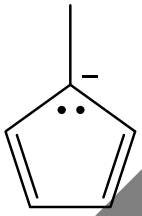
(a)



(b)



(c)



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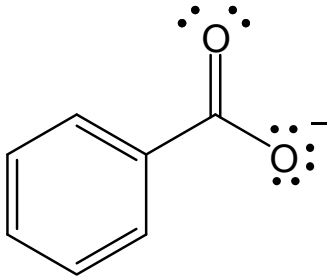
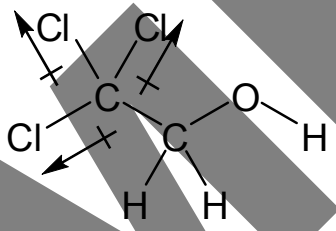


2.67 Being more electronegative than carbon, the three chlorine atoms inductively remove electron density from the carbon atom to which they are all attached. This effect propagates down the chain, ultimately reducing the electron density on the oxygen. This makes the oxygen-hydrogen bond weaker and the molecule more acidic.



SAMPLE