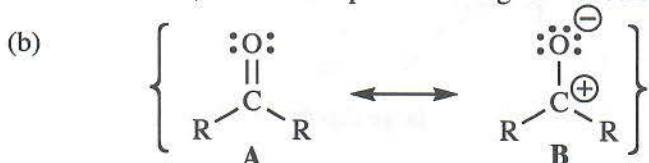


CHAPTER 2—ACIDS AND BASES; FUNCTIONAL GROUPS

2-1

$$(a) 2.4 D = 4.8 \times \delta \times 1.23 \text{ \AA}$$

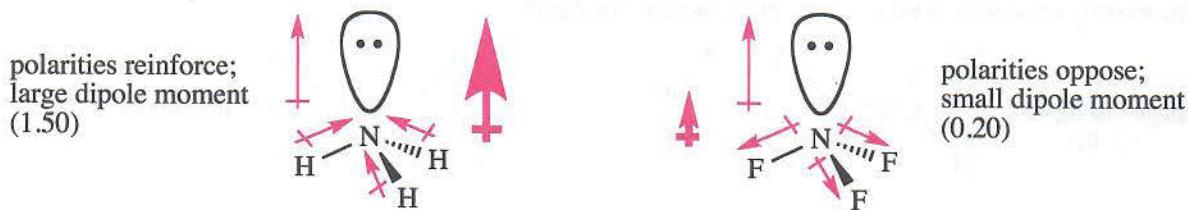
$\delta = 0.41$, or 41% of a positive charge on carbon and 41% of a negative charge on oxygen



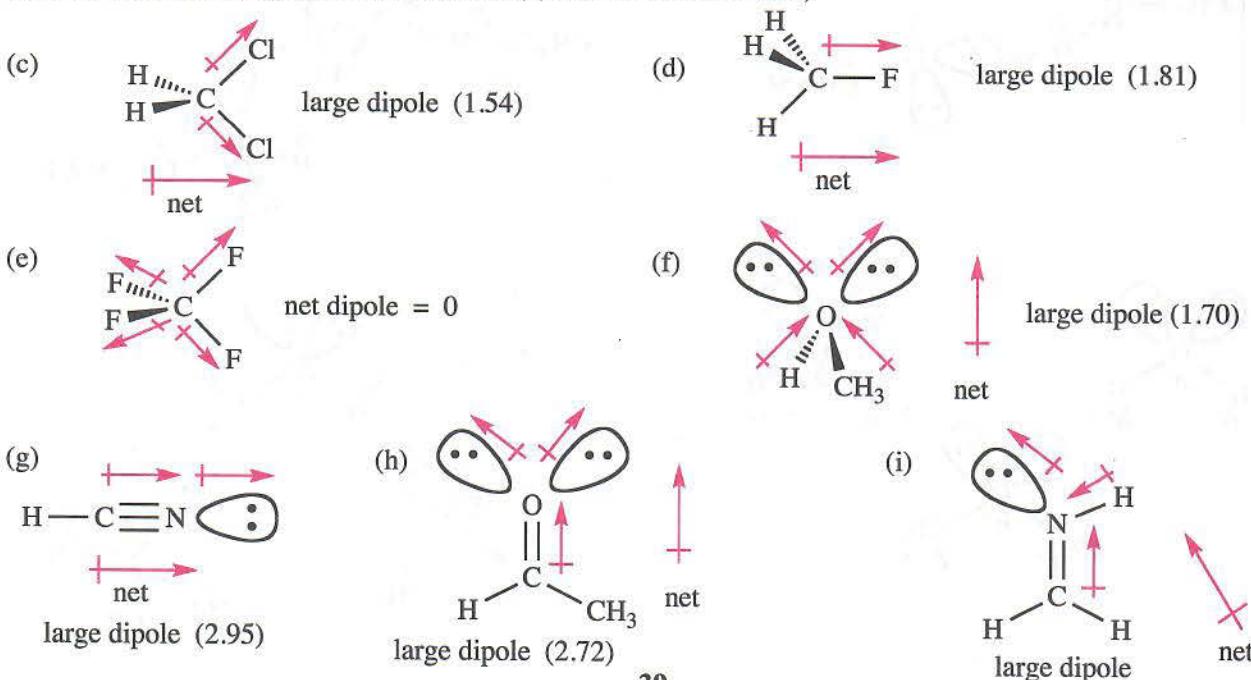
Resonance form A must be the major contributor. If B were the major contributor, the value of the charge separation would be between 0.5 and 1.0, meaning >50% of a positive charge on C and >50% of a negative charge on O. Even though B is "minor", it is quite significant, explaining in part the high polarity of the C=O.

2-2

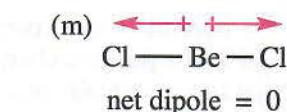
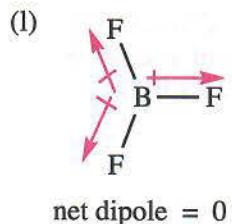
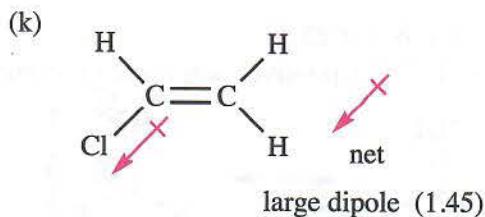
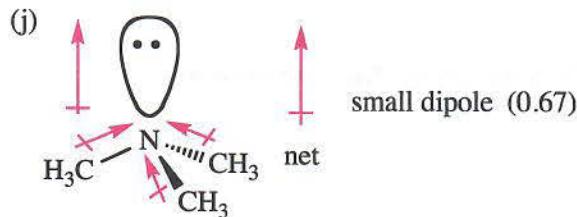
Both NH_3 and NF_3 have a pair of nonbonding electrons on the nitrogen. In NH_3 , the *direction* of polarization of the N—H bonds is *toward* the nitrogen; thus, all three bond polarities and the lone pair polarity reinforce each other. In NF_3 , on the other hand, the direction of polarization of the N—F bonds is *away* from the nitrogen; the three bond polarities cancel the lone pair polarity, so the net result is a very small *molecular* dipole moment.



2-3 Some magnitudes of dipole moments are difficult to predict; however, the direction of the dipole should be straightforward, in most cases. Actual values of molecular dipole moments are given in parentheses. (Each halogen atom has three nonbonded electron pairs, not shown below.) The C—H is usually considered nonpolar. (Parts (a) and (b) are solved in the text.)

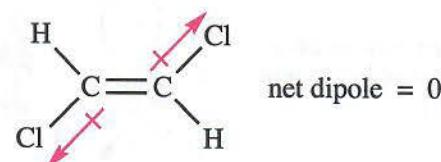
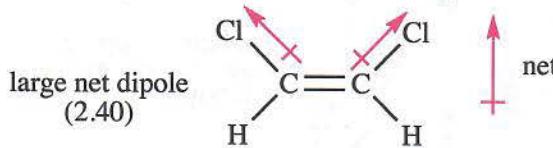


2-3 continued

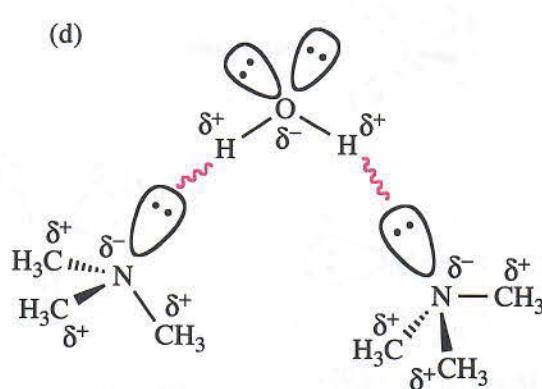
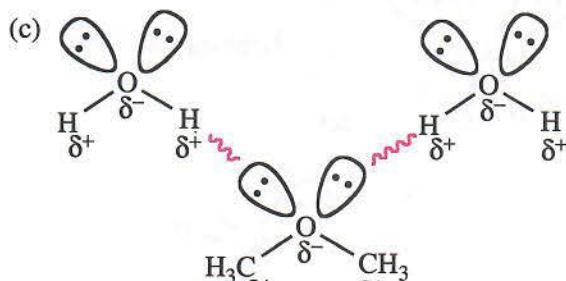
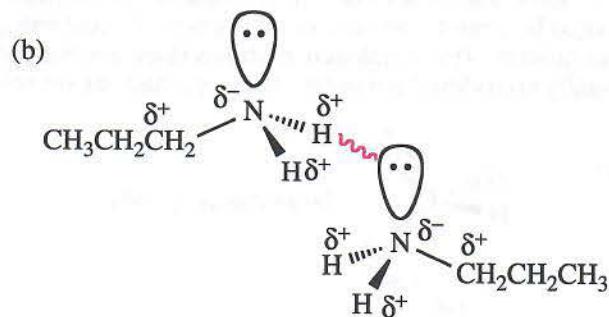
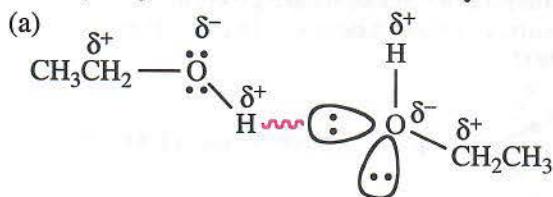


In (l) and (m), the symmetry of the molecule allows the individual bond dipoles to cancel.

2-4 With chlorines on the same side of the double bond, the bond dipole moments reinforce each other, resulting in a large net dipole. With chlorines on opposite sides of the double bond, the bond dipole moments exactly cancel each other, resulting in a zero net dipole.

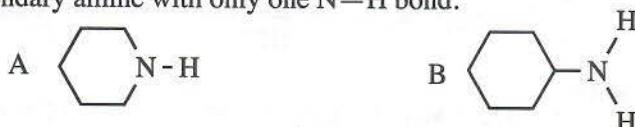


2-5 Hydrogen bonds are shown as wavy bonds.



2-6

- (a) $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$ has less branching and boils at a higher temperature than $(CH_3)_3CC(CH_3)_3$.
- (b) $CH_3(CH_2)_5CH_2OH$ can form hydrogen bonds and will boil at a much higher temperature than $CH_3(CH_2)_6CH_3$, which cannot form hydrogen bonds.
- (c) $CH_3CH_2CH_2CH_2OH$ can form hydrogen bonds and boils at a higher temperature than $CH_3CH_2OCH_2CH_3$.
- (d) $HOCH_2(CH_2)_4CH_2OH$ can form hydrogen bonds at both ends and has no branching; it will boil at a much higher temperature than $(CH_3)_3CCH(OH)CH_3$.
- (e) $(CH_3CH_2CH_2)_2NH$ has an N—H bond and can form hydrogen bonds; it will boil at a higher temperature than $(CH_3CH_2)_3N$, which cannot form hydrogen bonds.
- (f) The second compound shown (B) has the higher boiling point for two reasons: B has a higher molecular weight than A; and B, a primary amine with two N—H bonds, has more opportunity for forming hydrogen bonds than A, a secondary amine with only one N—H bond.

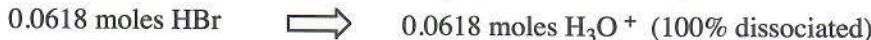


2-7

- (a) $CH_3CH_2OCH_2CH_3$ can form hydrogen bonds with water and is more soluble than $CH_3CH_2CH_2CH_2CH_3$, which cannot form hydrogen bonds with water.
- (b) $CH_3CH_2CH_2OH$ is more soluble in water because it has one fewer carbon than $CH_3CH_2OCH_2CH_3$.
- (c) $CH_3CH_2NHCH_3$ is more water soluble because it can form hydrogen bonds with water; $CH_3CH_2CH_2CH_3$ cannot form hydrogen bonds.
- (d) CH_3CH_2OH is more soluble in water. The polar O—H group forms hydrogen bonds with water, overcoming the resistance of the nonpolar CH_3CH_2 group toward entering the water. In $CH_3CH_2CH_2CH_2OH$, however, the hydrogen bonding from only one OH group cannot carry a four-carbon chain into the water; this substance is only slightly soluble in water.
- (e) Both compounds form hydrogen bonds with water at the double-bonded oxygen, but only the smaller molecule (CH_3COCH_3) dissolves. The cyclic compound has too many nonpolar CH_2 groups to dissolve.

2-8

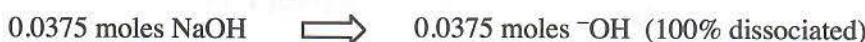
$$(a) 5.00 \text{ g HBr} \times \frac{1 \text{ mole HBr}}{80.9 \text{ g HBr}} = 0.0618 \text{ moles HBr}$$



$$\frac{0.0618 \text{ moles } H_3O^+}{100. \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{0.618 \text{ moles } H_3O^+}{1 \text{ L solution}}$$

$$pH = -\log_{10} [H_3O^+] = -\log_{10} (0.618) = \boxed{0.209}$$

$$(b) 1.50 \text{ g NaOH} \times \frac{1 \text{ mole NaOH}}{40.0 \text{ g NaOH}} = 0.0375 \text{ moles NaOH}$$



$$\frac{0.0375 \text{ moles } ^{-}\text{OH}}{50. \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \frac{0.75 \text{ moles } ^{-}\text{OH}}{1 \text{ L solution}} = 0.75 \text{ M}$$

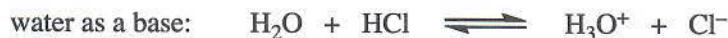
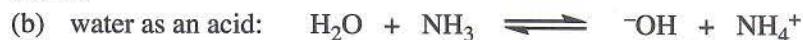
$$[H_3O^+] = \frac{1 \times 10^{-14}}{[^{-}\text{OH}]} = \frac{1 \times 10^{-14}}{0.75} = 1.33 \times 10^{-14}$$

$$pH = -\log_{10} [H_3O^+] = -\log_{10} (1.33 \times 10^{-14}) = \boxed{13.88}$$

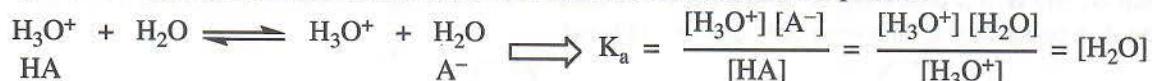
(The number of decimal places in a pH value is the number of significant figures.)

2-9

(a) By definition, an acid is any species that can donate a proton. Ammonia has a proton bonded to nitrogen, so ammonia can be an acid (although a very weak one). A base is a proton acceptor; that is, it must have a pair of electrons to share with a proton. In theory, any atom with an unshared electron pair can be a base. The nitrogen in ammonia has an unshared electron pair so ammonia is basic. In water, ammonia is too weak an acid to give up its proton; instead, it acts as a base and pulls a proton from water to a small extent.



(c) Hydronium acting as an acid in water solution will have this chemical equation:



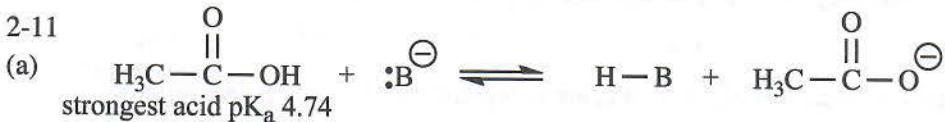
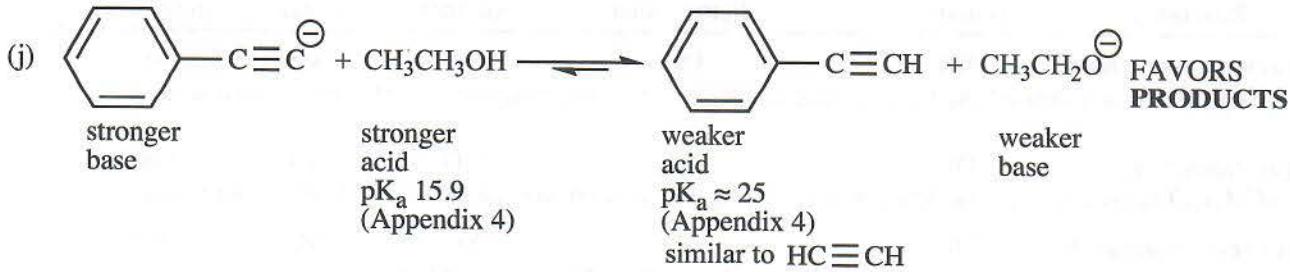
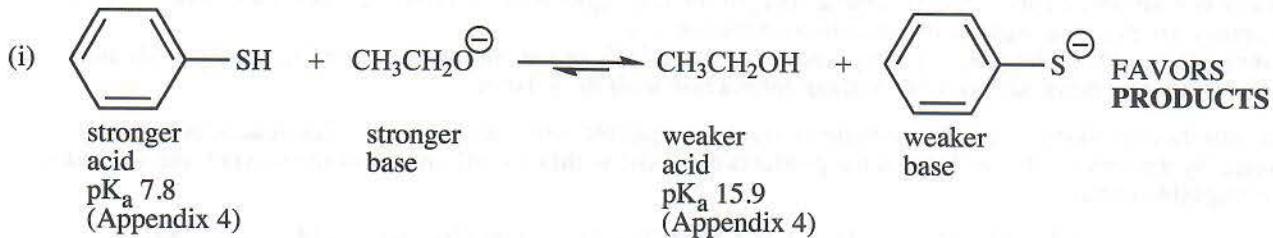
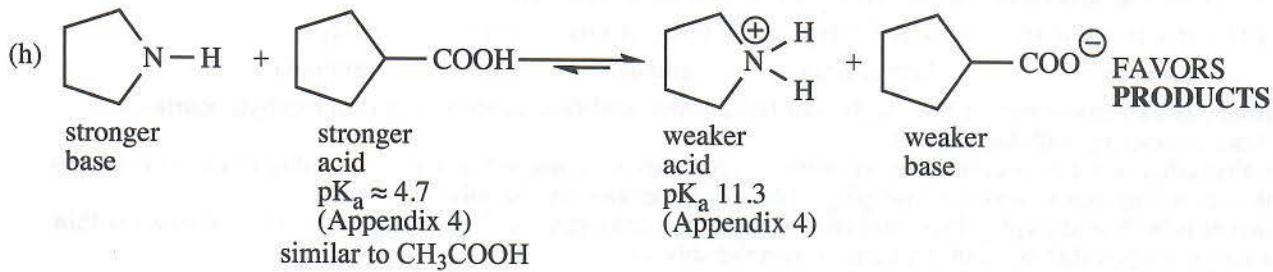
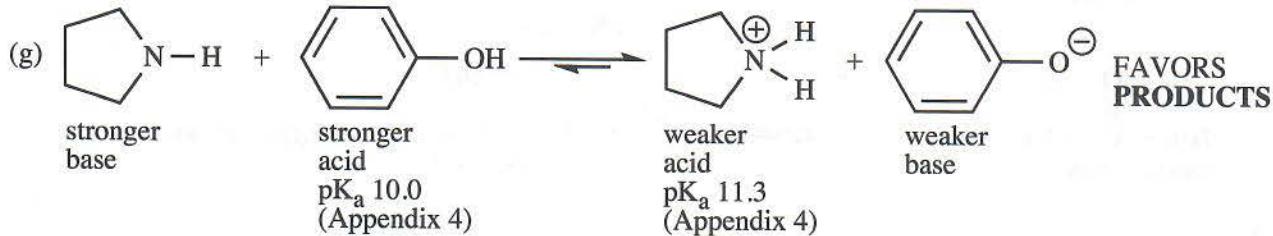
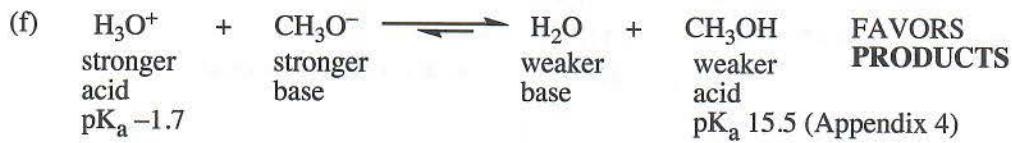
$$[\text{H}_2\text{O}] = \frac{1000 \text{ g H}_2\text{O}}{1 \text{ L H}_2\text{O}} \times \frac{1 \text{ mole H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 55.55 \text{ M} = K_a \quad \xrightarrow{\text{pK}_a = -\log(55.55)} \quad \underline{\underline{-1.74}}$$



2-10 Values are from Table 2-2, or, as noted, from Appendix 4 in the text.

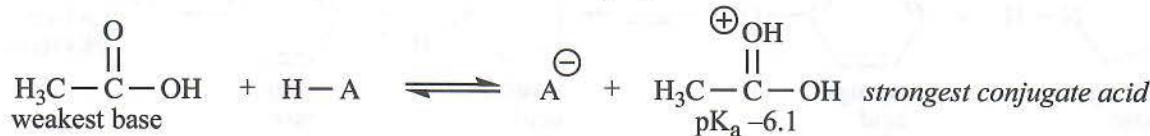
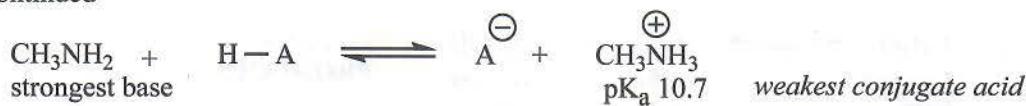
- | | | |
|--|-----------------------------|--|
| <p>(a) $\text{HCOOH} + \text{CN} \rightleftharpoons \text{HCOO}^- + \text{HCN}$
stronger acid
$\text{pK}_a 3.76$</p> | <p>FAVORS
PRODUCTS</p> | <p>Part (a) is already solved in the text.</p> |
| <p>(b) $\text{CH}_3\text{COO}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{O}^-$
weaker base
$\text{pK}_a 15.5$
(Appendix 4)</p> | <p>FAVORS
REACTANTS</p> | |
| <p>(c) $(\text{CH}_3)_2\text{CHOH} + \text{NaNH}_2 \rightleftharpoons (\text{CH}_3)_2\text{CHO}^- \text{Na}^+ + \text{NH}_3$
stronger acid
$\text{pK}_a \approx 15.9$
(estimated from Table 2-2)</p> | <p>FAVORS
PRODUCTS</p> | |
| <p>(d) $\text{Na}^+ \text{OCH}_3 + \text{HCN} \rightleftharpoons \text{HOCH}_3 + \text{Na}^+ \text{CN}$
stronger base
$\text{pK}_a 9.22$</p> | <p>FAVORS
PRODUCTS</p> | |
| <p>(e) $\text{HCl} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{Cl}^-$
stronger acid
$\text{pK}_a -7$</p> | <p>FAVORS
PRODUCTS</p> | |

2-10 continued



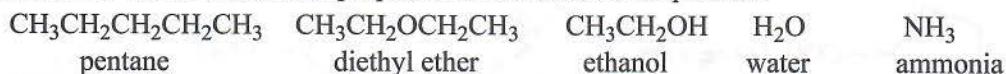
2-11 continued

(b)



2-12

First, review the structures and properties of the solvents in question.

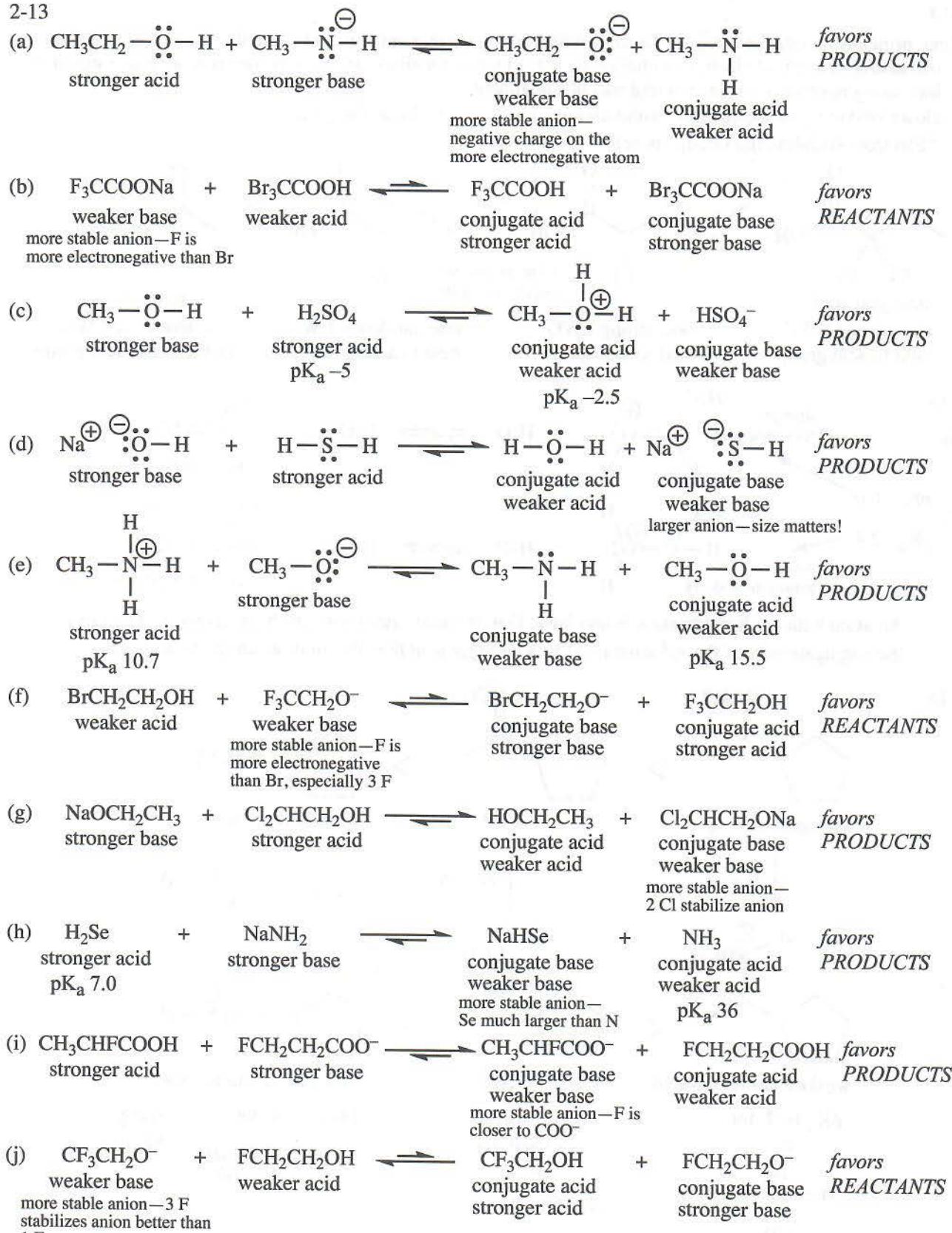


- Pentane is a hydrocarbon, neither acidic nor basic. Any acid-base reaction can occur in hydrocarbons without interacting with the solvent.
- Diethyl ether is not acidic, so reactions with strong bases are compatible, but it is weakly basic, so reactions with very strong acids (stronger than $\text{pK}_a -3.6$) will be leveled by the solvent.
- Ethanol is both acidic ($\text{pK}_a 15.9$) and basic (pK_a of the conjugate acid -2.4), so only acids and bases within this range are possible without interaction with the solvent.
- Water is both acidic ($\text{pK}_a 15.7$) and basic (pK_a of the conjugate acid -1.7), so only acids and bases within this range are possible without interaction with the solvent.
- Ammonia is both acidic ($\text{pK}_a 36$, very weak) and basic (pK_a of the conjugate acid 9.2), so only acids and bases within this range are possible without interaction with the solvent.

This question is asking, "Are the ultimate products compatible with the solvents?" The reactants may be leveled by the solvent, but as long as the products can exist within the pK_a limits of the solvent, the solvent is an acceptable choice.

Reaction	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ pentane	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ diethyl ether	$\text{CH}_3\text{CH}_2\text{OH}$ ethanol	H_2O water	NH_3 ammonia
(a) very strong base	OK	OK	NO	NO	OK
	HC≡CLi is a strong base from an acid of $\text{pK}_a 25$. It is not compatible with alcohols and water.				
(b) strong base	OK	OK	NO	NO	OK
	$(\text{CH}_3)_3\text{COLi}$ is a strong base from an acid of $\text{pK}_a 18$. It is not compatible with alcohols and water.				
(c) very strong acid	OK	NO	NO	NO	NO
	The protonated ring compound has $\text{pK}_a -3.8$. It is compatible only with pentane.				
(d) strong base	OK	OK	NO	NO	OK
	$(\text{CH}_3)_3\text{CONa}$ is a strong base from an acid of $\text{pK}_a 18$. It is not compatible with alcohols and water. <small>also a reactant</small>				
(e) very strong acid	OK	NO	NO	NO	NO
	The protonated oxygen compound has $\text{pK}_a -7.3$. It is compatible only with pentane.				
(e) strong acid	OK	OK	OK	OK	NO
	The protonated oxygen compound has $\text{pK}_a 0.0$. It is compatible with the four solvents except ammonia.				

2-13

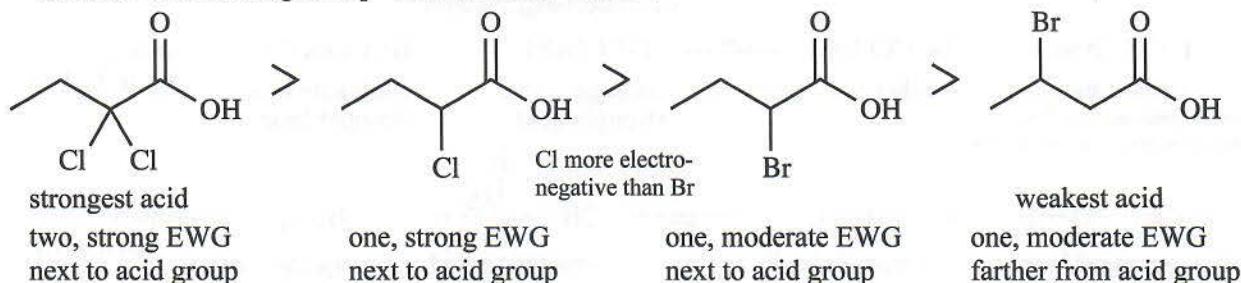


2-14

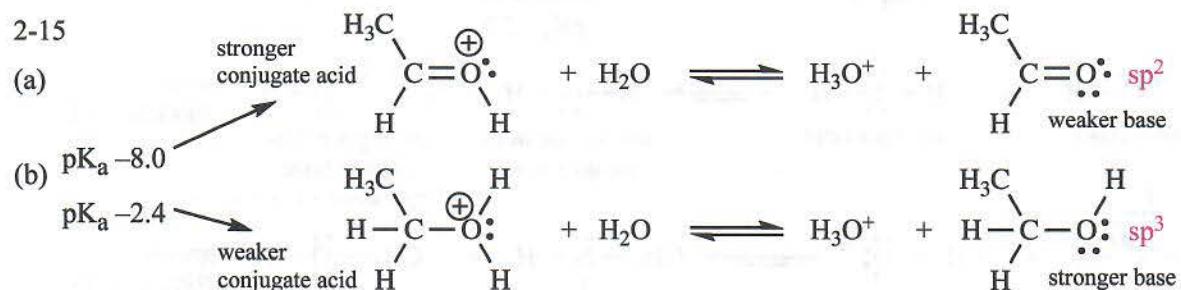
Three principles guide the effect of electron-withdrawing substituents on acid strength. Acidity is increased by:

- increasing strength of electron-withdrawing substituents; for single atoms, this means more electronegative;
- increasing number of electron-withdrawing substituents;
- closer proximity of the electron-withdrawing substituents to the acidic group.

"Electron-Withdrawing Group" is abbreviated "EWG".

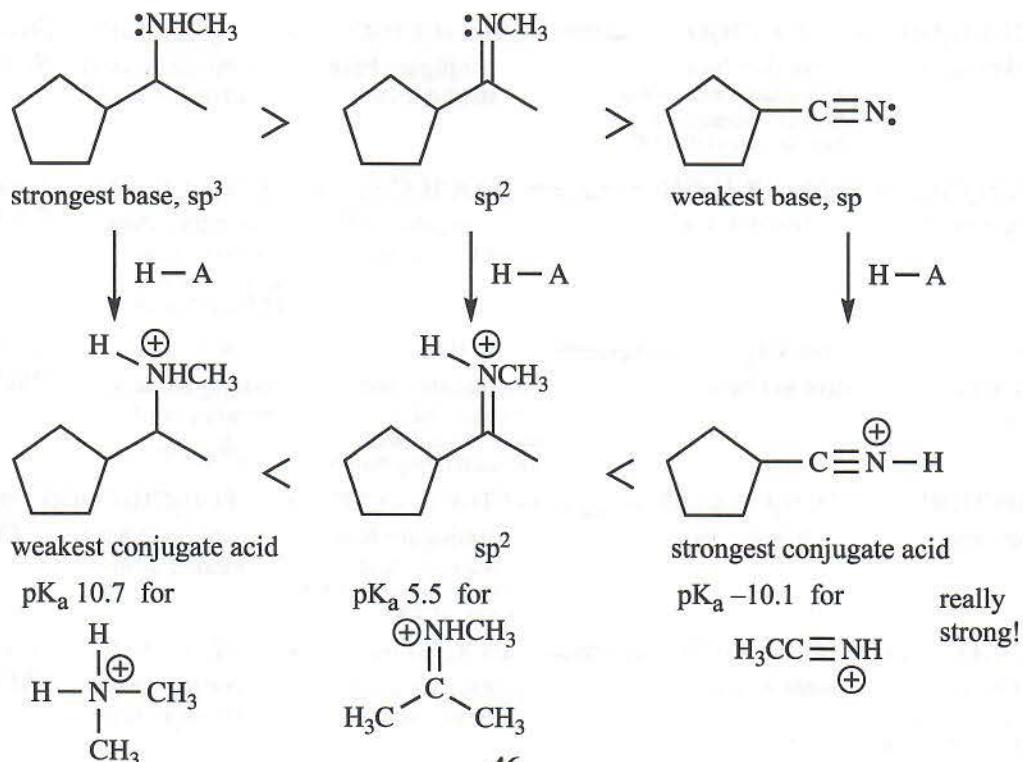


2-15



An atom with sp^2 hybridization is less basic than the same atom with sp^3 hybridization. Therefore, the conjugate acid of the sp^2 atom must be a stronger acid than the atom when sp^3 hybridized.

2-16

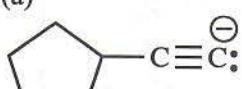


2-17

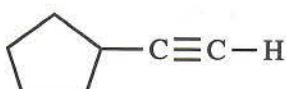
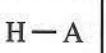
When comparing basic atoms, sp^3 atoms are stronger bases than sp^2 , which are stronger than sp .

Conjugate acids have the opposite order: H on sp is stronger than H on sp^2 , which is stronger than H on sp^3 .

(a)



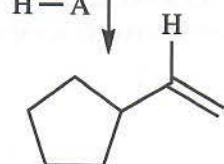
weaker base, sp



stronger conjugate acid

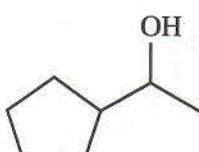


stronger base, sp^2

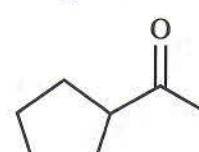
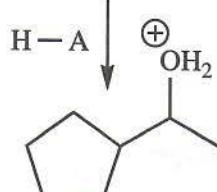


weaker conjugate acid

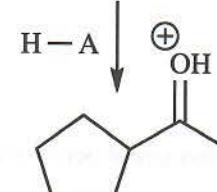
(b)



stronger base, sp^3

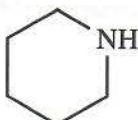


weaker base, sp^2

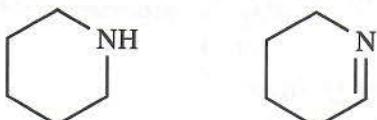
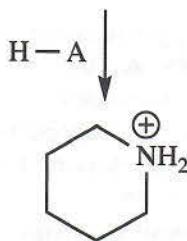


weaker conjugate acid stronger conjugate acid

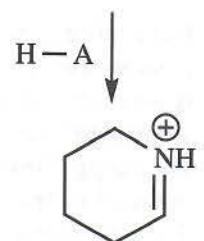
(c)



stronger base, sp^3



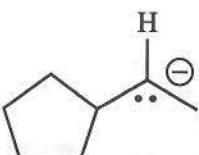
weaker base, sp^2



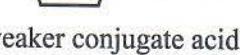
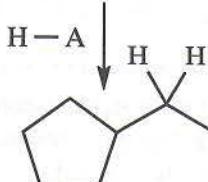
weaker conjugate acid stronger conjugate acid

(d)

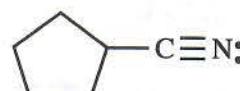
These structures are not the same comparison as in the other problems. They differ by a more important feature than hybridization: an anion at an sp^3 carbon is always going to be a stronger base than a neutral nitrogen.



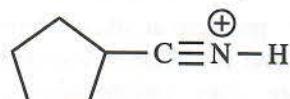
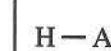
stronger base,
anion and sp^3



weaker conjugate acid



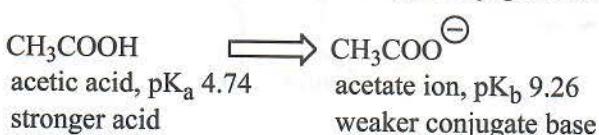
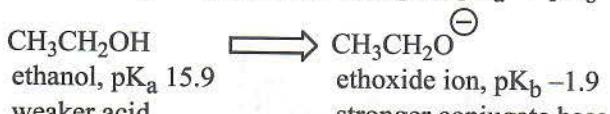
weaker base, neutral
N and sp



stronger conjugate acid

2-18

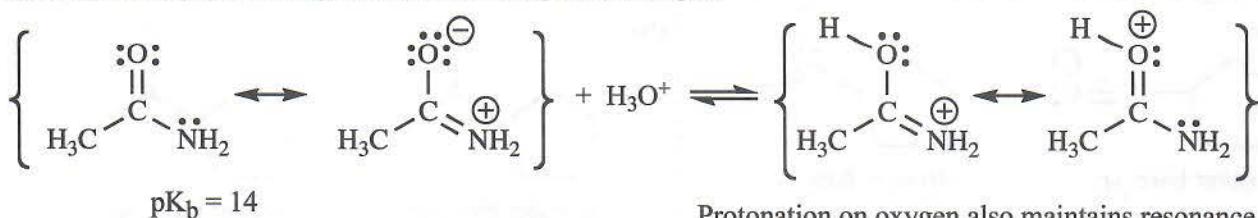
Recall that for any conjugate acid-base pair, $pK_a + pK_b = 14$. Applying this to the structures in question:



The strength of an acid is determined by the stability of its conjugate base. In this case, the resonance stabilization of the acetate ion explains its weaker basicity.

2-19

The resonance forms of acetamide show that the oxygen, not the nitrogen, is the likely site of protonation because the oxygen has a higher electron density than nitrogen.

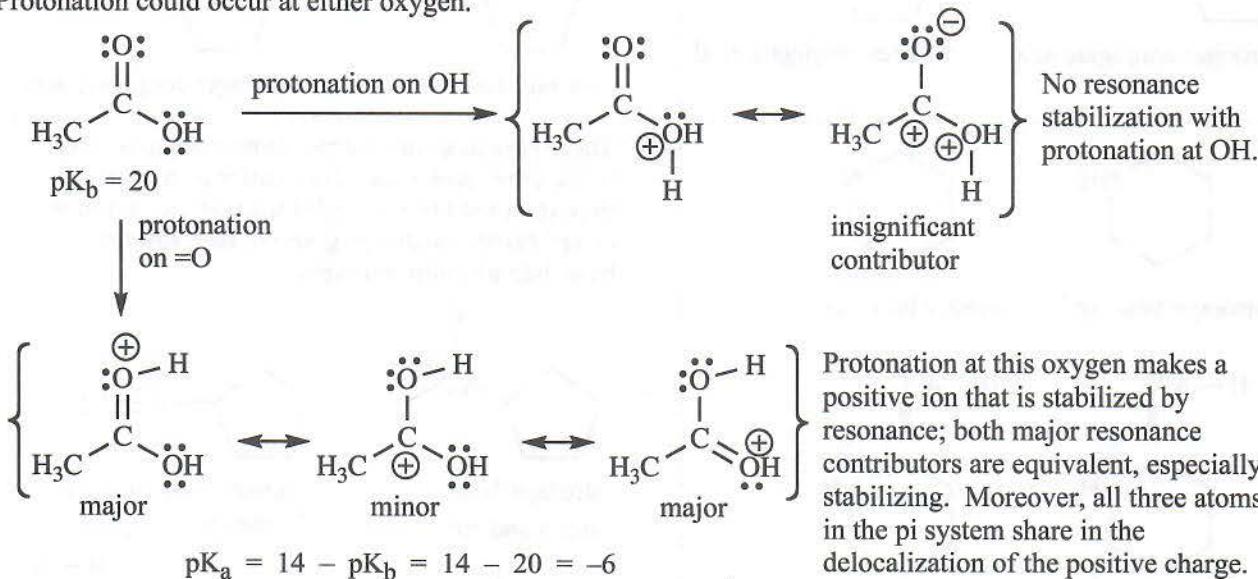


Protonation on oxygen also maintains resonance stabilization, unlike protonation on nitrogen which interrupts resonance stabilization.

$$\text{pK}_a = 14 - \text{pK}_b = 14 - 14 = 0$$

2-20

Protonation could occur at either oxygen.

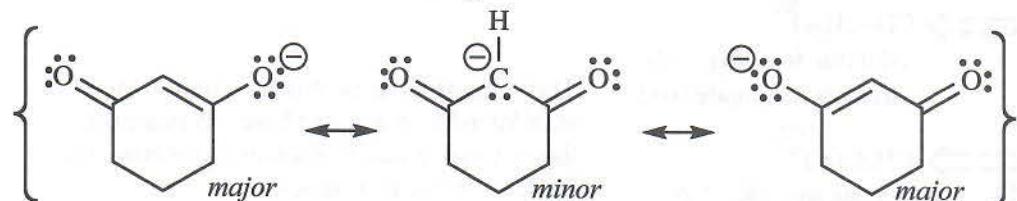


2-21 *The strength of an acid is determined by the stability of its conjugate base.*

This problem analyzes resonance stabilization of conjugate bases, which in this problem are anions except for part (g). The conjugate base that has more resonance forms that are significant contributors will be more stable, and therefore its conjugate acid is the stronger acid.

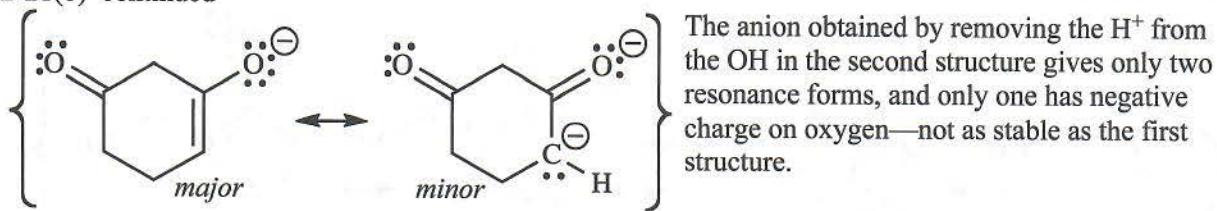
Part (a) was solved in the textbook.

(b) The anion of the first structure has three significant resonance contributors, two of which are equivalent (particularly stable) and with negative charge on the more electronegative atoms; high stabilization of the anion makes the first structure the stronger acid.

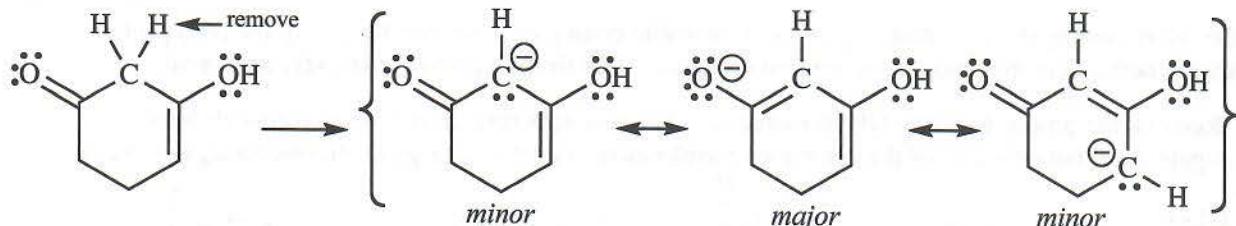


See the next page for the resonance forms of the other conjugate base.

2-21(b) continued



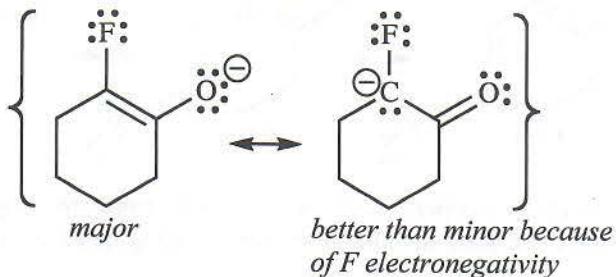
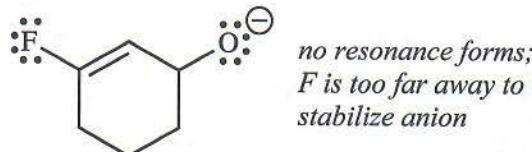
However, there is another choice of which H⁺ to remove. Removing an H from the CH₂ between the two oxygens also gives a resonance-stabilized anion:



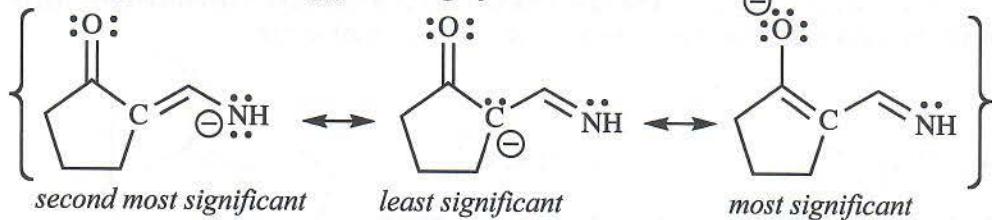
Arguably, the CH is a better proton to remove than the OH because of greater resonance stabilization, but either of the anions from the second structure is less stable than the anion from the first structure. **The first structure is still the stronger acid.**

(c) The most acidic H⁺ from the first structure is the OH. The anion from removing this H⁺ is not stabilized by resonance, and the F is too far away to have any significant inductive effect.

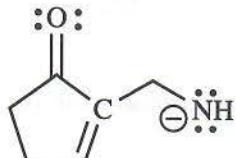
The anion from the second structure has two resonance forms, the second of which is even more stable because of the electronegativity of F. Therefore, **the second structure is the stronger acid.**



(d) Removing an H⁺ from NH₂ gives a highly stabilized anion:

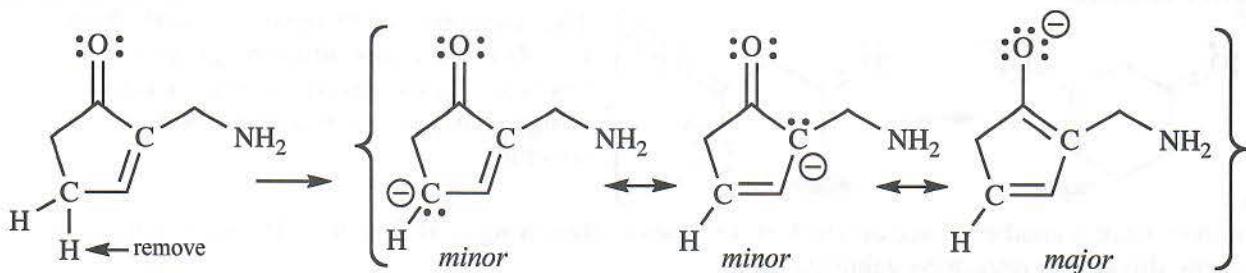


There are two choices for which H⁺ to remove from the second structure. If we want a direct comparison with the resonance-stabilized anion directly above, we should look at removing an H⁺ from the N, giving this conjugate base with no resonance stabilization.



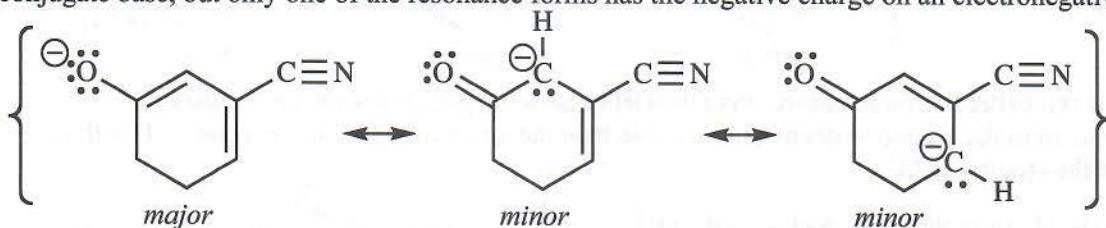
See the next page for the resonance forms of the other conjugate base.

2-21(d) continued

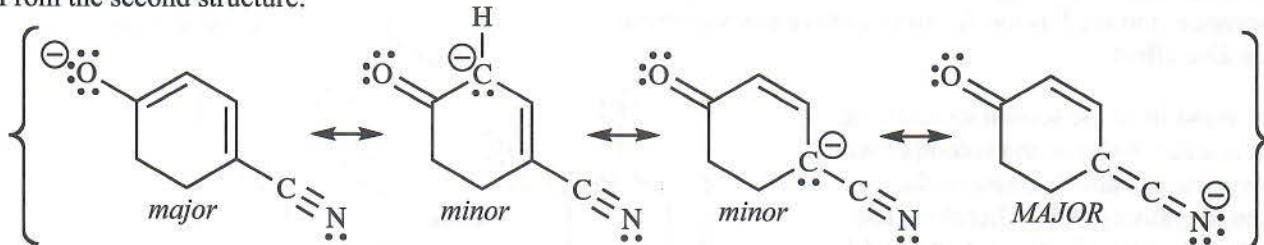


Although removing the CH_2 proton gives a more stable conjugate base than removing the NH_2 proton, neither is better than the anion from the first structure. **The first structure is the stronger acid.**

(e) Remove the proton from the OH in each case. The first structure gives a resonance-stabilized conjugate base, but only one of the resonance forms has the negative charge on an electronegative atom.

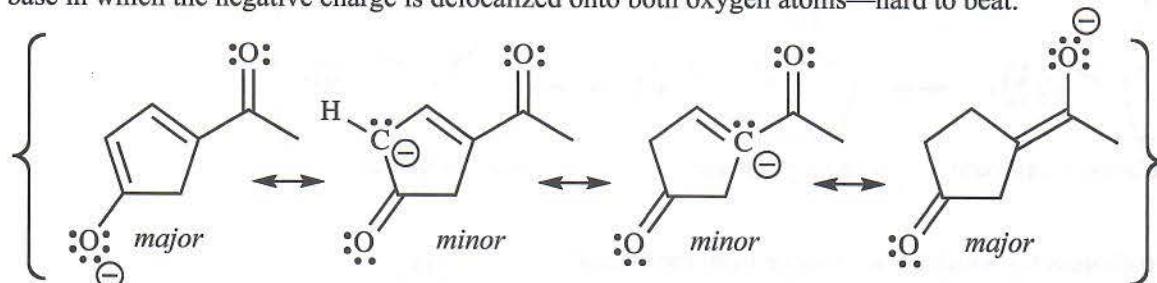


From the second structure:



Woo hoo! With the proper placement of the CN group, the negative charge can be delocalized onto the N as well as the O, making this the more stable conjugate base. **The second structure is the stronger acid.**

(f) Remove the proton from the OH in each case. The first structure gives a resonance-stabilized conjugate base in which the negative charge is delocalized onto both oxygen atoms—hard to beat.

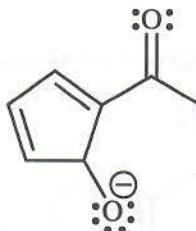


See the next page for the structure of the other conjugate base.

2-21(f) continued

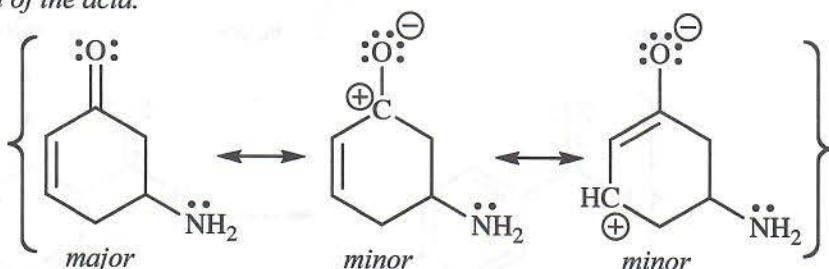
The conjugate base of the second structure shows that there is no resonance stabilization of the anion.

Therefore, the first structure is the stronger acid.

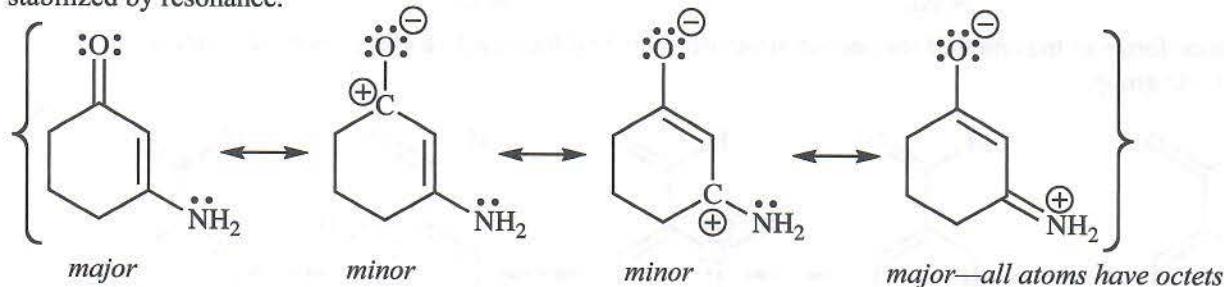


(g) The conjugate bases of these structures are not anions, yet the same principle applies: *the stability of the conjugate base determines the strength of the acid.*

After one of the NH protons is removed from the first structure, the conjugate base is a structure that has no charge and the NH₂ is not stabilized by resonance.



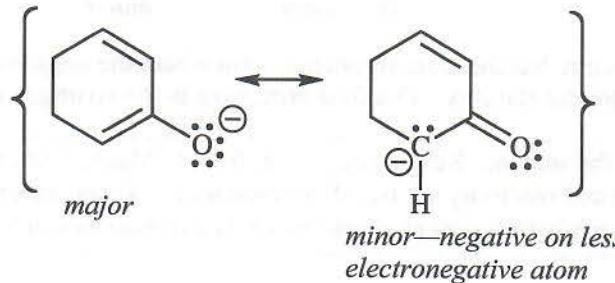
After one of the NH protons is removed from the second structure, however, the conjugate base is highly stabilized by resonance.



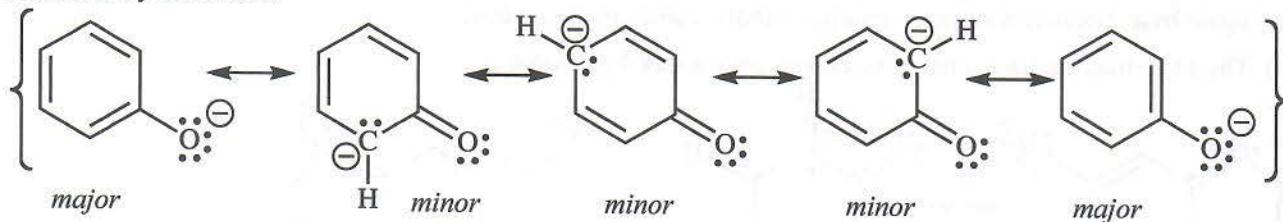
Because it has the more stable conjugate base, the second structure is the stronger acid.

(h)

After the OH proton is removed, the first structure is stabilized by resonance only to a small degree.



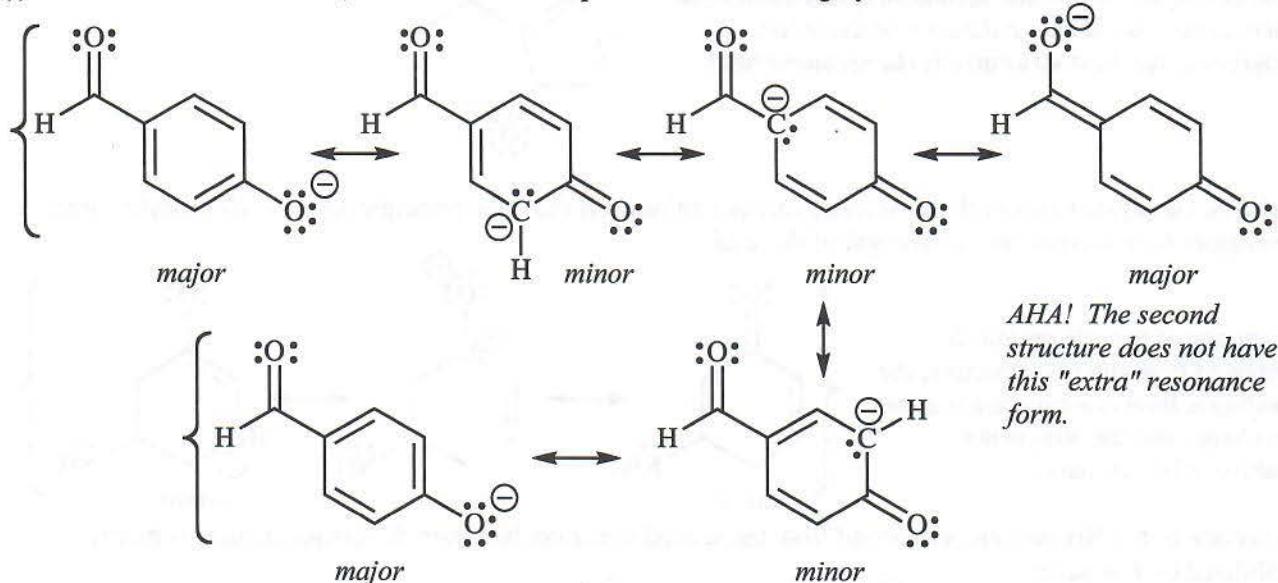
After one of the OH protons is removed from the second structure, however, the conjugate base is highly stabilized by resonance.



Because it has the more stable conjugate base, the second structure is the stronger acid.

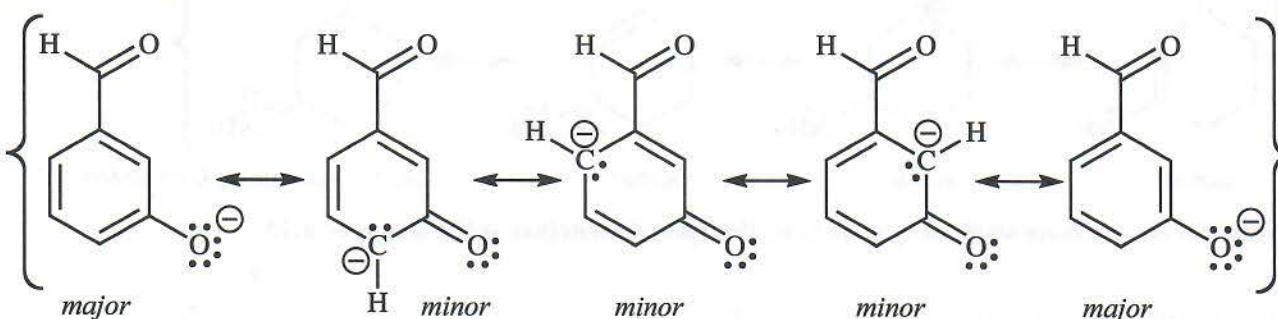
2-21 continued

(i) In both of these structures, removal of the OH proton results in a highly stabilized anion.



AHA! The second structure does not have this "extra" resonance form.

Resonance forms of the anion of the second structure show that the negative charge is never delocalized on the C=O group.



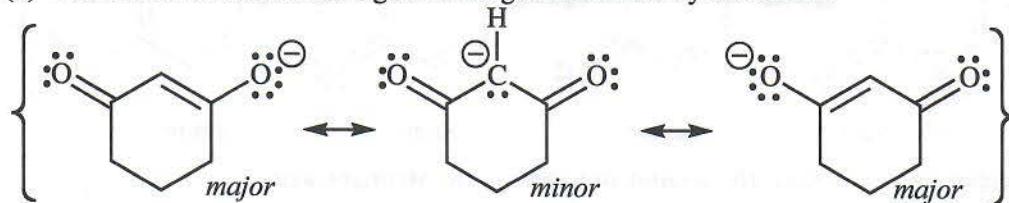
The first structure has the extra resonance form where the negative charge is delocalized onto the C=O, resulting in greater stability. **The first structure is the stronger acid.**

Note to the student: Resonance is your friend. Many, if not most, of the effects of structure on stability and reactivity are based on resonance, and understanding how to draw resonance forms, and when to apply the concept of resonance, is a critical tool in your success in solving problems.

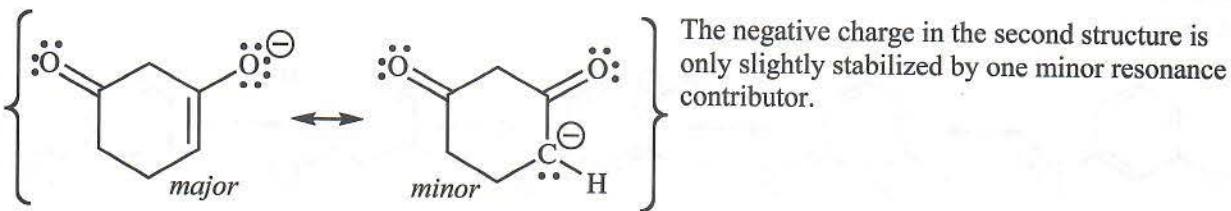
2-22

The more stable the anion, the less basic it will be. This is the corollary of: a stronger acid has a weaker conjugate base, because a stronger acid has a more stable conjugate base.

(b) The first structure has its negative charge delocalized by resonance.

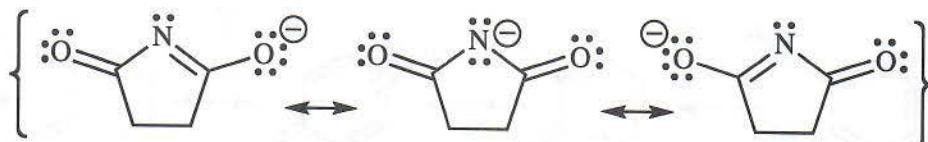


2-22(b) continued

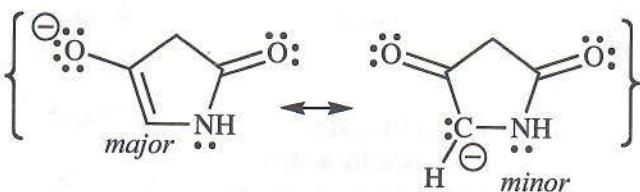


Because the first structure is more stable because of greater resonance delocalization of the negative charge, **the second structure will be the stronger base**. Note that this is the same as problem 2-21(b), just from the other side of the equation.

(c) The first structure has the negative charge delocalized onto two oxygens and a nitrogen:

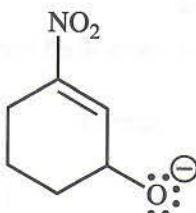


The second structure has the negative charge delocalized onto one oxygen and a carbon:

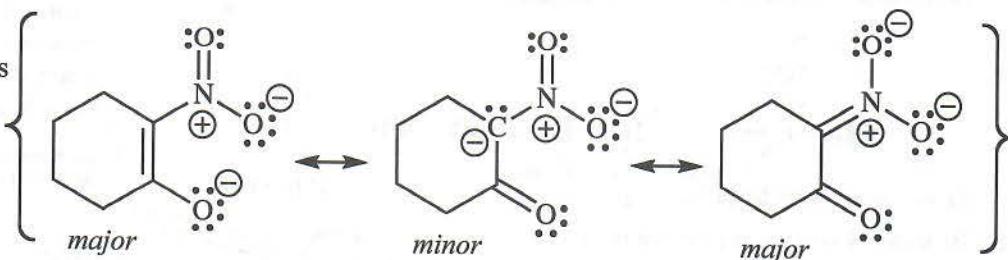


Because the first structure is more stable because of greater resonance delocalization of the negative charge, **the second structure will be the stronger base**.

(d) Even though there is resonance between the C=C and the NO₂ group, the first structure has the negative charge on oxygen that is not delocalized by resonance.



The second structure has the negative charge delocalized onto two oxygens:

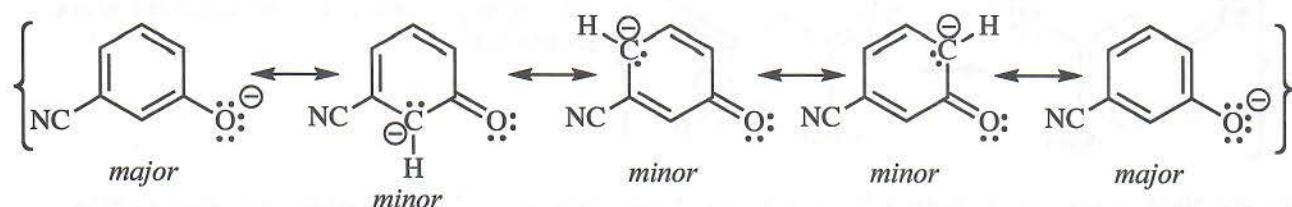


Because the second structure is more stable because of greater resonance delocalization of the negative charge, **the first structure will be the stronger base**.

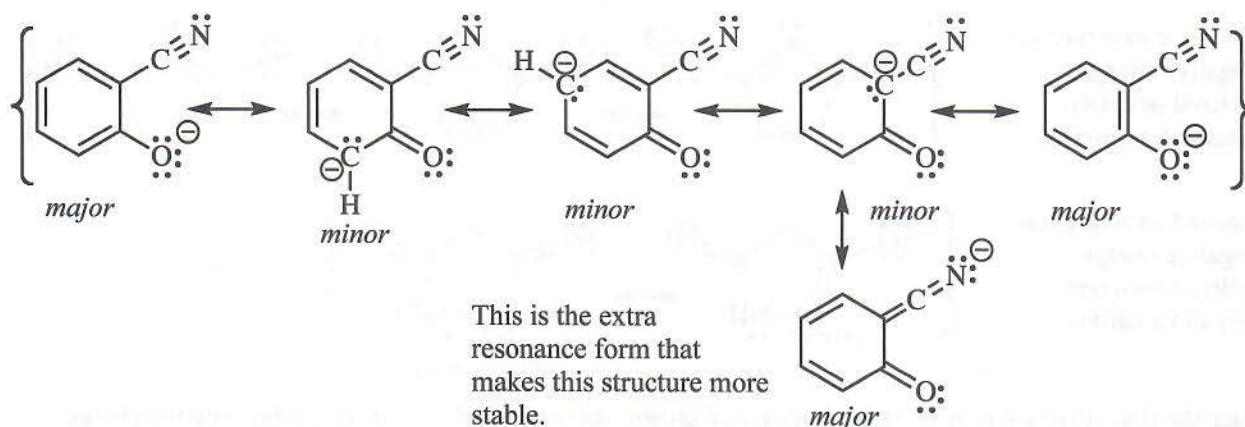
(e) As shown on the next page, the negative charge in both structures is highly delocalized by resonance, but only the second structure has the negative charge on the oxygen and the nitrogen. Because the second structure is more stable, **the first structure will be the stronger base**.

2-22(e) continued

First structure:



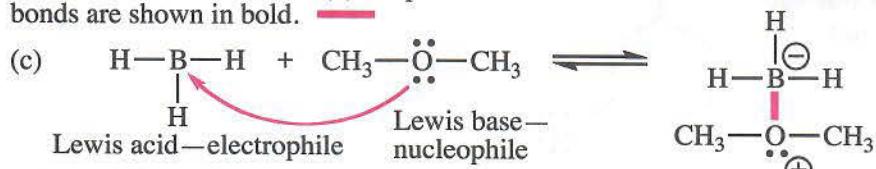
Second structure:



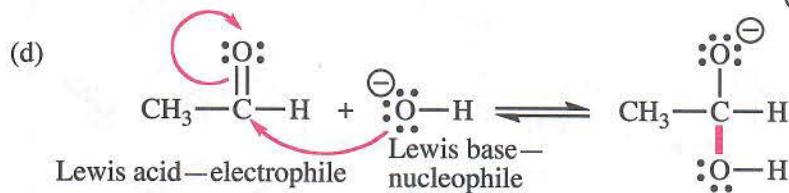
This is the extra resonance form that makes this structure more stable.

The first structure will be the stronger base.

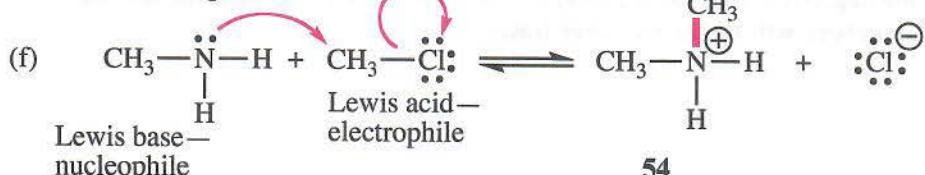
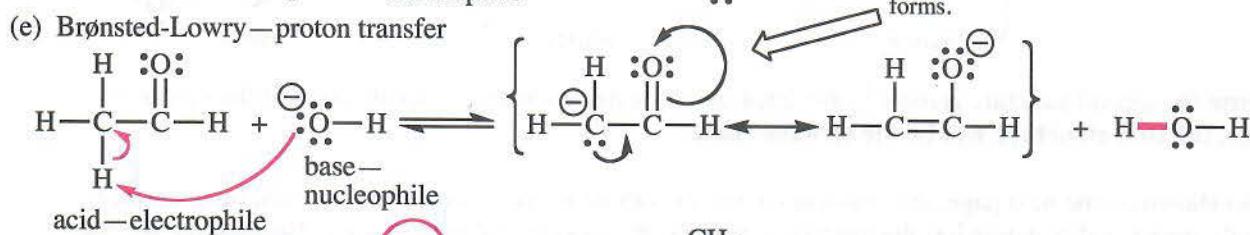
2-23 Solutions for (a) and (b) are presented in the Solved Problem in the text. Here, the newly formed bonds are shown in bold.



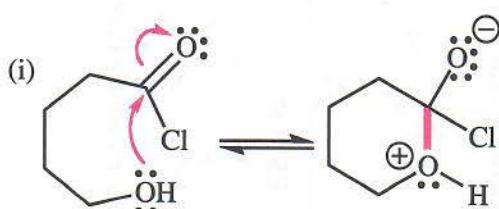
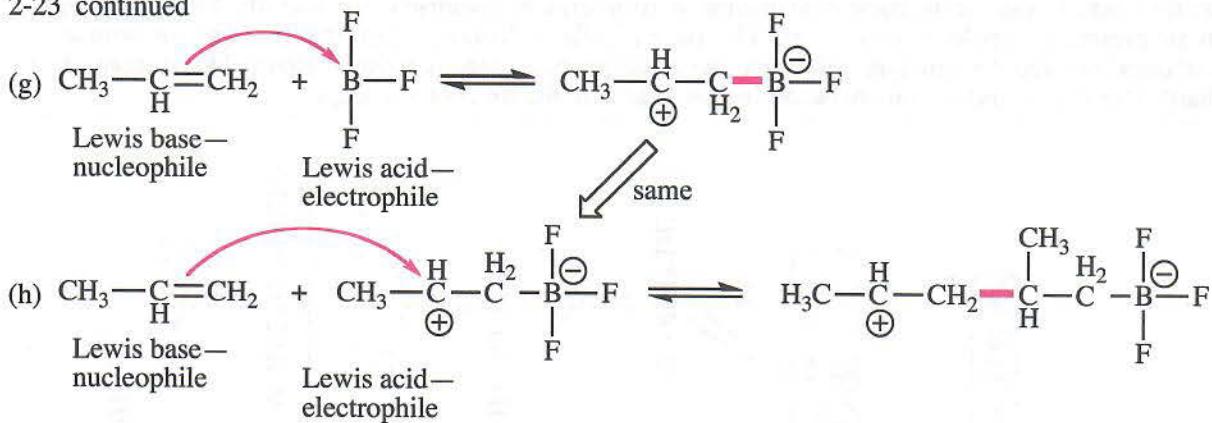
Curved arrows that show electron movement are shown here and in the text in red. Arrows within resonance forms that show *imaginary* movement are in green in the text, and in black here.



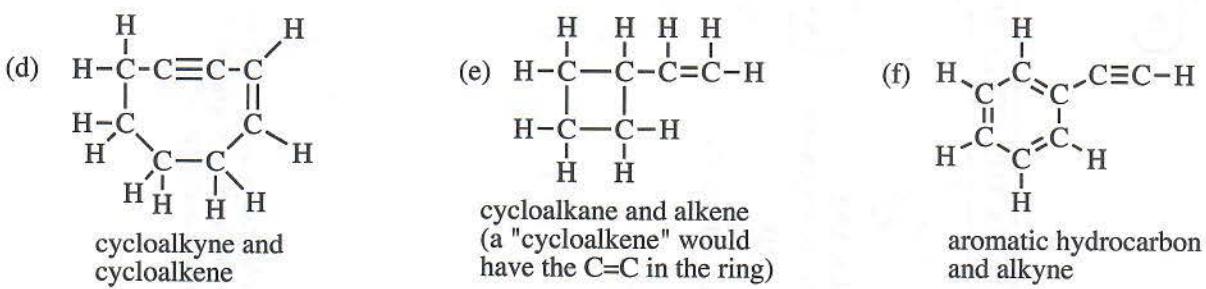
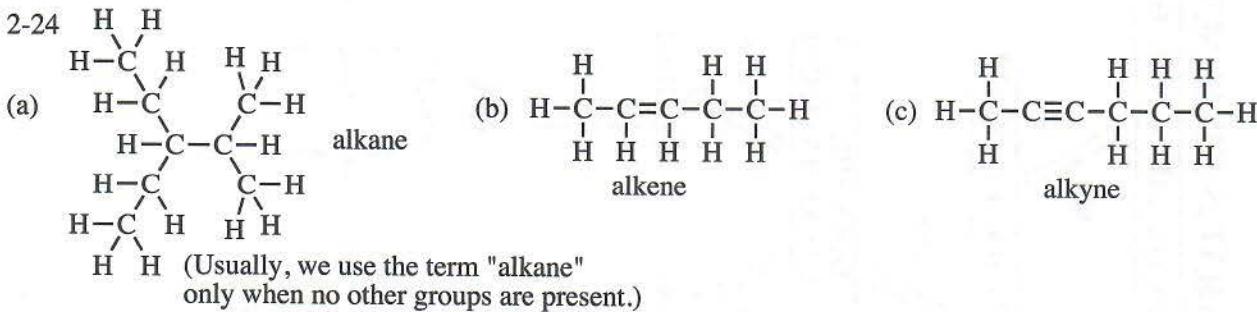
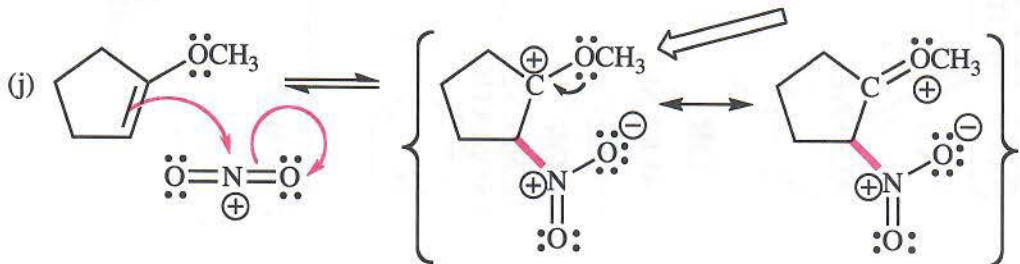
The problem asks for the *imaginary* movement of electrons in the resonance forms.



2-23 continued

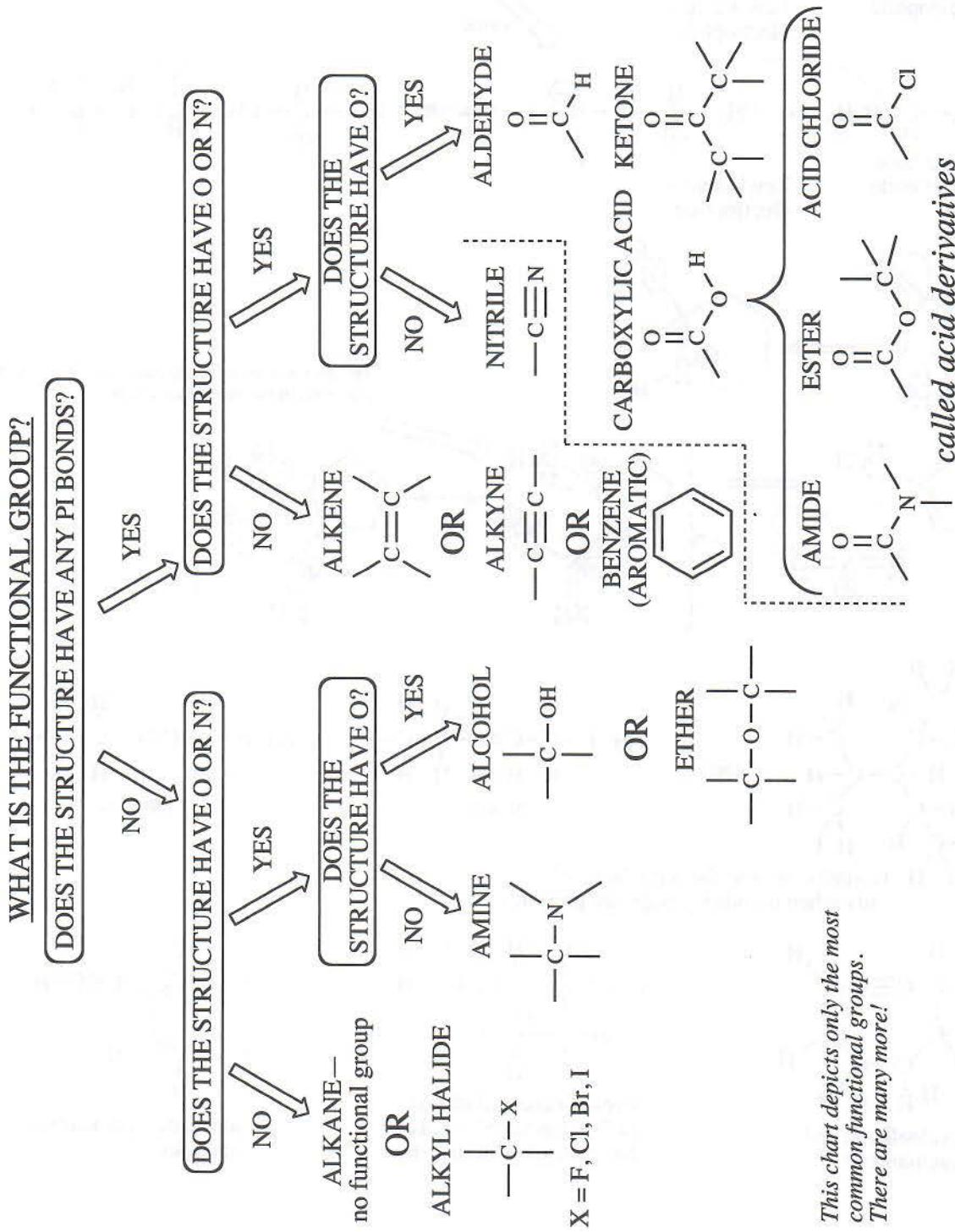


The problem asks for the *imaginary* movement of electrons in the resonance forms.

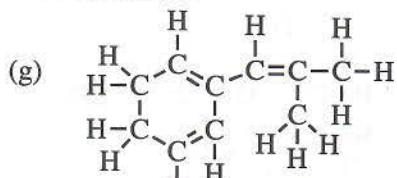


continued on page 57

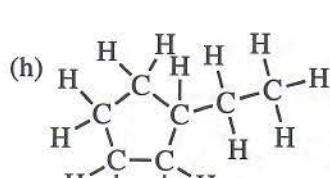
Note to the student: One of the most fundamental skills in organic chemistry is to identify what functional groups are present in a molecular structure. This page is called a "concept map" that prompts you with a series of questions about a structure, leading to the determination of the functional group. Do not memorize this chart! Use it as an aid as you are becoming familiar with the functional groups.



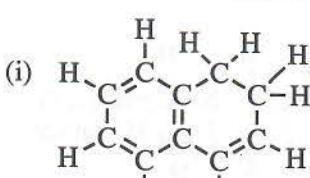
2-24 continued



cycloalkene and alkene

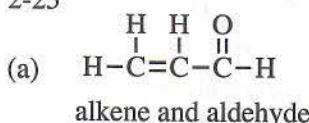


cycloalkane and alkane

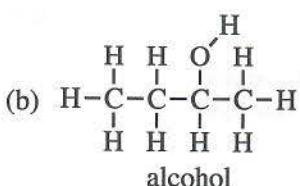


aromatic hydrocarbon
and cycloalkene

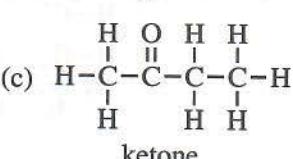
2-25



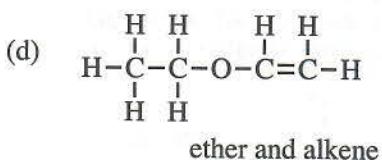
alkene and aldehyde



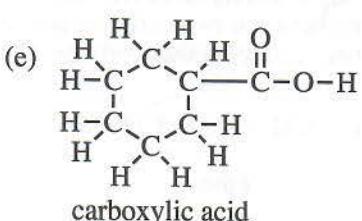
alcohol



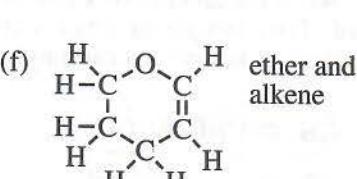
ketone



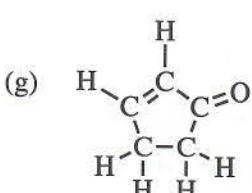
ether and alkene



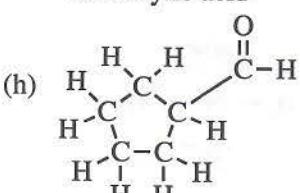
carboxylic acid



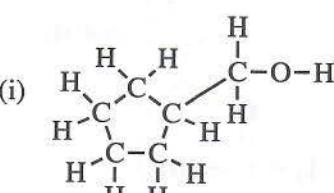
ether and
alkene



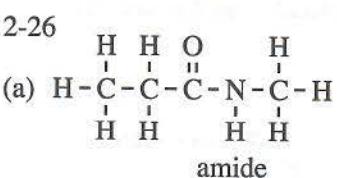
alkene and ketone



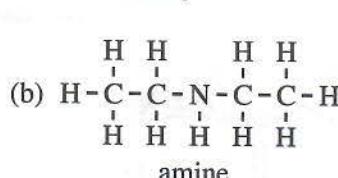
aldehyde



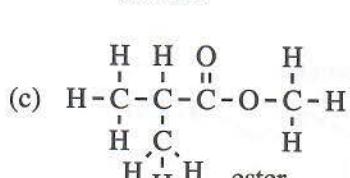
alcohol



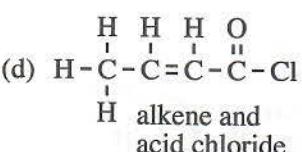
amide



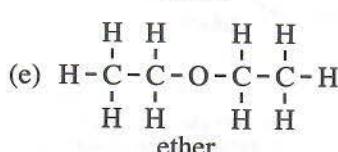
amine



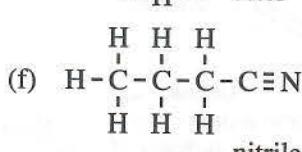
ester



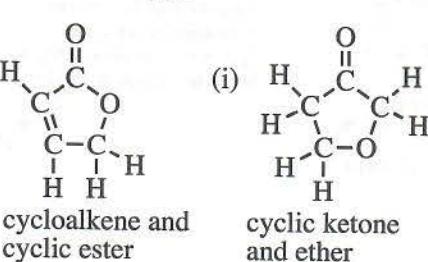
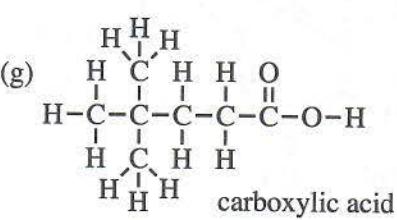
alkene and
acid chloride



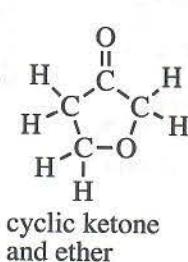
ether



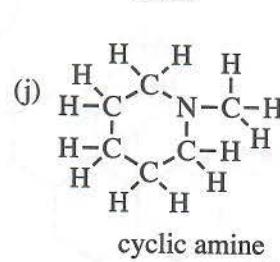
nitrile



cycloalkene and
cyclic ester

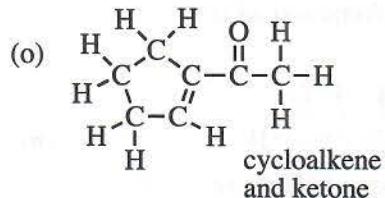
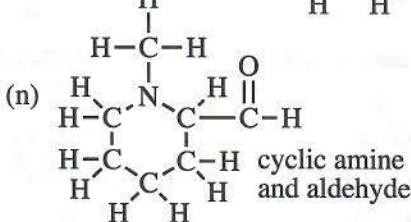
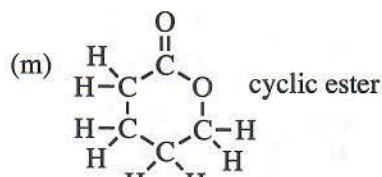
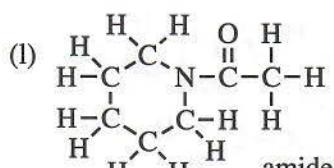
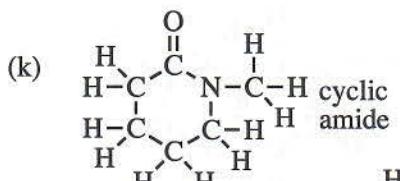


cyclic ketone
and ether

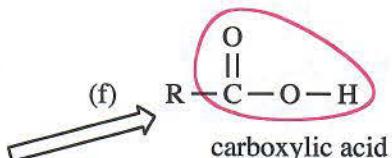
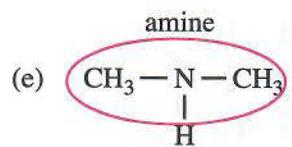
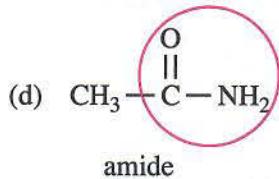
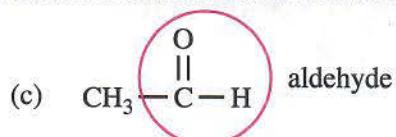
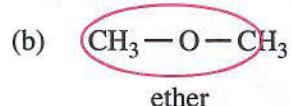
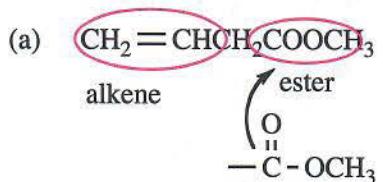


cyclic amine

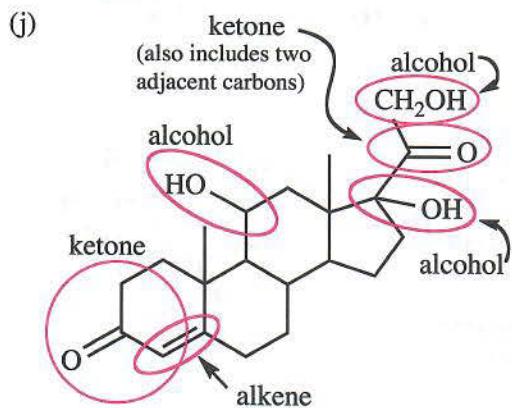
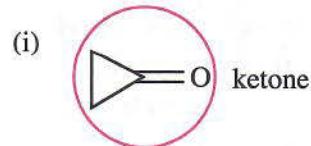
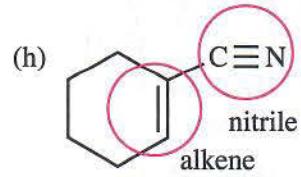
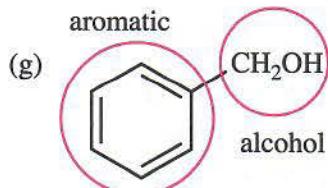
2-26 continued

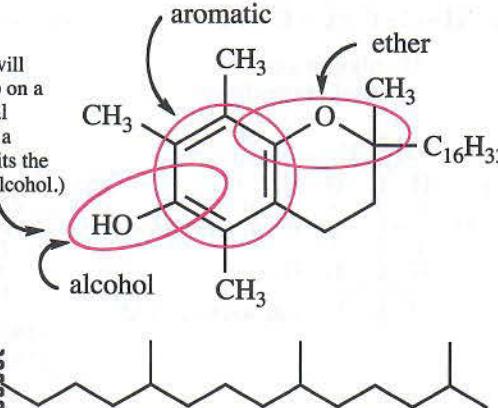


2-27 When the identity of a functional group depends on several atoms, all of those atoms should be circled. For example, an ether is an oxygen between two carbons, so the oxygen and both carbons should be circled. A ketone is a carbonyl group between two other carbons, so all those atoms should be circled.



R is the symbol that organic chemists use to represent alkyl groups. Sometimes, when the identity of the group does not matter, aryl groups or others can also be included in the R abbreviation.

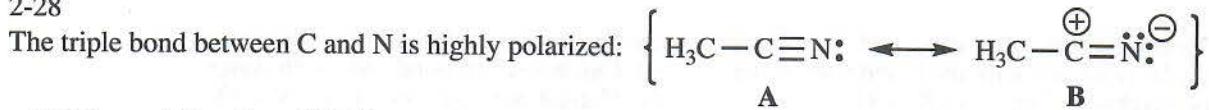


(k)  aromatic
ether
alcohol

(In later chapters, you will learn that the OH group on a benzene ring is a special functional group called a "phenol". For now, it fits the broad definition of an alcohol.)

This group is represented by $C_{16}H_{33}$ in the problem.

2-28

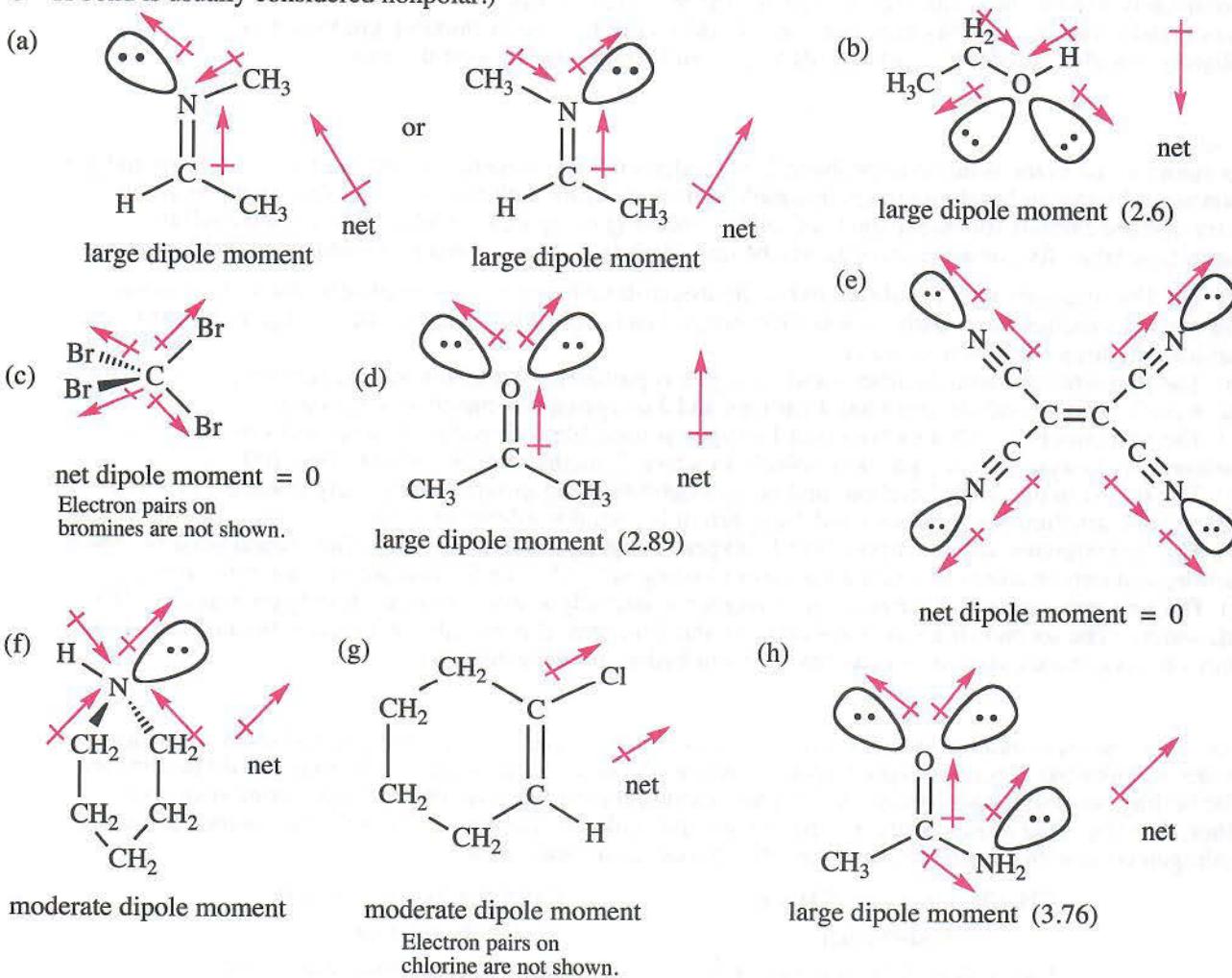


$$3.6 \text{ D} = 4.8 \times \delta \times 1.16 \text{ \AA}$$

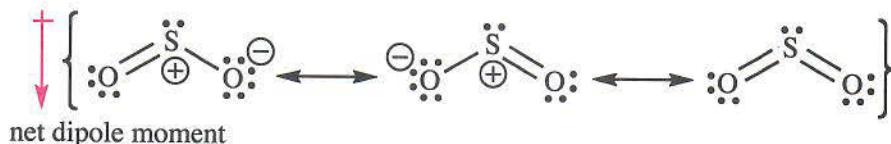
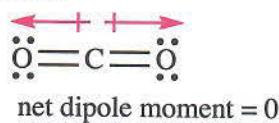
$\delta = 0.65$, or 65% of a positive charge on carbon and 65% of a negative charge on nitrogen

Resonance form **B** must be the major contributor. If **A** were the major contributor, the value of the charge separation would be between 0.0 and 0.5, meaning <50% of a positive charge on C and <50% of a negative charge on N.

2-29 Some magnitudes of dipole moments are difficult to predict; however, the direction of the dipole should be straightforward in most cases. Actual values of molecular dipole moments are given in parentheses. (The C—H bond is usually considered nonpolar.)



2-30 CO_2 is linear; its bond dipoles cancel, so it has no net dipole. SO_2 is bent, so its bond dipoles do not cancel.



2-31

- (a) Can hydrogen bond with itself and with water.
(c) Can hydrogen bond with itself and with water.
(e) Cannot hydrogen bond: no N or O.
(g) Can hydrogen bond only with water.
(i) Can hydrogen bond only with water.
(k) Can hydrogen bond only with water.
- (b) Can hydrogen bond only with water.
(d) Can hydrogen bond only with water.
(f) Cannot hydrogen bond: no N or O.
(h) Can hydrogen bond with itself and with water.
(j) Can hydrogen bond only with water.
(l) Can hydrogen bond with itself and with water.

Water solubility depends on the number of carbons and the number of hydrogen-bonding groups in a molecule, and to a lesser extent, on the shape of the molecule and its ability to form hydrogen bonds. A structure with one hydrogen-bonding group can carry in three carbons for sure, called "miscible", meaning completely soluble; four carbons will be partially soluble—these are borderline cases and are the most difficult to predict; five or more carbons will be only slightly soluble, which is sometimes called "insoluble".

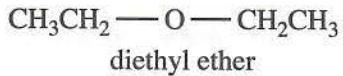
- completely soluble, miscible: (c) 3C; (g) 3C; (h) 3C; (i) 3C; (l) 2C;
- moderately soluble, possibly miscible: (a), (j), (k)—each has one H-bonding group and 4C;
- slightly soluble, "insoluble": (b) 6C; (d) 6C; (e) and (f) have no H-bonding group.

2-32

As summarized in the solution to problem 2-31, water solubility depends on the number of carbons and the number of hydrogen-bonding groups in a molecule. A structure with one hydrogen-bonding group can carry in three carbons for sure, called "miscible", meaning completely soluble; four carbons will be partially soluble; five or more carbons will be only slightly soluble, which is sometimes called "insoluble".

- (a) The first structure with 5 carbons and no hydrogen-bonding group is completely insoluble in water. The second structure has 4 carbons and 1 oxygen; it is miscible with water because oxygen's electron pairs can form hydrogen bonds with water.
- (b) The first structure with 5 carbons and 1 oxygen is partially soluble in water (tetrahydropyran, 8 g/100 mL water). The second structure has 4 carbons and 2 oxygens; it is miscible with water.
- (c) The first structure with 4 carbons and 1 oxygen is miscible with water. The second structure with 5 carbons and 1 oxygen is only partially soluble in water (2-methyltetrahydrofuran, 14 g/100 mL).
- (d) The first structure with 5 carbons and no hydrogen-bonding group is completely insoluble in water. The second structure has 6 carbons and 1 oxygen; it is partially soluble in water.
- (e) The first structure with 5 carbons and 1 oxygen is slightly soluble in water. The second structure has 5 carbons and two bromines—which do not form hydrogen bonds—and is completely insoluble in water.
- (f) The first structure with 5 carbons and 1 oxygen is partially soluble in water (tetrahydropyran, 8 g/100 mL water). The second structure has 4 carbons and 1 oxygen; it is miscible with water because the electron pairs on oxygen are exposed and can readily form hydrogen bonds with water.

2-33 Diethyl ether and butan-1-ol each have one oxygen, so each can form hydrogen bonds with water (water supplies the H for hydrogen bonding with diethyl ether); their water solubilities should be similar. The boiling point of butan-1-ol is much higher because these molecules can hydrogen bond with each other, thus requiring more energy to separate one molecule from another. Diethyl ether molecules cannot hydrogen bond with each other, so it is relatively easy to separate them.

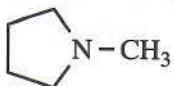


Can hydrogen bond with water;
cannot hydrogen bond with itself.

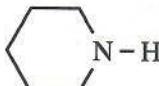


Can hydrogen bond with water;
can hydrogen bond with itself.

2-34



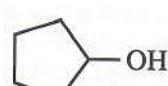
N-methylpyrrolidine
b.p. 81 °C



piperidine
b.p. 106 °C



tetrahydropyran
b.p. 88 °C



cyclopentanol
b.p. 141 °C

(a) Piperidine has an N—H bond, so it can hydrogen bond with other molecules of itself.

N-Methylpyrrolidine has no N—H, so it cannot hydrogen bond and will require less energy (lower boiling point) to separate one molecule from another.

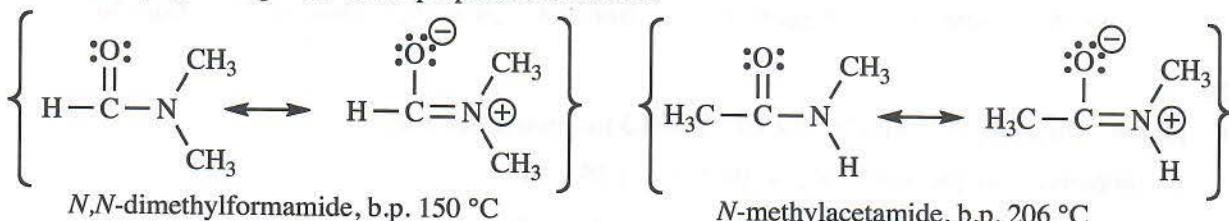
(b) Two effects need to be explained: 1) Why does cyclopentanol have a higher boiling point than tetrahydropyran? and 2) Why do the oxygen compounds have a greater difference in boiling points than the analogous nitrogen compounds?

The answer to the first question is the same as in (a): cyclopentanol can hydrogen bond with its neighbors while tetrahydropyran cannot.

The answer to the second question lies in the text, Table 2-1, that shows the bond dipole moments for C—O and H—O are much greater than C—N and H—N; bonds to oxygen are more polarized, with greater charge separation than bonds to nitrogen.

How is this reflected in the data? The boiling points of tetrahydropyran (88 °C) and *N*-methylpyrrolidine (81 °C) are close; tetrahydropyran molecules would have a slightly stronger dipole-dipole attraction, and tetrahydropyran is a little less "branched" than *N*-methylpyrrolidine, so it is reasonable that tetrahydropyran boils at a slightly higher temperature. The large difference comes when comparing the boiling points of cyclopentanol (141 °C) and piperidine (106 °C). The greater polarity of O—H versus N—H is reflected in a more negative oxygen (more electronegative than nitrogen) and a more positive hydrogen, resulting in a much stronger intermolecular attraction. The conclusion is that hydrogen bonding due to O—H is much stronger than that due to N—H.

(c) Resonance plays a large role in the properties of amides.

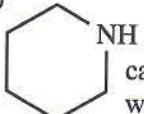


The first structure has no hydrogen bonding because it has no O—H or N—H bond, but it is a highly polar structure and has a large dipole moment, so its dipole-dipole intermolecular force is very high. The second structure has hydrogen bonding because of the N—H bond in addition to the strong dipole-dipole interaction, reflected in its higher boiling point. Both amides boil higher than the four at the beginning of the problem because of the dipole-dipole interactions that are accentuated by the resonance forms.

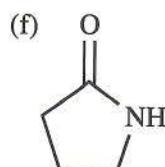
2-35 Higher-boiling compounds are the ones described.

- $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ can form hydrogen bonds with other molecules of itself.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ has a higher molecular weight than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ has less branching than $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ has a higher molecular weight AND a dipole-dipole interaction compared with $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

(e)



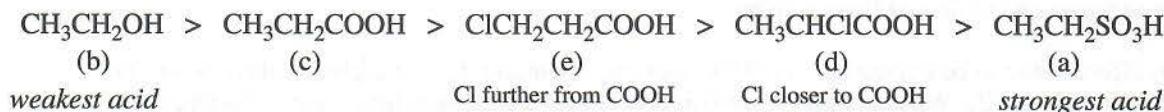
can form hydrogen bonds with other molecule of itself (actual bp 106°C; the other structure has bp 81°C).



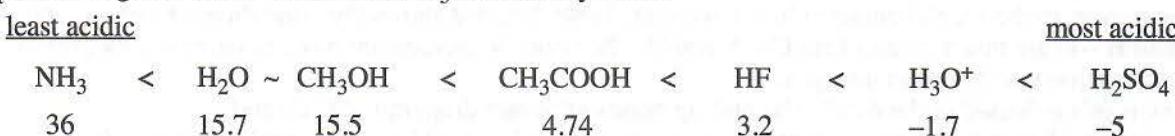
has two sites for hydrogen bonding, not just one, and a very strong dipole because of resonance (actual bp 245°C; the other structure has bp ≈102°C).

2-36 The strength of the acid depends on the stability of the conjugate base. The two primary factors governing the strength of organic acids are resonance and inductive effects; of these two, resonance is usually the stronger and more important effect.

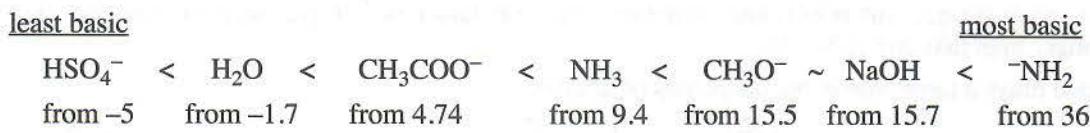
Any organic structure with an $-SO_3H$ in it is a very strong acid because the anion has three significant resonance contributors. An organic structure with $-COOH$ is moderately strong since the conjugate base has two significant resonance contributors. A structure with a simple $-OH$ does not have any resonance stabilization of the conjugate base, so it is the weakest acid. Within each group, inductive effects from an electronegative atom like Cl will have a small effect.



2-37 These pK_a values from the text, Table 2-2 and Appendix 4, provide the answers. The lower the pK_a , the stronger the acid. Water and CH_3OH are very close.



2-38 Conjugate bases of the weakest acids will be the strongest bases. The pK_a values of the conjugate acids are listed here. (The relative order of some bases was determined from the pK_a values in Appendix 4 of the textbook.)



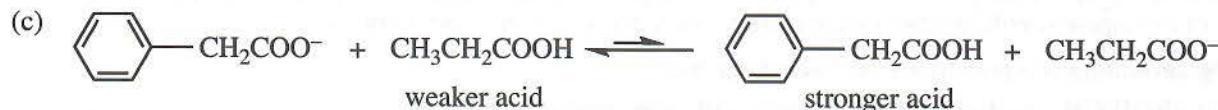
2-39

(a) $pK_a = -\log_{10} K_a = -\log_{10} (5.2 \times 10^{-5}) = 4.3$ for phenylacetic acid

for propionic acid, pK_a 4.87: $K_a = 10^{-4.87} = 1.35 \times 10^{-5}$

(b) Phenylacetic acid is 3.9 times stronger than propionic acid.

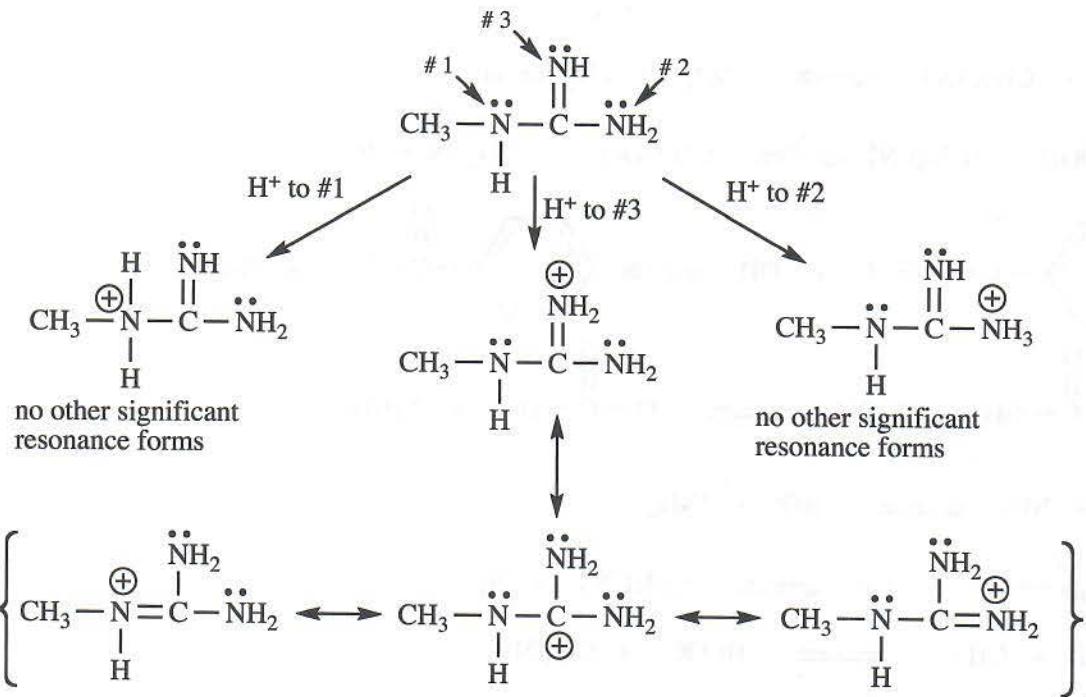
$$\frac{5.2 \times 10^{-5}}{1.35 \times 10^{-5}} = 3.9$$



Equilibrium favors the weaker acid and base. In this reaction, reactants are favored.

2-40

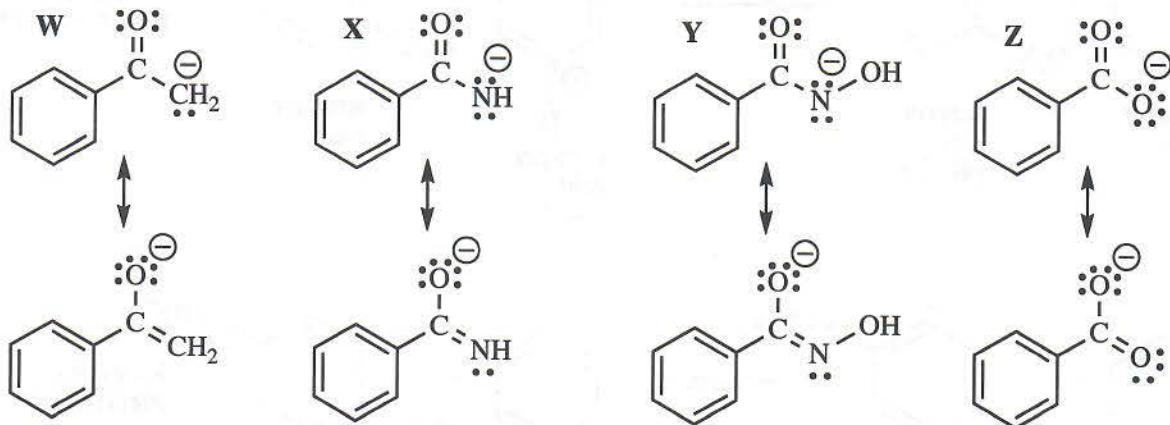
(a)



(b) Protonation at nitrogen #3 gives four resonance forms that delocalize the positive charge over all three nitrogens and a carbon—a very stable condition. Nitrogen #3 will be protonated preferentially, which we interpret as being more basic.

2-41 The critical principle: *the strength of an acid is determined by the stability of its conjugate base.*

(a) conjugate bases

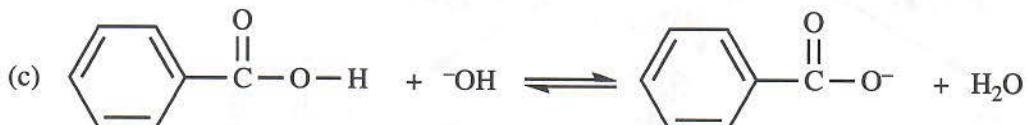


(b) X is a stronger acid than W because the more electronegative N in X can support the negative charge better than carbon, so the anion of X is more stable than the anion of W.

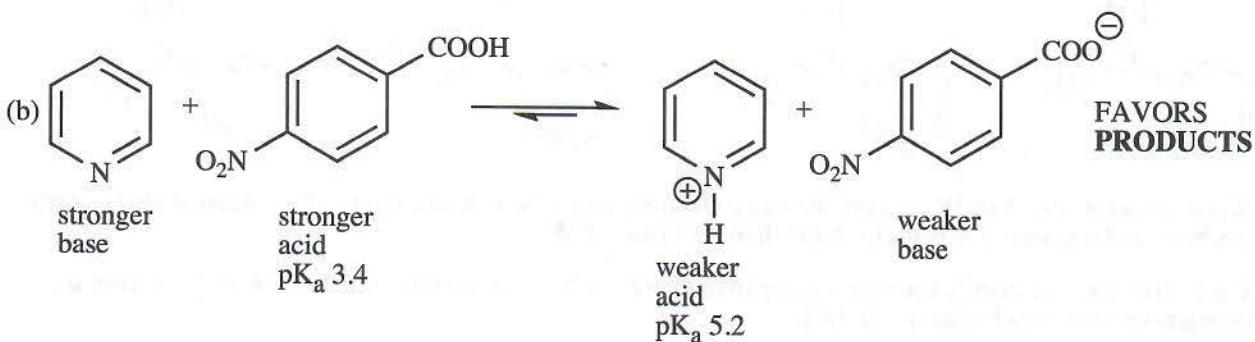
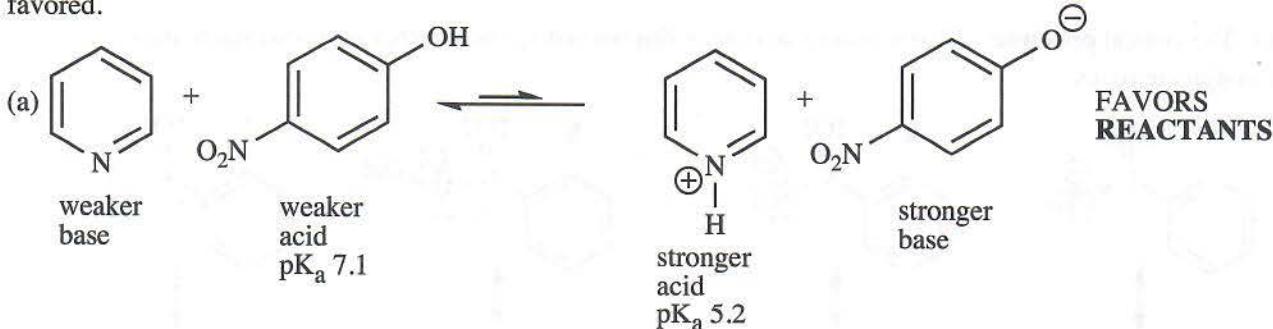
(c) Y is a stronger acid than X because the negative charge in Y is stabilized by the *inductive effect* from the electronegative oxygen substituent, the OH.

(d) Z is a stronger acid than Y because of two effects: O is more electronegative than N and can support the negative charge of the anion better, plus the anion of Z has two EQUIVALENT resonance forms, which is particularly stable.

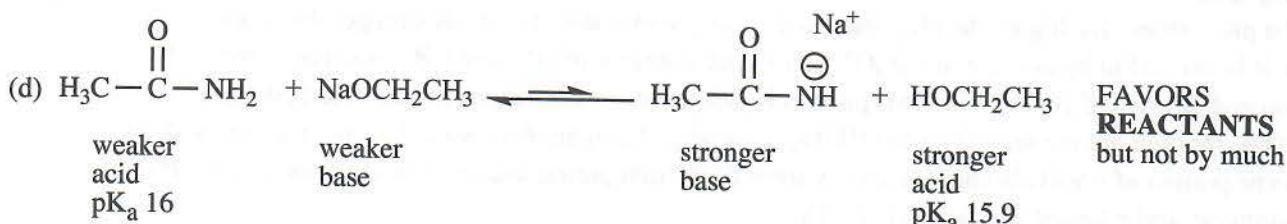
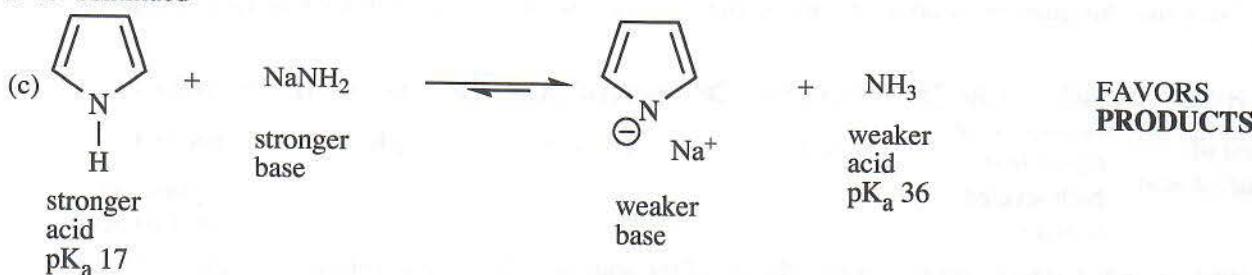
2-42



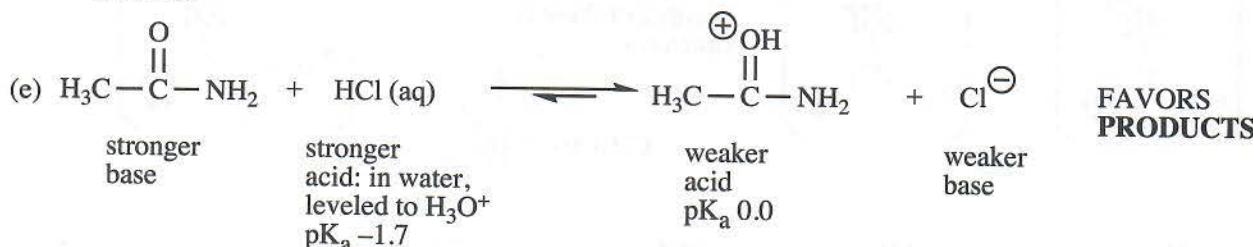
2-43 Values are from Appendix 4 in the text. The side of the equation with the weaker acid and base is favored.



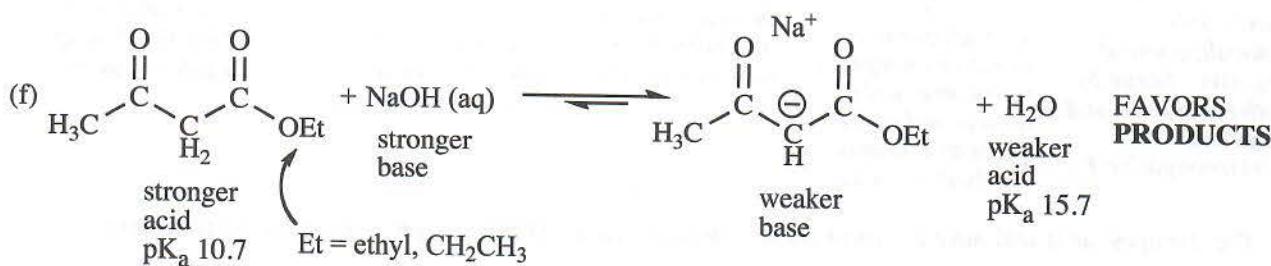
2-43 continued



The reaction in part (d) merits comment. Only 0.1 pK_a units separates the two acids in this equation. When pK_a values are measured in solvents other than water (any pK_a value higher than 15.7), the experimental error increases. Without specifying that these two pK_a values were measured in the same solvent, it is difficult to give the difference of 0.1 pK_a units much credence. Conclusion: the two sides of the equation are fairly equally matched, and the products and reactants would probably be close to 50:50. In one solvent, reactants may be favored, and in a different solvent, products favored.

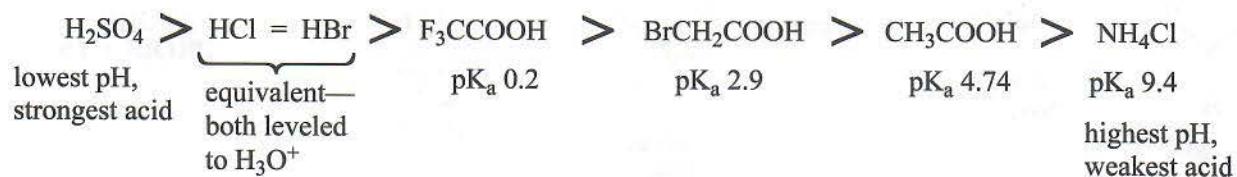


Recall from problem 2-19 that the site of protonation of the reactant is the O, not the N.



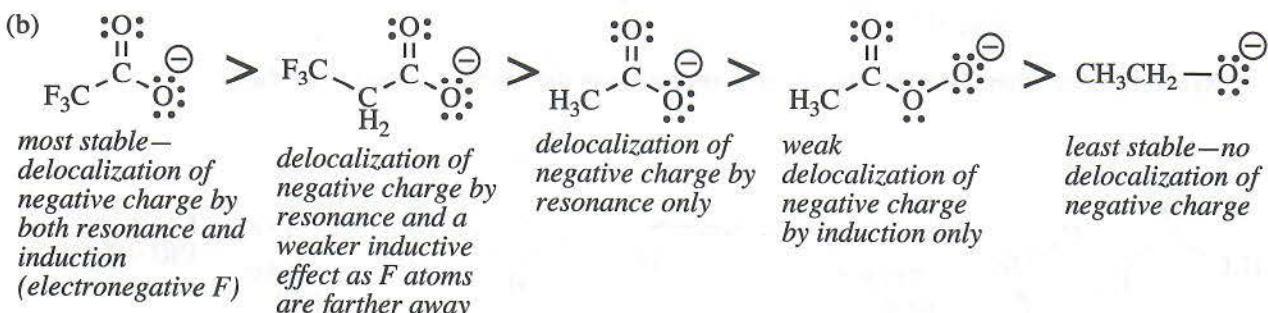
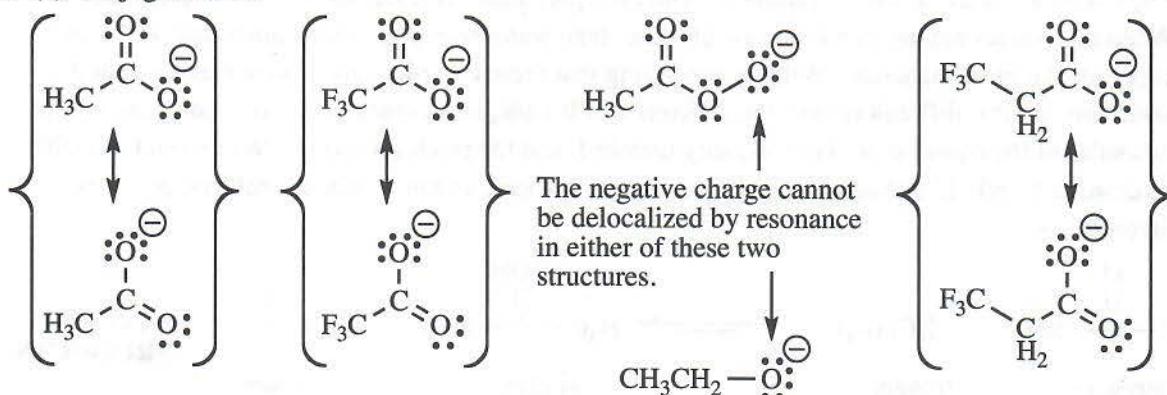
The most acidic proton in the reactant is the CH between the two C=O because of resonance stabilization of the resultant anion by both C=O. See the solutions to problems 1-8(g) or 1-43(c) for similar examples.

2-44 Note that this question is asking for the strength of the aqueous solution (pH), not just the strength of the acid.

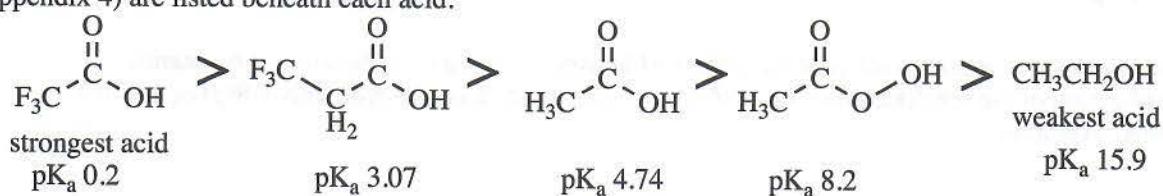


Explanation: For acids weaker than water, the pH of the aqueous solution will follow the sequence of the pK_a values: the higher the pK_a, the less they ionize in water. For acids stronger than water, they will be leveled to hydronium ion, H_3O^+ , so 1 molar solutions of HCl and HBr would be completely ionized, giving $[\text{H}^+] = 1\text{M}$. The exception is H_2SO_4 because it is a diprotic acid: the first proton is 100% ionized, but the second proton (HSO_4^-) has pK_a 2.0, higher than water but still a strong acid, so some portion of it will also be ionized in excess of the first proton, making this aqueous solution the strongest acid = lowest pH, with $[\text{H}^+] > 1\text{M}$.

2-45 (a) conjugate bases

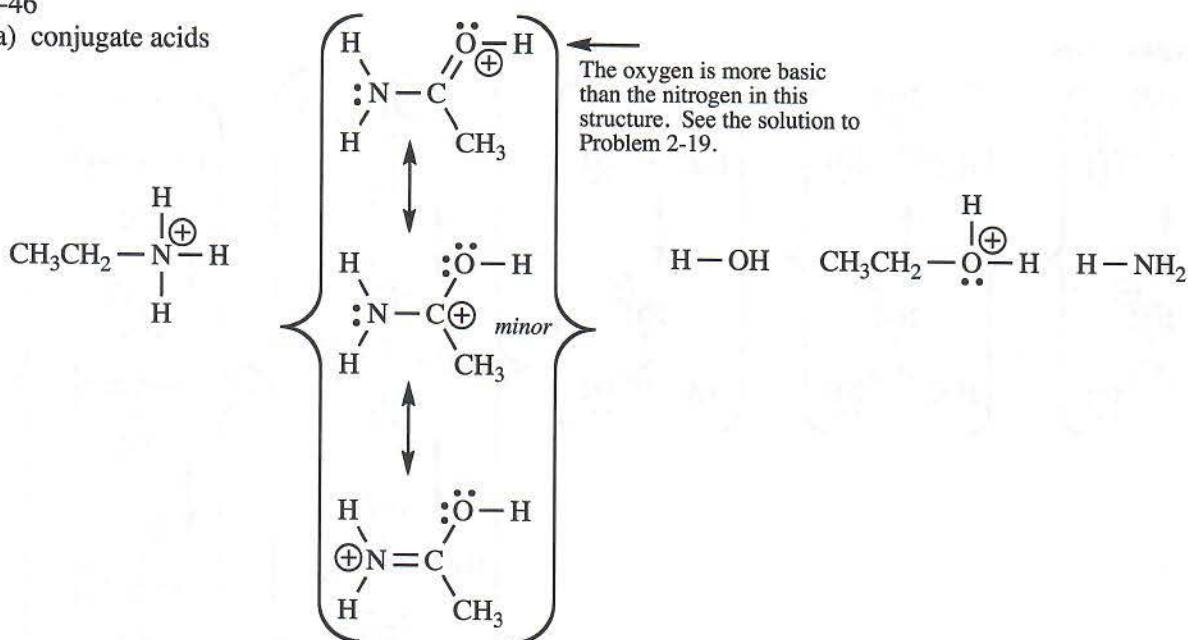
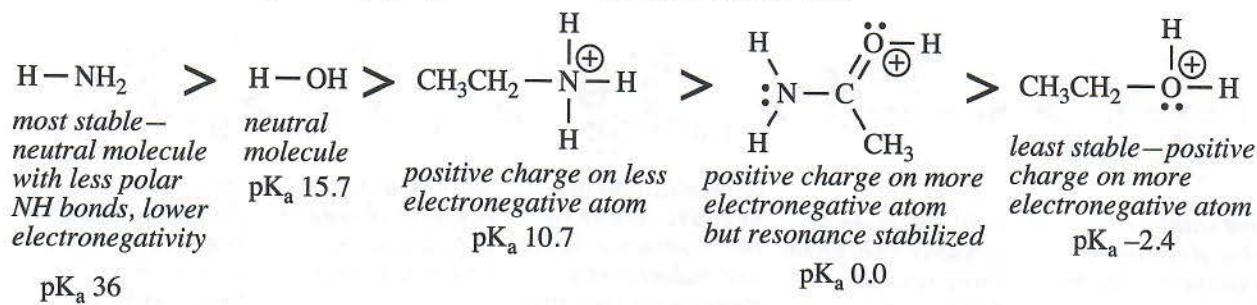


(c) The strongest acid will have the most stable conjugate base. The actual pK_a values (some from text Appendix 4) are listed beneath each acid.

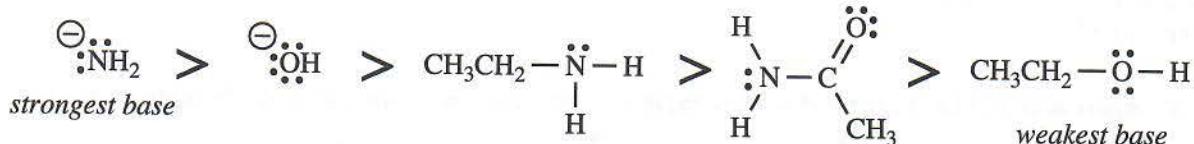


2-46

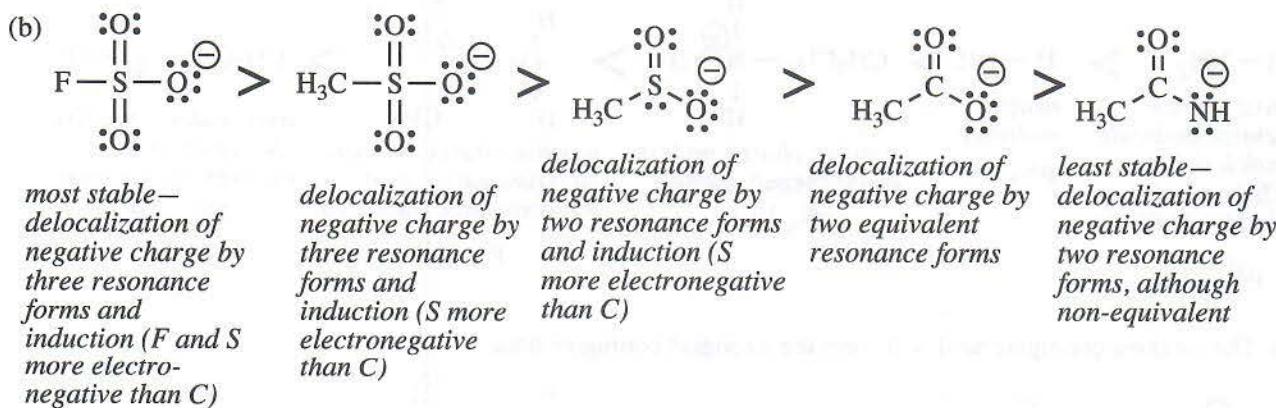
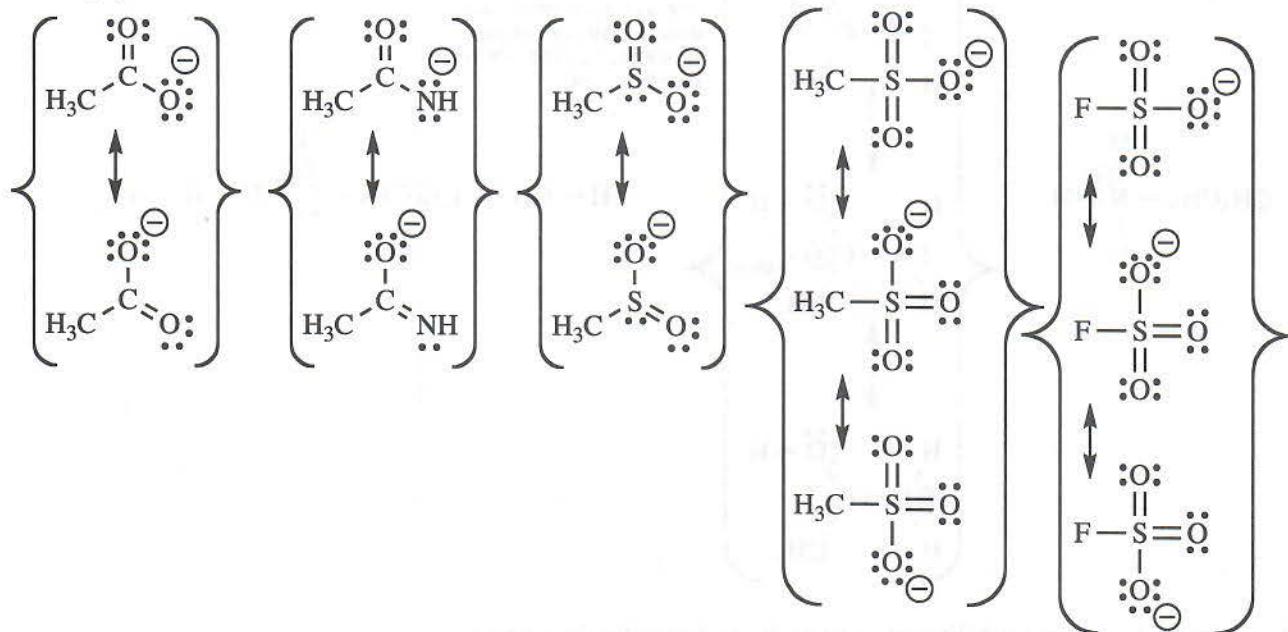
(a) conjugate acids

(b) order of decreasing stability (pK_a values from Appendix 4 in the text)

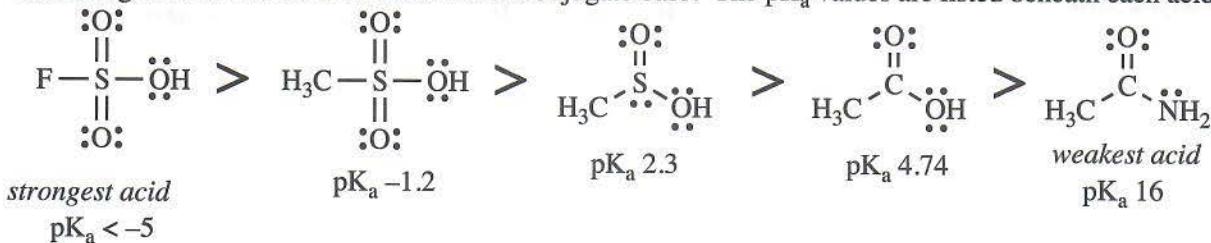
(c) The weakest conjugate acid will form the strongest conjugate base.



(a) conjugate bases

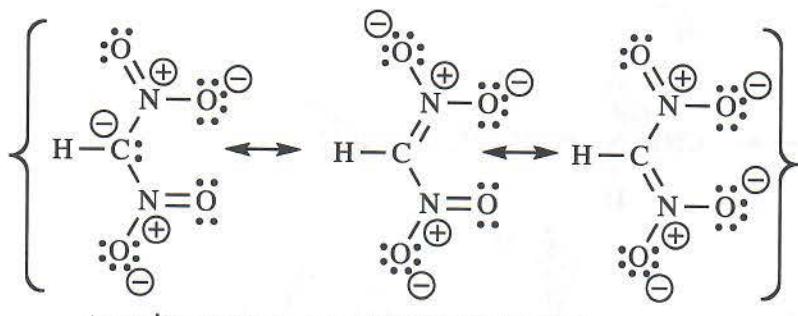
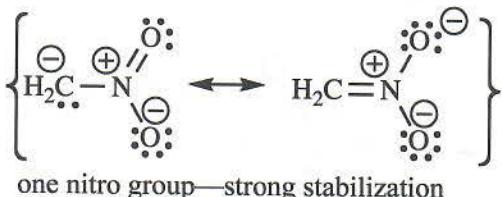
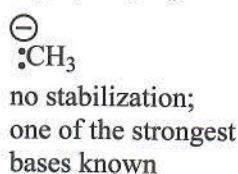


(c) The strongest acid will have the most stable conjugate base. The pK_a values are listed beneath each acid.

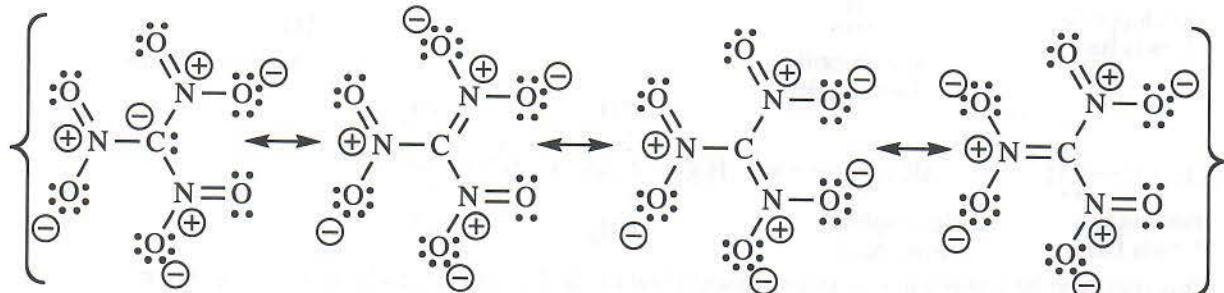


2-48

Of all the substituent groups in organic molecules, the nitro group, NO_2 , is the best electron-withdrawing group. Not only does it have three electronegative atoms that can stabilize negative charge by induction, but it also has very strong resonance stabilization. Adding just one nitro group to methane increase the acidity by 40 p K_a units!



two nitro groups—very strong stabilization



three nitro groups—maximum stabilization—essentially zero negative charge on central C

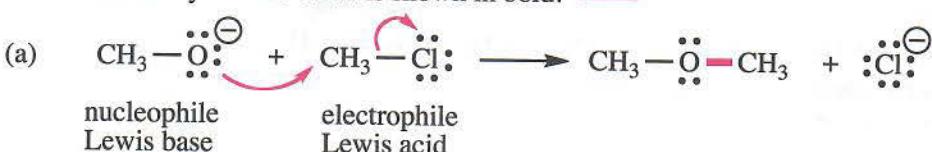
Each subsequent substitution of H by NO_2 increases the amount of the delocalization of the electron pair on C, stabilizing the anion.

2-49

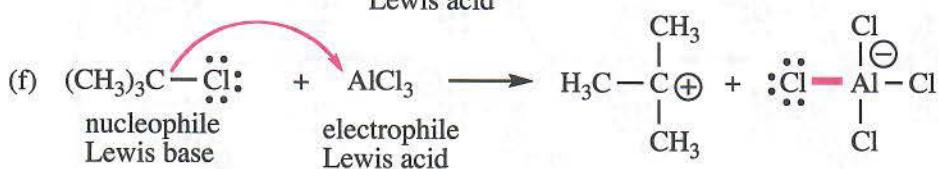
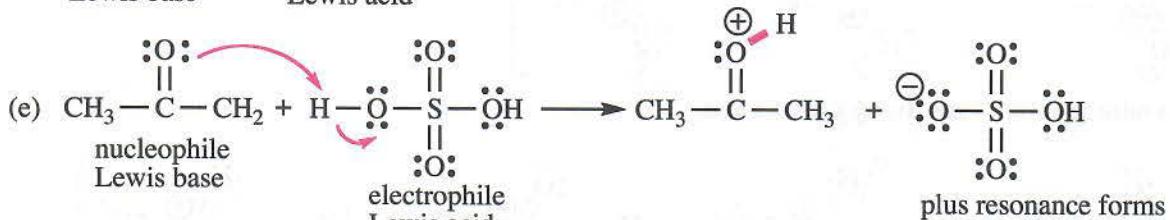
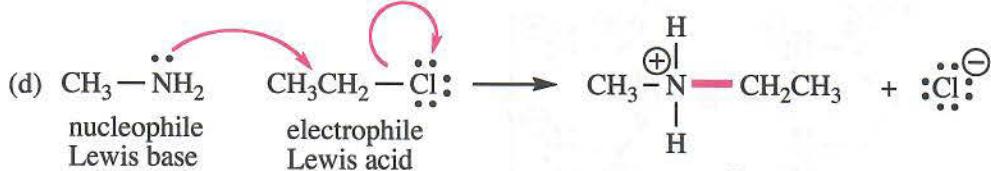
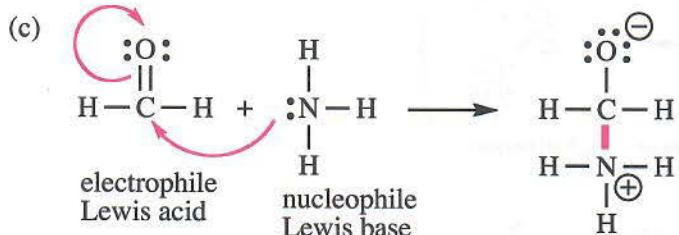
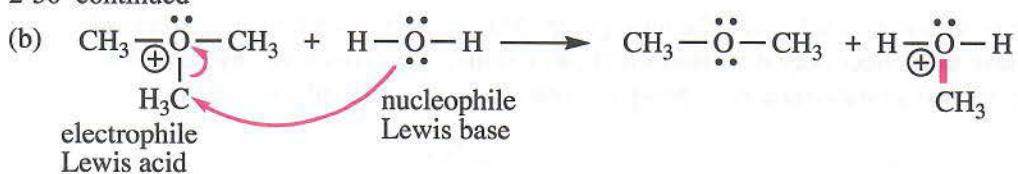


(b) The conjugate acid of CH_3Li is CH_4 . Text Appendix 4 gives the p K_a of CH_4 as 50, one of the weakest acids known. The conjugate base of one of the weakest acids known must be one of the strongest bases known.

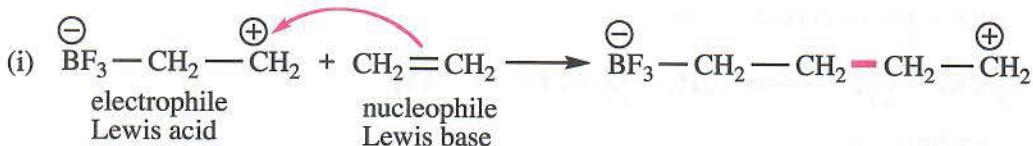
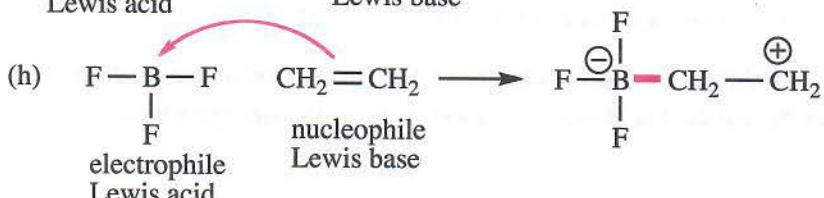
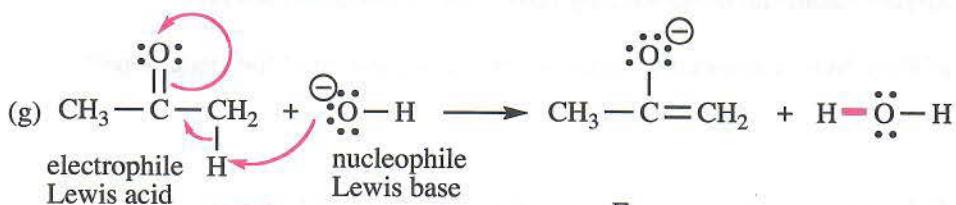
2-50 The newly formed bond is shown in bold. —



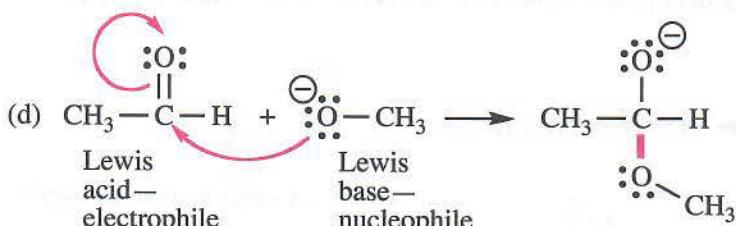
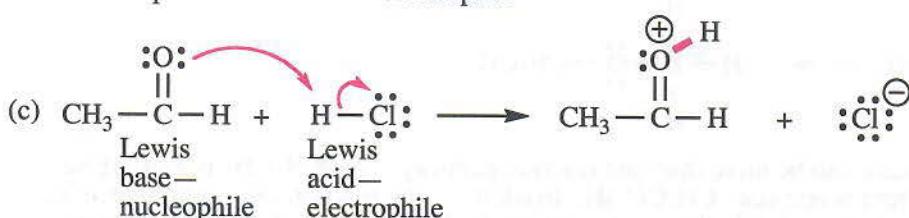
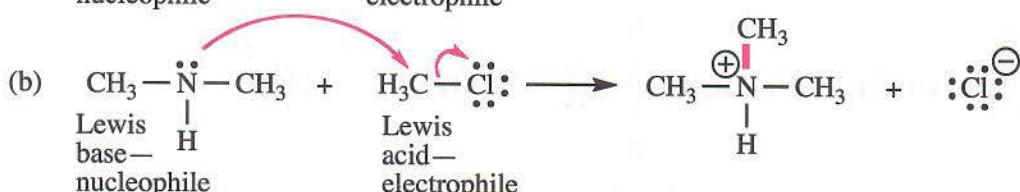
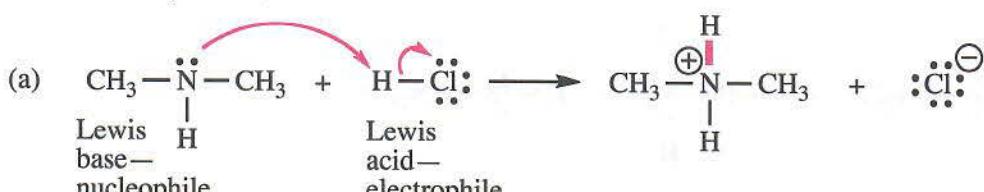
2-50 continued



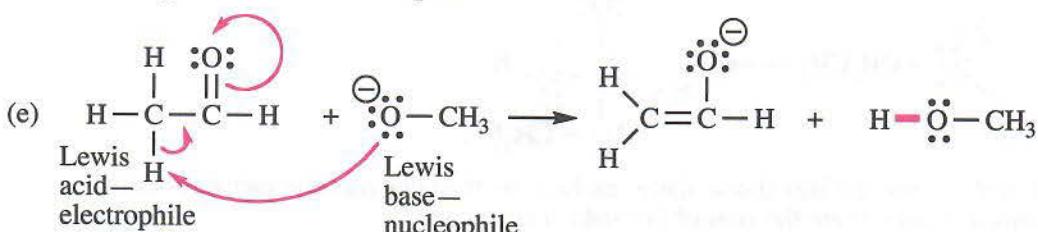
This may also be written in two steps: association of the Cl with Al, and a second step where the C—Cl bond breaks.



2-51 In each product, the new bond is shown in bold.

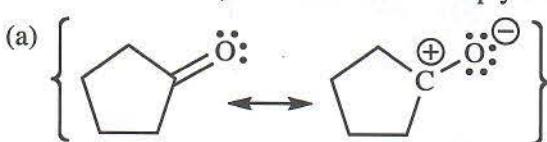


Notice in parts (d) and (e) that the identical reactants can generate two separate products.

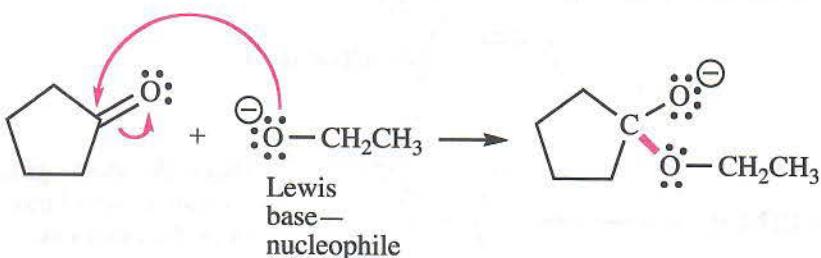


2-52 In each product, the new bond is shown in bold.

In each case, look for the atom that is the most positive because of induction or resonance, or is the most electron deficient (like boron with an empty orbital).

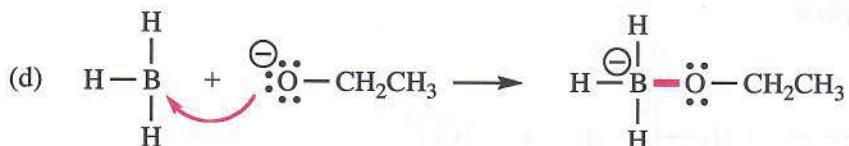
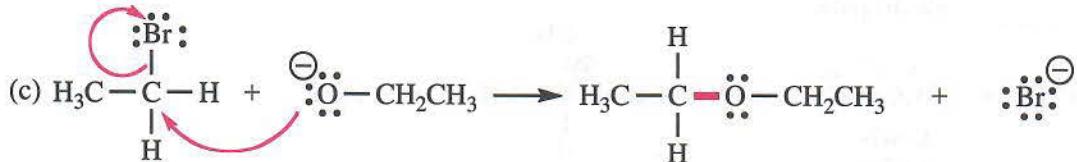
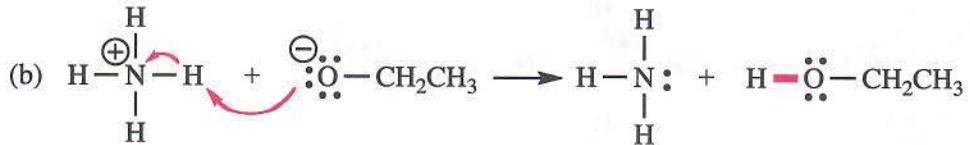


Resonance forms show that the C in a C=O group always has some (+) charge; this carbon is an electrophile. Nucleophiles will be attracted to it as shown here and in parts (e) and (f).

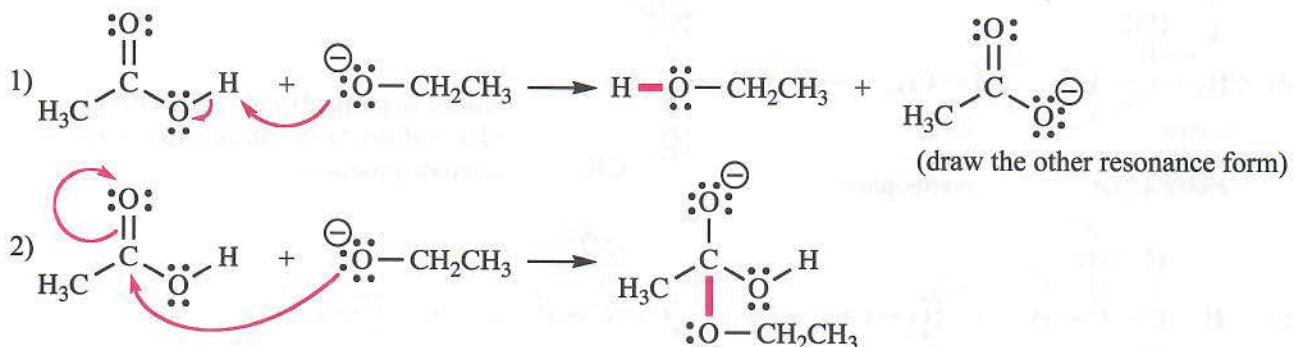


The Na^+ is a spectator ion and plays no active role in these reactions. It is not shown here to avoid clutter.

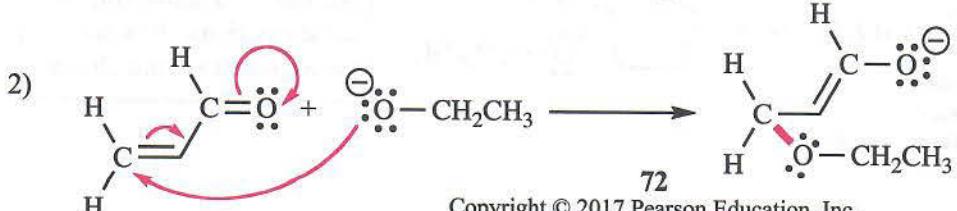
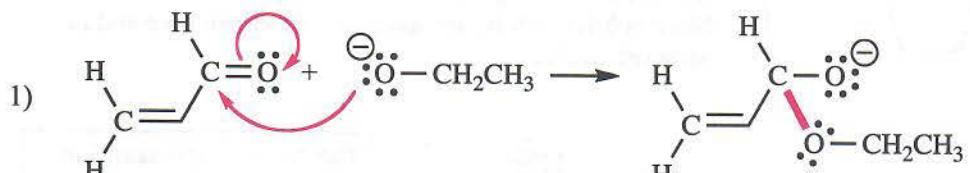
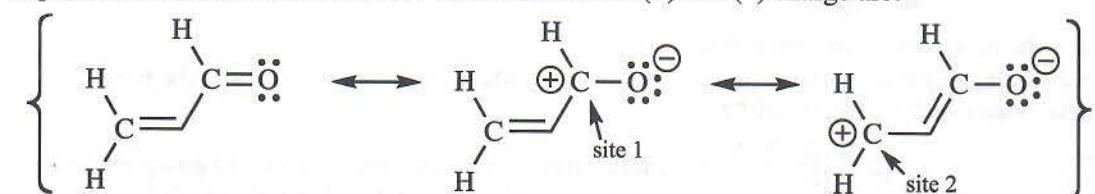
2-52 continued



(e) As shown in 2-51(d) and (e), there can be more than one reaction pathway. NaOCH₂CH₃ is a strong base and can quickly remove a proton from acetic acid, CH₃COOH. In addition, the reaction can occur at the C=O (see 2-52(a)) of acetic acid, although more slowly than proton removal which is one of the fastest reactions known.



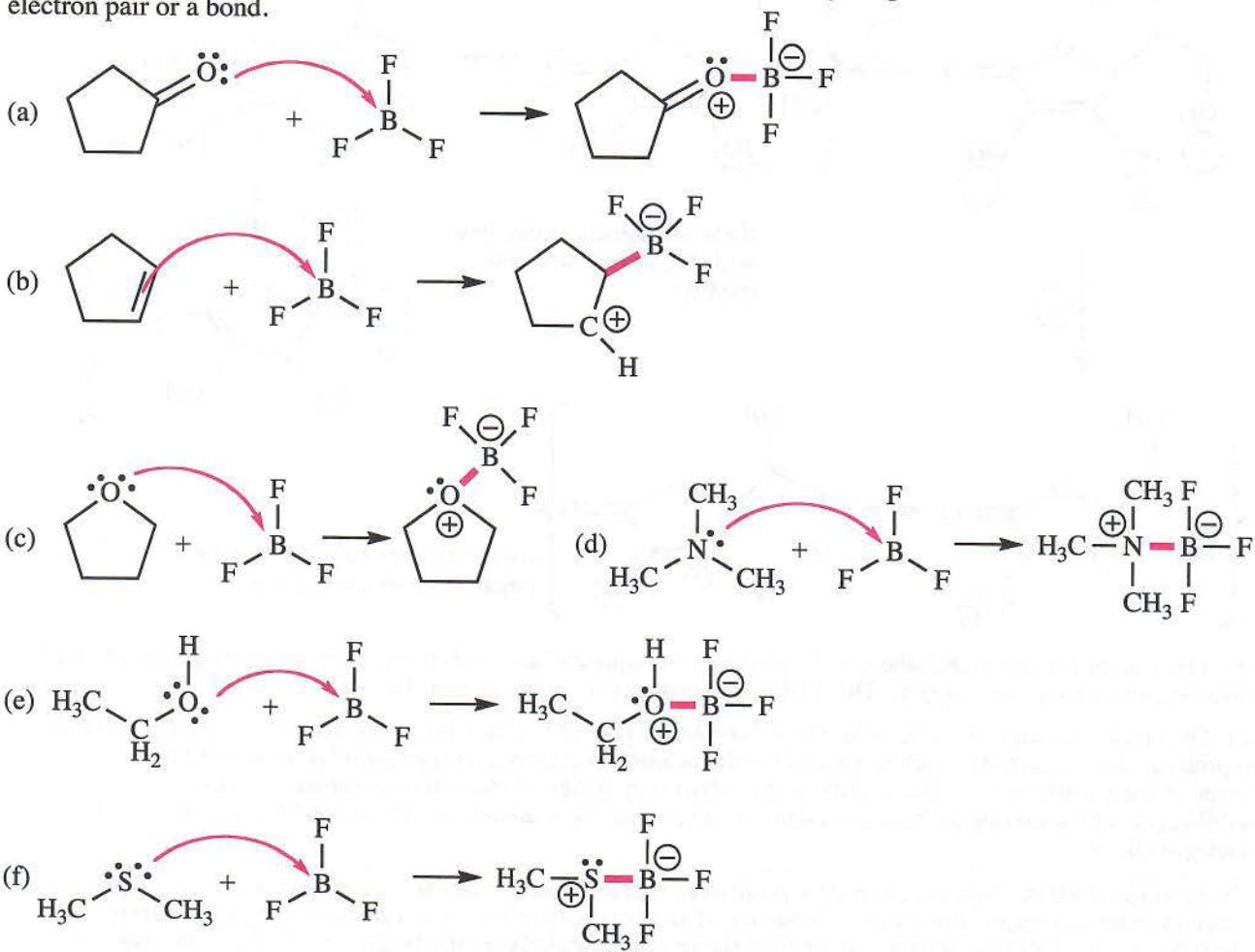
(f) As shown in 2-51(d) and (e), and 2-52(e) above, there can be more than one reaction pathway. Draw important resonance forms to reveal where the sites of (+) and (-) charge are.



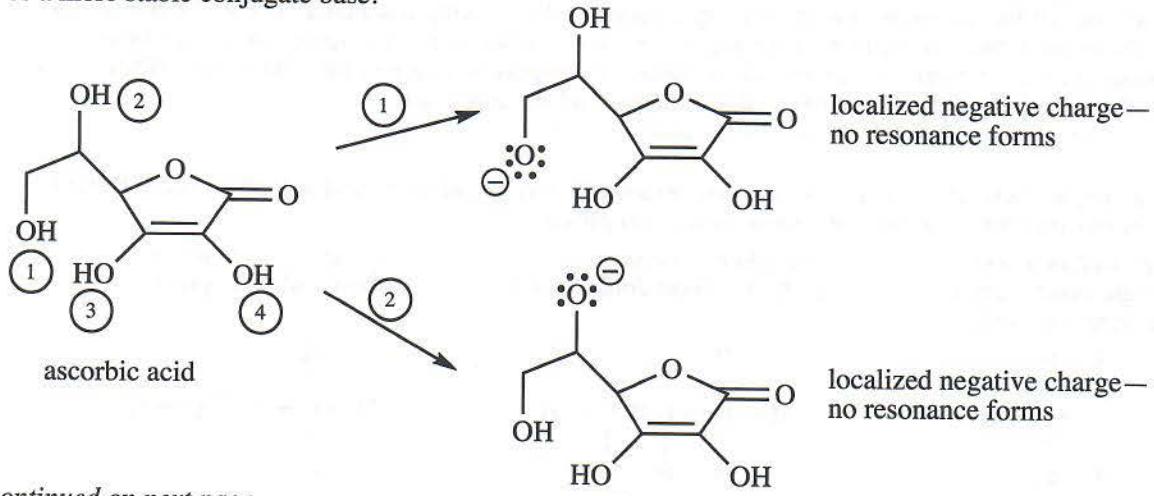
This is the most significant resonance contributor. Draw the other one.

2-53 In each product, the new bond is shown in bold.

In each case, look for an unshared electron pair, or an electron pair in a double or triple bond, to make a molecule nucleophilic. An arrow showing electron movement must always begin at an unshared electron pair or a bond.

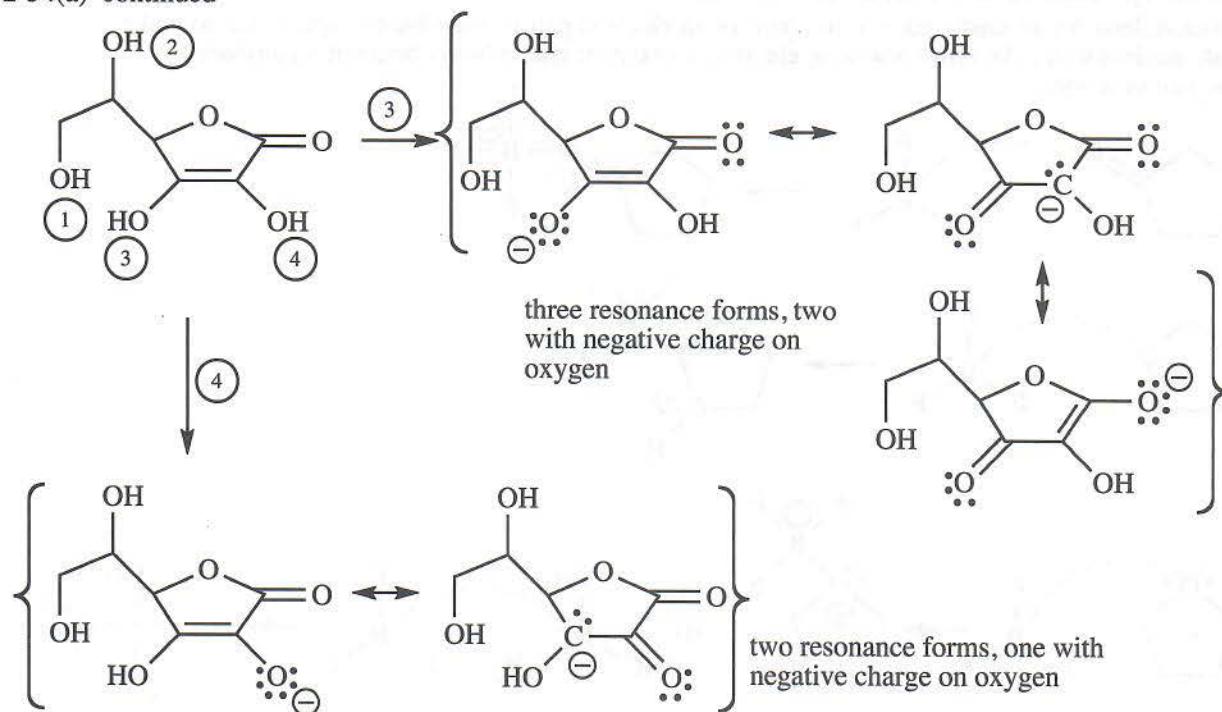


2-54 (a) Ascorbic acid has four OH groups that could act as acids. The ionization of each shows that one gives a more stable conjugate base.



continued on next page

2-54(a) continued



(b) The ionization of the OH labeled "3" produces a conjugate base with three resonance forms, two of which have negative charge on oxygen. This OH is the most acidic group in ascorbic acid.

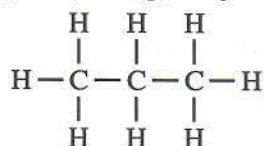
(c) The conjugate base of acetic acid, the acetate ion, CH_3COO^- , has two resonance forms (see the solution to problem 2-47), each of which has a $\text{C}=\text{O}$ and a negatively charged oxygen, similar to two of the resonance forms of the ascorbate ion. The acidity of these two very different molecules is similar because the stabilization of the conjugate base is so similar. *The strength of an acid is determined by the stability of its conjugate base.*

Note to the student: Organic chemistry professors will ask you to "explain" questions, that is, to explain a certain trend in organic structures or behavior of an organic reaction. The professor is trying to determine two things: 1) Does the student understand the principle underlying the behavior? 2) Does the student understand how the principle applies in this particular example?

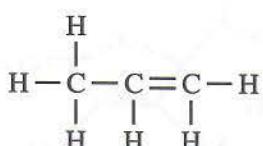
To answer an "explain" question, somewhere in your answer should be a statement of the principle, like: "*The strength of an acid is determined by the stability of its conjugate base.*" From there, show through a series of logical steps how the principle applies, like drawing resonance forms to show which acid has the most stable conjugate base through resonance or induction. Answering these questions is like crossing a creek on stepping stones. Each phrase or sentence is a step to the next stone. When strung together, the steps bridge the gap between the principle and the observation.

2-55 The examples here are representative. Your examples may be different and still be correct. What is important in this problem is to have the same functional group.

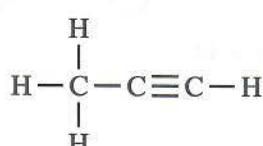
(a) alkane: hydrocarbon with all single bonds; can be acyclic (no ring) or cyclic



(b) alkene: contains a carbon-carbon double bond

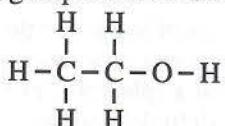


(c) alkyne: contains a carbon-carbon triple bond

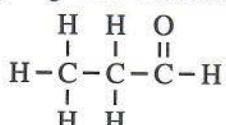


2-55 continued

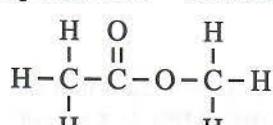
(d) alcohol: contains an OH group on a carbon



(g) aldehyde: contains a carbonyl group with a hydrogen on one side

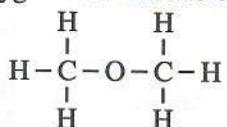


(j) ester: contains a carbonyl group with an O—C on one side



(m) nitrile: contains the carbon-nitrogen triple bond: $\text{H}_3\text{C}-\text{C}\equiv\text{N}$

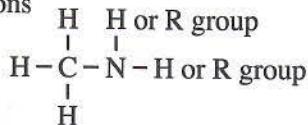
(e) ether: contains an oxygen between two carbons



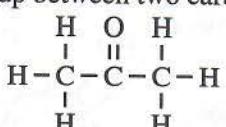
(h) aromatic hydrocarbon: a cyclic hydrocarbon with alternating double and single bonds



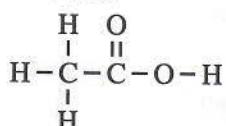
(k) amine: contains a nitrogen bonded to one, two, or three carbons



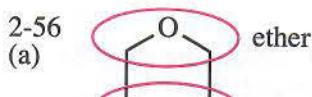
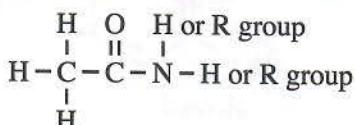
(f) ketone: contains a carbonyl group between two carbons



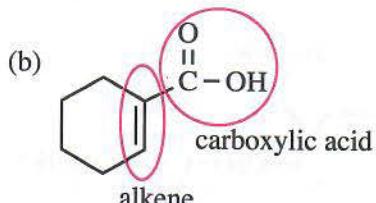
(i) carboxylic acid: contains a carbonyl group with an OH group on one side



(l) amide: contains a carbonyl group with a nitrogen on one side

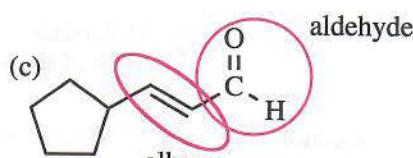


ether
ether



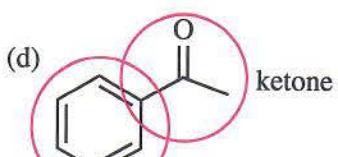
alkene

carboxylic acid



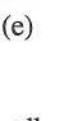
alkene

aldehyde

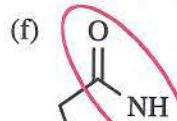
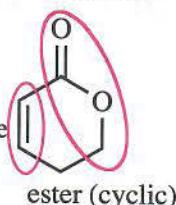


aromatic

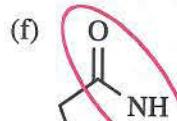
ketone



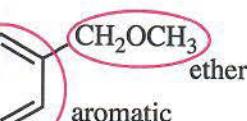
alkene



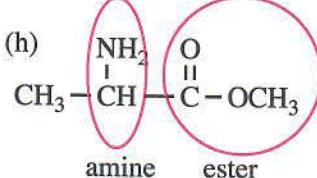
amide (cyclic)



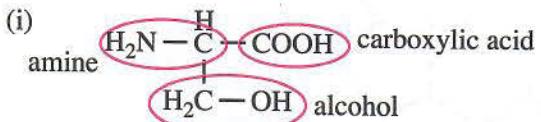
nitrile



aromatic



amine
ester



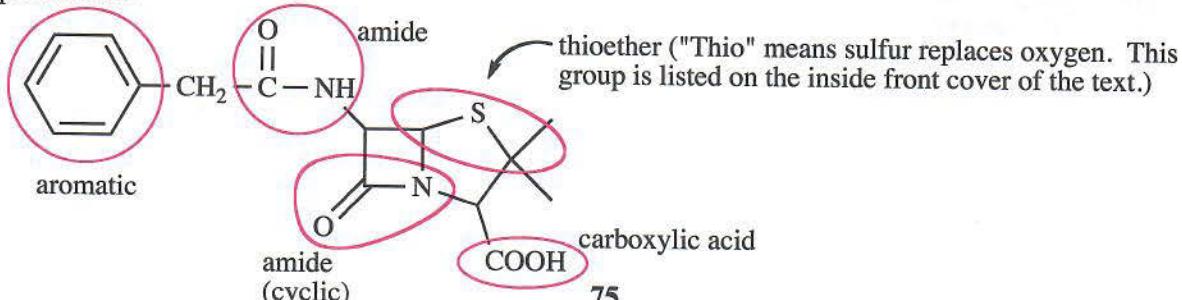
amine

carboxylic acid

alcohol

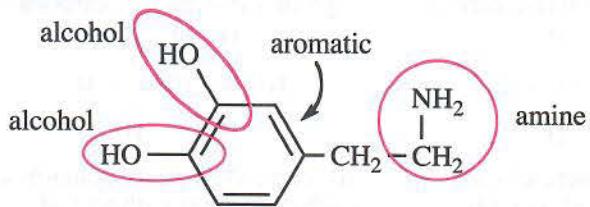
2-57

(a) penicillin G



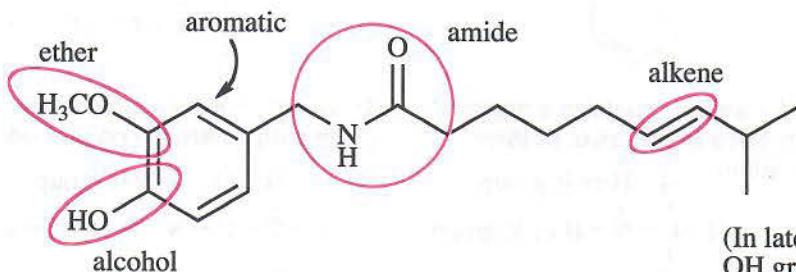
2-57 continued

(b) dopamine



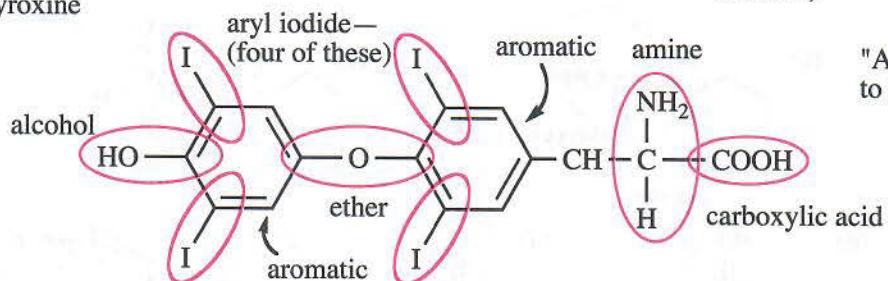
(In later chapters, you will learn that the OH group on a benzene ring is a special functional group called a "phenol". For now, it fits the broad definition of an alcohol.)

(c) capsaicin



(In later chapters, you will learn that the OH group on a benzene ring is a special functional group called a "phenol". For now, it fits the broad definition of an alcohol.)

(d) thyroxine



"Aryl" iodides are attached to aromatic rings.

(e) testosterone

